## THERMAL AND PHOTOCHEMICAL

## REACTIONS OF

BRIDGEHEAD HALOGEN COMPOUNDS

by

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..

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#### ABSTRACT

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A method of halogen exchange at normally unreactive bridgehead positions was developed utilizing the <u>in situ</u> generation of aluminum trihalides from aluminum foil and iodine, liquid bromine and gaseous chlorine in various solvents. The resulting solutions of aluminum iodide, bromide and chloride promoted rapid exchange of primary, secondary and tertiary halides under mild conditions and in high yield. Aromatic halides proved to be inert to the reaction conditions. Halogen exchange was shown to proceed from  $C1 \rightarrow Br$  $\rightarrow I$  as well as  $I \rightarrow Br \rightarrow C1$ . The rate of the reaction was found to follow the relative stability of the corresponding bridgehead carbenium ions i.e.  $1-tricyclo[3.3.1.1^{3,7}]$ decyl(adamantyl) > 1-bicyclo[2.2.2]octyl > 1-bicyclo-[2.2.1]heptyl>7 9-triptycenyl(9,10-0-Benzenoanthracene-9,10-dihydro).

Photochemical reactions of bridgehead halides of the adamantyl and bicyclo[2.2.1]heptyl systems were examined and found to follow both free radical and ionic pathways, the relative amount of each depending upon the halogen atom and the solvent used. Iodides reacted <u>via</u> an almost exclusive ionic pathway, chlorides <u>via</u> an exclusive free radical pathway and bromides via both pathways. With polyhalogen compounds the loss of halogen atoms was stepwise, no evidence for any "dehydro" or "propellane" type intermediates resulting from concerted loss of two halogens was found. The irradiation of bridgehead iodides in alcohols produced bridgehead ethers with bridgehead amides resulting from reaction in alkyl nitriles. Reaction in alkyl amines did not lead to bridgehead amines and reduction products were formed instead. Halogen exchange was observed for the irradiation of adamantyl iodides in halogenated solvents while for adamantyl bromides, chlorides and fluorides halogenation was found.

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The nuclear magnetic resonance spectra (<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F) of the halogenated bridgeheed derivatives of tricyclo[ $3.3.1.1^{3,7}$ ]decane (adamantane) showed anomalous chemical shifts upon successive addition of halogen atoms possibly due to interaction of the back lobes of the adamantane bridgehead carbon atoms.

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Crystal Ball

## Blind Guess

Slide Rule

Норе

Fear

and just a touch

of

Faith

Hal Clement

#### INTRODUCTION

The special character of reactions at the bridgehead positions of polycyclic systems was first noticed by Bartlett<sup>1</sup> in 1939. His proposal that these systems would be an ideal area to study reaction mechanisms and the preferred geometry of transition states has been proven over-whelmingly correct again and again over the past 36 years by many research groups around the world.<sup>2</sup>

The first example discovered involved the relative inertness of the 1-apocamphyl system.



At the time this work was published it was generally accepted that the only way in which one anion could replace another in any neutral molecule was via a Walden inversion (today known as the  $S_N^2$  displacement reaction). Bartlett reasoned that in the apocamphyl system (as well as other rigid polycyclic molecules) this type of displacement was impossible and that the observed inertness would be a result of the inherent instability of

- 1 -

the carbenium ion necessarily produced by a unimolecular reaction. This concept was later refined to suggest that carbenium ions would prefer a  $sp^2$  planar geometry allowing the three bonding orbitals to be as far apart as possible. The vacant p orbital would be at right angles to the plane of the bonding orbital. This planar arrangement has been supported by theoretical calculations<sup>3</sup> as well as by nmr<sup>4</sup> and infra-red studies<sup>5</sup> of several carbenium ion salts.

Thus in systems where the molecular geometry prohibits planarity a bridgehead carbenium ion reaction will be slower than for a system in which a planar intermediate could readily be formed<sup>2d</sup>. Therefore an examination of the rate of solvolysis for a series of bridgehead compounds would lead to a relative order of carbenium ion stabilities as shown below<sup>6</sup>: (the rates have been corrected for differences in the leaving group)





Br





1.0

2 x 10<sup>-2</sup>

7x10<sup>-3</sup>

 $2 \times 10^{-3}$ 

 $10^{-3}$ 

Br



100



10-8



1012



0°

10-16

This method of using relative rates is valid only if the transition states for the reactions all fall at the same point along the reaction coordinate. The assumption of equal degree of ionization has been made previously so that relative rates for a series of closely related compounds (eg. bridgehead bromides) may be taken to fairly well represent stability<sup>7</sup>.

The larger the size of the rings composing the bridged system the more readily will an  $sp^2$  hybridized carbon be accepted at the bridgehead. Therefore a continued increase in the ring size should lead to rate enhancement for bridgehead solvolysis relative to <u>t</u>-butyl halide. Two such examples are known and are shown below:<sup>8</sup>



Empirical force field calculations on bicyclo [3.3.3] undecane (manxane) indicate that a total of 6.8 kcal of strain energy would be relieved in going from the parent hydrocarbon to the bridgehead carbenium ion.<sup>8</sup> This is a result of the angle strain in the molecule (normal sp<sup>3</sup> hybridized carbon atoms have angles of 109.5° while in manxane calculations show  $4C_2C_1C_8 =$  $115.2^\circ$ ,  $4C_1C_2C_3 = 118.8^\circ$  and  $4C_2C_3C_4 = 118.2^\circ$ ).

This extreme reactivity is indicated by the fact that a pentane solution of manxane is spontaneously converted to the monoperoxide (X = 00H) by passing a stream of air through it. The chloride solvolyzes  $10^4$  times as fast as <u>t</u>-butyl chloride, and is totally converted to the alcohol (X = 0H) upon exposure to atmospheric moisture for a few minutes. Further calculations

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indicate that the presently unknown 1-chlorobicyclo  $\begin{bmatrix} 4.4.4 \end{bmatrix}$  tetradecane<sup>8</sup> will be even more reactive, solvolyzing approximately  $10^7$  times as fast as <u>t</u>-butyl chloride.

The above bridgehead compounds solvolyze over a range of 20 orders of magnitude. As a result of extreme nonreactivity the synthesis of bridgehead derivatives of the smaller ring systems has been difficult, often requiring long and roundabout routes. The bridgehead halogen compounds are the most useful intermediates. Some of the synthetic routes which have been employed to obtain them are shown below:



## Bridgehead Ionic Substitution

Because of the greater reactivity in the larger ring systems, direct



In all cases exclusive bridgehead bromination occurs because of the greater stability of the bridgehead carbenium ion over any of the secondary cations. Once isolated, the above bromides have been converted to the other bridgehead halogen compounds directly with concentrated acids or <u>via</u> the corresponding 1-hydroxy compounds. The reactions are exemplified for 1-bromoadamantane.



Peterson<sup>21</sup> has also found that bromine may replace other substituents as shown below:



As a result of the electron withdrawing nature of bromine, additional halogenation<sup>22</sup> requires more vigorous conditions with added Lewis acid catalysts. The same is true for alkyl substituted adamantanes as well.



46%

Under forcing conditions diamantane also reacts further to yield three disubstituted products<sup>16</sup>.



However, McKervey and co-workers have recently discovered that specific diamantane diols may be produced<sup>165</sup> by use of the fungus <u>Rhizopus Nigricans</u> as shown:





As a consequence of symmetry the other diamonoid hydrocarbon systems yield highly complex mixtures of products from Lewis acid brominations (if they do not also rearrange to substituted adamantanes under the reaction conditions).

Olah<sup>23</sup> has recently published a facile method of producing bridgehead and bridge halides from the corresponding alcohols with alkali halides in polyhydrogen fluoride - pyridine solution.



<u>Salt %3<sup>°</sup> %2<sup>°</sup></u> NaF 81 88 NaCl 40 40



NH4Br	80	70
КI	35	20

Stetter<sup>24</sup> has found that the adamantane ring may be chlorinated directly in  $CCl_4$  with aluminum chloride to yield a mixture of the monochloride and dichloride in 85% yield. Use of thionyl chloride in place of  $CCl_4$  led to the formation of the trichloride.



The only other direct method of synthesizing bridghead halides was found by Inamoto<sup>25</sup>. Hydride abstraction from 1-substituted adamantanes by <u>t</u>-butyl cation in the presence of hydrogen halides yielded the corresponding bridgehead halogen compound.



Bridgehead halides may also be produced by use of precursors to the diamonoid molecules. Rearrangement of <u>exo</u> or <u>endo</u>-tetramethylenenorbornane<sup>26</sup> and <u>exo</u> or <u>endo</u>-trimethylenenorbornane in the presence of aluminum chloride led to the formation of chlorinated adamantanes. Similarly, rearrangement of a hydrogenated norbornadiene dimer<sup>27</sup> in the presence of chlorosulphonic acid led to the production of 4,9-dichlorodiamantane.





An indirect method of synthesizing halogenated adamantanes has been electrophilic additions to dehydroadamantanes.

Work performed in this laboratory has shown that 1,3-dehydroadamantanes are formed from the reaction of 1,3-dihaloadamantanes with either sodium at room temperature or <u>n</u>-butyl lithium at  $-35^{\circ}$  C in diethyl ether with added HMPA<sup>30</sup>.



These highly reactive, oxygen sensitive dehydroadamantanes may be easily isolated by sublimation under nitrogen. The same ease of purification has been observed for 2,4-dehydroadamantane. Once isolated, both dehydroadamantanes may be used to synthesize substituted adamantanes.

Secondary halides have been isolated in low yields<sup>28</sup> from the hydrogen halide addition to 2,4-dehydroadamantane<sup>29</sup>.





major

Better yields have been realized from additions to 1,3-dehydroadamantane<sup>30,31</sup>.



As can be seen from the above examples the synthesis of tertiary or secondary adamantyl halides is relatively straightforward; however, the isolation of mixed bridgehead and bridge halides requires additional manipulations. <u>Syn</u> and <u>anti</u>-1,4-dihalides may be isolated from the Lewis acid catalyzed rearrangement of gem-adamantyl dihalides as shown below. The reactions are not clean however; the 1,4-dihalides must be separated from the other reaction products.





The isolation of 1,2-adamantyl dihalides first requires the synthesis of tricyclo  $[4.3.1.0.^{3,8}]$  decan-4-one (protoadamantanone) via the following route<sup>35</sup>.

ref 33



Upon treatment with  $PCl_5/PCl_3$  this ketone yields two products; the desired 1,2-dichloroadamantane and 4-chloroprotoadamantene<sup>36</sup> (which may be converted to the dichloride with boiling HCl). Treatment with  $PBr_5/PBr_3$  leads directly to 1,2-dibromoadamantane.



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Related to this, the 1,2-diiodide requires an extra synthetic step, production of the hydrazone<sup>37</sup>.



As can be seen from the above examples there are many ways of preparing halogenated adamantanes and other polycyclic hydrocarbons, but there have been few attempts made to convert one halide to another.

Methods of halogen exchange in acyclic systems have been known for many years<sup>38</sup> but most fail to work on tertiary centers. One of the earliest is the Finkelstein reaction<sup>39</sup> for converting primary chlorides and bromides to the corresponding iodides using NaI in acetone or a higher molecular weight ketone. The reaction proceeds because NaCl and NaBr are insoluble in the reaction medium pushing the equilibrium to the right.

RCH<sub>2</sub>X + NaI  $\sim$  RCH<sub>2</sub>I + NaX

Chlorine and bromine exchange may be performed but mixtures of products are usually observed. Secondary and tertiary halides may exchange, but at a greatly reduced rate compared to primary halides<sup>40</sup>. Schim<sup>41</sup> has used methanol as a solvent to achieve iodine exchange at a secondary position:

$$C_5^{H_{11}}C_{Br}^{CHCH_3} + NaI \xrightarrow{CH_3^{OH}} C_5^{H_{11}}C_{I1}^{CHCH_3}$$
 75%

Use of higher boiling and more polar solvents can speed up the reaction and increase yields but the procedure still works best for primary positions.



Miller<sup>44</sup> has used an extension of this reaction to convert tertiary and benzylic chlorides to the corresponding iodides using an excess of NaI in  $CS_2$  at 20<sup>o</sup> with a trace of FeCl<sub>3</sub>. Interestingly enough, primary and secondary halides fail to react.



Bromine to chlorine exchange has recently been reported by Vida<sup>45</sup> using silver difluorochloroacetate.



85%

Kagan and co-workers<sup>163</sup> have recently used graphite modified SbCl<sub>5</sub> to promote chlorine exchange. In the absence of graphite  $\ll$  chlorination occurs preferentially as shown below.



Filippo and co-workers<sup>46</sup> have also shown that MoCi<sub>5</sub> may be used to convert alkyl fluorides, bromides and iodides to the corresponding chlorides. Tertiary, secondary and primary halides exchange with rearrangement of primary halides occurring.



Kauer<sup>47</sup> has recently shown that iodine in normally unreactive positions will readily react with iodine monochloride to produce chlorides as shown below:



The relative ease of carrying out the reaction led Kauer to suggest that a bridgehead carbenium ion was not involved but rather the following mechanism was occurring:

$$RI + 2IC1 \xrightarrow{R} - I \xrightarrow{C1} + I_2$$
$$R-C1 + IC1$$

The above is supported by the early work of Thiele<sup>48</sup> who isolated an unstable dichloroiodo complex from the reaction of methyl iodide and IC1.

$$CH_3I + IC1 \xrightarrow{-80^\circ} CH_3IC1_2 \xrightarrow{-28^\circ} CH_3C1 + IC1$$

The reaction to replace halogen by fluorine at unactivated centres has been found to be difficult and to require more vigorous conditions<sup>49</sup>. Anhydrous silver fluoride has been used to synthesize the four possible bridgehead adamantyl fluorides in good yields<sup>50</sup>. Müller has also used it to exchange F for Cl in the diphenylbenzocyclopropene system as well<sup>51</sup>.

$$Ad(Br)_{x} \xrightarrow{Agr} Ad-(F)_{x} x = 1,2,3,4 60 - 80\%$$

. . .



Thus there are many different methods to interchange halogen atoms but until recently no one general procedure to effect complete exchange in both directions (i.e. Cl  $\longrightarrow$  Br  $\longrightarrow$  I as well as I  $\longrightarrow$  Br  $\longrightarrow$  Cl). This has been developed by Pincock and co-workers<sup>52</sup> for the bridgehead positions of adamantane, bicyclo [2.2.2] octane and bicyclo [2.2.1] heptane,

The fast and efficient exchange involves the <u>in situ</u> generation of the desired Lewis acid catalyst from aluminum foil and bromine in a halogenated solvent. Mono and tetra substituted adamantanes were rapidly exchanged in high yields. The smaller ring systems required more vigorous conditions but still proceeded in good yields. In the case of iodinated solvents the yields were lower due to side reactions, mainly reduction and polymerization.

#### Bridgehead Free Radical Chemistry

Unlike ionic reactions which proceed via exclusive formation of the bridgehead carbenium ion, free radical reactions of adamantanes yield both secondary and tertiary products. For this reason less work has been done on the free radical chemistry of the diamonoid hydrocarbons; the complex mixtures of products are often very difficult to separate and analyze completely.

One of the earliest studies involved the free radical chlorination of adamantane in various solvents  $^{53}$ .  $\bigwedge$ 







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In CCl<sub>4</sub> a fair amount of polychlorination was also observed but the identity of the products was not established.

Oda and co-workers<sup>54</sup> have also shown this competition between bridge and bridgehead abstraction in the reaction of adamantane with benzoyl peroxide and oxalyl chloride. Upon methanolysis an 82% yeild of the methyl esters was achieved (separable by distillation).



Studies by Tabushi<sup>55</sup> have established that the bridgehead adamantyl radical (a) was more readily formed than the bridge radical (b). He examined the competitive free radical halogenation of adamantane with benzoyl peroxide at  $90^{\circ}$  in various solvents.

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Table I Free Radical Halogenation of Adamantane

Reagent	Solvent	1-C1	2-C1	1-Br	2-Br
NBS	с <sub>6</sub> н <sub>5</sub> с1			45	55
$CH_2Br_2$	CH2Br2			75	25
CC1 <sub>4</sub>	cc1 <sub>4</sub>	89	11		
BrCC13	BrCC13	5		85	10

Experiments under 0<sub>2</sub> showed that only the bridgehead radical (a) could be trapped to form 1-adamantanol, i.e. it was long enough lived to allow competition between halogen exchange and trapping by oxygen.

The results in Table I also showed that steric effects were important; with the bulkier H abstractors (-CHBr<sub>2</sub> and -CCl<sub>3</sub>) more bridgehead products were observed.

Further studies with the Hunsdiecker reaction of 1 and 2-adamantane carboxylic acids showed the bridgehead radical to be less discriminating in its reactions  $^{56}$ .



(Later work showed that in the case of the bridgehead acid, halogen exchange via HgCl<sub>2</sub> was occurring<sup>55</sup> and that the ratio before exchange was actually 1.3:1.0; the secondary system did not undergo exchange). Thus the secondary radical selectively picked up a bromine atom while the bridgehead

radical preferred to pull a chlorine atom from the solvent. This suggests that the secondary (bridge) radical is actually the more stable.

This low selectivity of bridgehead radicals has also been shown by the same reaction with  $Br_2$  and HgO in  $CCl_4$  on  $bicyclo \left[2.2.2\right]$  octane-1-carboxylic acid<sup>57</sup>.



The actual competition between secondary and tertiary radicals usually depends on the nature of the abstracting agent. In some cases only bridgehead products are found. Billups<sup>58</sup> has found selective bridgehead abstraction in adamantane by the use of nitrogen cation radicals.

32%





However, this selectivity may be due in part to the possible formation of bridgehead carbenium ions in the strongly acidic reaction medium. No trace of secondary products were found from the carbene addition to adamantane utilizing a phase transfer  $agent^{59}$ .



Selective bridgehead radical formation was also observed in the photoacetylation of adamantane $^{60}$  as well as diamantane $^{61}$ .



However, attack on polycyclic hydrocarbons by nitrenes resulted in both secondary and tertiary products as shown by the following reaction<sup>62</sup>:  $R'-CH_3 + ROCN \longrightarrow ROCNH-CH_2-R'$ 

From this reaction the reactivities of the various positions was determined. (relative to cyclohexane = 1.0)



Thus the relative rates of reaction for the bridgehead positions were

1.0:0.3:0.07 for adamantyl to bicyclooctyl to bicycloheptyl. The corresponding ratios for bridgehead bromide solvolysis (carbenium ion intermediate) were  $1.0:10^{-3}:10^{-10}$ . Thus a free radical may be formed more readily than a carbenium ion at the bridgehead of the smaller ring systems.

Owens<sup>63</sup> has also found that free radical bromination with  $BrCC1_3$  leads mainly to bridgehead products (both halogenation and halogen replacement).



Further studies  $^{64}$  with photochemically generated Br atoms in  $CC1_4$  showed that mixed secondary and tertiary products resulted but no product analysis was performed.



X=Bror CI



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Wynberg<sup>65</sup> has reported an interesting study in which competition between free radical and carbenium ion intermediates was involved. Kolbe electrolysis of carboxylic acids normally follows the mechanism shown below:

In most cases the normal product in high yield is the dimer. However, in the case of adamantyl acids the following results were found.



Here the intermediate bridgehead free radical readily lost an electron to yield carbenium ion products exclusively while the secondary acid gave both cationic and free radical products. Therefore, in cases where a competition between cationic and free radical pathways exists the bridgehead substituted adamantanes prefer to react via the cationic one.

Ο

# Photochemistry of Alkyl Halides

The absorption of ultraviolet energy by alkyl halides has received extensive study but in nearly all cases involved homolytic carbon-halogen bond cleavage which led to free radical derived products <sup>66</sup>. Aromatic halide photochemistry has been examined only recently and in some cases

photochemical nucleophilic reactions are observed as well as reduction. In the only study of comparative reactivity of halides, Pinhey<sup>68</sup> found two reaction pathways for the excited aromatic halide.



He attributed the increase in the amount of reduction product to the decreasing strength of the C-X bond which would facilitate homolytic cleavage.

In a similar study, Bunce and co-workers examined the photochemistry of a series of halogenated naphthalenes in methanol<sup>69</sup>.



However, Kropp<sup>70</sup> has shown that not all alkyl halides react <u>via</u> a free radical pathway. In the 2-norbornyl system, completely different products

were observed from the irradiation of the iodide and bromide in diethyl ether.



Thus the norbornyl iodide appeared to react <u>via</u> an "ionic type" intermediate while the bromide reacted in a free radical manner. Further research on bridgehead halides<sup>71</sup> revealed that competitive ionic and free radical pathways were involved.



It was envisaged that initial excitation led to the formation of a radical pair which reacted <u>via</u> two modes. It could either undergo electron transfer to yield an ion pair which underwent nucleophilic attack by the solvent or hydrogen abstraction to yield the hydrocarbon. This was supported by irradiation in the presence of  $O_{2}$ .



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Thus trapping of the radical pair by  $0_2$  could favourably compete with electron transfer to the ion pair.

Since reactions at small ring bridgeheads are rare, slow, and usually inefficient, and since interchange of all halogen atoms had not been accomplished, the initial research reported in this thesis was concerned with developing an improved method of interconverting bridgehead halogen atoms. Special emphasis was placed on the isolation of iodides which might be photochemically induced to react to produce a variety of bridgehead substituted compounds in small bicyclic and tricyclic systems.

The irradiation of the diiodides would also be examined for any transient appearance of strained propellane type intermediates such as shown

below:



Finally, the photochemistry of bicyclic and tricyclic bridgehead chlorides, bromides, and iodides would be examined in order to determine if competing free radical and ionic type reaction pathways would be found as with the aromatic halogen compounds.

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#### RESULTS

In this section a brief account of the experimental results will be presented with little interpretation. A more complete analysis of the data will be found in the DISCUSSION section.

#### I Halogen Exchange

Since a recently published method of halogen exchange gave low yields of iodides<sup>52</sup>, the development of a milder but more efficient system was sought. The <u>in situ</u> generation of aluminum iodide from aluminum foil and elemental iodine in refluxing carbon disulfide was found to produce a very active catalyst which converted fluorides, chlorides and bromides to the corresponding iodide in high yield. Once the aluminum iodide was formed, the solution was cooled down to room temperature,  $0^{\circ}$ , or  $-50^{\circ}$ , depending upon the nature of the halogen compound. The substrate was then added and the exchange was complete within one minute. The same solvent was used to initiate bromine exchange as well; in this case the aluminum bromide was generated from aluminum foil and liquid bromine.

For chlorine exchange the aluminum chloride was generated from aluminum foil and gaseous chlorine in chloroform. Unfortunately, the use of carbon disulfide as solvent led to excellent yields of elemental sulfur, while the use of carbon tetrachloride as a solvent produced substantial amounts of hexachloroethane.

Primary, secondary and tertiary halides were all found to exchange readily while aromatic halides were inert under the reaction conditions. The structures of the halogenated adamantanes were verified by nmr analysis<sup>19</sup>.

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85%

CI<sub>6</sub>





93% ·Br J 78%



Rearrangement of secondary to tertiary positions was found to occur

slowly.



t = 5 hrratios:1 6 3 t = 22 hrratios:1 5 1

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<u>e</u>Br

Racemic 2-bromooctane was found to produce an 85% yield of the corresponding iodide. When (+)-2-bromooctane was used  $([\prec]_D = +29.4^{\circ}$  optical purity 66.5%) racemization was the major reaction pathway at room temperature; however, as the temperature was lowered the amount of inversion product increased as shown below.



Exchange of <u>cis</u> and <u>trans-4-t</u>-butylcyclohexyl chloride was also found to be temperature dependent; however, both isomers yielded the same <u>cis/trans</u> mixture of iodides at various temperatures as verified by nmr analysis<sup>152</sup>.



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The ease of the exchange reaction for bridgehead halides was found to follow the observed order for the solvolysis of bridgehead bromides<sup>26</sup>. That is, the adamantyl bridgehead exchange was extremely fast, the 1-norbornyl system very slow and the 1-bicyclooctyl intermediate in reactivity. A more detailed analysis of these results will appear in the DISCUSSION section.



This method of exchange using aluminum halide was compared to the use of ferric chloride in carbon disulfide. This ferric chloride reaction was found to be much slower and to require a large excess of Lewis acid to achieve complete chlorine exchange. Because of this relatively decreased activity, however, isolation of intermediate mixed halides was possible.





## II Photochemistry of Halides

## A) Photolysis of Bridgehead Halides in Alcohols

As found for the aromatic halides<sup>66, 66a</sup>, great differences in the type and ratio of products occurred for irradiation of bridgehead chlorides, bromides and iodides as shown below.



A comparison was made with the thermal reaction of 1-iodo and 1-bromoadamantane in refluxing methanol. After six hours the reactions were 35% and 10% completed and 90% and 60% completed after 24 hours. The photochemical reactions at approximately  $35^{\circ}$  C were completely finished after  $2\frac{1}{2}$  and 8 hours respectively. At room temperature 1-bromoadamantane showed no reaction after three weeks, while 1-iodoadamantane was 30% consumed.

Irradiation of di and triiodides gave good yields of the corresponding ethers. Irradiation of di- and tri-bromoadamantane on the other hand yielded mixtures of mono-, di- and trialkoxy adamantanes.



No 1,3-dehydroadamantane intermediates were detected, rather monitoring by glc indicated that a stepwise reaction was occurring. Workup of the photochemical reaction of dibromoadamantane in methanol before completion gave two intermediate bromo-adamantanes which reacted upon further irradiation to yield the observed products.



The same trends were found for the 1,4-diiodonorbornyl system, except that a higher percentage of hydrogen transfer relative to substitution by OCH<sub>3</sub> was observed.



When the reactions of the 1-haloadamantanes with methanol were repeated in the presence of  $0_2^{}$ , 1-adamantanol was produced at the expense



The reaction of adamantyl bromides could be stopped by the use of a Pyrex filter; iodides continued to react through Pyrex.

B) Production of Amides by the Photolysis of Bridgehead Halides in Alkyl Nitriles

With the use of alkyl nitriles as solvents, good yields of the corresponding alkyl amides were isolated. Here only the iodides were used; irradiation of the bromides also produced amides but at a much slower rate.

The bridge and bridgehead iodides reacted cleanly to yield the corresponding amides.



1,3-Diiodoadamantane reacted to yield the iodoamide which on further irradiation yielded the diamide with no trace of the monoamide.



The reaction of the norbornyl iodides produced a similar pattern, except that only the monoamide could be isolated.



In all cases it was found that the reaction was very slow and incomplete if extremely dry solvents were used. The best results were obtained by adding 2 - 3 drops of water to the solution of the iodide in the alkyl nitriles.

## C) Photolysis of Bridgehead Halides in Amine Solvents

The irradiation of 1-iodoadamantane in alcohols resulted in the formation of 1-alkoxyadamantanes. When the same reaction was repeated in

diethylamine solution, none of the product corresponding to reaction at nitrogen was observed. Instead, the reduction product adamantane predominated with a small amount of coupling to the carbon atom  $\ll$  to the nitrogen atom.  $\Lambda$ 



When the reaction was repeated in the presence of  $0_2$  the only compound isolated was 1-adamantanol i.e. the reduction pathway was being diverted by oxygen. Use of triethylamine or pyrrolidine as solvents led to the formation of adamantane in greater than 90% yield.

The addition of  $3,5-di-\underline{t}-butyl-4-hydroxytoluene$  (a free radical inhibitor) to the reaction in diethylamine and triethylamine slowed the reactions down and led to exclusive formation of adamantane.



However, irradiation in morpholine resulted in a 1:1 mixture of adamantane and the corresponding adamantylamine.



# D) Photolysis of Bridgehead Halides in Halogenated Solvents

The photochemistry of the four bridgehead monohaloadamantanes was examined in carbon tetrachloride and bromotrichloromethane. Irradiation in CCl<sub>4</sub> led to the formation of 4 main products plus substantial amounts of hexachloroethane.



The structures were assigned on the basis of nmr analysis and in the case of the <u>syn</u> and <u>anti</u>-1,4-dichlorides by comparison to authentic samples<sup>34</sup>. A more detailed description will be made in the <u>DISCUSSION</u> section.

In contrast, irradiation using BrCC1<sub>3</sub> as a solvent led to exclusive bromination of the bridgehead positions (longer reaction times eventually resulted in the formation of some secondary products).



Also there was no evidence for any hexachloroethane formation.

#### DISCUSSION

### A) Halogen Exchange

Since they are readily available, the brominated adamantanes were used as starting materials in the Lewis acid catalyzed exchanges of the other halogens. Reaction of adamantane and 1,3-dimethyladamantane in refluxing bromine for three hours<sup>15</sup> produced a near quantitative yield of the corresponding bridgehead monobromides. Due to the preferential formation of the bridgehead carbenium ion, no trace of any secondary isomers was observed.



The introduction of two or more bromine atoms required the presence of a Lewis acid catalyst<sup>73</sup>. Many different research groups have used various mixtures of co-catalysts to effect this substitution, but often with irreproduceable results<sup>22</sup>. It has been found that addition of very small amounts of "active" aluminum bromide<sup>74</sup> under carefully controlled conditions gave good yields of the higher brominated adamantanes.



The reaction most likely proceeds <u>via</u> the formation of the complex Br  $AlBr_4^{\textcircled{O}}$ . The positive bromine abstracts a hydride ion from adamantane to form the bridgehead carbenium ion which abstracts Br from the solvent to yield another bromine cation. Olah has found<sup>75</sup> that the 1-adamantyl cation is stabilized by interaction of the cation carbon with the back lobes of the other three bridgehead carbon atoms. Replacement by Br for H at these centers would decrease the size of the back lobes and lessen this stabilization effect. Thus further addition of bromine should be slower due to the decreased stability of the intermediate bridgehead carbenium ion. Consistent with this inductive effect is the experimental observation that the reaction to form the tetrabromide is very slow, requiring seven days in a sealed tube at  $170^{\circ}$ . Although the yield of 1,3,5,7-tetrabromoadamantane is low as a result of disproportionation reactions which lead to the formation of thick tars, the four 1-bromo, 1,3-di, 1,3,5-tri, and 1,3,5,7tetrabromoadamantanes were readily available and were used as the starting points for the halogen exchange studies.

The initial work was concerned with a mild method for the isolation of bridgehead iodides, for use in exchange and photolytic studies. Pincock and co-workers<sup>52</sup> had found that in halogenated solvents low yields of the iodides were obtained, side reactions leading to reduction and to polymerization predominated. This was probably due to the large excess (relative to substrate) of aluminum iodide present in the reaction mixture. Since it was desired that the exact amount of catalyst present be known, a nonhalogenated solvent, carbon disulfide, was chosen for further study. In this solvent the preparation of a solution of extremely active aluminum iodide was relatively facile.

Aluminum foil was torn into small pieces (with freshly washed and dried fingers) to expose fresh metal and placed with elemental iodine in a round bottomed flask. The flask was then heated at 80° for a few minutes to vapourize a few of the iodine crystals. At this point it was noted that dark specks were forming on the aluminum foil. The carbon disulfide was added and the purple solution was stirred under reflux for 45 minutes. At the end of this time the purple colour had been replaced by a light pink and most of the aluminum foil had been consumed. The solution of the active catalyst was then cooled down to room temperature and the brominated adamantane added.

It was soon found that an excess of aluminum foil was essential to the reaction. Excess iodine led to polymerization as the predominant pathway with low yields of the desired iodides. Initial studies with a 4:1 ratio of iodine to 1-bromoadamantane with an excess of aluminum foil led to rapid iodine exchange but upon standing at room temperature side reactions also occurred. After a great deal of time was spent testing reaction times and substrate ratios it was found that the best results were obtained utilizing an aluminum foil to iodine to 1-adamantyl bromide molar ratio of 4:0.75:1.0. The exchange was complete after 1 minute at room temperature and very little decomposition occurred upon standing at room temperature. It was later discovered that even better yields could be realized by running the reaction at  $-50^{\circ}$ . Here again the exchange was complete after 1 minute.

Thus it was found that this procedure produced a very active and mild iodine exchanging catalyst. For example, tetrabromoadamantane could be completely converted to the tetraiodide in 1 minute at room temperature, unlike the reaction using a halogenated solvent which required more forcing conditions<sup>52</sup>. This <u>in situ</u> generation of aluminum iodide was used to prepare

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all the possible adamantyl and 1,3-dimethyladamantyl bridgehead iodides.

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The method was extended to the exchange of other halogen atoms. As a result of these reactions, as described below, the 16 different mono, di, tri and tetrahaloadamantanes were made available. A study of the halogen effects on the  $^{13}$ C spectra of these molecules was made, the results of which will appear later on in this section.

Bromine exchange was not required as a result of the ease of synthesis of the brominated adamantanes. However, it was found that substitution of liquid bromine for elemental iodine in the above in situ generation of AlI<sub>3</sub> led to a solution of very active aluminum bromide. A halogen exchange reaction could then be performed to produce high yields of bromides from other halides. Preparation of the bromide catalyst was slightly different from that of the iodide. The aluminum foil and bromine were mixed with 2 ml of CS<sub>2</sub> and allowed to stand until the foil began blackening. (With no solvent present the exothermic reaction resulted in the evolution of large amounts of Br<sub>2</sub>). The rest of the solvent was added and the dark brown solution stirred under reflux for 1 hour which resulted in a light orange solution. This was cooled to room temperature and the bridgehead halide added as before.

Chlorine exchange was investigated by extending the reaction to the <u>in</u> <u>situ</u> generation of active aluminum chloride. Bubbling chlorine gas through a mixture of aluminum foil and  $CS_2$  at  $0^{\circ}$  led to a yellow solution. To this was added a small crystal of  $I_2$  in order to initiate an exothermic reaction which consumed most of the aluminum foil. Upon cooling to  $0^{\circ}$ , 1,3-dibromoadamantane was added and the reaction worked up after 2 minutes. Analysis of the solution by glc indicated that the desired exchange had occurred but upon evaporation a large amount of a dark yellow solid was isolated.

To establish what was taking place the reaction was repeated in the absence of the adamantyl dibromide. Again a yellow solid was obtained, which upon glc analysis at long retention times proved to be identical to elemental sulfur.

In order to eliminate this production of sulfur, the solvent system was changed from CS<sub>2</sub> to CCl<sub>4</sub>. The reaction was repeated under the same conditions with Cl<sub>2</sub> gas. A dark black solution was obtained to which the adamantyl dibromide was added. Workup this time again resulted in the isolation of a yellow solid. Repetition in the absence of the bromide again resulted in the same yellow solid which was shown to be identical to hexachloroethane.

Therefore, after major side reactions which successively oxidized the  $CS_2$  and radically coupled the  $CCl_4$ , it was decided to fall back upon the solvent used earlier<sup>5,2</sup>, i.e. chloroform. The use of  $Cl_2$  with aluminum foil in CHCl<sub>3</sub> generated a very active catalyst which produced chlorides in high yields at room temperature at a faster rate than observed for the AlCl<sub>3</sub> generated previously by Pincock and co-workers<sup>5,2</sup>. For example, the conversion of 1,3,5,7-tetrabromoadamantane to the tetrachloride was complete in 15 minutes at room temperature while the previous method required 20 hours.

For fluorine exchange AgF was used as reported earlier<sup>50</sup>. However, much better yields could be isolated by drying the silver fluoride under vacuum at 140<sup>°</sup> for 5 hours before use. This eliminated the formation of alcohols and resulted in 70 - 85% yields of the corresponding fluorides.

positions of any mono, di, tri or tetrahaloadamantane could be effected. Since

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the formation of iodides was to be used for the production of starting materials for photochemical studies, the iodine exchange reaction was studied further.

It was found that even the relatively inert C-F bond would react with this catalyst system to yield the corresponding iodide.



Next of interest was to determine if primary and secondary cyclic and acyclic halides could also be exchanged to the corresponding iodides without the elimination to olefins, rearrangement and/or polymerization which may proceed with these systems. Miller<sup>44</sup> has recently found a method of converting tertiary and benzylic chlorides to the corresponding iodides using NaI in carbon disulfide at room temperature with a trace of FeCl<sub>3</sub> as catalyst. The reaction proceeds in high yields but is quite slow ( 10 -72 hours). The heterogeneous reaction was thought to occur via a closely held complex or ion pair.

RC1 + FeCl<sub>3</sub> + I<sup>-</sup>  $\longrightarrow$   $R \stackrel{C1}{\underset{I}{\underset{I}{\atop}} FeCl_{3}$   $\stackrel{--}{\longrightarrow} RI + FeCl_{3} + CI<sup>-</sup>$ The reaction still proceeded using mercuric chloride in place of ferric chloride but failed completely if a soluble iodide (nBu<sub>4</sub>NI) was used. The use of AlCl<sub>3</sub> in place of FeCl<sub>3</sub> gave no exchange at all. Interestingly, the reaction failed completely for primary or secondary chlorides which easily react via the Finkelstein reaction<sup>39</sup>.

 $RCH_2C1 + NaI \longrightarrow RCH_2I + NaC1$ 

The use of aluminum iodide generated <u>in situ</u> was found to readily exchange primary and secondary halides. However, in most cases the observed

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yields were lower than for the tertiary halides.



Analysis of the product from the reaction of 1-chlorobutane by nmr showed no trace of any rearrangement products. The exchange on 2-bromooctane produced 2-iodooctane again with no observeable rearrangement. The reaction of optically active bromide was found to be temperature dependent. The exchange of (+)-2-bromooctane (obtained from Norse Chemical Co. $[\alpha]_D =$ 29.4° optical purity = 66.5%<sup>76</sup>) was performed at 4 different temperatures with the amount of optically active iodide increasing with decreasing temperature.



Even at low temperatures the major product arose via racemization with

15% due to inversion at  $-65^{\circ}$ . Complete racemization may imply that a free carbenium ion is present which may undergo attack by I<sup>-</sup> from either side or racemization may arise from repeated exchange without the presence of a carbenium ion.

A similar exchange on <u>cis</u> and <u>trans</u>  $4-\underline{t}$ -butylcyclohexyl chloride also yielded iodides, the ratio of which were temperature dependent. The same ratio (determined by nmr integration) of iodides was formed from either stereoisomeric chloride at various temperatures. This result suggested a common intermediate, likely a tightly held ion pair.



The reactions with the <u>t</u>-butyl cyclohexyl chlorides were worked up after 1 minute (analysis of the reaction at  $-55^{\circ}$  over a period of 1 hour indicated that the ratio of products did not change).

By using the above ratios at the various temperatures, the energetics of the cis-trans mixtures could be determined. From  $K = \frac{\text{equat I}}{\text{axial I}}$ 

$$\Delta G^{\circ} 298 = -0.55 \text{ kcal/mole}$$

and from a plot of log K versus 1/T the following values could be determined.

$$\triangle H = +2.34$$
 kcal/mole  
 $\triangle S = +9.98$  eu

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The value of  $\triangle G^{O}$  compares well with results found by other researchers as shown below:



 $X = CN \qquad \triangle G^{\circ} \ 339 = -0.25 \ \text{kcal/mole}^{77}$  $X = OH \qquad \triangle G^{\circ} \ 298 = -0.54 \ \text{kcal/mole}^{78}$  $X = CO_2 \text{Et} \qquad \triangle G^{\circ} \ 298 = -1.0 \ \text{kcal/mole}^{79}$ 

Therefore, for the iodides and the other cis-trans isomers the equatorial isomer is more stable at higher temperatures due to its greater degree of freedom ( $\Delta$ S overides the contribution by $\Delta$ H).

The above results from the optically active 2-octyl and <u>cis</u> and <u>trans</u> 4-<u>t</u>-butylcyclohexyl systems seemed to point to an ion-pair type intermediate rather than a free carbenium ion. Rearrangement as well as olefinic products could be expected if a free carbenium ion was involved.

This marked resistance to rearrangement was also observed with the exchange on the secondary position of adamantane. The exchange of 2-bromoadamantane at  $0^{\circ}$  led to a 95% yield of the corresponding secondary iodide. Stirring the solution at room temperature for 5 hours produced no change. However, refluxing the solution gradually led to the formation of the bridgehead isomer. A small amount of adamantane was observed as well as a trace of the 1,3-diiodide.



An increase in the concentration of the solution led to an increase in

the rate of the rearrangement. This is in accord with similar apparent 1,2-shifts in the adamantyl system.  $^{80}$ 

Direct intramolecular 1,2-shifts are believed to be strongly inhibited in these systems. For a facile exchange to occur a dihedral angle of  $0^{\circ}$ between the vacant p orbital and the C-R bond (R = migrating group) would be desired. In the adamantyl system the dihedral angle for the tertiary cation is  $60^{\circ}$  while for the secondary cation it is  $90^{\circ}$ .



Therefore these 1,2-shifts are thought to be intermolecular in nature. This is supported by work on the Koch-Haaf reaction<sup>80</sup> of 2-adamantanol. The ratio of tertiary to secondary product was found to be concentration dependent which is expected for an intermolecular process.



A similar concentration dependence was observed for the interconversion of 1- and 2-adamantanol in concentrated  $H_2SO_4^{\phantom{1}80}$ .

For the apparent 1,2-methyl shifts an intramolecular mechanism has been

found to exist<sup>81</sup>. Specifically labelled  $2-{}^{14}$ C adamantane was treated with AlBr<sub>3</sub> in CS<sub>2</sub> for 14 days at 25°. This led to 1.9% of carbon scrambling. However, treatment for 8 hours at 110° led to 78% scrambling as shown via the following mechanism.



A similar mechanism was found for the 2 to 1-methyladamantane interconversion<sup>82</sup>. In this case, however, the presence of the methyl groups enhanced the reactivity; the reaction was complete after 5 days at 25°.

The same type of rearrangement has been found for the biadamantane<sup>83</sup> system as well. Stirring a solution of either 1,1' or 2,2'-biadamantane<sup>84</sup> with  $AlBr_3$  in cyclohexane at 60<sup>°</sup> leads to the same mixture of three isomers at equilibrium.



This supports the calculated values of the strain energy for the 3  $biadamantanes^{85}$ .

Table II Strain Energy of Isomeric Biadamantanes

Strain Energy kcal/mole

21.46
19.70
23.04
6.87

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Similar complex mixtures have been observed from the Lewis acid catalyzed bromination of 1,1-biadamantane<sup>86</sup>. However, the products have not been fully characterized.

In spite of the possibility of this rearrangement, the reaction of  $\underline{\text{in situ}}$  generated AlCl<sub>3</sub> or AlI<sub>3</sub> with 3,3'-dibromo-1,1'-biadamantane produces the corresponding chloride and iodide with no rearrangement. The same is true for the silver fluoride promoted exchange.



Thus it was found that secondary and primary halides, as well as bridgehead halides, could be exchanged in high yields under very mild conditions. Aromatic halides were found to be inert under the reaction conditions. In systems prone to rearrangement or elimination (eg. cyclohexyl, 1-butyl, 2-octyl halides) the unrearranged products could easily be isolated.

The ease of the exchange was also found to parallel the expected relative stability of the corresponding bridgehead carbenium ion. The reaction of 1,4-dichlorobicyclo  $\begin{bmatrix} 2.2.1 \end{bmatrix}$  heptane to the diiodide proceeded in low yields (45%) and required 4 days in refluxing carbon disulfide (bp 46°). The large amount of polymeric material was due to the ten fold excess of aluminum iodide required to totally consume the starting material. A more rapid reaction was observed by the use of refluxing cyclohexane (bp 80°) as solvent. Here the diiodide was isolated in 74% yield after 12 hours. The iodine exchange on 1,4-dichlorobicyclo  $\begin{bmatrix} 2.2.2 \\ 2.2.2 \end{bmatrix}$  octane was found to be intermediate in rate between the norbornyl and adamantyl systems<sup>72</sup> as shown below.

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The ultimate test of this exchange method was on the very unreactive triptycenyl system shown below:



The attempted iodine exchange on 9-chlorotriptycene<sup>89</sup> failed in refluxing cyclohexane, decalin and para-xylene (3 fold excess of AlI<sub>3</sub>, solution stirred under reflux for 4 days). In all cases the 9-chlorotriptycene was recovered unchanged, the darkening of the solution in decalin and xylene was found to be due to reactions of the solvent with the aluminum iodide. No trace of the triptycenyl iodide or reduction to the parent hydrocarbon was observed. This confirms the estimate that the bridgehead position of triptycene would be at least 10<sup>9</sup> times less reactive than the bridgehead positions of bicyclo[2.2.2] octane<sup>2d</sup>.



The major reason for this extreme inertness is due to the non-flexible nature of the carbon skeleton. Theoretical work<sup>90</sup> has suggested that bridgehead carbenium ions do not reach planarity, instead an optimum geometry is achieved. This can be visualized by examining the bridgehead carbenium ion of adamantane<sup>26</sup>. The angle at the bridgehead would prefer to be  $120^{\circ}$ , (sp<sup>2</sup> hybridization) however as flattening at this position occurs the nonbridgehead angles decrease in size resulting in increased strain.



Figure I Relationship of Strain Energy versus Angle Size in 1-Adamantyl Cation

N.R.



For  $\theta$  to be  $120^{\circ} \phi$  would have to decrease to  $90^{\circ}$  from  $109.5^{\circ}$ ; if no flattening occurred  $\theta$  would be  $109.5^{\circ}$  as would  $\phi$ . Therefore a certain amount of bending could occur to make  $\theta = 113^{\circ}$  and  $\phi = 104^{\circ}$  for an optimum geometry of lowest strain energy. It is therefore clear that in systems where the molecule is less flexible the carbenium ion will not be as stable and less likely to form. The triptycene system may be considered by examining the x-ray data.



 $= 105.3^{\circ}$ 

X = H

X = Br  $\theta = 107.5^{\circ}$   $\phi = 110.7^{\circ}$  ref<sup>92</sup> Now if one assumes the values for X = C1 to be between those for X = H and X = Br it is apparent that if flattening of the bridgehead occurs to make  $\theta$  approach 120° then  $\phi$  must also approach 90°. However, unlike the adamantane case,  $\phi$  for the triptycenyl system would prefer to be 120° (since it is at an sp<sup>2</sup> hybridized carbon atom). Any flattening of the bridgehead will increase the overall strain energy by decreasing the value of  $\phi$  further away from its normal value of 120°. Therefore a consideration of angle strain alone suggests that the 9-triptycenyl carbenium ion would be very unstable and reluctant to form.

 $= 113.1^{\circ}$ 

ref<sup>91</sup>

The bicyclo [2.2.2] octyl system is not as strained and will permit a bridgehead carbenium ion more readily<sup>93</sup>.



This unreactiveness of the 9-triptycenyl system now leads to a more detailed examination of the mechanism by which this aluminum halide promoted exchange takes place.

Miller's proposal<sup>44</sup> of a loose complex of the Lewis acid and the substrate (see page 42) appears reasonable except that for the aluminum halide reactions there will be no free I<sup>-</sup> available as a result of the excess aluminum foil present. Miller also found that AlX<sub>3</sub> did not react in his system. However, if we consider initial front side attack by the aluminum halide, a loose complex will result.

$$R - X + Ali_{3} \xrightarrow{rapid} R \xrightarrow{X} Ali_{2} \text{ or } RX \cdots Ali_{3}$$

$$R - I + Ali_{2}X \xrightarrow{rapid} R^{+} Ali_{3}X^{-}$$

This loose complex could exist in equilibrium with a tightly held ion pair composed of the bridgehead carbenium ion plus the aluminum halide anion. The concentration of this ion pair at any one time would probably be quite small but once formed would rapidly abstract an iodide ion to produce the bridgehead iodide (or other halide depending upon which Lewis acid was being used). This tightly held ion pair would also explain why at room temperature no rearrangement of the 2-iodoadamantane (secondary iodide) to 1-iodoadamantane (bridgehead iodide) occurs and why elimination to olefins in other systems is minimized. Higher temperatures are required for the equilibration of products and for any intermolecular rearrangement of the product, possibly through more fully formed carbenium ions.

The difference in rates of the adamantyl, bicyclo[2.2.1] heptyl, bicyclo[2.2.2] octyl and triptycenyl systems (see page 49) also support the above mechanistic analysis. A faster overall reaction would result from the intermediary of a relatively stable carbenium ion pair. The relative rates of the exchange are in the same order as the rates of the solvolysis of the bridgehead bromides (see page 2 of INTRODUCTION).

However, a full carbenium ion intermediate is not likely because of the lack of rearrangement or elimination products as shown before. Also informative are the results of extended reaction times on the 1,4-dihalobicyclo[2.2.2] octane system. In this case rearrangement of the ring system does occur to yield mixtures of bicyclo[3.2.1] octyl and bicyclo[2.2.2] octyl

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The above is contrary to the results found by  $01ah^{94}$  from the reaction of 1-chlorobicyclo[2.2.2] octane in SbF<sub>5</sub> - SO<sub>2</sub>ClF at -78°. Reaction occurred instantly to form the bicyclo[3.3.0]-1-octyl cation.



The super acid results would tend to suggest that free carbenium ions are not involved in the Lewis acid promoted halogen exchanges. The extended reaction times were also used in an attempt to rearrange the bicyclo[2.2.1] heptyl to the bicyclo[3.1.1] heptyl system but without success. The rearrangement of the bicyclooctyl and not the bicyclo heptyl are indirectly supported by theoretical calculations on the parent hydrocarbons by Schleyer and co-workers<sup>85</sup>.

Table III	Strain	Energy	of	Bicyclic	Systems
	Compour	nd			
		•	•		

A





16.98

Strain Energy kcal/mole

12.95

12.06

12.49

35.85

In addition to the difference in carbenium ion stabilities, the effect of Lewis acidity on the exchange reaction was also examined. One would expect aluminum halides to be better reagents as a result of their greater Lewis acid strength<sup>164</sup> relative to ferric halides. However in Miller's study<sup>44</sup> AlCl<sub>3</sub> was ineffective as compared to FeCl<sub>3</sub>. A comparison of the two procedures indicates that the <u>in situ</u> generated AlI<sub>3</sub> is much more reactive.

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As a complement to the above, a study was made of the ability of FeCl<sub>3</sub> versus <u>in situ</u> generated AlCl<sub>3</sub> to promote exchange of bromine for chlorine. It was found that FeCl<sub>3</sub> was effective but that both a large excess of the Lewis acid and longer reaction times were required.





t=15min



Refluxing conditions were required to achieve complete exchange with FeCl<sub>3</sub>. One advantage, however, is that room temperature reactions allowed the isolation of mixed halide species.



Therefore it appeared that the strengths of the respective Lewis acids also affected the rate of the reaction, the weaker FeCl<sub>3</sub> requiring a longer time to achieve complete exchange.

With either FeX<sub>3</sub> or AlX<sub>3</sub> the same general mechanism should apply for the exchange of the bridgehead halides. In the case of the bridge substituted isomers one might consider backside attack a likely possibility. However, the reaction at the secondary carbon of adamantane by nucleophilic backside attack has been found to be relatively unimportant due to significant nonbonded interactions with the axial hydrogen atoms as shown below:



Whiting has found  $^{95}$  that  $S_N^2$  type reactions do not occur and the following tosylates solvolyze with excess retention over inversion.



Elegant studies by Schleyer<sup>96</sup> and co-workers have further indicated that solvolysis of 2-substituted adamantanes does not involve nucleophilic attack. Adamantanes substituted in the 2 position solvolyze in much the same fashion as the bridgehead isomers and completely differently from usual secondary compounds. The most convincing evidence on this point has been presented in a study of solvolysis in the presence of azide ion. When the addition of  $N_3^-$  causes a rate enhancement and a corresponding alteration in the distribution of products a bimolecular ( $S_N$ 2) type reaction may be suspected<sup>97</sup>.

Schleyer and co-workers have investigated the effect of azide ion on the solvolysis of 3 alkyl derivatives  $^{98}$  in 80% aqueous ethanol.

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		·,	·	% Yields		
Substrate	NaN <sub>3</sub>	$k \ge 10^5 \text{ sec}^{-1}$	RN3	ROH	ROEt	
1-adamanty1	0.00	12.6	0.0	49	51	•
bromide	0.02	13.0	0.4	41	58	
0.01M	0.04	13.2	0.4	45	54	
75 <sup>0</sup>	0.06	14.2	0.6	43	56	
2-adamantyl	0,00	1.94	0.0	71	29	•
tosylate	0.02	2.10	0.1	68	31	
0.01M	0.04	2.17	0.4	66	33	•
75 <sup>0</sup>	0.06	2.26	0.7	65	34 .	
2-propvl	0.00	5.75	0	10	0	•
tosvlate	0.02	8.27	31	6	9	•
0.01M	0.04	12.5	54	4	6	
50 <sup>0</sup>	0.06	16.9	65	3.	5	

Table IV Effect of Added Azide on the Rate of Solvolysis

Thus the 1 and 2-adamantyl compounds solvolyze in the same way with and without azide ion. Very little adamantyl azide is formed and only a small increase in the rate of reaction is observed. The "normal" secondary derivative reacts completely differently which one would expect for an  $S_{\nu}^{2}$  type solvolysis. Therefore, the halogen exchange reaction should also proceed <u>via</u> the same pathway for both bridgehead and bridge halogens of the adamantane ring structure.

As a result of the steric inhibition of backside attack at the secondary positions of adamantane it was anticipated that various secondary and mixed tertiary and secondary adamantyl halides could be selectively exchanged. The 1,2-adamantyl dichloride was cleanly converted to the dibromide and diiodide with no trace of any of the other isomers.

X=Br

The same reaction was repeated for the gem dichloride. In this case rearrangement was the major pathway. At low temperatures the reaction could be quenched to yield two dibromides easily separated by glc.



The minor component was found to be the unrearranged gem dibromide, the major being the <u>syn</u>-1,4-dibromide (a small amount of the corresponding <u>anti</u> isomer was also present). The <u>syn</u> dibromide was collected by glc and assigned on the basis of melting point and nmr chemical shifts<sup>99</sup>.

When the reaction was repeated under iodine exchange conditions at low temperatures two products were again observed by glc. However, the gem diiodide could not be isolated. Upon preparative tlc or column chromatography only adamantanone plus a small amount of 2-iodoadamantane was obtained.



The major product from the reaction was identified as <u>syn</u>-1,4-diiodoadamantane on the basis of its similar nmr to the <u>syn</u>-1,4-dichloride and <u>syn</u>-1,4-dibromide (see nmr DISCUSSION section).

In this case there was no trace of any of the <u>anti-1,4</u> isomer by glc or nmr analysis. When the reaction was repeated at room temperature a 70% yield of the syn-1,4-diiodide was realized.

The corresponding chlorine exchange on the gem dibromide was also examined. In this case an 87% yield of the 1,4-dichlorides was observed. The product consisted of 81% <u>syn</u> and 19% <u>anti</u> by nmr. Interestingly when this mixture was treated under iodine exchanging conditions a 74% yield of <u>syn-1,4-diiodoadamantane</u> was observed with no trace of the <u>anti</u> isomer by nmr or glc analysis.



This preferential formation of the  $\underline{syn}-1,4$  isomer has also been found by Geluk who treated a mixture of the 1,4 diols with  $\underline{SOCl}_2^{100}$ .



This is in spite of the fact that one would expect that the anti isomer (diequatorial) would be the more stable and therefore the major product. McKervey<sup>34</sup> has also found that the gem dichloride will rearrange in the presence of AlCl<sub>3</sub> to yield the <u>syn</u> isomer as the major product.

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However, Yang<sup>99</sup> has found that the <u>syn</u> isomer will slowly rearrange to the <u>anti</u> isomer in the presence of AlCl<sub>3</sub> in  $CS_2$ .



Therefore even though the <u>syn</u> isomer appears to be the less stable it is the major product in all the above halogen exchange reactions.

As can be seen from the above discussion the aluminum halide promoted halogen exchange is a general reaction for primary, secondary and tertiary halides. Even very unreactive small ring bridgehead halides will react by use of a higher boiling solvent. The procedure is very mild and proceeds in high yields. Aromatic halides are inert to the reaction conditions.

# B) Photochemistry of Bridgehead Halides

The ultraviolet spectra<sup>101</sup> of a series of alkyl halides indicate that bromides absorb at around 200 - 220 nm and iodides at 240 - 260 nm with molar extinction coefficients from 2 - 7 x  $10^2$ . This absorption is due to the  $n \rightarrow \sigma$  \* transition of the halogen atom. Chlorides were found to absorb below 200 nm. Introduction of a second halogen on the same atom was found to move  $\lambda$  max to longer wavelengths and increase  $\varepsilon$  by a factor of 2 - 3. For studies of the synthetic possibilities of photochemical substitutions of halogenated adamantanes it was desireable to obtain the uv spectra of a

<u>Table V</u> I	Jltraviolet Spect	ra of Adamanty	1 Halides
Compound	<u>M 10<sup>-4</sup></u>	Solvent	<u>λ max nm</u>
1-AdI	2.48	снзон	263
2-AdI	3.34	снзон	257
1,3-AdI,	1.69	СНЗОН	267
1,3-AdI,	4.38	CH <sub>2</sub> C1 <sub>2</sub>	266
1,2-AdI2	3.72	CH <sub>2</sub> C1 <sub>2</sub>	267
syn 1,4-Ad	1.59	снзон	260
syn 1,4-Ad	2.70	CH <sub>2</sub> C1 <sub>2</sub>	260
1-C1, 3-IA	2.16	снзон	265
Me,AdI	3.38	снзон	264
Me,AdI,	1.41	СНЗОН	266
1-Ad-Ad-I	1.15	СНЗОН	264
AdIa	1.30	снзон	271
AdI	2.88	CH <sub>2</sub> C1 <sub>2</sub>	272
AdI,	2.28	CH2C12	280

series of adamantyl halides.

2,2-AdBr,

AdBr,

From the above table it may be seen that the  $\varepsilon$  values are 5 - 10 times as large for an ordinary alkyl halide. Introduction of additional iodine atoms moves the  $\lambda$  max to longer wavelengths with an increase in the extinction coefficient. Adamantyl bromides absorb at very low wavelengths, the tetrabromide at 208 nm.

снзон

ch<sub>3</sub>cn

CH3OH

7.28

0.37

3.46

240

208

259

1) Photolysis of Adamantyl Halides in Alcohol Solvents

The initial study of the photochemical reaction of halides using alcohols as solvents indicated the absorption of light energy resulted in a very rapid reaction compared with simple solvolysis. A comparison of the thermal and photochemical results is shown below.

<u>ε 10</u>3

1.29 1.11 2.25 2.47 1.45 1.89 1.93 1.11 1.18 2.62 2.78 3.39 3.58 4.82

1.02

4.60

1.71



Method	Time	Conversion
$hv = 35^{\circ}$	2½ hours	100%
thermal (reflux)	6 hours	35%
thermal (reflux)	24 hours	90%
thermal 25°	3 weeks	30%

The same reaction for 1-bromoadamantane was 100% complete after 8 hours photochemically and only 60% complete after refluxing in methanol for 24 hours.

Initial excitation of the C-X bond would lead to promotion of an n electron to the  $\sigma^*$  antibonding orbital of the halogen atom. This excited halide could then undergo homolytic cleavage to a radical pair or heterolytic cleavage to an ion pair as shown below:



Hydrogen abstraction by the bridgehead radical would yield adamantane while nucleophilic attack by the alcohol solvent on the bridgehead carbenium ion would yield the adamantyl ether. This duality of reaction pathways is exemplified below:


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The irradiation of the bromide gave a larger amount of the product derived from hydrogen atom transfer from the solvent (presumably a free radical pathway). The iodide gave excellent yields of the nucleophilic type product (carbenium ion pathway). The irradiation of 1-iodoadamantane in alcohols proved to be a rapid general method of producing high yields of the corresponding alkoxyadamantane. (In all cases < 5% of adamantane was observed)



X = I

 $\begin{array}{l} \texttt{R} = \texttt{Me, Et, NPr, iPr, nBu, iBu} \\ -\texttt{CH}_2\texttt{CH}_2\texttt{OH}, -\texttt{CH}_2\texttt{CH}_2\texttt{OCH}_3 \end{array}$ 

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 $t = 2\frac{1}{2}$  hours

The only alcohol tried which did not yield the desired ether was  $\underline{t}$  - butanol. In that case the only product isolated was 1-adamantanol.



Other reports<sup>102</sup> have stated the difficulty in preparing <u>t</u>-butoxyadamantane, presumably due to the facile loss of the <u>t</u>-butyl cation leading to 1-adamantanol.

The irradiation of 2-iodoadamantane in methanol also produced the corresponding secondary methyl ether with no trace of the rearranged bridgehead ion. Thus the bridge carbenium ion was not sufficiently longlived to undergo rearrangement to the tertiary cation.



The 1,3-adamantyl dihalides also underwent reaction in alcohols as shown below:



As with the monohalides the diiodide reacted almost exclusively via a carbenium ion type pathway and the dibromide via the free radical pathway as well as the cationic one. The dichloride yielded only a reduction product with no trace of any nucleophilic type products at all. As the strength of the carbon-halogen bond increases, the amount of reduction products increases as well.

Pinhey<sup>68</sup> has observed the reverse trend in a study of the irradiation of <u>meta</u> halogen substituted phenols in alcoholic solution. The results



He attributed the change to the fact that before nucleophilic attack by ROH could occur, the excited state would have to develop appreciable charge separation. If the carbon halogen bond energy is high then this charged pathway can compete favourable with homolytic cleavage. However, with the weaker carbon-iodine bond, homolytic cleavage leading to the free radicals would predominate yielding reduction products.

With the adamantyl halides the rate of the reaction to form the ion pair or carbenium ion appears to be faster than the homolytic cleavage. Therefore, with the weak carbon-iodine bond the majority of the reaction is via heterolytic cleavage.

The isolation of 1-methoxyadamantane from the irradiation of 1,3-dibromoadamantane at first suggested the possible intermediacy of dehydroadamantane which was then attacked by a molecule of solvent.



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However, monitoring the reaction by glc indicated than no dehydroadamantane was present<sup>103</sup>. Instead a stepwise reaction was occurring, substantiated by the isolation of two brominated intermediates which disappeared upon further irradiation.



Workup of the reaction before completion allowed the isolation of these two intermediates by column chromatography and preparative glc.

The same two competing reaction pathways were observed for the irradiation of 1,3,5-trihaloadamantanes.



The 1,3,5,7-tetrahalides were not examined because of their extremely low solubility in alcohols.

The competition between carbenium ion and free radical pathways was also supported by 0<sub>2</sub> studies. Irradiation in the presence of 0<sub>2</sub> (a good radical trapping agent) led to the production of bridgehead alcohols in place of products previously formed by hydrogen atom transfer from the solvent.

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The cationic pathway was relatively unaffected by the  $0_2$ , only the free radical pathway could be trapped. The intermediate hydroperoxide (X = 00H) would be reduced to the corresponding alcohol upon workup. Kropp<sup>71</sup> has also observed this trapping by  $0_2$  in the study of the 1-halo-bicyclo [2.2.1] heptyl system. However, in this case more of the cationic pathway was affected by the presence of  $0_2$ .



The isolation of the reduction product in the presence of  $0_2$  was suggested to occur <u>via</u> nucleophilic attack by solvent on the excited state to form the bridgehead carbanion which led to the reduction product.



This pathway was found to yield norbornane with 18% D incorporated at the bridgehead. Thus the carbanion was a minor path in the production of the hydrocarbon.

The same irradiation using CH<sub>3</sub>OD as solvent was performed using 1-bromoadamantane. Isolation of the adamantane produced and study by mass spectrometry indicated that only a 3% incorporation of D had taken place. This result suggests that with 1-bromoadamantane only a very small amount of the bridgehead carbanion pathway is involved. This reluctance of forming the bridgehead carbanion of adamantane has been found by other workers as well<sup>104</sup>.

Two cases were discovered where the contribution of the free radical pathway was enhanced. Irradiation of either 1-iodo or 1-bromoadamantane in methanol with added NaCN led to an increase in the amount of adamantane formed. This was probably due to increased electron transfer by CN<sup>-</sup>.



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The irradiation of 1-bromo-3-chloroadamantane also yielded a relatively large amount of free radical product.



Irradiation of the iodo-chloride produced the chloroether with no trace of 1-chloroadamantane.

Since little or no radical derived products (reduction to adamantane) are found in the photolysis of mono, di and triiodides, the reactions occur almost exclusively via the carbenium ion pathway. The norbornyl system studied by Kropp<sup>71</sup> cannot support a positive charge at the bridgeheads as readily as the adamantyl system<sup>2c</sup>, so that more free radical nature is expected and found here for the iodides. To further support this fact the irradiation of the 1,4-diiodide was studied.



Further irradiation yielded the two ethers with the diether as the major product. The same reaction was studied in CH<sub>3</sub>OD which resulted in a 17% incorporation of deuterium at the bridgehead of the monoether. Thus with two iodines there is still a significant contribution by the carbanion pathway. In the norbornyl system the major path is still cationic but with more free radical contribution than with the adamantyl system.

Later studies indicated that the 1-bromoadamantane reaction could be

quenched by the use of a Pyrex filter; however, 1-iodoadamantane continued to react. The reason for this may be seen from the following graph and the fact that Pyrex stops any light with a wayelength shorter than 275 nm. Figure II Ultraviolet Spectra of Bridgehead Adamantyl Iodides



The  $\lambda$  max for the adamantyl bromides is at very short wavelengths, the value for 1,3,5,7-tetrabromoadamantane is 208 nm. Thus in using a Pyrex filter no excitation of the C-Br bond may occur. However, the iodides absorb above 275 nm so that they continue to react through Pyrex.

Since the photochemistry of halides is divided into two paths (ionic and free radical) at some early stage of reaction, a discussion of the various pathways of photoexcitation seems in order. The photochemical promotion of electrons is schematically represented in the following diagram<sup>105</sup>. Figure III Jablonski Diagram for Excited States



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Initially one has a solution of a compound in its ground state which is being irradiated by ultraviolet radiation. Absorption of a photon results in the excitation of an electron <u>via</u> a symmetry-allowed transition to the first singlet excited state  $S_i$ . This may be due to a  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ , or  $n \rightarrow \sigma^*$  depending upon the type of chromophore in the molecule. Once in  $S_i$  the excited state may follow three possible paths. Path b represents fluorescence i.e. a return to the ground state with the release of energy in the form of ultraviolet radiation. Path c is a radiationless deactivation to the ground state, the energy appearing in the form of heat. The third possibility is known as intersystem crossing (path d) to the upper vibrational levels of the first triplet excited state. Collisions with the surroundings reduce the state to its lowest vibrational level (path f). The T<sub>i</sub> state also has a radiative deactivation to the ground state (phosphorescence) (path h) and a nonradiative pathway (path g).

The T<sub>1</sub> state is lower in energy than S<sub>1</sub>. Since the electron in T<sub>1</sub> and the ground state have parallel spins they may not occupy the same space at the same time (Pauli principle) and therefore electron-electron repulsion is reduced relative to the S<sub>1</sub> state. Direct excitation to T<sub>1</sub> is symmetry forbidden so that once formed it is rather long lived compared to S<sub>1</sub> which has an allowed deactivation pathway (fluorescence path b). The radiationless pathways c and g are normally quite slow compared to the other possible paths. The relative population of the T<sub>1</sub> state depends upon the rate of intersystem crossing (path d). Spin-orbital coupling is required to "mix" the S<sub>1</sub> and T<sub>1</sub> states to some extent for crossing to occur. This coupling is greatest when one of the electrons involved in the transition is in an orbital close to a heavy atom such as N, O or halogen. This enhancement of





An increase in the size of the heavy atom has three effects on  $S_1$  and  $T_1$ . First a greater population of  $T_1$  would result due to a greater rate of inter-system crossing. Secondly, a greater yield of phosphorescence (path h) relative to fluorescence (path b) should be observed as a consequence of the greater population of  $T_1$ , and finally the lifetime of  $T_1$  should decrease since the fluorescence would be more "allowed" as a result of the greater spin-orbital coupling. The third result may be illustrated by the following table of phosphorescence ( $T_1$ .) lifetimes and the rate constants for intersystem crossing from  $S_1$  to  $T_1$  (solvent is a mixture of ethanol, isopentane and ether) for some halogenated naphthalenes.

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Table VI Triplet Lifetimes and the Rate of Intersystem Crossing

		к <b>S</b> — т <sup>105</sup>	lifetime <sup>107</sup> (sec)
×	X = H	$1 \times 10^{6}$	2.5
$\sim$	F	$5 \times 10^{5}$	1.4
	C1	$5 \times 10^{7}$	$2.3 \times 10^{-1}$
$\checkmark\checkmark$	Br	$2 \times 10^9$	$1.4 \times 10^{-2}$
	I	$3 \times 10^{10}$	$2.3 \times 10^{-3}$

Therefore it may easily be seen that an iodine atom promotes very efficient and rapid intersystem crossing with a bromine, chlorine and fluorine atom progressively less effective. The lifetimes of the T<sub>1</sub> states decrease as the size of the halogen increases. However, the lifetime of the S<sub>1</sub> state is exceedingly short ( $t = 10^{-6}$  to  $10^{-9}$  sec) so that in most systems the T<sub>1</sub> state has the greatest probability of undergoing chemical reaction.

With all the above discussion in mind the photochemistry of the bridgehead halogen compounds may be examined more closely. A possible mechanism for the reaction would be as follows. The initial excitation of an n electron on the halogen atom would lead to the S, state. Intersystem crossing as a result of the heavy atom effect would lead to a T, state, the population of which would be greatest for the iodides relative to bromides and chlorides.

The intermediary of triplet states in the irradiation of 1-iodoadamantane was demonstrated by quenching studies with 1,3-pentadiene. A methanol solution of a 20:1 molar ratio mixture of 1,3-pentadiene and 1-iodoadamantane was irradiated through pyrex. The time required for complete reaction was 11 hours. In the absence of the 1,3-pentadiene the reaction was complete after  $2\frac{1}{2}$  hours. Normally when T<sub>1</sub> states are produced they persist long enough to undergo phosphorescence or inter and/or intramolecular reaction. However, in the presence of a molecule which has a triplet energy less than that of the substrate T<sub>1</sub> then energy transfer may occur to form the triplet state of the quencher and return the substrate triplet to its ground state. The choice of filters should be such that only the substrate absorbs energy.

Therefore in the reaction of 1-iodoadamantane the 1,3-pentadiene quenches the T<sub>1</sub> state and slows the reaction of the adamantyl iodide down. The reaction does not stop since the concentration of methanol is much greater than that of the quencher so that eventually all of the adamantyl iodide reacts with the solvent to form 1-methoxyadamantane. 1,3-Pentadiene has an E<sub>T</sub> of 53 kcal/mole so that the E<sub>T</sub> of 1-iodoadamantane must be above this value.

Sensitization is the reverse process of quenching. A molecule which absorbs energy with fast intersystem crossing to form a  $T_i$  state is used to transfer energy to the  $T_i$  state of the substrate. Here only the sensitizer should absorb energy so that direct excitation of the substrate does not occur. The  $T_i$  state of the sensitizer should also be of higher energy than the  $T_i$  state of the substrate for efficient energy transfer to take place.

Sensitization studies were performed on 1-bromoadamantane in methanol with a 5-6 to 1 ratio of sensitizer to adamantyl bromide. There was no reaction after 24 hours irradiation through Pyrex with any of the sensitizers used. The compounds and their  $E_{T}$  values are shown below<sup>108</sup>.

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m · 1· 3 · · · · · · · · ·

## Table VII Triplet Energies of Various Sensitizers

Sensitizer	E <sub><b>T</b> kcal/mole</sub>
benzene	80
acetophenone	73.6
benzophenone	68.5
fluorene	67.6
phenanthrene	66.6
anthracene	60.9
l-naphthaldehyde	59.5

Rather than adamantyl bromide, the adamantyl iodide would have been a better model to study but unfortunately the molecule continued to react through all filters tried so that sensitization studies were not possible.

Therefore it could not be conclusively established that triplet states were responsible for the reactions of the adamantyl halides in alcoholic solution but they were strongly suspected. Promotion of an n electron to the  $\sigma$  \* orbital would result in decreased stability of the carbon halogen bond. At the wavelength of absorption there is more than enough energy available for cleavage of the C-X bond as shown below<sup>109</sup>.

Table VIII Energy Conversion Table<sup>105</sup>

Table IX Average Carbon-Halogen

λ		$(\mathbf{F}_{2} - \mathbf{F}_{1})$		bond Scrength				
A°	1	kcal/mole	eV	Bond	Bond Energy			
2,000 2,500 3,000	50,000 40,000 33,333 28,571	143.0 114.4 95.3	6.20 4.96 4.13 2.54	C-F C-C1 C-Br C-I	116 kcal/mole 78 68 51			

Once in the long lived (relative to  $S_1$ )  $T_1$  state bond cleavage could occur to yield either an ion pair or radical pair. The decreased reactivity of the adamantyl chlorides and bromides may be explained by the slower rates of intersystem crossing to the  $T_1$  states and also the fact that the  $\lambda$  max for these compounds lie below 200 nm. The major portion of the energy given off by the high pressure mercury lamp is above 240 nm so that a longer time would be required to populate the T, states of these bridgehead halides.

Another possibility exists, however, which has not been eliminated. The free radical and carbenium ion products may arise from the two different excited states. For 1-iodoadamantane the rate of formation of T, may be so fast that only a small amount of free radical product (derived from reaction of S,) results. With 1-bromoadamantane the slower rate of intersystem crossing may allow for more radical products derived from S<sub>1</sub>. A great deal more work remains to be done to determine the exact mechanism by which these excited states undergo reaction.

As a result of the nearly exclusive formation of carbenium ion type products from the irradiation of bridgehead iodides other solvents were tried to determine if other nucleophilic type products could be isolated.

# 2) Irradiation of Bridgehead Halides in Alkyl Nitrile Solvents

A photochemical reaction of adamantyl bromides and iodides with nitriles was discovered by accident during an attempt to photochemically synthesize 1-cyanoadamantane. Irradiation of a solution of 1-iodoadamantane and sodium cyanide in DMSO yielded 88% adamantanol and 8% cyanoadamantane (reaction in the absence of NaCN yielded 1-adamantanol exclusively). Therefore, CH<sub>3</sub>CN was tried as another solvent to dissolve both the iodide and sodium cyanide. Irradiation through quartz for 24 hours yielded a yellow solid which contained a strong carbonyl in the infra-red. The purified compound was shown to be 1-acetamidoadamantane. It was thought to be formed <u>via</u> the following mechanism;



The initially formed bridgehead carbenium ion was attacked by a solvent molecule to yield the nitrilium cation which was rapidly attacked by water to form the observed amide. When carefully dried CH<sub>3</sub>CN was used, the reaction was found to be very slow and incomplete. The best results were obtained by the addition of 2 drops of water to the acetonitrile solution of the iodide. The reaction of 1-bromoadamantane was found to be very slow relative to the iodide.

The reaction was shown to be applicable to other nitriles and proceeded in good yields.



This mild reaction was in marked contrast to the strongly acidic conditions required for the Ritter reaction<sup>110</sup>.



Good yields were also found by Miller for the aniodic reaction of substituted adamantanes<sup>111</sup>.



Vincent has also used the aniodic reaction to produce 2-substituted amides<sup>112</sup>.



The above two methods are well known to proceed <u>via</u> intermediate carbenium ions so that the photochemical amide formation probably involves them as well.

Irradiation of 1,3-diiodoadamantane was found to lead to the formation of the diamide <u>via</u> the easily isolated iodo-amide intermediate. No trace of the monoamide was observed.



Interestingly the same reaction worked for <u>exo</u>-2-iodonorbornane to produce the corresponding secondary amides.



The irradiation of 1,4-diiodonorbornane led to the formation of two products.



Irradiation of the purified iodo-amide led to the formation of the bridgehead mono amide with no evidence for any of the diamide product. Unlike the adamantyl case the norbornyl iodoamide reacted exclusively <u>via</u> a free radical type mechanism to lead to only the reduction product.

## 3) Irradiation of Bridgehead Halides in Amine Solvents

It was initially hoped that due to the tendency of adamantyl iodides to undergo photochemical cationic pathways that irradiation in various amines would lead to adamantylamines. However, irradiation in diethylamine led to a rapid consumption of starting material with the formation of two free radical derived products.



Repetition of the reaction with 0<sub>2</sub> bubbling through the solution led to the formation of 1-adamantanol exclusively. Thus only a free radical pathway exists for the iodide in diethylamine. When the free radical trapping agent 3,5-di-t-buty1-4-hydroxytoluene was added to the solution the only product isolated was adamantane, and the reaction required 9 hours to go to completion.

A solution of adamantyl iodide in triethylamine yielded adamantane (88%) plus the HI salt of the solvent after 15 minutes of irradiation. In the presence of 3,5-di-t-butyl-4-hydroxytoluene the reaction required 6 hours for completion. The same result was observed with pyrrolidine as

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solvent; the only product was adamantane. This same reductive behaviour has also been observed for the irradiation of halogenated anthracenes with alkyl amines<sup>113</sup>.

In morpholine, however, a 1;1 ratio of free radical and carbenium ion type product were observed.



The bridgehead amine was identical to that produced by the solvolysis of 1-adamantyl iodide in reluxing morpholine for 60 hours.

Again, as with the reactions in alcohols, two explanations may be used for the experimental results. The free radical reaction may result from the S, state which is rapidly trapped by a solvent molecule. On the other hand, if the bridgehead adamantyl radical is formed from the T, state, specific solvent interaction may favour its formation relative to when ROH was the solvent and carbenium ion products predominated. The speed of the reaction in  $\text{Et}_3N$  suggests that trapping of the bridgehead radical occurs almost immediately before any significant amount of carbenium ion can be formed.

The excited state produced in morpholine may be more solvated than in the other alkyl amines so that both the adamantyl cation and free radical are formed. A comparison of the relative rates of reaction for the following three reactions is very interesting:



As the solvent polarity increases (dielectic constant =/4), the time of the reaction increases as well as the relative amount of carbenium ion type products. This suggests that whatever the excited state is, that solvation effects appear to be important and that the competition between free radical and carbenium ion pathways may be controlled by the choice of solvents.

### 4) Irradiation of Bridgehead Halides in Halogenated Solvents

In contrast to ionic reactions of adamantane, free radical substitution occurs at both bridge and bridgehead positions. Photochemical chlorination of adamantane<sup>53</sup> with  $Cl_2$  in various solvents led to mixtures of 1 and 2-chloroadamantane. However, a "fair degree" of polychlorination was found to occur when carbon tetrachloride was used as the solvent. The complex mixture of products was not separated.

With this in mind comparative photochemical reactions of adamantane in  $CH_{2}Cl_{2}$ ,  $CHCl_{3}$  and  $CCl_{4}$  were performed (no  $Cl_{2}$  present). After irradiation for 48 hours the  $CH_{2}Cl_{2}$  solution showed no reaction, the  $CHCl_{3}$  solution consisted of 68% adamantane, 30% 1-chloroadamantane and 2% 2-chloroadamantane. The

CCl<sub>4</sub> solution contained six chlorinated adamantanes plus large amounts of hexachloroethane. Separation of these products proved difficult.

To minimize the separation problems, the photochemical chlorination of a series of mono-substituted adamantanes in CCl<sub>4</sub> was examined. Irradiation of 1-chloroadamantane for 48 hours resulted in the complete consumption of the starting material. Glc analysis showed the mixture to consist of hexachloroethane plus 4 chlorinated adamantanes. Elution down a silica gel column with 30-60 petroleum ether yielded the hexachloroethane. The chlorinated adamantanes were washed from the column with CHCl<sub>3</sub> and eluted with petroleum ether down a long alumina column. The crude isomers were purified by preparative glc. Comparison with authentic samples showed the products to be 1,3-dichloroadamantane, <u>anti</u>-1,4-dichloroadamantane, <u>syn</u>-1,4dichloroadamantane, and 1,3,5-trichloroadamantane in order of elution from the column.



There was no evidence for any of the 1,2-dichloride isomer at all. Selective abstraction of H<sup>•</sup> by various agents has been found to be a function of the size of the abstracting species, as shown in Figure VI. The larger the agent the greater the amount of bridgehead radical formed<sup>55</sup>. This is similar to the effects which inhibit  $S_N^2$  type solvolysis reactions of 2-adamantyl species (see page 56).

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Therefore, with a large abstracting agent like  $\cdot \text{CCl}_3$  abstraction of an H• next to a C! atom will be sterically very unfavourable so that the abstraction occurs at the 3 or 4 position instead.



This mixture of bridgehead and bridge chlorides is in marked contrast to the work of Billups<sup>58</sup> in which only bridgehead chlorides were isolated.



However, the strong acid solution may actually be forming bridgehead carbenium ions. The above photochemical reaction should be an exclusive free radical reaction.

The same photochemical chlorination was repeated with 1-fluoro and 1-bromoadamantane. The same four products were observed plus hexachloroethane.





X=F,Br

Isolation of the products was <u>via</u> column chromatography and preparative glc as before. The isomers eluted in the same order as for the case where X = C1 and were assigned on the basis of their similar nmr spectra.

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In view of the above results the same reactions were repeated using bromotrichloromethane as the solvent. Irradiation of a solution of adamantane yielded only 1 and 2-bromoadamantane with no trace of any chlorinated products. This is supported by work of Eichler<sup>114</sup> who found that abstraction of Br. from  $\text{ErCCl}_3$  by the bridgehead adamantyl radical was 29 times faster than abstraction of Cl. from  $\text{CCl}_4$  by the same radical.

Quite unexpectedly, the irradiation of 1-substituted adamantanes in BrCC1<sub>3</sub> led to the exclusive formation of bridgehead products. This procedure proved to be a facile way of synthesizing mixed adamantyl halides as shown below.



Also of interest was that no hexachloroethane was produced as shown by glc analysis. The steric effects for •CCl<sub>3</sub> abstracting H• from 1-substituted adamantanes should be the same in CC1<sub>4</sub> and BrCC1<sub>3</sub> and yet mixed bridge and bridgehead products are observed in CC1<sub>4</sub> while only bridgehead products are found in BrCC1<sub>3</sub>. (At longer reaction times in BrCC1<sub>3</sub> secondary products started to form as well, as shown by glc.) Placing additional substituents at the other bridgeheads leads to secondary products as well.



The reasons for the difference in behaviour of  $CCl_4$  and  $BrCCl_3$  are not clear. The absence of  $C_2Cl_6$  in the  $BrCCl_3$  suggests that very efficient H abstraction by  $\cdot CCl_3$  may be taking place and therefore no coupling to form  $C_2Cl_6$  occurs. The exclusive bridgehead radical formation follows from the bulkiness of the trichloromethyl radical as seen before. In the case of  $CCl_4$  solution the low selectivity could result from Cl being the abstracting agent. Because of its small size abstraction could lead to both bridge and bridgehead radicals. The  $\cdot CCl_3$  radicals would to a large extent couple to form hexachloroethane.

The irradiation of 1-iodoadamantane in either  $CC1_4$  or  $BrCC1_3$  led to substitution of the iodine by chlorine and bromine with traces of dihalides.



The same type of substitution for various substituted aromatic iodides in  ${\rm CCl}_{\rm A}^{-115}$  has been observed.



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Thus it may be ascertained  $f_{rom}$  the above reactions that the irradiation of bridgehead halogen compounds leads to the production of both free radical and carbenium ion type intermediates. The relative amount of each depends upon the nature of the halogen atom as well as the type of solvent being used for the reaction.

C. Discussion of Spectral Results

#### I) Mass Spectra:

This technique proved to be exceedingly valuable in the analysis of various substituted adamantanes. Two papers have appeared in the literature; the first a complete study of twenty 1-substituted adamantanes<sup>116</sup> and the second a study of eight 2-substituted adamantanes<sup>117</sup>.

Bridgehead mono substituted adamantanes were found to fragment via two pathways. For most alkyl groups and halogen atoms loss of X<sup>•</sup> was the preferred fragmentation.



X=halogen,R, NO<sub>2</sub> However, for groups which could stabilize a +ve charge the major fragment corresponded to loss of a  $C_4H_9$  radical<sup>38</sup> with formation of a substituted phenyl cation.



With the 2-substituted adamantanes the major fragment was due to loss of HX or X from the molecular ion  $^{39}$ .



The same pattern was observed for the amide photoproducts of the two adamantyl iodides.

Table X Fragmentation Pattern for Adamantyl Amides

A		Pt	P-C4 <sup>H</sup> 9	P-X
$f \rightarrow $	X=NHCMe	81	100	10
V Kx	O X=NHCPr	65	69	100
A	0	P <sup>+</sup>	P-X	P-HX
$\downarrow \uparrow^{x} \longrightarrow$	X=NHCMe	1.00	27	49
	X=NHČ₽r	100	45	35

The same was observed for the corresponding norbornyl amides.

Table XI Fragmentation Pattern of Norbornyl Amides



In both the norbornyl and adamantyl the 2-substituted amides underwent fragmentation, losing HX as a major pathway. The bridgehead isomers preferred to lose an alkyl radical  $(C_4H_9^{\bullet} \text{ and } C_2H_5^{\bullet})$  to yield a resonance stabilized carbenium ion. With the 1-substituted adamantanes, when R = Pr the resulting cation from P-C\_4H\_9 was not as stable as when R = Me.

This decreased stability of the phenyl substituted cation as the size of R increased was also found in the mass spectra of various 1-alkoxyadamantanes. The loss of OR increased as the size of R increased. Table XII Fragmentation Pattern of 1-Alkoxyadamantanes

	<b>P</b> <sup>+</sup>	P-C4 <sup>H</sup> 9	P-OR
R = Me	25	100	8
= Et	41	100	22
= nPr	70	100	92
= iPr	51	100	41
= nBu	50	71	100
= iBu	3	4	100
= nPn	16	32	100
$= CH_2 CH_2 OH$	16	7	100
$= CH_2CH_2OCH_3$	11	4	100

The same preference for loss of OR as the size of R increased was also found for the 1,3-diethers.

Table XIII Fragmentation Pattern of 1,3-Dialkoxyadamantanes

	Р	P-C4 <sup>H</sup> 9	P-OR
R = Me	26	100	26
= Et	39	100	28
= nPr	45	100	74.
= iPr	40	100	81
= iBu	. 5	9	100

II) Infrared Spectra:

Detailed analysis of the infrared spectra of substituted adamantanes has received little attention<sup>118</sup>. Its main use in this study was for comparitive purposes; the spectra for monohalides were very similar as were those for dihalides and so on. The spectra for the halogenated biadamantanes are shown below as examples (run as KBr pellets). <u>Figure VII</u> Infrared Spectra of 3,3'-Dihalo-1,1'-Biadamantanes





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The pattern for secondary substituted adamantanes is not so similar, but is still comparable. This is shown above for the three <u>syn-1,4-dihalo-</u> adamantanes (CC1<sub>4</sub> solution). Thus an unknown halogenated adamantane could be assigned as disubstituted, trisubstituted or whatever by comparison with the spectra of known compounds.

#### III) <u>Nuclear Magnetic Resonance</u>

#### a) <u>H</u> (Proton)

This technique was by far the most useful for the analysis of derivatives of adamantane. The assignments are readily made from the chemical shifts and integrated intensities. Of special importance in the case of bridgehead compounds is the absence of strong coupling. Because of the rigid character of the adamantane skeleton, there is no possibility of appreciable distortion of the expected 60° angle between vicinal hydrogen atoms. Where measurable the J values between protons have been found to be 2.6 Hz. All protons in the molecule are strongly dependant upon the nature of the substituents<sup>19</sup>.

A typical example is shown below for 1-bromoadamantane. ( solvent is CS<sub>2</sub>) <u>Figure IX</u> Proton NMR Spectrum of 1-Bromoadamantane



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Only three different types of protons are present in the spectrum. There are two types of  $\delta$  protons but they generally resonate together so that the  $\delta$  protons (at 1.73) are slightly broader than the  $\beta$  protons (at 2.28) The  $\delta$  protons being furthest from the substituent usually occur closest to the value for adamantane itself ( $\delta = 1.78$ ). The  $\delta$  protons always are found as a featureless broad band.

In many cases some of the resonances may overlap with each other. In these instances switching to an aromatic solvent like benzene causes spectacular shifts of the resonances. This is shown below for 1-methoxy-adamantane in  $CS_2$  and  $C_6H_6$ .

Figure X Proton NMR Spectra of 1-methoxyadamantane



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In CS<sub>2</sub> solution the  $\beta$  and  $\delta$  protons resonate at essentially the same position. Changing the solvent to benzene causes an upfield shift in these positions. Interestingly, in all cases investigated here the  $\beta$  carbons (those closest to the substituent) are affected the least; they undergo the smallest solvent shift. Since studies have shown no evidence for a stable 1:1 type complex of substrate and solvent, it was suggested that the dipole moment of the substrate caused some weak ordering of the solvent which was geometrically but not thermodynamically equivalent to a complex<sup>119</sup>.

Thus by utilizing the two solvents mentioned above the analysis of the nmr spectra of bridgehead adamantyl halides is relatively straightforward. This is due to the fact that chemical shifts induced by various substituents are remarkably additive<sup>19</sup>. Knowing the magnitudes of these shifts one can accurately estimate the chemical shifts for di, tri and tetrasubstituted adamantanes. The results for monosubstituted adamantanes are shown below. The substituent shifts (subs) are the observed chemical shift of the halo compound minus that for adamantane.

<u>Table XIV</u>	Proton	and	Substituent	Shifts	of	1-Haloadamantanes
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$\square$	Pr B	CS_	solut	C.H. solution					
L	Vx -	F	C1	Br	I	F	C1	Br	I
ß	obs	1.81	2.08	2.28	2.62	1.83	2.06	2.26	2.50
1	subs	+.04	+.31	+.51	+.85	+.06	+.29	+.49	+.73
ጉ		2.18	2.08	2.04	1.92	1.94	1.80	1.70	1.60
U		+.31	+.21	+.17	+.05	+.07	07	17	27
C	·	1.62	1.69	1.73	1.88	1.36	1.38	1.40	1.42
δ		15	08	04	+.11	41	39	37	35

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The above substituent shifts are +ve for a downfield shift and -ve for an upfield shift (based up  $\delta = 1.77$  for the bridge protons of adamantane and 1.87 for the bridgehead protons).

Using the above substituent shifts together with the additivity principle, one may calculate the expected spectrum for any di, tri or tetrahalide. 1,3-dihalides have four different types of protons and the results are shown in the following table compared with the calculated values.



 $\beta = 1.77 + .51 + .51 = 2.79$  $\beta \delta = 1.77 + .51 - .04 = 2.24$  $\delta = 1.87 + .17 + .17 = 2.21$  $\delta = 1.77 - .04 - .04 = 1.69$ 

Table XV Experimental and Calculated Proton Chemical Shifts of 1,3-Dihaloadamantanes  $\Lambda$ 

A		cs <sub>2</sub>	solutio	on	C6H6 solution				
XX	X	F	C1	Br	I	F	C1	Br	I
R	obs	1.98	2.36	2.78	3.26	2.04	2.40	2.77	3.20
P	calc.	1.85	2.39	2.79	3.47	1.89	2.45	2.75	3.23
βб	obs	1.80	2.04	2.26	2.60	1.53	1.73	1.93	2.20
	calc.	1.66	2.00	2.24	2.73	1.42	1.67	1.89	2.15
x	obs	2.37	2.28	2.26	1.92	1.85	1.63	1.58	1.23
0	calc.	2.49	2.29	2.21	1.97	2.01	1.73	1.53	1.33
C	obs.	1:50	1.62	1.73	1.92	0.97	1.00	1.10	1.23
δ	calc.	1.47	1.61	1.69	1.99	0.95	0.99	1.03	1.07

Trisubstituted adamantanes have 3 different types of protons as shown by the spectra for the triiodide  $(CS_2)$ .



The calculated and observed results for all the trihalides are shown in the following table.

\_\_\_\_\_\_\_\_\_\_\_\_

Table XVI

Experimental and Calculated Proton Chemical Shifts of 1,3,5-Trihaloadamantanes

L <sub>X</sub>	8	cs,	2 solut:	ion		C6H6 solution				
	<i>₽₽</i> δ	F	C1	Br	I	F	C1	Br	I	
085	obs.	1.99	2.32	2.74	3.23	1.87	2.08	2.40	2.87	
рръ	calc.	1.70	2.31	2.75	3.58	1.48	1.96	2.38	2.88	
рѕѕ	obs.	1.75	1.95	2.25	2.58	1.30	1.42	1.61	1.93	
	calc.	1.51	1.92	2.17	2.84	1.01	1.32	1.52	1.80	
$\mathbf{v}$	obs.	2.47	2.46	2.41	1.97	1.63	1.42	1.40	0.95	
	calc.	2.80	2.50	2.38	2.02	2.08	1.66	1.36	1.06	

For the tetrahalides, since all the protons are now equivalent, only a single line is observed.



The same additivity relationship may be used for the dimethyladamantyl halides and halogenated biadamantanes. The results for these compounds are not included in tabular form.

As may be seen from Tables XIV to XVII the agreement between the observed and calculated chemical shifts is quite good for the chlorides  $(\pm .03 \text{ ppm in } \text{CS}_2, \pm .11 \text{ in } \text{C}_6\text{H}_6)$  and bromides  $(\pm .04 \text{ ppm in } \text{CS}_2, \pm .08 \text{ in } \text{C}_6\text{H}_6)$ . However, the agreement is not as good for the fluorides  $(\pm .22 \text{ ppm in } \text{CS}_2, \pm .27 \text{ in } \text{C}_6\text{H}_6)$  and iodides  $(\pm .20 \text{ ppm in } \text{CS}_2, \pm .08 \text{ in } \text{C}_6\text{H}_6)$ .

The protons directly adjacent to the halogen atoms deviate to the greatest extent. In CS<sub>2</sub> the  $\beta$  protons (adjacent to two halogens) of the fluorides appear at a lower field (deshielding effect) than expected and the deviation increases as the number of halogen atoms increase (deviation of di = +.13 ppm, tri = +.29,tetra = +.49). The  $\beta$  protons of the iodides follow the reverse trend, appearing at a higher field (shielding effect) than expected (deviation of di = -.21 ppm, tri = -.35, tetra = -.51). In CS<sub>2</sub> the  $\beta'$  protons (adjacent to one halogen atom) of the fluorides and iodides follow the same trend as the  $\beta$  protons. For the fluorides the deviations are for di = +.14 ppm, and tri = +.24; for the iodides the deviations for di = -.13 ppm, and tri = -.26. When the solvent is changed to benzene the deviations of observed and calculated for the  $\beta$  and  $\beta'$  protons of the

iodides disappear (average deviation = -.C5 ppm) while those of the fluorides increase slightly (deviation of  $\beta$  protons of di = +.15 ppm, tri = +.39, tetra = +.61 and deviation of  $\beta'$  protons of di = +.11 ppm, tri = +.29).

Although the deviations from additivity in calculated chemical shifts indicate a cooperative effect of increased number of halogens in adamantane, plots of observed chemical shift of the  $\beta$  and  $\beta'$  protons in CS<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> versus the number of halogen atoms are still essentially straight lines (Figures XII and XIII). In both solvents the  $\beta$  and  $\beta'$  protons of the adamantyl fluorides appear at the highest field and the iodides at the lowest field. This is expected from the anisotropic effects at  $\beta$  carbon atoms<sup>120</sup>. This downfield shift of I > Br > Cl > F decreases regularly as the number of halogen atoms increase. As may be seen from the similar slopes of the lines in Figure XII and XIII the effects of the 4 halogens in CS<sub>2</sub> are the same.

Figure XII

Observed Chemical Shift of the  $oldsymbol{eta}$  Protons versus Number of Halogen Atoms

 $\beta$  protons are adjacent to 2 halogen atoms



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The effect of the 4 halogens are also the same in  $C_6H_6$ . The difference between the slopes in  $CS_2$  and  $C_6H_6$  may be ascribed to the weak ordering of the solvent by the solute as proposed by Fort<sup>119</sup>. No evidence for a 1:1 complex was found and the authors suggest that the dipole of the solute causes a "cage-like" construction around the adamantyl halide. Rapid exchange of the solvent molecules involved in the "cage" with molecules from the bulk of the solvent would give the results of a 1:1 complex on the NMR time scale but would not be thermodynamically equivalent to one. As may be seen from Tables XIV to XVII the solvent shift increases as the number of halogens increase and is greatest for the protons furthest away from the substituent ( $\beta < \delta < \delta$ ). Also of interest is the fact that the shift is greatest for the iodides (as shown for the trihalides below). In all cases an upfield shift is observed.
Table XVIII Benzene Solvent Shifts for 1,3,5-trihaloadamantanes

888		Solvent	Shifts (CS	$_2 \rightarrow C_6^{H_6}$	)
Ax	X =	F	C1	Br	I
Fr 7	ββδ	0.12	0.24	0.34	0.35
x	βδδ	0.45	0.53	0.64	0.65
ββδ	۲	0.84	1.04	1.01	1.02

\*Shifts are in ppm upfield from the resonance in CS<sub>2</sub> solution.

Now turning to an examination of the  $\Upsilon$  protons one notices that the fluorides resonate at the lowest field, indicative of an inductive order  $F > Cl > Br \neg I$ . The downfield shift of F relative to I is the reverse of the order observed for the  $\Upsilon$  protons of <u>n</u>-propyl halides<sup>121</sup> and various halogenated steroidal systems<sup>122</sup>. It has been suggested that this reversal of order for the  $\Upsilon$  protons of the 1-adamantyl system was due to the overlap of the rear lobes of the bridgehead bonding orbitals<sup>119</sup>, <sup>73</sup>. This concept of near lobe overlap has also been suggested to account for the same downfield trend from Br to F in a halogenated cholestane system. This back lobe interaction will be examined later in the thesis in an examination of the <sup>13</sup>C and <sup>19</sup>F nmr of these bridgehead halides.

As may be seen from Tables XV and XVI the agreement between calculated and observed chemical shifts of the  $\checkmark$  protons is good for the bromides  $(\pm .04 \text{ ppm in } \text{CS}_2, \pm .04 \text{ in } \text{C}_6\text{H}_6)$  and iodides  $(\pm .05 \text{ ppm in } \text{CS}_2, \pm .10 \text{ in}$  $\text{C}_6\text{H}_6)$ . The agreement is not as good for the fluorides  $(\pm .23 \text{ ppm in } \text{CS}_2, \pm .31 \text{ in } \text{C}_6\text{H}_6)$  and chlorides  $(\pm .02 \text{ ppm in } \text{CS}_2, \pm .17 \text{ in } \text{C}_6\text{H}_6)$ . The direction of the deviation for the  $\checkmark$  protons of the fluorides is opposite to that for the  $\beta$  and  $\beta'$  protons (see page96). The  $\circlearrowright$  protons of the fluorides appear at a higher field than expected from the additivity relationship. A plot of the chemical shift of the  $\circlearrowright$  protons versus the number of halogen atoms produces a straight line as shown in Figure XIV.





If the interaction of the back lobes of the bridgehead bonding orbitals is important, then placing halogen atoms in place of hydrogen should result in a reduction of charge density at the remaining bridgehead carbon atoms. The chemical shift of this  $\chi$  hydrogen would therefore move to lower field, the magnitude of the shift should increase as the number of halogen atoms at the bridgeheads increased and should be greatest when the most electronegative halogen (fluorine) is present. This is indeed observed in CS<sub>2</sub> solution as can be seen in Figure XIV. The effects of F, Cl, and Br are similar while the introduction of additional I atoms has only a very small effect. The situation is completely different in benzene solution where upfield shifts are observed with an increase in the number of halogens. In fact the plot in C<sub>6</sub>H<sub>6</sub> is very similar to the C<sub>6</sub>H<sub>6</sub> plots of the  $\beta$  and  $\beta'$  hydrogens in Figures XII and XIII. A possible explanation is that the deshielding effects of the halogen atoms in CS<sub>2</sub> solution are offset by the greater shielding effects<sup>41</sup> caused by interaction of the solute with the benzene solvent molecules as seen on page 99. These interesting  $\Im$  effects will be examined further in the discussion of the<sup>13</sup>C and <sup>19</sup>F nmr spectra of these molecules.

As a further test of the accuracy of this additivity relationship for bridgehead positions of adamantane a series of mixed halides were studied as shown in Tables XIX and XX.

CS<sub>2</sub> solution

Table XIX

HS

Experimental and Calculated Proton Chemical Shifts of 1-Chloro-3-Haloadamantanes

C6H6 solution

С	17	L/X									
X:	μ.	H1	H2	Н3	H4	Н5	H1	H2	Н3	Н4	Н5
F	obs	2.23*	1.81*	2.01	2.35	1.55	2.24*	1.55*	1.75	1.85	1.00
	calc.	2.12	1.73	1.93	2.39	1.52	2.12	1.44	1.65	1.87	0.97
Br		2.56	2.26	2.06	2.26	1.67	2.55	1.88	1.74	1.61	1.05
		2.59	2.20	2.04	2.25	1.64	2.55	1.87	1.69	1.63	1.01
Ī	•	2.88	2.48	2.16	2.16	1.75	2.76	2.08	1.80	1.42	1.13
		2,93	2.54	2.19	2.13	1.80	2.79	2.11	1.71	1.53	1.07

\* J = 5.5 Hz

<u>Tab</u>	<u>le XX</u> Hs	Exper: Haload	Experimental and Calculated Chemical Shifts of 1,3-Dihalo-5- Haloadamantanes								
×	Ar Hy Hy	, Ha X	CS	2 <sup>solu</sup>	tion			C6 <sup>H</sup> 6 so	olution		
	μ,	H1	H2	Н3	H4	Н5	H1	H2	НЗ	Н4	Н5
X =	Br obs	2.68	2.36 <sup>a</sup>	2.15	2.46	1.67 <sup>b</sup>	2.44	2.13	1.58	1.47	1.32
Y =	F cal	c 2.64	.2.28	2.09	2.52	1.73	2.34	1.95	1.48	1.60	1.09
X =	I	3.14	3.00	2.50	2.06	2.35	2.82	2.68	1.92	1.10	1.75
Y =	Br	3.43		2.69	2.14	2.60	2.85	2.64	1.87	1.16	1.56
Х =	C1	2.42	2.56	2.02	2.36	2.16	2.12	2.27	1.43	1.57	1.57
Y =	Br	2.35	2.51	.1.96	2.46	. 2.12	1.99	2.16	1.30	1.56	1.48
X =	C1	2.39	2.20 <sup>a</sup>	1.93	2.47	1.80 <sup>b</sup>	2.12	1.97 <sup>a</sup>	1.41	1.58	1.26
Y =	F	2.24		1.85	2.60	1.65	1.94	1.73	1.26	1.80	1.05
X =	Br	2.70	2.56	2.18	2.37	2.06	2.42	2.27	1.59	1.45	1.45
Y =	C1	2.71	2,55	2.16	2.42	2.00	2.36	2.18	1.50	1.43	1.32
a)	J = 5.	5 Hz	Ъ) J	= 3.5	Hz						

As may be seen from the tables deviations again occur but are smaller overall than when only one type of halogen is present. The deviation for fluorides in  $CS_2$  is  $\pm .09$  ppm,  $\pm .14$  in  $C_6H_6$ ; for iodides in  $CS_2 \pm .13$  ppm and  $\pm .06$  in  $C_6H_6$ ; and for chlorobromides in  $CS_2 \pm .04$  ppm and  $\pm .06$  in  $C_6H_6$ . As before the deviations of iodides in  $CS_2$  disappear in benzene solution while the deviations of the fluorides are present in both solvent systems.

Therefore, as may be seen from the above discussion, the proton nmr of bridgehead substituted adamantanes is an extremely valuable and simple technique to investigate inductive and aniosotropic effects of substituents as well as the possible presence of back lobe interactions in a well defined and rigid system. The nmr of 2-substituted adamantanes are more complicated than the bridgehead isomers as a result of lower symmetry making complete analysis difficult. The spectrum of 2-bromoadamantane is shown below (CC1<sub>4</sub> solution).

Figure XV Proton NMR Spectrum of 2-Bromoadamantane



The proton  $\propto$  to bromine is easily identified because of its low field resonance at  $\xi$ =4.52. The AB system at  $\xi$ =2.36 and  $\xi$ =1.58 (J = 12 Hz) belong to the protons  $\delta$  to the bromine atom on the syn side of the molecule. The axial protons exist in a 1,3 diaxial arrangement with the Br atom and therefore will be more deshielded ( $\xi$ =2.36) than the equitorial protons<sup>46</sup> which appear at  $\xi$ =1.58. The other resonances have been assigned but

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required double resonance techniques<sup>123</sup>.

Substituent shifts may be calculated and predictions made for 1,2, 1,4 and 2,4-adamantyl isomers but the agreement is not as good as for the bridgehead isomers<sup>100</sup>, 34, 124

In the case of the 1,4 isomers assignment may be made on the basis of the 1,3 diaxial arrangement of the proton and halogen atom as seen above. For <u>syn-1,4-dichloroadamantane</u> the  $\delta$  axial protons are deshielded by the axial secondary Cl atom. Also the bridgehead atom causes deshielding so that the doublet occurs further downfield than for 2-bromoadamantane at  $\delta = 2.65$ . Following this reasoning the downfield shift for the dibromide and diiodide should be even greater. This is indeed observed experimentally, as shown below.

Figure XVI

Proton NMR Spectra of syn-1,4-dihaloadamantanes



 $H_{\alpha} X$ Ha

X =	Ha	H∝
CI	2.65	4.11
Br	2.93	4.46
I	3.24	4.82



Therefore it has been seen that proton nmr is a useful method by which various halogenated adamantanes may be studied. The additivity relationship appears to hold for other substituents as well<sup>19</sup>. A study of the carbon nmr spectra of these halogenated adamantanes was undertaken to determine if the additivity relationship at carbon would be equally useful.

b) <sup>13</sup>C nmr spectra

Substituent effects have formed a large part of the work on early <sup>13</sup>C nmr studies<sup>125</sup>, but the correlation of chemical shifts with molecular and electronic characteristics has been unreliable when molecules with dynamic geometry are used. The adamantyl system, because of its rigid and well defined geometry, is an ideal model to study substituent effects.

A typical example is shown for 1-bromoadamantane.

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With wide band 'H decoupling all the resonances appear as singlets; the peak heights represent a combination of the number of carbon atoms plus their type. For example, quaternary carbons attached to bromine give weak absorptions while  $CH_2$  carbons give much stronger absorptions. Initial studies in this area have differentiated the  $\mathcal{F}$  and  $\mathcal{S}$  carbons for all the monohaloadamantanes<sup>126</sup> by means of off-resonance decoupling.

From the <sup>13</sup>C chemical shifts of the monohalides, the substituent shifts could be used to calculate the expected carbon chemical shifts for the di, tri and tetrahalides.



Table XXI <sup>13</sup>C Chemical Shifts of 1-mono-Haloadamantanes

Substituent

Carbon Atom and Associated Substituent Shift<sup>b</sup>

	X		β		8		8	
H	28.4	(0.0)	37.7	(0.0)	28.4	(0.0)	37.7	(0.0)
F <sup>C</sup>	92.4	(64.0)	42.7	(5.0)	31.4	(3.0)	35.9	(-1.8)
C1	68.6	(40.2)	47.5	(9.8)	31.3	(2.9)	35.4	(-2.3)
Br	66.2	(37.8)	49.3	(11.6)	32.5	(4.1)	35.5	(-2.2)
I	50.7	(22.3)	52.3	(14.6)	33.0	(4.6)	35.6	(-2.1)
CNd	30.3	(1.9)	40.0	(2.3)	27.2	(-1.2)	35.8	(-1.9)

<sup>a</sup>Shifts reported in ppm downfield from tetramethylsilane.

<sup>b</sup>The substituent shifts in parentheses is the chmical shift of the halo compound minus the chemical shift of adamantane. Positive shifts correspond to lower field.

<sup>C</sup>  $J_{CF}$  values are  $J_{\alpha} = 184$  Hz,  $J_{\beta} = 17.8$  Hz,  $J_{\delta} = 10.6$  Hz and  $J_{\delta} < 2$  Hz. <sup>d</sup>CN = 125.1

A sample calculation for 1,3-diiodoadamantane, using these substituent shifts of the monohalides, is shown below.



 $\alpha = 28.4 + 22.3 + 4.6 = 55.3$   $\beta' = 37.7 + 14.6 + 14.6 = 66.9$   $\beta = 37.7 + 14.6 - 2.1 = 50.2$   $\delta' = 28.4 + 4.6 + 4.6 = 37.6$  $\delta = 37.7 - 2.1 - 2.1 + 33.5$ 

The above substituent shifts differ slightly from those found by earlier workers but this is not surprising as different solvent systems were used in the three cases<sup>126</sup>.

The calculated and observed chemical shifts for all the di, tri and tetrahalides are shown in the following three tables.

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Table XXII Experimental and Calculated Chemical Shifts of 1,3-di-Haloadamantanes $^{oldsymbol{lpha}}$ 

ubstituent	X	B	B	8	۶
$\mathbf{F}^{\mathbf{b}}$	93.4(95.4)	48.0(47.7)	41.2(40.9)	31.5(34.4)	34.3(34.1)
C1	66.9(71.6)	56.6(57.3)	45.7(45.2)	33.8(34.2)	33.5(33.1)
Br	62.0(70.3)	59.1(60.9)	46.9(47.1)	34.9(36.6)	33.6(33.3)
I	44.8(55.3)	64.6(66.9)	49.9(50.2)	36.6(37.6)	33.7(33.5)

<sup>a</sup>Calculated values in parentheses.

 $J_{CF}$  values are  $J_{\alpha_1} = 188$  Hz,  $J_{\alpha_a} = 13.3$  Hz,  $J_{\beta}' = 19.0$  Hz, and  $J_{\beta} = 16.0$  Hz and J > = 10.3 Hz.

<u>Table XXIII</u>	Experimental	and Calculated	Chemical
	Shifts of 1.	3.5-Trihaloadama	antanes 🏊



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FЬ	
C1	1
Br	

Ι

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à.	- (	P	هر	8
Б	92.4(98.4)	46.9(45.9)	39,9(39,1)	28.1(37.4)
L į	64.5(74.4)	54.4(55.0)	43.8(42.9)	33.5(37.1)
r	58.1(74.4)	56.8(58.7)	44.8(44.9)	36.3(40.7)
	39.3(59.9)	61.7(64.8)	47.4(48.0)	39.5(42.2)

<sup>a</sup>Calculated values in parentheses.

 $J_{CF}$  values are  $J_{\alpha_1} = 191 \text{ Hz}$ ,  $J_{\alpha_2} = 14.8 \text{ Hz}$ ,  $J_{\beta'} = 18.8 \text{ Hz}$ ,  $J_{\beta} = 16.9 \text{ Hz}$ and  $J\gamma = 12.0$  Hz.



Table XXIV Experimental and Calculated Chemical Shifts of 1,3,5,7-tetra-Haloadamantanes<sup>a</sup>

Substituent

Ъ

L	æ	B
F	90.4 (101.4)	46.2 (44.1)
C1	62.3 ( 77.3)	52.8 (52.7)
Br	54.2 ( 78.5)	54.9 (56.5)
I	31.1 ( 64.5)	59.7 (62.7)

<sup>a</sup>Calculated values in parentheses.

 $J_{CF}$  values are  $J_{\alpha}$  = 192 Hz,  $J_{\alpha}$  = 17.2 Hz, and  $J_{\beta}$  = 19.4 Hz.

As may be seen from the tables XXII to XXIV, the observed chemical shifts for the secondary carbon atoms ( $\beta$  and  $\beta'$ ) agree quite well to those calculated using the additivity relationship while the bridgehead carbons ( $\ll$  and  $\delta$ ) resonate at a higher field than expected. This is shown in the following table.

Table XXV	Average Deviation for Di, Tri and Te	of Observed trahalides	from Calculated	Chemical	Shifts
Carbons	F	C1	Br	I.	
æ	-6.3	-9.9	-16.3	-21.5	
<i>β</i> '	+1.3	<u>+</u> 0.5	-1.8	- 2.8	
β	<u>+</u> 0.5	<u>+</u> 0.7	<u>+0.2</u>	<u>+</u> 0.5	
ጽ	-6.1	-2.0	-3.0	- 1.9	

Good agreement is observed for the secondary carbon atoms adjacent to one halogen atom ( $\beta$ ) with larger deviations for the  $\beta'$  carbons. The bridgehead carbons, however, all experience large upfield shifts relative to the shifts

expected from additivity.

Linear relationships were observed in plots of the chemical shifts of the  $\beta$  and  $\beta'$  carbon atoms versus the number of halogen atoms as seen in the following figure.

Figure XVIII

Chemical Shift of  $\beta$  and  $\beta$  Carbons versus Number of Halogen Atoms



Downfield shifts in the order I > Br > Cl > F are observed for the  $\beta$ and  $\beta'$  carbons and this shift decreases regularly as the number of halogens increases. This is expected from the anisotropic effects at  $\beta$  carbons<sup>127</sup> and has been observed in other systems<sup>125b</sup>. This shielding effect increases as the number of halogens is increased, moving the resonances to higher field. As can be seen from the similar slopes the effect is nearly the same for the four different types of halogen atoms. Although the  $\prec$  carbon atoms of the halogenated adamantanes deviate to the largest extent ( $\prec$  carbon of the tetraiodide appears 33.4 ppm upfield from the value predicted by additivity) a plot of the chemical shift versus the number of halogen atoms yields straight lines as shown in the following graph.



Chemical Shift of  $\thickapprox$  Carbons versus Number of Halogen Atoms



The order is the reverse of that observed with the  $\beta$  and  $\beta'$  carbon atoms in that an inductive order is observed i.e. deshielding increases with an increase in the electronegativity; F > Cl > Br > I. However, additional halogens do not cause further deshielding; instead, the chemical shifts of the  $\prec$  carbons move progressively upfield. As can be seen from the slopes in Figure XIX, this shielding effect is greatest for the iodides. This results in a 33.4 ppm deviation upfield for the tetraiodide from the value calculated

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from additivity. These deviations at the  $\propto$  positions of halogenated adamantanes have also been observed by Pehk <u>et al</u><sup>126a</sup> who found small upfield shifts for the following two bromides. No explanation for these deviations was suggested.



The deviations at the  $\propto$  position of the multihalogenated adamantanes are much larger, the average for the twelve compounds is 13.5 ppm upfield from that expected by additivity.

In spite of this deviation from additivity the chemical shifts of the  $\ll$  carbons follow a more regular pattern than found for the halogenated methanes<sup>128</sup>. The results for those compounds are shown below. The fluoro-methanes have been found to exhibit constantly increasing deshielding<sup>129</sup> as the number of F atoms is increased from 1 - 4.

Table XXVI Chemical Shift of Various Halogenated Methanes

Compound	Chemical shift (relative to TMS)
CH <sub>4</sub>	- 2.3
CH <sub>3</sub> C1	25.0
CH <sub>3</sub> Br	10.0
CH <sub>3</sub> I	-20.7
CH <sub>2</sub> C1 <sub>2</sub>	54.0
CH <sub>2</sub> Br <sub>2</sub>	21.4
CH2I2	-54.0
CHC13	77.5
CHBr <sub>3</sub>	12.2
CHI3	-140
CC14	96
CBr	-29

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Thus as can be seen, the fluorides and chlorides exhibit constantly increasing deshielding while iodides show constantly increasing shielding with increased number of halogen atoms. Bromides initially exhibit deshielding but then begin to show shielding effects for 3 and 4 bromine atoms. These changes have been ascribed to a combination of steric, inductive and polarization effects<sup>128</sup>. Direct steric effects should be absent in the bridgehead substituted adamantanes so that the  $\prec$  carbon chemical shifts could be viewed as inductive deshielding in the order of F > Cl > Br > Icombined with the shielding effects due to the polarizability of the halogen atoms in the order of I > Br > Cl > F. With the  $\prec$  carbons this polarizability factor appears to be the dominant one as the number of halogens increase.

The same upfield shifts in the order I > Br > Cl are found for the  $\propto$  carbons of the two bicyclic systems shown below. The  $\beta$  and  $\beta$  carbons also follow the same order observed for the adamantyl system i.e. downfield shift in the order I > Br > Cl.

Table XXVII

Carbon Chemical Shifts of 1,4-Dihalobicyclo [2.2.1] heptane and [2.2.2] octane

ß	1×
4 X	

X =

	X	$\checkmark$			X	- X B		
	æ	B'	B	X =	X	ß		
Ħ	36.5	38.6	29.5	Н	23.9	25.8		
C1	65.6	54.0	39.8	C1	64.1	37.8		
Br	56.4	56.4	41.9	Br	58.9	40.2		
I	29.9	61.3	45.7	I	38.9	43.9		

The polarizability effects on the  $\propto$  carbon atoms of these two bicyclic system are compared with the adamantyl system in the following table. Table XXVIII

Carbon and Substituent Shift of Dihalides



<sup>a</sup> Value in bracket = chemical shift of  $\propto$  carbon of the dihalide - chemical shift of  $\propto$  carbon in the parent hydrocarbon.

The shielding effects of the halogen atoms are largest for the bicyclo [2.2.1] heptyl system with the greatest effect due to two iodine atoms, the  $\propto$  carbon appears 6.6 ppm upfield from the  $\propto$  carbon of the parent hydrocarbon.

The unsubstituted bridgehead carbon atoms ( $\mathcal{F}$ ) in the halogenated adamantanes also deviate, but to a lesser extent than the  $\prec$  carbons. However, unlike the straight lines found in Figure XIX, the plot of chemical shift of the  $\mathcal{F}$  carbon atoms versus the number of halogen atoms is not linear as shown below in figure XX. As with the  $\beta$  and  $\beta$  carbons the iodides exhibit the largest deshielding; however, unlike the other positions the addition of another halogen atom at an  $\propto$  carbon results in a further increase of the deshielding of the  $\mathcal{F}$  carbons. Addition of a third halogen atom results in further deshielding of the  $\mathcal{F}$  carbon of the triiodide and tribromide while shielding is observed for the  $\mathcal{F}$  carbon of the trichloride and trifluoride. Especially puzzling is the fact that an unsubstituted ( $\mathcal{F}$ ) bridgehead carbon is shifted downfield by an increased number of iodine or bromine atoms at the other bridgeheads while the substituted ( $\infty$ ) bridgehead carbon itself is shifted upfield by the addition of iodines or bromines at



the other bridgehead positions.

Number of Halogens, n in  $C_{10}H_{16-n}X_n$ 

"Peculiar" influences of the heavier halogen atoms on the  $\chi$  position have been noted previously<sup>126a</sup>. However, a unified basis for the chemical shift effects at all positions by halogens remains unavailable. A major factor must involve the interaction of the non-bonded 1,3 carbon atoms. This is supported as presented above, by the good correlation of observed and calculated shifts for the  $\beta$  and  $\beta'$  and  $\delta$  carbons for all of the haloadamantanes but the complete lack of correlation for the bridgehead  $\ll$ and  $\chi$  carbon atoms.

These same effects are shown by the <sup>13</sup>C nmr spectra of a series of mixed 1,3 dihalides as shown below.



## Table XXIXExperimental and Calculated Chemical Shifts of<br/>1-Halo-3-halo-adamantanes

5	ubst:	itue	nt	-1		R'	12	R.	×	c
		_a		A X	ay	Ρ	PY	<i>P</i> ^	0	0
	X =	F	obs.	92.4	66.8	52.2	45.8	40.7	32.5	33.9
	Y =	C1	calc.	95.3	71.6	52.2	45.7	40.4	34 <b>.3</b>	33.6
	X =	Br	obs.	62.2	66.8	57.8	45.6	46.9	34.2	33.6
	Y =	C1	calc.	69.1	72.7	59.1	45.3	47.0	35.4	33.2
	X =	I	obs.	43.5	66.3	60.6	45.5	49.8	34.7	33.6
	Y =	C1	calc.	53.6	73.2	62.1	45.4	50.0	35.9	33.3
	X =	$\mathbf{F}^{\mathbf{b}}$	obs.	92.2	62.0	53.8	47.3	40.9	33.3	34.2
	Y =	Br	calc.	96.5	69.2	54.3	47.5	40.5	35.5	33.7

- <sup>a</sup>  $J_{CF}$  values are  $J_{xx} = 188.5$  Hz,  $J_{xy} = 11.7$  Hz,  $J_{\beta'} = 19.5$  Hz,  $J_{\beta x} = 18.0$  Hz, and  $J_{\delta'} = 9.8$  Hz.
- <sup>b</sup>  $J_{CF}$  values are  $J_{x} = 188.7 \text{ Hz}$ ,  $J_{x} = 10.8 \text{ Hz}$ ,  $J_{\beta'} = 20.0 \text{ Hz}$ ,  $J_{\beta_x} = 16.8 \text{ Hz}$ , and  $J_{\delta'} = 9.6 \text{ Hz}$ .

Again, excellent agreement is found for the  $\beta$ ,  $\beta'$  and  $\delta$  carbons with deviations (average 1.6 ppm) for the  $\delta$  carbons and as large as 10 ppm for the  $\propto$  carbon atoms. However, in general the additivity rule holds quite well and is very useful in assigning the chemical shifts observed to the specific carbon atoms. This is shown in the following three tables for 1,3dimethyladamantyl halides and 3,3'-dihalo-1,1'biadamantanes.



# Table XXXExperimental and Calculated Chemical Shifts of1,3-Dimethy1-5-haloadamantanes

X =		C1	C2	C3	C4	C5	C6	C7	C8
Н	obs. calc.	43.8 43.5	29.3 29.0	36.1 35.5	29.3 29.0	43.8 43.0	30.5 30.0	51.7 50 <b>.9</b>	30.9
Fa	obs. calc.	48.4 48.2	93.0 93.0	40.9 40.5	31.5 32.0	42.0 41.4	34.6 33.0	53.0 49.1	29.4
C1	obs. calc.	53.4 53.0	69.0 69.2	45.9 45.3	32.0 31.9	41.7 40.9	34.6 32.9	49.6 48.6	29.6
Br	obs. calc.	54.9 54.8	65.7 66.8	47.3 47.1	32.5 33.1	41.5 41.0	53.2 34.1	49.4 48.7	29.7
I	obs. calc.	58.2 57.8	55.9 51.3	50.5 50.1	33.1 33.6	41.7 41.1	35.6 34.6	49.6 48.8	29.5

<sup>a</sup>  $J_{CF}$  values are:  $J_1 = 17.5 \text{ Hz}$ ;  $J_2 = 184 \text{ Hz}$ ;  $J_3 = 17.5 \text{ Hz}$ ;  $J_4 = 9.5 \text{ Hz}$ ;  $J_6 = 9.5 \text{ Hz}$ .



Table XXXIExperimental and Calculated Chemical Shifts of1,3-Dimethy1-5,7-Dihaloadamantanes

X =		C1	C2	C3	C4	C5	C6
F <sup>a</sup>	obs. calc.	47.6 45.5	93.9 96.0	47.6 46.4	35.5 36.0	49.3 47.3	28.6
C1	obs. calc.	54.7 55.1	66.5 72.1	51.5 50.7	36.7 35.8	47.9 46.3	28.5
Br	obs. calc.	57.3 58.7	61.5 70.9	52.8 52.6	38.3 38.2	47.7 46.5	28.7
I	obs. calc.	62.4 64.7	43.0 55.9	55.6 55.7	39.3 39.2	47.5 46.7	28.6.

<sup>a</sup>  $J_{CF}$  values are  $J_1 = 18.8$  Hz;  $J_{a} = 186$  Hz;  $J_{a} = 13.6$  Hz;  $J_3 = 15.6$  Hz;  $J_4 = 10.0$  Hz.



<u>Table XXXII</u> Experimental and Calculated Chemical Shifts of 3,3'-Dihalo-1,1'-Biadamantanes

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X =	C1	C2	C3	C4	C5	C6	C7
H obs. sub shift	29.2 +0.8	35.3 -2.4	36.6 +8.2	35.3 -2.9	29.2 +0.8	37.6 -0.1	37.6 -0.1
F <sup>a</sup> obs. calc.	93.7 93.2	41.0 40.3	41.6 39.6	34.2 33.5	31.0 32.2	42.3 42.6	35.5 35.8
C1	70.0 69.4	45.9 45.1	41.5 39.5	33.7 32.0	31.6 32.1	47.1 47.4	35.1 35.3
Br	67.7 67.0	47.6 46.9	42.6 40.7	33.7 33.1	32.6 33.3	48.9 49.2	35.4 35.4
I	48.6 51.2	50.6 49.9	43.1 41.2	33.6 33.2	33.1 33.8	52.1 52.2	35.4 35.5

<sup>a</sup>  $J_{CF}$  values are  $J_1 = 183$  Hz;  $J_2 = 17.0$  Hz;  $J_3 = 9.6$  Hz;  $J_5 = 10$  Hz;  $J_6 = 17.0$  Hz

Again, good agreement is found for all the secondary carbon atoms with small deviations for the  $\propto$  and  $\checkmark$  carbon atoms. As a further test of the additivity relationship, the <sup>13</sup>C spectra of a series of 1-alkoxyadamantanes were obtained as shown in Table XXXIII. With these substituent shifts the expected chemical shifts for the diethers could be compared with the experimental values as shown in Table XXXIV. Unlike the halogenated adamantanes, no deviations were observed for the  $\propto$  carbons, good agreement was found for these and the  $\beta$ ,  $\beta'$  and  $\xi$  carbon atoms. However, the  $\flat$  carbons again showed some "peculiar" shielding effect<sup>126a</sup> causing deviations from 1.8 to 2.5 ppm upfield.



Table XXXIII

 $^{13}$ C Chemical Shifts of 1-Alkoxyadamantanes

Carbon Atom and Associated Substituent Shift

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	R =	حر	ß	۲	8		
	Me <sup>a</sup> c	obs. 72.2	41.0	30.5	36.6		
		+43.8	+3.0	+2.1	-1.1		
	Et <sup>b</sup>	72.2	41.7	30.6	36.6		
		+43.8	+3.7	+2.2	-1.1		
	Pr <sup>C</sup>	71.8	415	30.6	36 5		
		+43.4	+3.5	+2.2	-1.2		
	d Bard	70 /		<b>00</b> (			
	IFT	/2.4 +44.0	42.5 +4 5	30.6	36.5		
	0		• • • •	12.2	-1.2		
	nBu	72.3	43.0	30.9	36.8		
		+43.6	+3.8	+2.4	-0.9		
	$iBu^{f}$	72.3	43.0	30 9	36.8		
		+43.9	+5.0	+2.5	-0.9		
		70 5					
	nen-	/2.5 +44 1	41.0 +3.6	30.7	36.7		
			13.0	τ <b>ζ</b> ο <b>ງ</b>	-1.0		
a)	-CH <sub>3</sub>	$CH_3 = 47.$	6				
Ъ)	-CH <sub>2</sub> CH <sub>3</sub>	$CH_2 = 55.$	0; $CH_3 = 16.6$				
c)	-CH2CH2CH3	$OCH_2 = 61$	.5; CH <sub>2</sub> = 24.2;	$CH_3 = 10.8$			
d)	-CH(CH <sub>3</sub> ) <sub>2</sub>	CH = 61.3	; $CH_3 = 26.3$				
e)	-CH2CH2CH2CH	$3 \qquad OCH_2 = 59$	.6; CH <sub>2</sub> = 33.0;	CH <sub>2</sub> = 19.6; CH <sub>3</sub>	$_{3} = 14.0$		
f)	-CHCH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	OCH = 66.	OCH = 66.8; $CH_3 = 23.3$ ; $CH_2 = 31.8$ ; $CH_2 = 10.7$				
g)	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH	$_{2}^{CH}_{3}$ $^{OCH}_{2}$ = 59	.7; CH <sub>2</sub> = 28.7;	$CH_2 = 22.8; CH_2$	$= 22.8; CH_3 = 14$	4.2	



### Table XXXIV

Experimental and Calculated Chemical Shifts for 1,3-Dialkoxyadamantanes

R =		æ	B	β	ጽ	δ
Me <sup>a</sup>	obs.	74.6	44.2	39.8	30.8	35.4
	calc.	74.3	43.7	39.6	32.6	35.5
Et <sup>b</sup>	obe	76.2	45.4	40.7	30 . 9	35.5
ЦС	calc.	74.4	45.1	40.3	32.8	35.5
nPr <sup>C</sup>	obs.	74.1	45.4	40.6	30.8	35.5
	calc.	74.0	44.7	40.0	32.8	35.3
iPr <sup>d</sup>	obs.	74.7	47.2	41.5	30,9	35.5
	calc.	74.6	46.7	41.0	32.8	35.3
iBue	obs.	74.7	47.7	41.8	30,9	35.4
204	calc.	74.8	47.7	41.8	33.4	35.9
			( <b>a a</b>			

a)  $OCH_3$   $OCH_3 = 63.7$ b)  $OCH_2CH_3$   $CH_2 = 55.4$ ;  $CH_3 = 16.4$ c)  $OCH_2CH_2CH_3$   $OCH_2 = 61.9$ ;  $CH_2 = 24.0$ ;  $CH_3 = 10.8$ d)  $-OCH(CH_3)_2$   $OCH_2 = 62.0$ ;  $CH_3 = 25.2$ e)  $-OCHCH_3_{CH_2}CH_3$  OCH = 67.3;  $CH_3 = 22.9$ ;  $CH_2 = 31.6$ ;  $CH_3 = 10.4$ 

As a further test, three unsymmetrically disubstituted adamantanes were examined, the results of which are shown in Table XXXV.



Table XXXVExperimental and Calculated Chemical Shifts of UnsymmetricalDisubstituted Adamantanes

-*		C1	C2	C3	C4	C5	C6	C7
$X = F^{a}$	obs.	93.3	46.9	74.7	40.4	31.3	41.9	35.0
Y = OEt	calc.	94.6	46.4	75.2	39.6	33.6	41.6	34.8
$X = Br^b$	obs.	63.8	53.1	73.9	40.0	32.9	48.2	34.6
Y = OEt	calc.	68.4	53.0	76.3	39.2	34.7	48.2	34.4
$\begin{array}{l} X = F^{C} \\ Y = CN \end{array}$	obs.	90.0	44.6	34.0	38.7	30.3	41.3	34.1
	calc.	91.2	45.0	33.3	38.2	30.2	40.8	34.0

a)  $J_1 = 185.6 \text{ Hz}$ ,  $J_2 = 17.0 \text{ Hz}$ ,  $J_3 = 11.4 \text{ Hz}$ ,  $J_5 = 10.2 \text{ Hz}$ ,  $J_6 = 17.6 \text{ Hz}$ OCH<sub>2</sub> = 55.8, CH<sub>3</sub> = 16.2

b) 
$$OCH_2 = 55.6$$
,  $CH_3 = 16.2$ 

c)  $J_1 = 186.0 \text{ Hz}$ ,  $J_2 = 19.4 \text{ Hz}$ ,  $J_3 = 10.0 \text{ Hz}$ ,  $J_5 = 10.2 \text{ Hz}$ ,  $J_6 = 18.0 \text{ Hz}$ CN = 123.4

Again, it is only the bridgehead carbon atoms which experience significant deviations from the calculated values. A comparison of these deviations as a function of the substituent may be seen in Table XXXVI for various substituted halides.



Table XXXVIDeviation from Additivity for Bridgehead Carbons of<br/>Substituted Adamantyl Halides

	X =	F	C1	Br	I
$Y = F^{a}$	ح× حγ ک	-2.0 -2.0 -2.9	-4.8 -2.9 -1.8	-7.2 -4.3 -2.2	NA <sup>b</sup>
Y = C1	. Xy X	-2.9 -4.8 -1.8	-4.7 -4.7 -0.4	-6.9 -5.9 -1.2	-10.1 -6.9 - 1.2
Y = Br	& x & y &	-4.3 -7.2 -2.2	-5.9 -6.9 -1.2	-8.3 -8.3 -1.7	NA
Y = I	Х Х Х	NA	-6.9 -10.1 -1.2	NA	-10.5 -10.5 -1.0
Y = 1-Ad	४ ४ ४	+0.5 +2.0 -1.2	+0.6 +2.0 -0.5	+0.7 +2.1 -0.7	-2.6 +2.1 -0.7
Y = OEt	ax xy X	-1.3 -0.5 -2.3	NA	-4.6 -2.4 -1.8	NA
Y = CN	d x x y x	-1.2 -0.7 +0.1	NA	NA	NA

a) -ve deviations refer to upfield shifts

b) NA = Compound Not Available

Several interesting trends may be seen from Table XXXVI. In all cases halogen atoms cause an upfield deviation at the bridgehead positions. For the substituted carbons ( $\ll$ ), the deviation is largest for iodine, for the unsubstituted carbons (%) fluorine causes the largest deviation. For the halogenated biadamantanes the carbon bearing the halogen atom ( $\propto$ ) is not affected to a large extent but  $\propto_{\gamma}$  experiences a downfield deviation which seems to be independent of the nature of the halogen atom. As seen from Table XXXIV, no deviation occurs for the  $\propto$  carbon atoms of the diethers. The dihalides experience a large deviation at the  $\propto$  carbon as seen from Table XXXVI. Replacement of one of the halogen atoms by an ethoxy group also results in an upfield deviation of the  $\propto_x$  carbon atom, the magnitude of which is about 60% of that caused by a halogen atom.

The above results provide further support for the concept that nonbonded effects are important at the 1,3 positions of the adamantane system. The possibility that such interactions would also appear in the  $^{19}$ F spectra of these molecules was examined in the following section.

C) <sup>19</sup>F nmr Spectra

As a further measure of the influence of substituents on chemical shifts around the adamantane ring structure, the  $^{19}$ F spectra of a series of substituted fluoroadamantanes (in CCl<sub>4</sub>) were examined. The results are presented in Table XXXVII.



Table XXXVII ''F Chemical Shifts of Substituted 1-Fluoroadamantanes Fluorine Atom and Associated Substituent Shift

Rl	R2	R3	Chemical Shift <sup>a</sup>	Substituent Shift <sup>b</sup> (SCS)
н	н	н	-128.0	0.0
Н	1-Ad	H	-127.8	+0.2
Н	н	F	-132.5	-4.5
Н	н	C1	-133.0	-5.0
Н	Н	Br	-131.6	-3.6
Н	н	CN	-133.9	-5.9
H	н	OCH2CH3	-132.5	-4.5
H	H	NHCCH 3	-132.2	-4.2
H	F	F	-138.9	-10.9
Н	C1	C1	-136.4	-8.4
Н	Br	Br	-133.2	-5.2
F	F	F	-148.5	-20.5
H	CH <sub>3</sub>	CH 3	-132.9	-4.9
F.	CH3	CH3	-139.8	-11.8
C1	CH3	CH3	-137.0	-9.0
Br	CH <sub>3</sub>	CH <sub>3</sub>	-135.9	-7.9

-137.2

-132.4

-4.4

-9.2

a) Chemical shift in ppm relative to internal  $CFC1_3$ 

anti

syn

b) Chemical Shift of the substituted fluoroadamantane-chemical shift of fluoroadamantane. Negative values indicate an upfield shift. In all cases (except when R2 = 1-adamantyl) an upfield shift of the <sup>19</sup>F resonance is observed by the addition of various substituents. This upfield shift is inconsistent with theories concerning the effect of electron-withdrawing substituents on chemical shifts. In the fluoromethanes the <sup>19</sup>F resonance is greatly shifted to lower field<sup>131</sup>, consistent with an inductive order, the magnitude of the shift increasing as the number of F atoms is increased. This downfield shift is not observed with the adamantyl fluorides; in fact the addition of F atoms results in the largest upfield shifts relative to 1-fluoroadamantane (see Table XXVII).

Dewar and co-workers<sup>132</sup> have proposed that some form of substituentinduced structural change may be involved with various fluorinated anthracenes; however, these effects should be relatively unimportant for the rigid adamantyl system. These upfield shifts have also been found for the bicyclo[2.2.2]octyl system as shown below<sup>130</sup>.

These upfield shifts were also largely ascribed to a structural change induced by the electron-withdrawing substituent possibly leading to an increase in the C-F bond order. However, as Table XXXVII indicates, for substituted fluoroadamantanes significant upfield shifts are observed for both electronegative and electropositive substituents. The largest upfield shifts are due to fluorine atoms but the effect is not restricted to fluorine nor specific position of substituent. Table XXXVII indicates that a fluorine, two bridgehead methyls, ethoxy group, cyano, acetamido, bridgehead chlorine, <u>anti</u>-4-chlorine or two bromine atoms all cause a substituent-induced chemical shift of about 5 ppm upfield. A study by Wahl<sup>133</sup> has shown that various alkyl groups also produce an upfield substituent shift as shown in Table XXXVIII.



Table XXXVIII

Fluorine and Substituent Chemical Shifts of Alkyl-Substituted l-Fluoroadamantanes

R1	R2	R3	Chemical Shift	Substituent Shift
н	Н	Н	-130.0	0.0
н	Н	CH <sub>3</sub>	-132.8	-2.8
H	CH <sub>3</sub>	CH <sub>3</sub>	-135.3	-5.3
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	-137.8	-7.8
Н	Н	Et	-132.3	-2.3
H.	H	iPr	-131.2	-1.2
Н	Н	t-Bu	-130.1	-0.1

This seemingly electron-withdrawing nature of the methyl group is also supported by solvolysis studies of methyl substituted 1-bromoadamantanes. The successive addition of bridgehead methyl groups to 1-bromoadamantane reduces the rate by approximately 30%. The other alkyl groups show an increase in rate<sup>134</sup>. However, the acidities of alkyl substituted adamantane carboxylic acids suggest that methyl is more electropositive than hydrogen<sup>135</sup>. <u>Table XXXIX</u> Acidities of Substituted 1-Adamantane Carboxylic Acids

\_₽	R	рКа
	Н	6.78
	Me	6.88
V Kaan	Et	6.95
V COOH	iPr	7.02

It has been suggested that replacement of hydrogen by methyl (or alkyl) may produce a small change in geometry which is reflected by the <sup>19</sup>F chemical shifts and the solvolysis ratio of adamantyl derivatives. This effect would be less pronounced for the  $_{pKa}$  values since the reaction site is further removed from the adamantane nucleus. Therefore it would be better to consider alkyl groups as being polarizable groups rather than being electropositive or electronegative relative to hydrogen<sup>136</sup>. This polarizing nature of alkyl groups may also be seen in Table XL.



Table XL Solvolysis of 4-Substituted 1-Bicyclo 2.2.2 Octyl Brosylates

Substituent (	<b>R)</b>		10 <sup>5</sup> k; sec <sup>-1</sup>	kR/kH
H			11.3	1.0
t-Bu		1	6.2	0.55
iPr			4.7	0.43
Et			4.0	0.36
Me			3.4	0.30
C <sub>6</sub> H <sub>5</sub>	• •		0.8	0.07
CN			0.003	0.0002

In the above case all alkyl groups appear to be electron withdrawing relative to hydrogen. However, the authors take this to mean that the difference is not entirely inductive in nature, rather that replacement of hydrogen causes a change in the hybridization at that bridgehead which slightly alters the geometry of the other bridgehead position, therefore sterically affecting the rate of reaction.<sup>136</sup>

The peculiar upfield shift in <sup>13</sup>C and <sup>19</sup>F nmr of the bridgehead carbons and fluorine atoms may therefore be a result of small, subtle, and <sup>\*</sup> yet significant structural changes brought about by changes in the hybridization of a bridgehead carbon atom at which hydrogen has been replaced by some other

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substituent.

#### CONCLUSIONS

It has been shown that the use of <u>in situ</u> generated aluminum halides leads to a very mild and general method for the interchange of non-aromatic halides in high yield. The reaction is thought to proceed <u>via</u> a tightly held ion pair of the aluminum halide and starting material. Even normally inert small ring bridgehead positions will react to produce exchanged products in good yield.

The irradiation of bridgehead halides in various solvents has been found to yield products from bridgehead carbenium ion and free radical pathways, the relative amount of each dependent upon the type of halide and the solvent used. No evidence for the intermediacy of any propellane type compounds was found.

The carbon-13 and fluorine-19 nmr spectra of bridgehead halogenated adamantanes have indicated some inner-lobe type interaction of the 4 bridgehead carbon atoms, the exact nature of which was not determined.

#### SUGGESTIONS FOR FURTHER STUDY

It would be interesting to determine the exact nature of the excited states involved in the photochemical reactions of the adamantyl halides. The quantum yields for the reactions of the iodides and bromides would be useful to determine why the iodides react at a much faster rate than the bromides and chlorides. A filter to stop the reaction of the iodide could also be used to try various sensitizers to initiate the reaction.

A second area worthy of examination would be the photochemical bromination reaction in BrCCl<sub>3</sub>. This reaction could be used to lead to otherwise difficult to synthesize bromides which could react to produce interesting dehydroadamantanes as shown below.



Finally, a third area would be an attempt to quantitatively explain the somewhat puzzling  ${}^{13}$ C and  ${}^{19}$ F nmr results of the halogenated adamantanes. Some form of theoretical treatment should be made to try and satisfactorily explain all of the observed results.

#### EXPERIMENTAL

#### General:

Melting points (uncorrected) were obtained with a Thomas Hoover capillary melting point apparatus using sealed tubes.

Infra-red spectra were recorded on a Perkin-Elmer 137 spectrophotometer with 0.493 mm sodium chloride solution cells using carbon tetrachloride as the solvent (unless otherwise stated). Band positions are reported on the frequency  $(cm^{-1})$  scale and intensities as strong (s), medium (m), weak (w), broad (b), shoulder (sh).

Ultraviolet spectra were obtained using a Gilford 240 spectrophotometer. Proton (<sup>1</sup>H) nuclear magnetic resonance spectra were recorded using a Varian Associates T-60, HA-100 or XL-100 spectrometer. All samples were run as 10 - 15% solutions in carbon disulfide, deuterochloroform, carbon tetrachloride or benzene with the chemical shifts expressed in parts per million (ppm) relative to internal tetramethylsilane at  $\delta = 0.0$ . Fluorine (<sup>19</sup>F) nmr spectra were obtained with a Varian Associates T-60 spectrometer. The samples were run as 10 - 30% solutions in carbon tetrachloride and the chemical shifts were expressed in ppm relative to internal trichlorofluoro--methane. The carbon (<sup>13</sup>C) nmr spectra were recorded on a Varian Associates CFT-20 spectrometer in CDCl<sub>3</sub> solution with wide band proton (<sup>1</sup>H) decoupling. Again the chemical shifts were expressed as ppm relative to internal tetramethylsilane at  $\delta = 0.0$ .

Low resolution mass spectra were recorded on an Atlas CH-4b spectrometer with high resolution work on an Atlas AEI-MS-902. The intensities of the fragments were reported as percentages of the base peak (100%). Both instruments were operated at 70 ev. Gas-liquid partition chromatography (glpc) was performed on a Perkin-Elmer 900 Gas Chromatograph utilizing a flame ionization detection system with helium as the carrier gas ( $\approx 60$  ml/min.)

The column used was a 6' by 0.125'' 8% OV-17 on Chromosorb W AW-DMCS 80/100 mesh.

Temperature programming was routinely used as exemplified below.

$$125^{\circ}$$
 (4)  $\xrightarrow{16^{\circ}}$   $250^{\circ}$ 

i.e. the column temperature was maintained at  $125^{\circ}$  for 4 minutes then heating at  $16^{\circ}$  per minute took place until a final temperature of  $250^{\circ}$  was achieved.

Preparative glpc was performed on a Varian aerograph model 90-P using helium as the carrier gas ( $\approx$  80 ml/min.).

The column used was a 5' x 0.25" 10% Carbowax 20m on Chromosorb W 80/100 mesh.

The samples were collected in Dry Ice-isopropanol cooled vessels.

Microanalytical results were obtained by Mr. P. Borda of this department.

Photochemical reactions were carried out in quartz or pyrex tubes equipped with condenser and a take-off joint for sampling. The light source was a GE UA-3 360 watt high pressure mercury lamp in a water cooled quartz immersion well. The reaction vessels were suspended approximately 10 cm from the immersion well and the whole system surrounded by aluminum foil to minimize loss of light. The solutions were degassed well with L - grade nitrogen for 15 minutes before irradiation or with 0<sub>2</sub> gas bubbled through the solution during the reaction.

Methanol was purified by refluxing over magnesium metal followed by

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distillation (bp  $63^{\circ}$ ) and storage in brown bottles under N<sub>2</sub>.

Dimethyl sulfoxide was stirred over molecular sieves (5 A) then distilled at reduced pressure over calcium hydride.

Acetonitrile was distilled from  $P_2O_5$  then redistilled over  $K_2CO_3$ (bp 81°) and then stored under  $N_2$  in dark bottles.

Carbon disulfide was stirred over molecular sieves before use.

All other solvents were either reagent or spectrograde and used without further purification.

Sodium cyanide was washed well with absolute ethanol then dried under vacuum at  $120^{\circ}$  for five hours before use. Similarly, LiBr, LiI, LiClo<sub>4</sub> and AgF were all dried at  $140^{\circ}$  under vacuum for 6 hours before use.

Aluminum oxide for column chromatography was obtained from McArthur Chemical Co. and had a pH range of 9.5 - 10.0. Silica gel was 60 - 120 mesh and was obtained from BDH.

Thin layer chromatography was performed on glass plates coated with 2.0 mm of silica gel containing uv - 254 fluorescent indicator from Binkman Instruments.

#### 1-Bromoadamantane



Procedure of Landa<sup>15</sup> was followed. To a 200 ml round bottomed flask equipped with a stirring bar, condenser and drying tube containing 20.0 g (147 mmoles) of adamantane (Aldrich) was added 40.0 ml of  $H_2SO_4$  washed bromine.

The solution was allowed to reflux with stirring for three hours whereupon the evolution of HBr had ceased. The reaction mixture was cooled to room temperature and poured onto 250 g of ice and 200 ml of CCl<sub>4</sub>. Solid sodium bisulfite was added with stirring to destroy excess  $Br_2$ . The solution was added to a separatory funnel and the organic layer washed with aqueous sodium carbonate and then water. After drying over MgSO<sub>4</sub> and Norit the solution was evaporated to yield a yellow solid which was eluted with 30 - 60 petroleum ether down an alumina column to yield 30.2 g (95%) of fluffy white crystals, mp 118° - 119° (11t<sup>18</sup> 119 - 120°). IR - 1455(s), 1343(m), 1290(s), 1105(m), 1030(s), 980(m), 955(s), 778(s) <u>NMR</u> (CS<sub>2</sub>) - unresolved doublet 2.28, (6H),  $\beta$ ; broad singlet 2.04, (3H),  $\gamma$ ;

unresolved doublet 1.73, (6H),  $\delta$  .

1,3-Dibromoadamantane



Into a 200 ml round bottomed flask equipped with stirring bar, condenser and drying tube was placed 10.0 g (73.5 mmole) of adamantane.
The flask was cooled to  $0^{\circ}$  and 40.0 ml of  $H_2SO_4$  washed  $Br_2$  was added. To this was cautiously added 120 mg of anhydrous  $AlBr_3$  which resulted in a rapid evolution of HBr. The solution was allwed to warm to room temperature and stirred for 0.5 hours followed by stirring at  $50^{\circ}$  for 0.5 hours. The flask was then cooled to  $0^{\circ}$  once again and 220 mg of anhydrous  $AlBr_3$  added. After the evolution of HBr had ceased the solution was stirred at room temperature for 0.75 hours followed by stirring at  $50^{\circ}$  for 0.75 hours. The solution was cooled to room temperature and worked up as before to yield a light yellow solid. Glc showed one main peak ( $200^{\circ}$ ) with traces of the mono and tri-bromides (t = 2, 1.2 and 3.5 minutes respectively).

Recrystallization from pentane yielded 15.3 g (73%) of white crystals mp 108 -  $109^{\circ}$  (lit<sup>22b</sup> 108 -  $109^{\circ}$ )

<u>IR</u> - 1460(s), 1340(m), 1320(s), 1290(s), 1020(s), 1000(m), 955(m), 700(s)
<u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - singlet 2.77, (2H), β ; unresolved doublet 1.93, (8H), βδ; broad singlet 1.58, (2H), γ ; unresolved triplet 1.10, (2H), δ .

1,3,5-Tribromoadamantane



To a stirred solution of 10.0 g (73.5 mmole) of adamantane and 40.0 ml of  $H_2SO_4$  washed bromine in a 200 ml round bottomed flask equipped with condenser and drying tube at 0° was added 220 mg of anhydrous AlBr<sub>3</sub>. After the initial evolution of HBr had ceased the reaction mixture was warmed to room temperature and stirred for two hours. Upon cooling once more to 0° 270 mg of AlBr<sub>3</sub> was added and the solution allowed to stir at room temperature until the evolution of HBr had ceased. The solution was then allowed to

reflux with stirring for 18 hours. Workup as before yielded a dark yellow solid which was shown to consist of one major peak by glc ( $200^{\circ}$  t = 2 min.).

Recrystallization from methanol yielded 18.4 g (76%) of white crystals mp 125 - 126<sup>o</sup> (lit<sup>22b</sup> 126 - 127<sup>o</sup>). <u>IR</u> - 1455(m), 1340(w), 1330(w), 1310(s), 1035(m), 975(m), 715(m) <u>NMR</u> (CS<sub>2</sub>) - singlet 2.74, (6H),ββ§; singlet 2.25 (1H), §; singlet 2.41,

(6H), **BSS**.

1,3,5,7-Tetrabromoadamantane



The same procedure for the preparation of the tribromide was followed. After the 18 hour reflux the solution was cooled to room temperature and transferred to a Carius tube which was then frozen in liquid nitrogen and sealed under vacuum. The tube was placed in a metal bomb and heated at  $175^{\circ}$  for six days. The tube was frozen in liquid N<sub>2</sub> again, then opened. Workup as before yielded a dark brown solid which consisted of 85% tetrabromide and 15% tribromide (OV - 17 200° t = 12.0 and 8.0 min. respectively). Three recrystallizations from CCl<sub>4</sub> yielded 12.5 g (37%) of a white solid mp 246 - 248° (lit <sup>22b</sup> 246 - 248°). IR - 1450(m), 1318(s), 1220(m), 998(m), 855(s) <u>NMR</u> (CS<sub>2</sub>) - singlet 2.65, (12H). 1-Bromo-3,5-dimethyladamantane



To a 200 ml round bottomed flask equipped with condenser and drying tube at 0° was placed 10.0 g (61.0 mmole) of 1,3-dimethyladamantane (Sunoco) and 40.0 ml of  $H_2SO_4$  washed  $Br_2$ . After the initial evolution of HBr had ceased the mixture was refluxed in an oil bath with stirring for three hours. Workup as before yielded a light yellow liquid which showed one peak by glc (125(4)  $\xrightarrow{32}$  200° t = 6.5 min.). Distillation afforded 13.48 g (91%) of a colourless oil, bp 66 - 68° (0.12 mm) (lit<sup>137</sup> 67 - 69° (0.03 mm)).

<u>IR</u> - 1455(s), 1370(w), 1320(m), 1280(w), 1170(m), 975(m), 935(m), 920(m) 895(m)

<u>NMR</u> (CS<sub>2</sub>) - singlet 0.87, (6H), CH<sub>3</sub>; singlet 1.20, (2H), H1; singlet 1.38, (4H), H<sub>2</sub>; singlet 1.95, (4H), H<sub>3</sub>; singlet 2.10, (3H), H<sub>4</sub> + H<sub>5</sub>.

1,3-Dibromo-5,7-dimethyladamantane



To a stirred mixture of 10.0 g (61.0 mmole) of 1,3-dimethyladamantane and 40.0 ml of  $H_2SO_4$  washed  $Br_2$  in a 200 ml round bottomed flask equipped with condenser and drying tube at 0° was added 100 mg of anhydrous  $AlBr_3$ . After the evolution of HBr had ceased the mixture was stirred at room temperature for 0.5 hours then at 50° for 0.5 hours. After cooling to 0° Another 100 mg of  $AlBr_3$  was added and the solution stirred at room temperature for 0.75 hours and at 50° for 0.75 hours. Workup as before yielded a light yellow solid which was recrystallized from hexane to yield 11.0 g (74%) of white crystals, mp 114 - 115° (lit<sup>138</sup> 115 - 116°).

- <u>IR</u> 1455(s), 1378(w), 1355(w), 1340(m), 1318(s), 1238(m), 1180(m), 940(w), 907(m)
- <u>NMR</u> (CS<sub>2</sub>) singlet 0.93, (6H), -CH<sub>3</sub>; singlet 1.23, (2H), H<sub>1</sub>; singlet 1.93, (8H), H<sub>2</sub>; singlet 2.60, (2H), H<sub>3</sub>.

1,1'-Biadamantane



The biadamantane was prepared by Ken Waldman,a 4th year summer student, in 1971 by the procedure of Reinhardt<sup>83</sup>. mp 288 - 289° (lit<sup>83</sup> 290°) <u>IR</u> (KBr) - 1438(s), 1342(s), 1330(s), 1300(m), 1100(m), 1034(m), 961(m), 813(m)

<u>NMR</u> (CS<sub>2</sub>) - unresolved doublet 1.64, (12H),  $\beta$ ; unresolved doublet 1.73, (12H),  $\delta$ ; broad singlet 1.94, (6H),  $\delta$ .

3,3'-Dibromo-1,1'-biadamantane



To a 200 ml round bottomed flask equipped with condenser and drying tube at  $0^{\circ}$  was added 6.7 g of crude biadamantane. To this was added 40.0 ml of H<sub>2</sub>SO<sub>4</sub> washed Br<sub>2</sub>. After the moderate evolution of HBr had ceased the solution was stirred under reflux for three hours. Workup as before yielded 9.2 g of a yellow solid which was shown by nmr and glc to contain some of the monomer. Subsequent analysis of the starting material showed it to contain substantial amounts of monobromoadamantane. This was removed by washing the crude solid with methanol.

The solid was then recrystallized from  $CCl_4$  to yield 5.2 g of a white solid, mp 232 - 234° (lit<sup>83</sup> 236°)

<u>IR</u> (KBr) - 1440(s), 1340(s), 1320(s), 1300(s), 1237(s), 1132(m), 1102(m), 1020(s), 982(m), 947(s), 890(w), 815(sb), 762(s), 684(sb)

<u>NMR</u> (CS<sub>2</sub>) - unresolved doublet 1.58, (12H), H<sub>1</sub> + H<sub>5</sub>; singlet 2.10, (4H), H<sub>4</sub>; singlet 2.20, (12H), H<sub>1</sub> + H<sub>3</sub>.

## General Procedure for Iodine Exchange

Into a 100 ml round bottomed flask equipped with stirring bar, condenser and drying tube was placed the desired amount of aluminum foil torn into small pieces. To this was added the iodine crystals and the contents stirred at 80° in an oil bath until part of the iodine had vapourized, coating the aluminum foil. Next was added the carbon disulfide through the top of the condenser resulting in a dark purple solution. This mixture was stirred under reflux until a light pink colour had replaced the original purple and most of the aluminum foil had been broken up into very small pieces (usually requiring 45 to 60 minutes). The reaction vessel was then removed and cooled down to either room temperature,  $0^{\circ}$  in an ice bath. or -50° in a Dry Ice-isopropanol bath depending upon the type of halide being used. The halide was then added directly and the reaction quenched by the addition of aqueous sodium bisulfite (usually after 2 minutes). Petroleum ether was added and the layers separated. The organic phase was washed with aqueous sodium carbonate, water and dried over MgSO<sub>4</sub>. Evaporation of the

solvent under reduced pressure yielded the crude iodide which was purified by distillation, column chromatography or recrystallization.

## General Procedure for Bromine Exchange

In this case the freshly torn aluminum foil was placed with 2 ml of CS<sub>2</sub> and then the desired amount of liquid bromine added. This solution was refluxed with stirring for several minutes and then the rest of the solvent was added. The rest of the procedure and workup was identical to that of the iodine exchange reaction.

# General Procedure for Chlorine Exchange

Unlike the iodine and bromine exchange reactions, carbon disulfide could not be used as a solvent for chlorine exchange. Use of chlorine gas with freshly torn aluminum foil in carbon disulfide led to a rapid oxidation of the solvent to yield elemental sulfur. A single run with 1,3-dibromoadamantane produced the desired 1,3-dichloride in a 1:10 ratio with elemental sulfur. Separation of the two products was tedious so that this method was abandoned.

Instead, to a mixture of freshly torn aluminum foil in reagent chloroform at  $0^{\circ}$  was added chlorine gas, saturating the solution. A small crystal of iodine was added, initiating an exothermic reaction in which the aluminum foil was broken up into small pieces. The solution was cooled to  $0^{\circ}$  again and the adamantyl bromide was added with stirring. The solution was quenched by the addition of water, the layers separated and the organic phase washed with aqueous sodium carbonate and water. After drying,the solvent was evaporated under reduced pressure to yield the crude chloride. Use of CCl<sub>4</sub> as the solvent led to the desired chlorine exchange but also produced major amounts of hexachloroethane as well.

### General Procedure for Fluorine Exchange

Into a three necked flask equipped with condenser, drying tube and stirring bar was placed the desired adamantyl bromide with a three to four fold excess of freshly dried silver fluoride with 75 ml of spectrograde cyclohexane. The mixture was stirred under reflux and stopped when glc indicated that starting material had been consumed. The solution was cooled, filtered and evaporated to yield the crude fluoride which was purified by distillation or column chromatography.

#### 1-Fluoroadamantane



To a solution of 4.0 g (18.6 mmole) of 1-bromoadamantane in 50 ml of reagent cyclohexane was added 5.5 g (43.0 mmole) of anhydrous silver fluoride. The mixture was allowed to reflux with stirring for  $4\frac{1}{2}$  hours. Filtration and evaporation yielded a light brown solid which was eluted with 30-60 petroleum ether down an alumina column to yield 2.48 (83%) of fluffy white crystals, mp 212 - 214° (sub) (lit<sup>18</sup> 210 - 212°)

- <u>IR</u> 1455(m), 1350(s), 1318(s), 1295(m), 1180(w), 1110(m), 1070(sb), 970(s), 920(s), 908(w), 835(sb)
- <u>NMR</u> (CS<sub>2</sub>) unresolved doublet 1.62, (6H), δ ; multiplet 1.81, (6H), β ; broad singlet 2.18, (3H), δ.

<u>NMR</u> (<sup>19</sup>F) - singlet -128.0 ppm.

The di, tri and tetrafluorides were prepared by Dr. K. Bhandari, a post-doctoral fellow in the spring of 1973.

1,3-Difluoroadamantane



 ${\rm Mp}^{50}$  240 - 241°

- <u>MS</u> 172(37), 129(77), 115(81), 97(51), 43(100)
- <u>IR</u> 2450(m), 1360(m), 1340(s), 1320(m), 1295(m), 1240(w), 1110(s),

1060(s), 1000(s), 945(s), 902(m), 835(sb)

<u>NMR</u>  $(C_6H_6)$  - triplet J = 5.5 Hz, 2.04, (2H),  $\beta$ ; broad singlet 1.85, (2H),  $\delta$ ; broad doublet, J = 3 Hz, 1.53, (8H),  $\beta\delta$ ; broad singlet, 0.97,

(2H), S .

<u>NMR</u>  $({}^{19}F)$  - singlet -132.5, SCS - 4.5\*.

<u>Analysis</u> - $C_{10}H_{14}F_2$		<u> </u>	<u> </u>	
	calculated	69.76	8.14	
	found	69.53	7.96	

\* SCS = Substituent Chemical Shift

1,3,5-Trifluoroadamantane



 $Mp^{50}$  244 - 245°

- <u>MS</u> 190(78), 133(84), 129(64), 115(92), 56(100)
- <u>IR</u> 1460(m), 1350(m), 1322(s), 1290(m), 1258(m), 1150(s), 1062(m), 1037(s), 995(s), 952(s), 895(w), 835(sb)

<u>NMR</u> (CS<sub>2</sub>) - broad multiplet, J = 3.5 Hz, 2.47, (1H), δ; broad doublet, J = 3.5 Hz, 1.99, (6H), ββδ; triplet, J = 2.5 Hz, 1.75, (6H), βδδ.
<u>NMR</u> (<sup>19</sup>F) - singlet, -138.9, SCS -10.9
<u>Analysis</u> - C<sub>10</sub>H<sub>13</sub>F<sub>3</sub>

calculated	63.16	6.84
found	62.88	6.92

1,3,5,7-tetrafluoroadamantane



$$\begin{split} & \text{Mp}^{50} \ 252 \ - \ 253^{\circ} \\ & \underline{\text{MS}} \ - \ 208(11), \ 152(11), \ 133(76), \ 129(25), \ 128(39), \ 115(14), \ 109(14), \ 56(100) \\ & \underline{\text{IR}} \ - \ 1460(\texttt{w}), \ 1450(\texttt{m}), \ 1325(\texttt{s}), \ 1250(\texttt{m}), \ 1060(\texttt{sb}), \ 1035(\texttt{sb}), \ 995(\texttt{w}), \\ & \overline{\text{N72}}(\texttt{s}), \ 930(\texttt{m}), \ 840(\texttt{sb}) \\ & \underline{\text{NMR}} \ (\text{CS}_2) \ - \ \texttt{quintet}, \ \texttt{J} \ = \ 3.5 \ \text{Hz}, \ 2.04, \ (12\text{H}) \\ & \underline{\text{NMR}} \ (^{19}\text{F}) \ - \ \texttt{singlet}, \ -148.5, \ \text{SCS} \ -20.5 \\ & \text{High Resolution Mass Spec} \ - \ C_{10}\text{H}_{12}\text{F}_4 \qquad \text{calculated} \ \ 208.0875 \\ & \text{found} \qquad 208.0865 \end{split}$$

1,3-Dimethy1-5-fluoroadamantane



To a reluxing solution of 3.0 g (12.4 mmole) of 1-bromo-3,5-dimethyladamantane in 50 ml of reagent grade cyclohexane was added 4.0 g (31.0 mmole) of freshly dried silver fluoride. The reaction was stopped after 3 hours, cooled, filtered and evaporated to yield a light yellow oil which showed one peak by glc  $(75^{\circ} (4) \xrightarrow{32})$  200, t = 6.8 min.). Distillation yielded 1.90 g (84%) of a colourless liquid, bp 34° (0.3mm). <u>MS</u> - 182(18), 167(100), 163(4), 147(9), 125(13), 111(28), 107(18)

- <u>IR</u> 1455(s), 1375(w), 1355(m), 1342(w), 1328(m), 1185(m), 1150(w), 1060(w), 1053(w), 1015(s), 970(m), 938(w), 915(w), 880(m)
- <u>NMR</u> (CS<sub>2</sub>) singlet, 0.88, (6H), -CH<sub>3</sub>; broad singlet, 1.11, (2H), H<sub>1</sub>; unresolved doublet, 1.28, (4H), H<sub>2</sub>; doublet, J = 5.5 Hz, 1.45, (4H), H<sub>3</sub>; broad triplet, J = 5.5 Hz, 1.64, (2H), H<sub>5</sub>; multiplet, J = 3 Hz, 2.20, (1H), H<sub>4</sub>

<u>Analysis</u> - $C_{12}H_{19}F$		<u> </u>	<u> </u>
	calculated	79.07	10.50
	found	79.07	10.60

1-Ethoxy-3-fluoroadamantane



To a solution of 400 mg (1.54 mmole) of 1-bromo-3-ethoxy-adamantane in 20 ml of cyclohexane was added 800 mg (6.36 mmole) of AgF. The solution was stirred under reflux for 3 hours. After filtration the solution was evaporated to yield a light yellow solid. Elution with 30-60 petroleum ether down an alumina column yielded 250 mg (82%) of a colourless oil. Sublimation of the oil at 60° (1 mm) yielded white needles. Mp 33 - 34.5°. <u>MS</u> - 198(60), 153(14), 141(100), 123(27), 113(32), 97(11), 95(8) <u>IR</u> - 1444(m), 1382(w), 1358(w), 1340(m), 1320(w), 1300(w), 1120(sb) 1060(s), 998(s), 913(m), 868(w)

$(C_6^{H_6}) - triplet, J = 7$	Hz, 1.11, (3H);	singlet, 1.15, (2)	H), H <sub>5</sub> ,; singlet
1.51, (4H), H <sub>3</sub> ; unreso	lved triplet, J	= 5.5  Hz, 1.69, (41)	H), H <sub>2</sub> ;
doublet, J = 5.5 Hz, 1	.94, (2H), H <sub>1</sub> ; b	road singlet, 2.02	, (2H), H <sub>4</sub> ;
quartet, $J = 7 Hz$ , 3.2	3, (2H)		
$(^{19}F)$ - singlet, -132.5	, SCS -4.5		
ysis - C <sub>10</sub> H <sub>10</sub> FO	C	• • • • • • • • • • • • • • • • • • •	

<u>Analysis</u> - $C_{12}H_{19}FO$	· · ·	<u> </u>	H
	calculated	72.69	9.66
	found	71.56	9.54
High Resolution MS	calculated	198.2814	
	found	198.2825	

1,3-Difluoro-5,7-dimethyladamantane

NMR

NMR



To a refluxing solution of 2.0 g (6.2 mmole) of 1,3-dibromo-5,7dimethyladamantane in 30 ml of reagent cyclohexane was added 5.0 g (39.2 mmole) of freshly dried silver fluoride. The reaction was stopped after 4 hours, cooled, filtered and evaporated to yield a yellow oil which showed one peak by glc (75(4)  $\frac{32}{200}$ , t = 6.8 min.). Distillation yielded 0.87 g (70%) of a colourless oil, bp 64<sup>o</sup> (0.7mm).

<u>MS</u> - 200(16), 185(100), 165(5), 129(37), 125(37)

<u>IR</u> - 1455(s), 1355(w), 1342(m), 1322(s), 1280(w), 1242(m), 1195(s), 1045(m) 1022(s), 987(s), 928(s), 918(w), 868**∦**m), 675(mb)

<u>NMR</u> - (CS<sub>2</sub>) - triplet, J = 5.5 Hz, 1.84, (2H), H<sub>3</sub>; unresolved doublet, 1.47, (8H), H<sub>2</sub>; broad singlet, 1.08, (2H), H<sub>1</sub>; singlet, 0.98, (6H), -CH<sub>3</sub>.
<u>NMR</u> (<sup>19</sup>F) - singlet, -139.8, SCS -11.8

<u>Analysis</u> - $C_{10}H_{18}F_2$	<u> </u>	H
calculated	71.97	9.06
found	71.76	9.20

3,3'-Difluoro-1,1'biadamantane



To a refluxing solution of 2.0 g (4.67 mmole) of 3,3'-dibromo-1,1'biadamantane in 40 ml of reagent cyclohexane was added 3.0 g (23.6 mmole) of freshly dried silver fluoride. The reaction was cooled to room temperature after four hours, filtered and evaporated to yield a light brown solid. This was eluted with 30-60 petroleum ether down a short alumina column to yield 1.10 g (76%) of fluffy white crystals, mp 227 - 229°.

<u>MS</u> - 306(29), 153(100), 152(20), 134(72)

<u>IR</u> (KBr) - 1510(s), 1450(m), 1350(w), 1342(w), 1330(w), 1300(w), 1135(w),

1100(w), 1070(m), 1015(m), 965(w), 935(m), 915(mb), 880(w)

<u>MMR</u> (CS<sub>2</sub>) - unresolved doublet, 1.48, (8H),  $H_2$ ; broad singlet, 1.54, (4H),  $H_5$ ; doublet, J = 5.5 Hz, 1.59, (4H),  $H_1$ ; unresolved doublet, 1.73, (8H),  $H_3$ ; broad singlet, 2.24, (4H),  $H_4$ .

<u>NMR</u> (<sup>19</sup>F) - singlet, -127.8, SCS +0.2

<u>Analysis</u> - $C_{20}H_{28}F_2$ -		<u>    C    </u>	<u>    H    </u>
	calculated	78.39	9.21
	found	78.49	9.34

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1-Chloroadamantane



The catalyst was prepared from 150 mg of aluminum foil with chlorine gas in 20 ml of chloroform. To this was added 500 mg (2.32 mmole) of 1-bromoadamantane. Workup after 10 minutes yielded a yellow solid which showed one peak by glc  $(125^{\circ}(4) \xrightarrow{32}) 200^{\circ}$ , t = 5.4 min.). Sublimation yielded 320 mg of a white solid, mp 164 - 165°  $(11t^{18} 164 - 165.5^{\circ})$ . <u>IR</u> - 1440(s), 1342(m), 1295(m), 1100(m), 1030(s), 980(w), 955(m), 690(m) 685(mb)

<u>NMR</u>  $(C_6H_6)$  - unresolved triplet, 1.38, (6H), S; broad singlet 1.80, (3H), S; broad doublet, 2.06, (6H),  $\beta$ .

1,3-Dichloroadamantane



The catalyst was prepared as above; from 500 mg of 1,3-dibromoadamantane (1.7 mmole) a yield of 320 mg (90%) of white crystals (after recrystallization from hexane) was produced, mp 129 - 130° (lit<sup>139</sup> 130 - 131°) <u>MS</u> - 206(5), 204(8), 171(32), 169(100), 133(12), 115(10), 105(5), 91(12) <u>IR</u> - 1445(s), 1360(w), 1340(s), 1320(s), 1295(s), 1158(m), 1110(m), 1040(s), 995(w), 968(s), 955(w), 850(sb), 780(mb) <u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - singlet, 1.00, (2H), §; broad singlet, 1.63, (2H), §; singlet, 1.73, (8H), β§; singlet, 2.40, (2H), §. 1,3,5-Trichloroadamantane



The catalyst was prepared as before; from 1.0 g (2.68 mmole) of 1,3,5-tribromoadamantane 565 mg (88%) of white crystals (from hexane) was produced. Mp 111 - 112° (1it<sup>139</sup> 112 - 113°) <u>MS</u> - 240(8), 238(9), 205(66), 203(100), 169(10), 167(12), 133(4), 91(17) <u>IR</u> - 1455(s), 1355(w), 1322(s), 1295(m), 1242(w), 1050(s), 978(m), 865(s), 855(msh)

<u>NMR</u> ( $C_6H_6$ ) - singlet, 2.08, (6H),  $\beta\beta\delta$ ; singlet, 1.42, (7H),  $\beta\delta\delta + \delta$ <u>1,3,5,7-Tetrachloroadamantane</u>



The catalyst was prepared as above; from 500 mg (1.1 mmole) of 1,3,5,7-tetrabromoadamantane 260 mg (85%) of white crystals (from benzene) was produced. mp 193 -  $194^{\circ}$  (lit<sup>52</sup> 194°)

<u>MS</u> - 276(11), 274(19), 272(20), 241(33), 239(100), 237(100), 204(26)

202(27), 125(36), 91(50)

<u>IR</u> - 1455(s), 1320(s), 1220(s), 992(m), 870(s), 857(wsh)

<u>NMR</u> (CS<sub>2</sub>) - singlet, 2.30, (12H)

1-Chloro-3,5-dimethyladamantane



The catalyst was prepared as above; from 500 mg (2.06 mmole) of 1-bromo-3,5-dimethyladamantane 380 mg (90%) of a colourless liquid was produced. bp 60 - 62° (0.8 mm) (lit<sup>140</sup> 84 - 86° (4mm)) <u>IR</u> - 1445(s), 1365(w), 1350(w), 1338(w), 1320(m), 1280(w), 1170(mb), 975(w), 938(w), 922(m), 908(m), 895(m), 835(m) <u>NMR</u> (CS<sub>2</sub>) - singlet, 0.89, (6H), -CH<sub>3</sub>; singlet, 1.17, (2H), H<sub>1</sub>; broad doublet, 1.35, (4H), H<sub>2</sub>; singlet, 1.74, (4H), H<sub>3</sub>; broad doublet, 1.93,

(2H), H<sub>5</sub>; broad singlet, 2.12, (1H), H<sub>4</sub>

1,3-Dichloro-5,7-dimethyladamantane



The catalyst was prepared as above; from 750 mg (2.33 mmole) of 1,3-dibromo-5,7-dimethyladamantane 480 mg (88%) of white crystals (from hexane) was produced. mp 95 - 96° ( $1it^{74}$  95.5 - 96.5°)

- <u>MS</u> 234(1), 232(3), 219(1), 217(3), 199(33), 197(100), 161(13), 141(17), 121(5), 119(9), 91(7)
- <u>IR</u> 1458(s), 1377(w), 1350(w), 1340(m), 1320(s), 1238(m), 1176(m), 998(w), 945(m), 938(m), 905(m), 852(s)
- <u>NMR</u> (CS<sub>2</sub>) singlet, 0.97, (6H), -CH<sub>3</sub>; singlet, 1.15, (2H), H<sub>1</sub>; singlet, 1.70, (8H), H<sub>2</sub>; singlet, 2.24, (2H), H<sub>3</sub>

3,3'Dichloro-1,1'-biadamantane



The catalyst was prepared from 500 mg of aluminum foil in 30 ml of chloroform, with chlorine gas at  $0^{\circ}$ . To this was added 1.0 g (2.36 mmole) of 3,3'-dibromo-1,1'-biadamantane. The solution was worked up after 1 minute to yield a light yellow solid which was eluted down a short alumina column with pentane to yield 0.67 g (85%) of a white solid. The mass spectrum showed the presence of a bromo-chloro compound in addition to the desired dichloride.

Elution down a larger alumina column with pentane yielded a white solid which was recrystallized from pentane to yield white crystals. mp 198.5 -  $200^{\circ}$ . <u>MS</u> - 340(2), 338(s), 303(1), 177(50), 169(28), 135(50), 134(80), 133(39),

121(43), 119(43), 107(66), 105(62), 91(100)

- <u>IR</u> (KBr) 1450(m), 1342(m), 1325(m), 1305(m), 1240(w), 1165(w), 1130(w), 1102(w), 1025(s), 985(w), 955(m), 830(s), 810(w), 768(s), 705(s)
- <u>NMR</u> (CS<sub>2</sub>) unresolved doublet, 1.51, (8H), H<sub>2</sub>; singlet, 1.60, (4H), H<sub>5</sub>; singlet, 1.87, (4H), H<sub>1</sub>; singlet, 2.00, (8H), H<sub>3</sub>, broad singlet, 2.17, (4H), H<sub>4</sub>.

High Resolution MS - C <sub>20</sub> H <sub>23</sub> C1 <sub>2</sub>	calculated	338.1508			
	found	338.1480			
Use of Ferric Chloride as an Exchanging Agent					

The reaction of bridgehead halides with  $\text{FeCl}_3$  in  $\text{CS}_2$  was found to be rapid on a small scale but increasing amounts of  $\text{FeCl}_3$  and reaction times were required on a larger scale. In all cases the bridgehead halide was

dissolved in 20 ml of CS<sub>2</sub> and the FeCl<sub>3</sub> added to the solution. <u>1-Haloadamantanes</u>

To a solution of 80 mg of 1-iodoadamantane in 20 ml of CS<sub>2</sub> was added 200 mg of FeCl<sub>3</sub>. The solution turned dark purple immediately and glc showed 1 peak, 1-chloroadamantane. The same reaction was repeated with 50 mg of 1-bromoadamantane and 160 mg of FeCl<sub>3</sub>. The solution turned dark orange immediately and glc showed 1-chloroadamantane to be the only product. 1,3-Dihaloadamantanes

To a solution of 60 mg of 1,3-diiodoadamantane in 20 ml of CS<sub>2</sub> was added 200 mg of FeCl<sub>3</sub>. The solution turned dark purple immediately and the corresponding dichloride was the only product by glc. The same reaction was repeated with 40 mg of 1,3-dibromoadamantane and 160 mg of FeCl<sub>3</sub>. After 1 hour the orange solution consisted of 70% 1,3-dichloroadamantane and 30% 1-bromo-3-chloroadamantane. No change in the ratios occurred over long reaction times.

# 1,3,5-Trihaloadamantanes

To a solution of 50 mg of 1,3,5-triiodoadamantane in 20 ml of  $CS_2$  was added 100 mg of FeCl<sub>3</sub>. The solution turned purple gradually over a period of 1 hour.

	C1 <sub>3</sub>	C1 <sub>2</sub> I	C1I <sub>2</sub>	I <sub>3</sub>
4 hours	-	-	1	1
22 hours	2	1		-
34 hours	only peak	-	-	-

The same reaction was repeated with 40 mg of the tribromide and 150 mg of FeCl<sub>3</sub>. Cl<sub>2</sub>Br ClBr<sub>2</sub> Br<sub>2</sub>

	° <u>*</u> 3	<sup>01</sup> 2 <sup>11</sup>		<sup>D</sup> 3
18 hours	-	1	2	3
40 hours	-	1.5	2	2
60 hours	-	2	3	1

The same reaction was repeated with 200 mg (.54 mmole) of the tribromide and 840 mg (5 mmoles) of FeCl<sub>3</sub> in 35 ml of refluxing  $CS_2$ .

	<sup>C1</sup> 3	Cl <sub>2</sub> Br	ClBr <sub>2</sub>	Br <sub>3</sub>
70 min.	2	4	4	1
150 min.	3	3	1	-
270 min.	5	1	_	_
300 min.	only product	-	-	-

The trichloride was isolated in 82% yield.

The FeCl<sub>3</sub> reaction was also performed with 1,4-diiodobicyclo[2.2.1]heptane. A solution of 170 mg (.5 mmole) of the diiodide with 840 mg (5 mmole) of FeCl<sub>3</sub> was stirred under reflux for 45 hours in 30 ml of  $CS_2$ . The only peak by glc was the corresponding dichloride which was isolated in 75% yield.

1-Iodoadamantane

The catalyst was prepared by heating 900 mg (3.5 mmole) of iodine with 380 mg (14.0 mmole) of aluminum foil in 35 ml of CS<sub>2</sub> for 45 minutes (original purple colour had been replaced by a light pink). The solution was cooled to room temperature and 1.0 g (4.7 mmole) of 1-bromoadamantane was added. The reaction was quenched after 2 minutes by the addition of aqueous sodium bisulfite, pentane added and the layers separated. The organic phase was washed with aqueous sodium carbonate, water and dried over magnesium sulfate. Evaporation yielded sticky orange crystals which showed one peak by glc ( $125(4) \xrightarrow{10} 250$ , t = 8.7 min.) Elution down a short alumina column with pentane yielded 0.90 (73%) of white crystals, mp 74 -75.5° ( $11t^{18}$  75 - 76°)

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<u>MS</u> - 262(trace), 135(84), 107(14), 105(19), 93(58), 92(23), 91(48), 79(100), 77(61)

<u>IR</u> - 1460(s), 1348(m), 1290(s), 1105(m), 1028(s), 980(w), 950(m), 670(m) <u>NMR</u> (CS<sub>2</sub>) - unresolved doublet, 2.62, (6H),  $\beta$ ; broad singlet, 1.92, (3H),

 $\lambda$  ; unresolved doublet, 1.88, (6H),  $\delta$  .

2-Iodoadamantane



The catalyst was prepared as before from 270 mg (10 mmole) of aluminum foil with 850 mg (3.35 mmole) of iodine in 35 ml of  $CS_2$ . After cooling to 0<sup>°</sup> in an ice bath, 1.0 g (4.7 mmole) of 2-bromoadamantane (Aldrich) was added with stirring. The reaction was quenched after 2 minutes and worked up as before to yield a light yellow oil. (one peak by glc 125(4)  $\xrightarrow{16}$  250<sup>°</sup>, t = 10.1 min.) Elution with 30-60 petroleum ether down a short alumina column yielded 1.14 g (95%) of fluffy white crystals, mp 47 - 48<sup>°</sup> (lit<sup>28</sup> 46 - 48<sup>°</sup>)

<u>IR</u> (CS<sub>2</sub>) - 1350(w), 1278(s), 1220(m), 1162(s), 1105(s), 1068(w), 1045(m), 1032(w), 988(w), 970(m), 958(w), 908(s), 820(m), 770(w), 720(s)

<u>NMR</u> (CS<sub>2</sub>) - multiplet, 4.84, (1H); multiplets, 1.58 - 2.50, (14H)

1,3-Diiodoadamantane



The catalyst was prepared as before from 550 mg (20.4 mmole) of aluminum foil and 1.3 g (5.1 mmole) of iodine in 35 ml of  $CS_2$ . After cooling to room temperature, 1.0 g (3.4 mmole) of 1,3-dibromoadamantane was added with stirring. The reaction was quenched after 8 minutes and worked up as before to yield an orange solid which consisted of one peak by glc (200°, t = 11.2 min.) Recrystallization from hexane yielded 1.04 g (78%) of white crystals, mp 110 - 111° (1it<sup>30a</sup> 110 - 111°)

<u>MS</u> - 388(trace), 261(100), 134(55), 133(40), 127(13), 119(14), 105(27), 91(56), 79(37), 77(35)

<u>IR</u> - 1455(s), 1338(m), 1316(s), 1284(s), 1238(m), 1144(w), 1105(w), 1018(s), 990(s), 955(s), 942(w), 785(sb)

<u>NMR</u> - singlet, 3.26, (2H), β; unresolved doublet, 2.60, (8H), βδ; singlet, 1.92, (4H), δ + δ.

1,3,5-Triiodoadamantane



The catalyst was prepared as before from 560 mg (20.8 mmole) of aluminum foil and 1.3 g (5.2 mmole) of iodine in 35 ml of  $CS_2$ . After cooling to room temperature, 1.0 g (2.68 mmole) of 1,3,5-tribromoadamantane was added. The reaction was quenched after 20 min. and worked up as before to yield 1.17 g (85%) of light yellow crystals (from benzene), mp 125 - 127°. <u>MS</u> - 516(trace), 387(100), 261(6), 260(8), 133(51), 132(17), 105(17),

91(42), 79(13)

<u>IR</u> - 1455(s), 1320(m), 1302(s), 1280(m), 1218(m), 1055(s), 955(m), 685(sb) <u>NMR</u> (CS<sub>2</sub>) - singlet, 3.23, (6H),  $\beta\beta\delta$ ; doublet, J = 3 Hz, 2.58, (6H),  $\beta\delta\delta$ ; multiplet, J = 3 Hz, 1.97, (1H),  $\delta$ .

<u>Analysis</u> - $C_{10}H_{13}I_3$		<u> </u>	<u>    H     </u>	<u> </u>
	calculated	23.37	2.55	74.08
	found	23.14	2.58	73.88

1,3,5,7-Tetraiodoadamantane



The catalyst was prepared as before from 380 mg (14.1 mmole) of aluminum foil with 895 mg (3.52 mmole) of iodine in 35 ml of CS<sub>2</sub>. After cooling to room temperature, 1.0 g (1.56 mmole) of 1,3,5,7-tetrabromoadamantane was added. The reaction was quenched after 30 minutes and worked up as before to yield 1.22 g (86%) of a light brown powder insoluble in most solvents. Recrystallization from either toluene or pyridine yielded white needles, mp >  $330^{\circ}$  (lit<sup>52</sup>= $370^{\circ}$ )

<u>MS</u> - 640(trace), 513(trace), 286(96), 285(94), 131(50), 130(39), 129(32), 116(28), 115(36), 91(100)

<u>IR</u> (CS<sub>2</sub>) - 1420(w), 1310(s), 1200(m), 980(m), 832(s), 705(w), 692(sb) <u>NMR</u> (CS<sub>2</sub>) - singlet, 3.18, (12H) 1,3-Dimethy1-5-iodoadamantane



The catalyst was prepared as before from 980 mg (3.86 mmole) of iodine and 275 mg (11.8 mmole) of aluminum foil in 30 ml of CS<sub>2</sub>. After cooling to room temperature, 1.25 g (5.15 mmole) of 1-bromo-3,5 -dimethyladamantane was added with stirring. The reaction was quenched after 2 minutes and worked up as before to yield a yellow oil which consisted of one peak by glc (125(4)  $\xrightarrow{32}$  200°, t = 7.6 min.) Distillation yielded a light pink liquid, 0.92 g (62%), bp 76 - 78° (0.34 mm). Glc provided an analytical sample.

 $\underline{\text{MS}} = 290(\text{trace}), 163(100), 107(60), 93(14), 91(14)$   $\underline{\text{IR}} = 1450(\text{s}), 1370(\text{w}), 1350(\text{w}), 1316(\text{m}), 1280(\text{m}), 1240(\text{m}), 1170(\text{s}), 970(\text{m}), 932(\text{w}), 918(\text{m}), 890(\text{s}), 695(\text{w}), 668(\text{m})$   $\underline{\text{NMR}} (\text{CS}_2) = \text{doublet}, J = 3 \text{ Hz}, 2.38, (2\text{H}), \text{H}_5; \text{singlet}, 2.22, (4\text{H}), \text{H}_3; \text{multiplet}, J = 3.5 \text{ Hz}, 1.94, (1\text{H}), \text{H}_4; \text{doublet}, J = 3 \text{ Hz}, 1.45, (4\text{H}), \text{H}_2; \text{singlet}, 1.27, (2\text{H}), \text{H}_1; \text{singlet}, 0.84, (6\text{H}), -\text{CH}_3.$   $\underline{\text{Analysis}} = \text{C}_{12}\text{H}_19\text{I} \qquad \underline{\text{C}} \qquad \underline{\text{H}}$ 

calculated	49.67	6.60
found	49.43	6.79

- 156 -





The catalyst was prepared as before from 310 mg (11.4 mmole) of aluminum foil and 860 mg (3.4 mmole) of iodine in 35 ml of CS<sub>2</sub>. After cooling to 0°, 750 mg (2.28 mmole) of 1,3-dibromo-5,7-dimethyladamantane was added with stirring. The reaction was stopped after 2 minutes and worked up as before to yield a yellow solid which showed one peak by glc  $(200(2) \xrightarrow{32} )$  250°, t = 4.4 min. SM = 2.9 min.) Elution with pentane down a short alumina column yielded 820 mg (86%) of white crystals mp 101.5 - 102.5° (1it<sup>30b</sup> 102 - 103°) MS - 289(100), 161(18), 160(15), 119(10), 107(14), 106(12), 105(10), 91(8) IR - 1455(s), 1375(w), 1343(w), 1330(w), 1308(s), 1222(m), 1162(m), 1118(m), 935(w), 920(w), 890(s), 695(s) NMR (CS<sub>2</sub>) - singlet, 3.07, (2H), H<sub>3</sub>; singlet, 2.25, (8H), H<sub>2</sub>; singlet, 1.37,

(2H), H<sub>1</sub>; singlet, 0.87, (1H), -CH<sub>3</sub>

3,3'-Diiodo-1,1'-biadamantane



The catalyst was prepared as before from 110 mg (4.0 mmole) of aluminum foil and 380 mg (1.5 mmole) of iodine in 40 ml of  $CS_2$ . After cooling to 0°, 428 mg (1.0 mmole) of 3,3'-dibromo-1,1'-biadamantane was added with stirring. The reaction was quenched after 2 min. and worked up

- 157 -

Hz

found

522.2552

1-Iodoadamantane



The catalyst was prepared as before from 190 mg (0.75 mmole) of iodine and 100 mg (3.7 mmole) of aluminum foil in 40 ml of  $CS_2$ . After cooling to 0°, 154 mg (1.0 mmole) of the fluoride was added. The reaction was quenched after 1 minute and worked up to yield an orange solid. Elution with petroleum ether down an alumina column yielded 220 mg (85%) of a white solid identical in all respects to 1-iodoadamantane. 1-Chloroanthracene



The procedure of Nonhebel<sup>141</sup> was followed. To a 3 necked 1 litre flask equipped with mechanical stirrer, condenser and drying tube was placed 17.8 g (100 mmole) of anthracene with 27.2 g (202 mmole) of anhydrous  $CuCl_2$  and 500 ml of  $CCl_4$ . The solution was stirred under reflux for 23 hours at which time glc showed a 60% reaction. An additional 10.0 g of  $CuCl_2$  was added and the solution refluxed for 5 hours. The dark yellow solution was filtered and evaporated to yield a dark brown solid. Recrystallization from petroleum ether (30-60) yielded 14.7 g (70%) of long yellow needles, mp 103 - 105° (1it<sup>141</sup> 104 - 106°) Triptycene



A modified procedure of Friedman<sup>89</sup> was used. A solution of 10.0 g (73 mmoles) of anthranilic acid in 50 ml of acetone was added dropwise to a refluxing solution of 7.0 g (44 mmoles) of anthracene and 9.3 g (79 mmoles) of <u>i</u>-amyl nitrite in 100 ml of  $CH_2Cl_2$ . The addition required  $2\frac{1}{2}$  hours, at the end of which the solution was washed with 5 x 75 ml of 10% HCl and dried over MgSO<sub>4</sub>. Evaporation yilded a thick black oil which was dissolved in 100 ml of xylene. To this was added 5.0 g of maleic anhydride and the solution was stirred under reflux for 30 minutes. The cooled solution was

poured in  $H_2O$  and  $CH_2Cl_2$  was added. The organic phase was washed with 5 x 75 ml of 10% KOH and dried over MgSO<sub>4</sub>. Evaporation of most of the solution yielded a dark oil which was frozen in a dry ice/acetone bath and filtered to yield a dark brown solid. This solid was placed on a long alumina column and eluted with petroleum ether (30-60). A total of 3.49 g (32%) of a fluffy white solid were isolated by this method. mp 251 - 252° (lit<sup>89</sup> 253 - 254°)

<u>NMR</u> (CDCl<sub>3</sub>) - multiplets, 7.37, (6H); multiplets, 7.00, (6H); singlet, 5.42, (2H)

9-Chlorotriptycene



The same procedure was used as for the preparation of triptycene<sup>89</sup> using 10.0 g (73 mmole) of anthranilic acid, 9.3 g (44 mmole) of 9-chloroanthracene, and 9.3 g (79 mmole) of <u>i</u>-amyl nitrite. After washing with 10% HCl the evaporated solid was dissolved in 50 ml of xylene and refluxed for 30 min. with 2.0 g of maleic anhydride.  $CH_2Cl_2$  was added to the cooled solution and the organic phase washed with 4 x 100 ml of 10% KOH. Evaporation of the dried solution yielded a black oil which was eluted with petroleum ether (30-60) down an alumina column. The first few fractions yielded 900 mg (10%) of residual starting material. Further elution with 5% ether-pet ether yielded triptycene plus 9-chlorotriptycene, then finally 4.7 g (37%) of a light yellow solid which was > 95% 9-chlorotriptycene by glc. Recrystallization from cyclohexane yielded light yellow cubes. mp 227 - 229<sup>°</sup> (lit<sup>142</sup> 228 - 229<sup>°</sup>)

<u>NMR</u> (CDC1<sub>3</sub>) - multiplet, 7.75, (3H); multiplet, 7.40, (3H); multiplet

7.05, (6H); singlet, 5.42, (1H) Attempted Exchange of 9-Chlorotriptycene

The catalyst for iodine exchange was prepared as before from aluminum foil and iodine in cyclohexane, n-octane, decalin and xylene. The 9-chlorotriptycene was added and the solutions refluxed for 4 days. The reactions in cyclohexane, octane and xylene showed no change by glc and the 9-chloride was isolated in > 90% yields. No triptycene could be seen by glc. The reaction in decalin showed peaks at shorter retention time than 9-chlorotriptycene or triptycene. Column chromatography on alumina yielded 9-chlorotriptycene plus a small amount of a yellow oil believed to be a result of reaction of the solvent since nmr indicated that there were no aromatic hydrogen atoms.

2,2-Dichloroadamantane



The procedure of McKervey was followed<sup>34</sup>. To a solution of 5.0 g (33.3 mmole) of adamantanone (Aldrich) in 10 ml (15.7 g, 115 mmole) of PCl<sub>3</sub> at 0<sup>o</sup> was added portionwise 9.2 g (43.0 mmole) of PCl<sub>5</sub> over a period of 1 hour. The yellow solution was warmed to room temperature and stirred overnight. The solution was poured into ice water and washed with chloroform. The organic layer was washed with water and dried over MgSO<sub>4</sub>.

Evaporation yielded a light yellow solid which was recrystallized from petroleum ether (30 - 60) to yield 5.80 g (85%) of long colourless needles. Mp 202 - 203<sup>o</sup> (lit<sup>34</sup> 203 - 204<sup>o</sup>).

- <u>MS</u> 206(6), 204(3), 171(58), 170(53), 169(100), 168(98), 166(23), 133(77) 91(100)
- <u>IR</u> 1460(wsh), 1445(s), 1345(m), 1330(w), 1265(m), 1214(w), 1095(m), 1062(w), 1045(w), 1038(m), 958(s), 945(w), 907(s), 843(sb)
- <u>NMR</u> (CC1<sub>4</sub>) broad singlet, 1.84, (8H); singlet, 2.40, (4H); singlet, 2.53, (2H)

2,2-Dibromoadamantane



The procedure of McKervey was followed<sup>34</sup>. To a solution of 2.5 g (16.7 mmole) of adamantanone in 10 ml of PBr<sub>3</sub> at 0<sup>°</sup> was added in small portions 7.5 g (17.4 mmole) of PBr<sub>5</sub> over a period of 1 hour. The orenge solution was worked up the same as for the gem dichloride to yield a dark yellow solid. This was recrystallized from 30-60 petroleum ether to yield 4.2 g (86%) of white needles (darkened on exposure to light, liberating HBr gas). Mp 161 -  $162^{\circ}$  (lit<sup>34</sup> 162 -  $163^{\circ}$ )

<u>MS</u> - no parent, 215(100), 213(100), 150(23), 134(14), 133(55), 91(41) <u>IR</u> - 1470(w), 1448(s), 1343(w), 1300(w), 1260(m), 1208(w), 1092(s), 1060(w) 1037(w), 957(s), 944(w), 898(s)

<u>NMR</u> - broad singlet, 1.93, (8H); singlet, 2.58, (4H); singlet, 2.77, (2H)

Rearrangement of 2,2-Dichloroadamantane



The catalyst was prepared as before from 200 mg (7.4 mmole) of aluminum foil and 164 ml (3.0 mmole) of bromine in 40 ml of refluxing  $CS_2$ . The solution was cooled to  $-50^{\circ}$  after 1 hour and 410 mg (2.0 mmole) of 2,2-dichloroadamantane was added with stirring. The reaction was worked up as before after 1 minute to yield a light orange solid which consisted of three peaks in the ratio of 1:2:4 by glc analysis. Preparative glc yielded the pure components. The first two compounds were shown to be the gem dichloride and gem dibromide by comparison with authentic samples. The major product was found to be <u>syn</u>-1,4-dibromoadamantane. Mp 108 -  $109^{\circ}$  (lit<sup>33</sup> 109 -  $110^{\circ}$ )

<u>MS</u> - parent(trace), 215(100), 213(100), 134(7), 133(35), 105(11), 91(19)

<u>IR</u> - 1465(w), 1445(m), 1342(m), 1325(w), 1300(w), 1285(m), 1250(m), 1188(w),

1180(w), 1100(m), 1028(w), 1020(s), 975(w), 942(m), 922(m)

<u>NMR</u> (CCl<sub>4</sub>) - multiplets, 1.85 - 2.40, (11H); doublet, J = 12 Hz, 2.95, (2H); singlet, 4.46, (1H)

The above reaction was repeated using 4.0 mmole of bromine to prepare the catalyst. The exchange was done at room temperature to yield the <u>syn-</u> 1,4-dibromide with only a trace of the gem dibromide.



To a solution of 1.0 g (4.88 mmole) of 2,2-dichloroadamantane in 40 ml of spectrograde  $CH_3NO_2$  was added 5.3 g (39.6 mmole) of anhydrous AlCl<sub>3</sub>. The solution was allowed to stir for 3 hours at room temperature, then poured into ice water. Carbon tetrachloride was added and the layers separated. The organic phase was washed with water and dried over MgSO<sub>4</sub>. Evaporation yielded a yellow oil which was shown to consist of 3 components by glc in the relative ratio of 2:8:1.  $(100(2) - \frac{8}{2}) = 200^{\circ}$ , t = 12.6, 13.2 and 14.7 min.) Elution down an alumina column with petroleum ether (30-60) yielded the three components which were further purified by preparative glc.

The first component proved to be <u>anti-1,4-dichloroadamantane</u>. Mp 130 - 131<sup>o</sup> (lit<sup>33</sup> 131.5 - 133.5<sup>o</sup>) <u>MS</u> - 206(4), 204(8), 171(31), 169(100), 133(14), 113(5), 105(5), 91(16) <u>IR</u> - 1465(wsh), 1445(s), 1360(w), 1340(m), 1335(m), 1280(w), 1220(m), 1100(m), 1025(s), 970(w), 942(m), 922(m)

<u>NMR</u> (CC1<sub>4</sub>) - singlet, 4.24, (1H); multiplets, 1.20 - 2.20, (13H)

The major product was found to be  $\underline{syn}-1,4$ -dichloroadamantane, mp 162 - 163° (lit<sup>33</sup> 157 - 159°)

<u>MS</u> - 206(3), 204(5), 171(32), 169(100), 133(18), 113(6), 105(6), 91(17)
<u>IR</u> - 1465(wsh), 1440(s), 1340(m), 1330(wsh), 1295(m), 1280(w), 1260(m), 1210(w), 1098(m), 1025(s), 970(w), 943(m), 920(s), 835(s), 777(mb)
<u>NMR</u> (CCl<sub>4</sub>) - broad singlet, 4.11, (1H); multiplets, 1.30 - 2.70, (11H);

doublet, J = 12 Hz, 2.65, (2H)

The minor product was found to be 1,4,4-trichloroadamantane, mp 153 -  $154^{\circ}$  (lit<sup>33</sup> 152 -  $153^{\circ}$ )

- <u>MS</u> 242(5), 240(6), 238(7), 205(68), 203(100), 170(7), 168(21), 131(21), 125(11), 113(19), 91(23)
- <u>IR</u> 1470(wsh), 1433(s), 1342(m), 1282(w), 1180(w), 1098(m), 1065(w), 1040(wsh), 1028(s), 972(m), 944(s), 925(s), 850(s), 835(sb)

<u>NMR</u> (CC1<sub>4</sub>) - multiplets, 1.70 - 2.90, (13H)

Protoadamantan-4-one 35



To a solution of 10.1 g (66.5 mmole) of 1-adamantanol in 200 ml of reagent benzene was added 32.6 g (73.6 mmole) of lead tetraacetate and 18.6 g (73.6 mmole) of iodine. The dark purple solution was stirred at 70° for 2 hours. The solution was filtered into an aqueous sodium bisulfite solution with stirring. The organic phase was then washed with aqueous sodium carbonate, water and dried over  $MgSO_4$ . Evaporation yielded the 7-iodomethylbicyclo[3.3.1]nonan-3-one as a dark oil.

<u>NMR</u> (CC1<sub>4</sub>) - doublet, J = 7 Hz, 2.92, (2H), -CH<sub>2</sub>I; multiplet, 0.90 - 2.40, (13H)

The crude oil was immediately dissolved in 20 ml of pyridine and stirred at 70<sup>°</sup> for 1<sup>1</sup>/<sub>2</sub> hours. The purple solution was poured into ice water/ pet ether and the layers separated. The organic layer was washed with aqueous sodium bisulfite, aqueous sodium carbonate, and water, then dried over  $MgSO_4$ . Evaporation yielded a light yellow solid which was eluted with petroleum ether (30-60) down an alumina column to yield 5.2 g (52%) of white crystals, mp 208 - 209<sup>o</sup> (lit<sup>35</sup> 210 - 212<sup>o</sup>) <u>MS</u> - 150(100), 108(18), 107(18), 106(14), 97(56), 80(32), 79(32),

68(15), 67(23), 66(33)

### IR - 1720(s)

<u>NMR</u> (CCl<sub>4</sub>) - broad multiplet, 2.67, (2H); broad singlet, 2.35, (4H); broad singlet, 1.88, (4H); singlet, 1.70, (4H)
<u>Chlorination of Protoadamantan-4-one</u><sup>36</sup>



To a solution of 2.0 g (13.3 mmole) of protoadamantan-4-one in 10 ml of PCl<sub>3</sub> in a 25 ml 3-necked flask equipped with condenser and drying tube at 0° was added 4.0 g (19.2 mmole) of PCl<sub>5</sub> in portions over a period of 1 hour. The solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into ice water, petroleum ether (30 - 60) added and the layers separated. The organic phase was washed with water and dried over MgSO<sub>4</sub>. Evaporation yielded a yellow oil which consisted of 3 components by glc (0V-17 100(2)  $\xrightarrow{10}$   $\rightarrow$ 200°, t = 7.4, 10.3, 11.8 min.) in the ratio of 63:13:24.

The compounds were isolated by preparative glc.

The first component was shown to be 4-chloroprotoadamantene (colourless oil).

<u>MS</u> - 170(16), 168(47), 133(81), 126(37), 113(32), 91(100)

<u>IR</u> - 1630(s), 1465(w), 1445(m), 1340(w), 1320(s), 1290(w), 1092(w), 1060(w) 1020(s), 950(w), 942(m), 905(m), 855(w)

The minor component was assigned as 4,4-dichloroprotoadamantane, mp  $98 - 99.5^{\circ}$ .

 $\underline{MS}$  - 206(5), 204(9), 171(33), 169(100), 133(24), 113(13), 91(28)

<u>IR</u> - 1455(s), 1340(w), 1322(w), 1308(m), 1180(m), 1162(w), 1105(w), 1062(m) 1045(w), 1020(m), 980(sb), 955(s), 917(s), 892(s), 878(s), 840(m), 670(s) <u>NMR</u> (CCl<sub>4</sub>) - multiplets, 1.40 - 3.10, (14H)

<u>Analysis</u> - $C_{10}H_{14}C_2$	<u> </u>	H
calculated	58.55	6.88
found	58.36	7.04

The third component was shown to be 1,2-dichloroadamantane, mp 179 -  $181^{\circ}$  (lit  $^{36}$  178 -  $180^{\circ}$ ,  $^{34}183 - 185^{\circ}$ )

 $\underline{MS} = 206(3), 204(6), 171(33), 169(100), 133(17), 113(8), 91(17),$ 

<u>IR</u> - 1450(s), 1340(m), 1284(m), 1222(w), 1100(m), 1032(s), 972(mb), 955(w), 852(s), 700(mb)

<u>NMR</u> (CC1<sub>4</sub>) - multiplets, 1.4 - 2.75, (13H); broad singlet, 4.25, (1H)

The above reaction was repeated with 1.5 g (10.0 mmole) of protoadamantan-4-one to yield a light yellow oil containing the same three products. This oil was placed in 50 ml of concentrated HCl and stirred under reflux for 30 hours. The white solid that was in the condenser was vashed out with  $CHCl_3$  and added to the washing of the acid solution. The organic phase was washed with water and dried. Evaporation yielded a yellow solid which was eluted with pentane down a short alumina column to yield 1.08 g (53%) of 1,2-dichloroadamantane which was identical in all respects to the material collected by glc above. 1,2-Dibromoadamantane



The procedure of McKervey was followed<sup>36</sup>. To a solution of 710 mg (4.72 mmole) of protoadamantan-4-one in 10 ml of PBr<sub>3</sub> at 0° was added portionwise over a period of 1 hour 2.50 g (5.22 mmole) of PBr<sub>5</sub>. The yellow solution was warmed to room temperature and allowed to stir for 48 hours. The orange oil was poured into ice water and worked up as above to yield a yellow solid. This was recrystallized from 30-60 petroleum ether to yield 0.64 g (51%) of colourless plates, mp 120 -  $121^{\circ}$  (1it<sup>36</sup> 122 -  $123^{\circ}$ ) <u>MS</u> - 294(2), 292(2), 215(100), 213(100), 133(26), 105(9), 91(29) <u>IR</u> - 1460(w), 1443(s), 1356(w), 1340(m), 1308(w), 1283(m), 1260(w), 1208(w),

1190(m), 1100(m), 1024(s), 970(m), 960(m), 950(m), 932(w), 925(w),680(s)
<u>NMR</u> (CC1<sub>4</sub>) - multiplets, 1.60 - 3.05, (13H); broad singlet, 4.46, (1H)
<u>Halogen Exchange on 1,2-Dichloroadamantane</u>



The catalyst was prepared as before from 100 mg (3.7 mmole) of aluminum foil and 382 mg (1.50 mmole) of iodine in 30 ml of  $CS_2$ . After refluxing for 45 min. the solution was cooled to  $-50^{\circ}$  in a Dry Ice/isopropanol bath and 205 mg (1 mmole) of the 1,2-dichloride added. The reaction was worked up as before after 15 min. (glc indicated that starting material was all gone after 30 seconds) to yield 405 mg of an orange solid. Elution with petroleum ether (30-60) down an alumina column yielded 320 mg
(82%) of a white solid which was recrystallized from pentane, mp 107 108.5° (lit<sup>37</sup> 106 - 108°)
<u>MS</u> - 388(6), 261(100), 216(3), 214(4), 134(20), 133(17), 105(6), 91(10)
<u>IR</u> - 1460(w), 1440(s), 1350(w), 1338(m), 1302(w), 1280(m), 1257(m),

1200(w), 1172(m), 1145(m), 1100(m), 1020(s), 972(m), 955(m), 945(m) 922(m), 665(s)

<u>NMR</u> (CC1<sub>4</sub>) - multiplets, 1.64 - 3.16, (13H); singlet, 4.98, (1H)

The same reaction was repeated using bromine to yield a 78% yield of 1,2-dibromoadamantane, identical to that produced by the bromination of protoadamantan-4-one.

Chlorine Exchange on 2,2-Dibromoadamantane



The catalyst was prepared as before from 300 mg (11.1 mmole) of aluminum foil in 45 ml of  $CHCl_3$  at 0° with chlorine gas being passed through the solution. The mixture was warmed to room temperature and a small crystal of iodine added. After the exothermic reaction which consumed most of the aluminum foil had ceased the black solution was cooled to 0° and 300 mg (1.02 mmole) of the 2,2-dibromide added. The reaction was worked up as before after 1 minute to yield an orange solid. Elution down a short alumina column with petroleum ether (30-60) yielded 180 mg (87%) of a white solid which was shown (by nmr) to consist of <u>anti</u>-1,4-dichloroadamantane (19%) and <u>syn</u>-1,4-dichloroadamantane (81%). Iodine Exchange on 1,4-Dichloroadamantane



The catalyst was prepared as before from 200 mg (7.4 mmole) of aluminum foil and 380 mg (1.5 mmole) of iodine in 40 ml of  $CS_2$ . The active catalyst solution was cooled to  $0^{\circ}$  and 160 mg (0.78 mmole) of a 80:20 mixture of <u>sym</u> and <u>anti-1</u>,3-dichloroadamantane was added. The reaction was worked up as before after 2 minutes to yield a dark oil which consisted of 1 peak by glc. Elution down a short alumina column with pentane yielded 220 mg (73%) of a light yellow solid which was recrystallized from pentane, mp 101 -102.5°.

<u>MS</u> - 388(trace), 261(100), 216(6), 214(7), 134(19), 133(18), 105(6), 91(12) <u>IR</u> - 1470(w), 1442(s), 1340(m), 1322(w), 1298(w), 1282(s), 1242(m), 1154(s), 1100(m), 1018(s), 967(w), 834(m), 915(s)

<u>NMR</u> (CC1<sub>4</sub>) - multiplets, 2.02 - 2.64, (11H); doublet, J = 12 Hz, 3.20, (2H); singlet, 4.84, (1H) ref 143

There was no evidence by glc or nmr for any of the anti-1,4-diiodide. Iodine Exchange on 2,2-Dichloroadamantane



The catalyst was prepared as before using 200 mg (7.4 mmole) of aluminum foil and 720 mg (3.0 mmole) of iodine in 30 ml of  $CS_2$ . The active catalyst system was cooled to  $-50^{\circ}$  in an isopropanol/Dry Ice bath and 410 mg (2.0 mmole)
of the 2,2-dichloride added. The reaction was quenched after 1 minute to yield a light pink solution which showed two peaks by glc. Evaporation yielded a dark orange oil which was purified by tlc (silica gel with 30-60 pet ether). Two major bands were separated and the components isolated by washing with chloroform. The first band yielded almost pure adamantanone (the CHCl<sub>3</sub> solution was dark purple). The second fraction consisted of mainly <u>syn</u>-1,4-diiodoadamantane with a small amount of 2-iodoadamantane.

The above reaction was repeated but this time the crude product was purified by column chromatography (alumina). Again, before chromatography only the two diiodide isomers were present but upon separation only the 1,4-diiodide was isolated along with 2-iodoadamantane and adamantanone.

The supposed gem diiodide present in the crude material could not be isolated as in the case of the bromine exchange reaction. 1-Chloro-3-iodoadamantane



To a solution of 1.0 g (2.53 mmole) of 1,3-diiodoadamantane in 50 ml of spectrograde CCl<sub>4</sub> in a 3-necked flask shielded from the light with aluminum foil at 0° was added  $130 \mu \ell$ (2.58 mmole) of iodine monochloride<sup>47</sup>. The solution became dark purple and was followed by glc. An additional  $45 \mu \ell$  of ICl was added after 1 hour. The reaction mixture was poured into ice water after 2 hours and shaken with aqueous sodium bisulfite. The organic phase was washed with aqueous sodium carbonate, water and dried over MgSO<sub>4</sub>. Glc showed two peaks of equal intensity (0V-17 125(2)  $\xrightarrow{16}$  250°, t = 5.2 and 7.8 min.). Evaporation yielded 0.92 g of a sticky yellow solid

which was collected by glc to yield 160 mg of the 1,3-dichloroadamantane and 190 mg of 1-chloro-3-iodoadamantane. The dichloride was identical in all respects to an authentic sample.

The chloroiodide had the following properties: mp 59.5 - 61<sup>o</sup> <u>MS</u> - 296(trace), 171(33), 169(100), 133(25), 113(10), 105(7), 93(10), 91(16) <u>IR</u> - 1452(s), 1338(s), 1318(s), 1285(s), 1262(w), 1246(w), 1145(w), 1103(m), 1022(s), 998(m), 958(s), 940(m), 840(s), 708(s)

<u>NMR</u> - (C<sub>6</sub>H<sub>6</sub>) - unresolved triplet, 1.13, (2H), H<sub>5</sub>; broad singlet, 1.42, (2H), H<sub>4</sub>; unresolved doublet, 1.80, (4H), H<sub>3</sub>; unresolved doublet, 2.08, (4H), H<sub>2</sub>; singlet, 2.76, (2H), H1

<u>Analysis</u> - C <sub>10</sub> H <sub>14</sub> C	11	<u> </u>	<u>    H     </u>
	calculated	40.50	4.76
	found	40.71	4.74

1,4-Dichlorobicyclo[2.2.1]heptane9



To a solution of 11.27 g (48.5 mmole) of crude 1,2,3,4-tetrachlorobicyclo [2.2.1] hept-2-ene\* in 150 ml of absolute ethanol was added 200 mg of 10% Pd/C with 20.2 g (200 mmole) of triethylamine. This solution was shaken on a Parr Hydrogenator at 43 psi for 1½ hours. The starting material was totally consumed as shown by glc. The catalyst was filtered off and water added. The solution was washed well with chloroform and the organic phase was washed with dilute HCl and water. The dried solution was evaporated to yield 8.5 g of a yellow solid which was shown to consist of the

\* Prepared by Dr. J. McKinley in 1971

1,4-dichloride plus two impurities of longer rentention time in the relative ratio of 8:1:1. Elution with petroleum ether (30-60) down an alumina column yielded 5.5 g (69%) of sticky white crystals which were recrystallized from pentane to yield white crystals, mp 77 - 78<sup>o</sup> (lit<sup>9</sup> 78 - 79<sup>o</sup>) <u>IR</u> (KBr) - 1450(m), 1312(s), 1264(s), 1240(m), 1210(s), 1010(s), 943(m),

857(s), 760(s)

<u>NMR</u>  $(C_6H_6)$  - singlet, 1.90, (2H); AB quartet, J = 8 Hz, 1.50 and 1.83, (8H) <u>1,4-Diiodobicyclo[2.2.1]heptane</u>



The catalyst was prepared as before from 3.8 g (140 mmole) of aluminum foil and 15.4 g (60.6 mmole) of iodine in 100 ml of carbon disulfide. The solution was refluxed for 45 minutes then 1.0 g ( $\pounds$ .06 mmole) of 1,4-dichlorobicyclo[2.2.1]heptane was added. The solution was stirred under reflux for 94 hours and then worked up as before to yield a dirty brown solid. Elution with petroleum ether (30-60) down an alumina column yielded 960 mg (46%) of a light yellow solid which was recrystallized from pentane to yield white crystals, mp 100 - 101° (1it<sup>52</sup> 101°)

Further elution yielded 85 mg of a white solid which was collected by preparative glc. mp  $79 - 80^{\circ}$ .

<u>MS</u> - 234(9), 232(20), 230(16), 206(48), 204(100), 202(78), 197(43), 195(46), 170(16), 168(51), 166(54), 160(22), 158(35)

<u>IR</u>  $(CS_2) - 1298(w)$ , 1280(s), 1238(w), 1224(m), 1200(w), 1180(w), 1154(w), 1120(m), 1092(m), 1074(m), 1038(s), 1014(m), 968(m), 880(w), 862(m), 849(m), 800(w), 736(s) <u>MMR</u>  $(C_6H_6)$  - multiplet, 1.26 - 2.00 <u>Analysis</u> - <u>C</u><u>H</u><u>I</u> 36.22 3.07 0.00

The rest of the material was a dark, thick oil of long retention time by glc (at least 3 peaks).



The catalyst was prepared as before from 1.6 g (60 mmole) of aluminum foil and 10.02 g (40 mmole) of iodine in 50 ml of reagent cyclohexane. After stirring under reflux for 40 minutes, 4.5 g (27.2 mmole) of the 1,4dichloride was added. The reaction was worked up after refluxing for 12 hours to yield a yellow solid. Elution with petroleum ether (30-60) down a silica gel column gave a small amount of side products; elution with diethyl ether yielded 6.5 g (73%) of a white solid which was recrystallized from pentane, mp 100 -  $101^{\circ}$ .

<u>IR</u> (KBr) - 1440(w), 1308(m), 1267(m), 1230(w), 1202(m), 990(s), 825(s), 748(s)

<u>NMR</u>  $(C_6H_6)$  - singlet, 2.00, (2H); AB quartet, J = 8 Hz, 1.78 and 1.40, (8H)



The catalyst was prepared as before from 50 mg of aluminum foil and chlorine gas at  $0^{\circ}$  in chloroform. A crystal of iodine was added and the solution refluxed in an oil bath. To this was added 50 mg of the 1,4-dichloride

- 174 -

and the solution stirred under reflux for 24 hours. Workup as before yielded a yellow solid identical in all respects to the starting material.



The catalyst was prepared as before from 55 mg (2.0 mmole) of aluminum foil and 127 mg (0.5 mmole) of iodine in 40 ml of carbon disulfide. After stirring for 40 minutes, 50 mg (.144 mole) of the 1,4-diiodide was added and the solution stirred under reflux for 60 hours. Workup as before yielded a yellow solid which was identical to starting material in all respects.

Exo-2-bromobicyclo[2.2.1] heptane



Procedure of Taylor<sup>144</sup> was followed. To a solution of 3.2 g (32 mmole) of norbornene in 40 ml of diethyl ether in a 100 ml 3-necked flask equipped with condenser and gas inlet tube at  $0^{\circ}$  was added dry HBr gas for a period of 1<sup>1</sup>/<sub>2</sub> hours. The solution was warmed to room temperature and allowed to stir overnight. The reaction mixture was poured into ice water and extracted with pentane. The organic layer was washed with aqueous sodium carbonate, water and dried over magnesium sulfate. Evaporation yielded a light yellow liquid which was distilled to yield 5.5 g (93%) of a colourless oil, bp 45° (2.5 mm) (lit<sup>145</sup> 96 - 97° (45 mm))

NMR (CDC13) - multiplets, 1.00 - 2.50, (10H); multiplet, 3.98, (1H)

Exo-2-iodobicyclo[2.2.1]heptane



The catalyst was prepared as before from 675 mg (25 mmole) of aluminum foil and 2.05 g (8 mmole) of iodine in 40 ml of carbon disulfide. The catalyst was cooled to room temperature and 2.10 g (12 mmole) of 2-bromonorbornane added. The reaction was stopped after 15 minutes and worked up as before to yield an orange oil. Distillation yielded 1.97 g (74%) of a light pink liquid, bp 29° (1.8 mm) (lit<sup>146</sup> 55 - 56° (3.0 mm)) <u>NMR</u> (CDCl<sub>3</sub>) - multiplets, 1.10 - 2.60, (10H); multiplet, 4.00, (1H) <u>Separation of cis and trans 4-t-butylcyclohexanol</u><sup>147</sup>

To an alumina column (1500 g) was placed 32.0 g of commercial cis/trans (30:70) 4- $\underline{t}$ -butylcyclohexanol and petroleum ether (30-60) was used as the elutant. After 14 litres of solvent (250 ml fractions) had been eluted 20% Et<sub>2</sub>0/pet ether was used. After 19 litres pure diethyl ether was used (fraction #76). At fraction #83 a white solid began appearing (pure cis alcohol). From here on 100 ml fractions were taken. Fractions #83 to #94 contained 19.8 g of pure trans alcohol while fractions #95 - #100 contained 1.8 g of a mixture of the two alcohols.



Cis

<u>NMR</u> (CDCl<sub>3</sub>) - singlet, 0.87, (9H); multiplets, 1.2 - 2.0, (9H); multiplet, 4.04, (1H)

Trans

<u>IR</u> (CC1<sub>4</sub>) - 3650(w), 3450(w), 1475(m), 1455(m), 1385(w), 1360(m), 1220(m), 1175(w), 1025(m), 1005(m), 955(s), 905(w)

<u>NMR</u> (CDCl<sub>3</sub>) - singlet, 0.87, (9H); multiplets, 1.0 - 2.0, (9H); broad singlet, 3.48, (1H)

Bromination of trans 4-t-butylcyclohexanol



To a 3-necked flask equipped with condenser and dropping funnel was placed 1.56 g (10.0 mmole) of trans 4-<u>t</u>-butylcyclohexanol. The flask was cooled to  $0^{\circ}$  and the dropping funnel charged with 2.98 g (11.0 mmole) of PBr<sub>3</sub> which was added dropwise over a period of 1<sup>1</sup>/<sub>2</sub> hours. The solution was allowed to warm to room temperature and stirred overnight. The reaction was quenched by the cautious addition of water. Addition of petroleum ether (30-60) and washing with aqueous sodium carbonate yielded a colourless solution which was shown by nmr to consist of the 3 and 4-bromo-<u>t</u>-butylcyclohexane isomers plus 4-<u>t</u>-butylcyclohexene. The relative ratios were 1:4:1 for the olefin; axial bromides; equitorial bromides<sup>148</sup>, 149. <u>NMR</u> (CDCl<sub>3</sub>) - singlet, 5.75, olefin; multiplet, 4.65 - 4.85, axial bromides; multiplet, 3.75 - 4.20, equitorial bromides Chlorination of cis/trans 4-t-butylcyclohexanol



To a 3-necked round bottomed flask equipped with condenser and dropping funnel was added 3.12 g (20.0 mmole) of cis/trans (30:70) 4-tbutylcyclohexanol. The flask was placed in an oil bath at  $80^{\circ}$  and the funnel was charged with 2.0 ml (31.0 mmole) of SOCl<sub>2</sub>. The dropwise addition took 20 minutes and the solution was stirred at  $80^{\circ}$  for 2 hours. The solution was cooled to room temperature and cautiously added to ice water. To this was added petroleum ether (30-60), the layers separated, and the organic phase washed with aqueous sodium carbonate and water. Evaporation of the dried solution yielded a yellow oil which was shown by nmr to consist of >90% 4-t-butylcyclohexene. An analytical sample was obtained by preparative glc.

- <u>IR</u> 1660(m), 1475(s), 1385(m), 1360(s), 1300(w), 1222(m), 1175(w), 1145(m), 1045(w), 942(w), 913(m), 876(m), 703(s)
- <u>NMR</u> (CDCl<sub>3</sub>) singlet, 0.87, (9H); multiplets, 1.2 2.2, (6H); singlet, 5.25, (2H)

Chlorination of cis-4-t-butylcyclohexanol



In a 2-necked flask equipped with condenser and dropping funnel containing 2.0 ml (31.0 mmole) of SOC1<sub>2</sub> was placed 2 ml of pyridine and

3.12 g (20.0 mmole) of cis-4-t-butylcyclohexanol<sup>150</sup>. The solution was heated to  $80^{\circ}$  and the SOCl<sub>2</sub> added dropwise over a period of 30 minutes. The solution was then stirred for 1½ hours. The cooled solution was cautiously added to water and worked up as before. Analysis by nmr showed the product to consist of the olefin (61%), cis chloride (14%) and the trans chloride (25%).

This mixture was placed with 1.0 g of KOH in 30 ml of 95% ethanol and stirred under reflux for 16 hours<sup>151</sup>. The cooled mixture was poured into water and extracted with pentane. Evaporation yielded a dark brown oil which was collected by glc to yield 650 mg of the olefin plus 510 mg of the trans-4- $\pm$ -butylcyclohexylchloride. Further analysis showed that the chloride contained 7% of the cis isomer as well.



<u>IR</u> - 1472(m), 1442(m), 1384(m), 1360(s), 1340(w), 1264(m), 1212(m), 1178(m), 1035(w), 998(s), 930(w), 900(m), 880(m)
<u>NMR</u> (CCl<sub>4</sub>) - singlet, 0.93, (9H); multiplets, 1.0 - 2.25, (9H); multiplet 3.69, (1H)

Chlorination of trans-4-t-butylcyclohexanol



The above reaction was repeated with the trans alcohol to yield a yellow oil which contained the olefin (65%) and chloride (35%). Collection

by glc yielded the cis chloride which was contaminated with 6% of the trans isomer.

<u>IR</u> - 1475(m), 1440(m), 1385(m), 1360(s), 1310(m), 1260(m), 1210(w), 1175(w) 1024(m), 1000(m), 927(w), 910(m), 862(s), 693(s)

<u>NMR</u> (CC1<sub>4</sub>) - singlet, 0.84, (9H); multiplets, 1.4 - 2.2, (9H); multiplet

4.37, (1H)

Chlorination of cis/trans 4-t-butylcyclohexanol



The above reaction was repeated with the commercial alcohol (30% cis, 70% trans) to give a light yellow oil which consisted of the olefin (58%) and the chlorides (42%). Collection by glc yielded the <u>t</u>-butyl chlorides which consisted of 70% cis and 30% trans by nmr integration.

Iodine exchange of cis/trans-4-t-butylcyclohexylchloride



The catalyst was prepared as before from 80 mg (3 mmole) of aluminum foil and 190 mg (0.75 mmole) of iodine in 30 ml of carbon disulfide. After refluxing for 40 minutes the solution was cooled to room temperature and 156 mg (0.84 mmole) of the 4-<u>t</u>-butylcyclohexyl chlorides added (70% cis, 30% trans). The reaction was worked up after 2 minutes to yield 220 mg (94%) of a light yellow oil which darkened (purple) rapidly on exposure to light. Glc showed one peak (no starting material) and nmr showed it to consist of the two isomeric iodides<sup>152</sup> by virtue of the two  $\propto$  hydrogens. (CCl<sub>4</sub> solution) cis iodide 4.94 (32%) trans iodide 4.04 (68%)

The same reaction was repeated on the pure cis and trans  $4-\underline{t}$ -butylcyclohexyl chlorides at room temperature and further studies were done at lower temperatures in Dry Ice solvent baths. In each case the catalyst was prepared as before and cooled to the appropriate temperature. The cyclohexyl chloride was dissolved in carbon disulfide and cooled to the temperature of the ice bath before addition. Analysis was again made by nmr.



73

70

41

t	rans	

 $\frac{25^{\circ}}{2 \text{ min}}$ 

 $\xrightarrow{25^{\circ}}{2 \text{ min}}$ 

 $\xrightarrow{-55^{\circ}}{2 \text{ min}}$ 

 $\xrightarrow{-65^{\circ}}{2 \min}$ 

 $\xrightarrow{-55^{\circ}}$ 

8 min

 $\overrightarrow{63 \text{ min}}$ 

cis

trans  $\xrightarrow{-35^{\circ}}{2 \text{ min}}$ 

cis

cis

trans

46	
35	
35	
40	
38	

27

30

54

65

65

60

62

59

2-Bromooctane



To a 200 ml 3-necked round bottomed flask equipped with stirring bar and dropping funnel containing 4.5 ml (13g, 48.0 mmole) of PBr<sub>3</sub> was placed 6.0 g (46.0 mmole) of 2-octanol. The flask was immersed in an ice bath at  $0^{\circ}$  and the PBr<sub>3</sub> added dropwise over a period of 1½ hours. The solution was warmed to room temperature and allowed to stir overnight. The mixture was then heated at 80° for 1 hour and poured into ice water and extracted with petroleum ether (30-60). The organic phase was washed with aqueous sodium carbonate, water then dried over MgSO4. Distillation yielded 5.0 g (75%) of a colourless liquid, bp 90° (30 mm), (lit<sup>153</sup> 76° (18 mm))

The exchange on 2-bromooctane at 25<sup>°</sup> gave a 85% yield of the corresponding iodide.

<u>IR</u> (neat) - 1460(s), 1376(m), 1280(w), 1250(w), 1202(m), 1165(s), 1135(s),

1078(wb), 790(m), 728(m)

<u>NMR</u> (CS<sub>2</sub>) - multiplets, 0.9 - 2.0, (16H); multiplet, 4.06, (1H)
<u>Iodine Exchange on (+)-2-Bromooctane</u>



99.78 mg in 5.0 ml of CS<sub>2</sub>

≪= +0.079

cell constant = 0.744

 $\left[\alpha\right] D = \frac{\alpha}{C1}$ 

 $= (+) \frac{100 \times 0.079 \times .05 \times 0.744}{0.1 \times .09978}$ 

The catalyst was prepared as before and the reaction was done at four different temperatures with approximately 65 mg of the optically active bromide each time. The product was identical by IR, glc and nmr to that of the reaction using racemic material. The reaction in all cases was quenched after 2 minutes to give an 82% yield of the corresponding iodide.

• • • • •	المعتقد المحاصف المعاجب المتعاقب المتعاقب	•• •	
Temperature	Rotation of Io	dide	+00% pure
25 <sup>°</sup>	obs 0.0 <sup>°</sup>	corr 0.0°	64. 20
0 <sup>0</sup>	-2.2 <sup>°</sup>	-3.3°	04.2
-53 <sup>0</sup>	-8.7 <sup>0</sup>	-13.1°	· ·
-65 <sup>0</sup>	-9.8°	- 14.7 <sup>0</sup>	

Hexabromocyclopentadiene



The catalyst was prepared from 2.16 g (80 mmole) of aluminum foil and 2.75 ml (8.0 g, 50 mmole) of liquid bromine in 40 ml of carbon disulfide. After refluxing for 40 minutes the aluminum foil had been torn up to small pieces and the solution was a light orange. The mixture was cooled to room temperature and 2.54 g (10.0 mmole) of hexachlorocyclopentadiene was added with stirring. The reaction was quenched and worked up as before after 20 minutes to yield 4.7 g (93%) of a dark oil which solidified on standing. Tlc showed one spot ( $R_f = 0.91$ , SM = 0.73) on silica gel plates with petroleum ether (30-60) as the developing solvent. Recrystallization from pentane yielded pale yellow crystals, mp 83 - 84° (lit<sup>154</sup> 82 - 83°)  $\frac{fR}{CS_2}$  - 1192(s), 1155(w), 1138(w), 1095(m), 910(m), 810(w), 745(s), 715(m)  $C_5Br_6$  <u>IR</u> (CS<sub>2</sub>) of C<sub>5</sub>Cl<sub>6</sub> - 1225(s), 1185(m), 1140(s), 1024(w), 978(w), 968(w), 862(w), 807(s), 710(s), 680(s)

1-Iodobutane



The catalyst was prepared as before from 640 mg (24 mmole) of aluminum foil and 2.0 g (8 mmole) of iodine in 30 ml of carbon disulfide. After 40 minutes the solution was cooled to 0<sup>°</sup> and 930 mg (10 mmole) of 1-chlorobutane was added. Workup as before after 2 minutes yielded 1.23 g (68%) of a light pink liquid identical in all respects to authentic 1-iodobutane. Analysis by nmr showed no trace of the secondary or tertiary isomers.

Iodocyclohexane



The catalyst was prepared as above from 500 mg (18.5 mmole) of aluminum foil and 2.45 g (9.2 mmole) of iodine in 40 ml of carbon disulfide. After stirring under reflux for 40 minutes the solution was cooled to room temperature and 2.0 g (12.3 mmole) of cyclohexyl bromide was added. Workup as before after 2 minutes yielded 2.04 g (78%) of a colourless liquid, bp  $38^{\circ}$  (2.7 mm) (lit<sup>153</sup> 68° (10 mm)) IR (CS<sub>2</sub>) - 1340(m), 1330(m), 1240(s), 1170(s), 1095(s), 1080(w), 1035(w), 1020(m), 992(s), 920(m), 885(s), 870(m), 855(m), 814(s) NMR (CS<sub>2</sub>) - multiplets, 1.20 - 2.30, (11H); multiplet, 4.27, (1H) Iodine Exchange on Bromobenzene



The catalyst was prepared as before from 500 mg (18.5 mmole) of aluminum foil and 2.54 g (10.0 mmole) of iodine in 40 ml of carbon disulfide. After refluxing for 40 minutes, 500 mg (3.19 mmole) of bromobenzene was added. No reaction was observed after 24 hours, so a portion of the solution was added to a carbon disulfide solution of 1-chloroadamantane. Complete conversion to iodoadamantane was observed. The solution was worked up after refluxing for 6 days to yield only starting material.

The same was found for the reaction of 1,2-dichlorobenzene and 1-bromonaphthalene -no iodide formation occurred.

Exchange on 1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene

\_\_\_\_\_ NR

The catalyst was prepared as before from 90 mg (3.9 mmole) of aluminum foil and 246 mg (0.97 mmole) of iodine in 20 ml of carbon disulfide. After refluxing for 40 min., 100 mg (0.43 mmole) of the tetrachloride was added. No reaction had occurred after 2 hours so a portion of the mixture was added to a carbon disulfide solution of 1-chloroadamantane. An immediate 100% conversion to 1-iodoadamantane occurred. The reaction was worked up after 24 hours to yield only residual starting material. Photochemical Reactions of Bridgehead Halides

A) Using Alcohols as Solvent



To a quartz tube was added 215 mg (1 mmole) of 1-bromoadamantane with 70 ml of the alcohol being used. The solution was degassed for 10 minutes with L grade nitrogen, a condenser added, and irradiated for approximately eight to twenty hours. Analysis by glc showed no trace of starting material with two products, adamantane and the alkoxyadamantane. With  $R = CH_3$ - and  $CH_3CH_2$ - the yields of adamantane were 21 and 19% respectively.

The solution was washed with aqueous sodium bisulfite, then petroleum ether was added and the layers separated. The organic phase was washed with aqueous sodium carbonate, water, and then dried over anhydrous magnesium sulfate. Preparative glc yielded the pure adamantyl ether. The same procedure was used in the photolysis of 262 mg (1 mmole) of adamantyl iodide. Here the reaction was much faster and the yield of adamantane in all cases was less than 5%.

a)  $R = CH_3$ -

- $\underline{MS} = 166(25), 135(8), 124(5), 109(100),$
- <u>IR</u> 1442(m), 1340(m), 1300(m), 1200(w), 1165(m), 1105(s), 1085(s), 1040(m) 890(m)
- <u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) unresolved triplet, 1.51, (6H), δ; unresolved doublet, 1.73, (6H), β; broad singlet, 2.00, (3H), δ; singlet, 3.13, (3H), -OCH<sub>3</sub>

850(wb)

- <u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) singlet, 0.93, (1H), -OH; unresolved triplet, 1.50, (6H), S; unresolved triplet, 1.65, (6H), B; broad singlet, 1.97, (3H), S; multiplet, 3.45, (4H), -OCH<sub>2</sub>CH<sub>2</sub>O-
- f)  $R = CH_2CH_2OCH_3$
- <u>MS</u> 210(100), 153(4), 135(100), 93(20), 80(26)
- <u>IR</u> 1445(m), 1360(w), 1350(m), 1300(m), 1240(w), 1200(m), 1120(sb), 1090(s), 1038(w), 983(m), 960(w), 924(m), 880(w)
- <u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) unresolved triplet, 1.47, (6H), §; unresolved doublet, 1.69, (6H), β; broad singlet, 1.96, (3H) §; singlet, 3.14, (3H), -OCH<sub>3</sub>; multiplet, 3.42, (4H), -OCH<sub>2</sub>CH<sub>2</sub>O-

<u>Analysis</u> - $C_{13}H_{22}O_2$		<u> </u>	H
	calculated	74.24	10.54
	found	74.16	10.60

- g)  $R = -C CH_2^3 CH_3$
- MS = 208(3), 179(17), 152(4), 135(100)
- <u>IR</u> 1448(m), 1362(m), 1350(m), 1300(w), 1165(w), 1105(sb), 1080(s), 1030(m), 1000(m), 945(w), 880(w)

 $\underbrace{\text{NMR}}_{1.12, (3H), -CH_3; \text{ multiplet}, J = 7 \text{ Hz}, 0.93, (3H), -CH_3; \text{ doublet}, J = 7 \text{ Hz}, 1.12, (3H), -CH_3; \text{ multiplet}, 1.40 - 1.60, (2H), -CH_2; \text{ unresolved} triplet, 1.54, (6H), & ; unresolved doublet, 1.75, (6H), & ; broad singlet, 2.01, (3H), & ; multiplet, J = 7 \text{ Hz}, 3.55, (1H), -OCH \\ \underbrace{\text{High Resolution MS}}_{\text{High Resolution MS}} - C_{14}H_{24}O \qquad \text{calculated} \qquad 208.3468 \\ \text{found} \qquad 208.3470 \end{aligned}$ 

h)  $R = CH_2CH_2CH_2CH_3$ <u>MS</u> - 208(50), 151(71), 135(100), 95(43) <u>IR</u> - 1450(m), 1350(m), 1300(m), 1185(w), 1115(s), 1085(s), 1025(w), 975(wb), 935(w), 915(w) <u>NMR</u>  $(C_6H_6)$  - triplet, J = 7 Hz, 0.91, (3H),  $-CH_3$ ; unresolved triplet, 1.51, (6H),  $\delta$ ; multiplet, 1.35 - 1.60, (4H),  $-CH_2CH_2$ -; unresolved doublet, 1.74, (6H),  $\beta$ ; broad singlet, 1.99, (3H),  $\delta$ ; triplet, J = 7 Hz, 3.34, (2H),  $-OCH_2$ 

High Resolution MS -  $C_{14}H_{24}O$ calculated208.3468found208.3465

- i) R = -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
   <u>MS</u> 222(16), 165(32), 135(100), 95(32)
   <u>IR</u> 1450(m), 1350(m), 1300(m), 1285(w), 1185(w), 1115(s), 1090(s), 1055(w), 940(wb), 915(w)
- <u>NMR</u>  $(C_6H_6)$  triplet, J = 7 Hz, 0.89, (3H), -CH<sub>3</sub>; multiplet, 1.35 -1.60, (6H), -(CH<sub>2</sub>)<sub>3</sub>-; unresolved triplet, 1.51, (6H),  $\delta$ ; unresolved doublet, 1.75, (6H),  $\beta$ ; broad singlet, 1.99, (3H),  $\delta$ ; triplet, J = 7 Hz, 3.34, (2H), -OCH<sub>2</sub> <u>Analysis</u> - C<sub>15</sub>H<sub>26</sub>O C H

$\frac{\text{nalysis}}{15} - C_{15}H_{26}O$		C	<u>H</u>
	calculated	81.02	11.78
	found	80.98	11.90

Solvolysis of Monohalides in Methanol

A solution of 100 mg (.46 mmole) of 1-bromoadamantane in 25 ml of methanol was stirred under refluxing conditions. After 6 hours 10% reaction had occurred with 60% after 24 hours. Similarly, a solution of 100 mg (.38 mmole) of 1-iodoadamantane in 25 ml of refluxing methanol showed 35% reaction after 6 hours and 90% after 24 hours. The photochemical reactions were completely finished in 8 hours and 2½ hours respectively. 2-Methoxyadamantane



A solution of 262 mg (1 mmole) of 2-iodoadamantane in 70 ml of methanol was irradiated through quartz in the same manner as the bridgehead isomer. Workup as before after 4 hours yielded the secondary ether (96%) plus adamantane (4%).

<u>IR</u> - 1462(w), 1455(m), 1380(m), 1365(w), 1223(w), 1200(m), 1182(m), 1105(sb), 985(m), 975(m), 940(m), 910(w)

<u>NMR</u>  $(C_6H_6)^{28}$  singlet, 3.18, (4H); doublet, J = 11 Hz, 2.21, (2H); doublet, J = 11 Hz, 1.31, (2H); multiplets, 1.58 - 1.98, (10H)

1,3-Dimethoxyadamantane



A well degassed solution of 388 mg (1 mmole) of 1,3-diiodoadamantane in 70 ml of methanol was irradiated for 4 hours through quartz. The diether was the major product (0V-17 125(4)  $\xrightarrow{32}$  200°, t = 8.4 min.) with a 4% yield of adamantane. Workup as before yielded the crude ether which was purified by glc.

<u>MS</u> - 196(26), 165(19), 139(100), 109(28), <u>IR</u> - 1455(m), 1365(m), 1325(w), 1300(m), 1280(w), 1190(m), 1150(m), 1115(s), 1072(s), 1050(m), 980(m), 915(s), 875(w) <u>NMR</u>  $(C_6^{H_6})$  - unresolved doublet, 1.28, (2H),  $\delta$ ; broad doublet, 1.58, (8H),  $\beta\delta$ ; singlet, 1.81, (2H),  $\beta$ ; broad singlet, 2.02, (2H),  $\delta$ ; singlet, 3.10, (6H), -OCH<sub>3</sub>

$\frac{\text{Analysis}}{12} - C_{12}H_{20}O_2$		<u> </u>	<u>H</u>
	calculated	73.43	10.27
	found	73.13	10.41

An authentic sample of the dimethoxyl compound was prepared by the method of Owen<sup>63</sup>. Into a 3-necked flask equipped with condenser, stirring bar and drying tube was placed 3.0 g (10.2 mmole) of freshly prepared Ag0<sup>15b</sup> and 100 ml of freshly distilled methanol. The mixture was stirred under reflux and followed by glc. Additional AgO was added (1.5 g every 24 hours) and the reaction cooled and filtered after 92 hours. Evaporation yielded a thick yellow oil which was eluted with petroleum ether (30-60) down an alumina column. The first fractions yielded 50 mg of a white solid while further elution gave the diether which was distilled, bp 63 - 65° (0.17 mm) to give a colourless oil identical in all respects to the photolytic product. The minor component was found to be 7-methylenebicyclo[3.3.1]-nonan-3-one, mp 160 - 161° (1it<sup>157</sup> 161 - 162°)

- <u>IR</u> 1720(s), 1460(m), 1400(m), 1360(w), 1335(m), 1220(m), 1155(w), 1100(w), 1090(m), 1060(m), 905(s), 880(m)
- <u>NMR</u> (CS<sub>2</sub>) singlet, 1.88, (2H); broad multiplet, 2.28, (10H); singlet, 4.65, (2H)

Attempted Synthesis of 1-t-butoxyadamantane



A solution of 262 mg (1 mmole) of 1-iodoadamantane in 70 ml of spectrograde <u>t</u>-butanol was irradiated through quartz for 4 hours. Workup as before yielded a white solid which was identical in all respects to 1-adamantanol. Careful drying and distillation of the <u>t</u>-butanol produced the same result with no trace of the <u>t</u>-butoxyadamantane.

Irradiation in the presence of cyanide ion



A solution of 140 mg (0.65 mmole) of 1-bromoadamantane with 200 mg (4.08 mmole) of NaCN in 75 ml of freshly distilled CH<sub>3</sub>OH was irradiated through quartz for 24 hours. Workup as before yielded a yellow solid which consisted of adamantane (41%) and 1-methoxyadamantane (59%).

The same reaction was repeated with 170 mg (0.65 mmole) of 1-iodoadamantane and 150 mg (3.06 mmole) of NaCN in 75 ml of CH<sub>3</sub>OH. The reaction was worked up after 2 hours to yield adamantane (15%) and 1-methoxyadamantane (85%). There was no evidence for any 1-cyanoadamantane in either reaction. Irradiation\_in DMSO with added NaCN



A solution of 270 mg (1.03 mmole) of 1-iodoadamantane with 300 mg (6.13 mmole) of NaCN in 75 ml of freshly distilled dimethyl sulfoxide was irradiated through quartz for 5 hours. The solution was worked up as before to yield a yellow oil shown to contain residual solvent. The oil was dissolved in petroleum ether (30-60) and washed five times with water and redried to yield a white solid. Glc showed it to consist of adamantane (4%), 1-adamantanol (88%), and 1-cyanoadamantane (8%).

The three products were collected by glc and were identical in all respects to authentic samples.

The same reaction was repeated in the absence of NaCN resulting in a quantitative yield of 1-adamantanol.

## Irradiation of 1,3-Dichloroadamantane

A degassed solution of 150 mg (0.73 mmole) of 1,3-dichloroadmantane in 70 ml of absolute ethanol was irradiated through quartz as before for 45 hours. Workup as before yielded a white solid which was shown to consist of a 1:1 mixture of starting material and 1-chloroadamantane. There was no trace of any ethoxy adamantanes. - 194 -

1.3-Diethoxyadamantane



A well degassed solution of 400 mg (1.03 mmole) of 1,3-diiodoadamantane in 70 ml of absolute ethanol was irradiated through quartz for 10 hours. Workup as before yielded a yellow oil which was collected by glc. <u>MS</u> - 224(39), 179(28), 167(100), 139(10), 123(16), 111(9), 95(11), 93(11) <u>IR</u> - 1448(m), 1382(m), 1360(w), 1344(m), 1322(w), 1300(m), 1280(w), 1122(s), 1100(msh), 1076(s), 1002(m), 880(w)

found

224.1758

1,3-Dipropoxyadamantane



A solution of 400 mg (1.13 mmole) of 1,3-diiodoadamantane in 70 ml of 1-propanol (degassed well with nitrogen) was irradiated through pyrex for 11 hours. Workup as before yielded a yellow oil which was collected by glc. <u>MS</u> - 252(45), 195(100), 193(74), 153(16), 151(32), 111(18), 95(24), 93(26) <u>IR</u> - 1455(m), 1345(m), 1320(w), 1300(m), 1120(s), 1078(s), 1030(m), 932(w), 908(m)  $\underbrace{\text{NMR}}_{(2_{6}H_{6})} - \text{triplet, J} = 7 \text{ Hz, 0.93, (6H), -CH}_{3}; \text{ unresolved triplet, 1.31,} (2H), & \text{$(1.42 - 1.70, (4H), -CH}_{2}-; \text{ broad doublet, 1.62,} (8H), & \text{$(3.5, (2H), $(2H), $(2H), $(2H), $(2H), $(2H), $(3.5, (2H), $(2H), $(2H), $(3.5, (2H), $(3.5$ 

1,3-Diisopropoxyadamantane



A well degassed solution of 400 mg (1.03 mmole) of 1,3-diiodoadamantane in 70 ml of reagent 2-propanol was irradiated through quartz for 17 hours. Workup as before yielded a thick yellow oil which was collected by glc. <u>MS</u> - 252(40), 195(82), 193(66), 167(13), 153(32), 152(17), 151(100), 150(15), 111(63), 109(19), 107(16), 95(34), 93(33)

<u>IR</u> - 1450(m), 1376(w), 1360(m), 1342(w), 1320(w), 1300(w), 1175(w), 1130(m), 1108(s), 1048(s), 980(mb), 912(w)

<u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - doublet, J = 6 Hz, 1.09, (12H), -CH<sub>3</sub>; unresolved triplet, 1.30, (2H), δ; doublet, J = 3 Hz, 1.58, (8H), βδ; singlet, 1.80, (2H), β; broad singlet, 2.05, (2H), δ; multiplet, J = 6 Hz, 3.72, (2H), -CH
<u>High Resolution MS</u> - C<sub>16</sub>H<sub>28</sub>O<sub>2</sub> calculated 252.2088
found 252.2111

## 1,3,5-Trimethoxyadamantane



A solution of 100 mg (.19 mmole) of 1,3,5-triiodoadamantane in 70 ml of methanol was degassed with nitrogen and irradiated through quartz for 6 hours. The triether was the major product with a 6% yield of adamantane. The ether was purified by glc.

MS = 226(45), 195(100), 169(90), 139(58), 123(89)

- <u>IR</u> 1445(m), 1350(w), 1315(m), 1290(m), 1220(w), 1185(m), 1230(m), 1180(sb), 1050(w), 1010(w), 970(m), 920(m)
- <u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) doublet, 1.44, (6H), βδδ; unresolved doublet, 1.73, (6H), ββδ; multiplet, 2.03, (1H), δ; singlet, 3.06, (9H), -OCH<sub>3</sub>

<u>Analysis</u> - $C_{13}H_{22}O_3$		<u> </u>	H
	calculated	68,99	9.79
	found	69.06	9.74

1,3-Dimethy1-5-methoxyadamantane



A degassed solution of 300 mg (1.04 mmole) of 1,3-dimethy1-5-iodoadamantane in 70 ml of methanol was irradiated through quartz for 3 hours. Workup as before yielded the crude ether containing 5% of 1,3-dimethy1adamantane. Purification was by preparative glc.  $\underline{MS} - 194(47)$ , 163(39), 137(100), 123(86), 107(39), 91(14) <u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - singlet, 0.85, (6H), -CH<sub>3</sub>; singlet, 1.01, (2H), H<sub>1</sub>; unresolved doublet, 1.20, (4H), H<sub>3</sub>; singlet, 1.41, (4H), H<sub>2</sub>; unresolved doublet, 1.60, (2H), H<sub>5</sub>; multiplet, 2.08, (1H), H<sub>4</sub>; singlet, 3.16, (3H), -OCH<sub>3</sub>
<u>Analysis</u> - C<sub>13</sub>H<sub>22</sub>O
<u>C</u>
<u>H</u>
calculated 80.35
11.41
found
80.22
11.44

1,3-Dimethoxy-5,7-dimethyladamantane



A degassed solution of 300 mg (0.72 mmole) of 1,3-diiodo-5,7-dimethyladamantane in 70 ml of methanol was irradiated through quartz for 4 hours. Workup as before gave the crude ether containing 4% of 1,3-dimethyladamantane. Purification was made by preparative glc.

<u>MS</u> - 224(39), 193(89), 153(100), 137(70), 121(55),

<u>IR</u> - 1460(m), 1380(w), 1345(m), 1300(w), 1250(wb), 1220(m), 1210(m),

1195(w), 1095(sb), 1020(w), 970(m), 915(m), 855(m)

<u>NMR</u> (CS<sub>2</sub>) - singlet, 0.89, (6H), -CH<sub>3</sub>; singlet, 1.01, (2H), H<sub>1</sub>; singlet,

1.22, (8H),  $H_2$ ; singlet, 1.45, (2H),  $H_3$ ; singlet, 3.04, (6H), -OCH<sub>3</sub> <u>Analysis</u> -  $C_{14}H_{24}O_2$  <u>C</u> <u>H</u> calculated 74.95 10.78 found 74.76 10.70 Irradiation of 1,3-Dibromoadamantane



A degassed solution of 300 mg (1.02 mmole) of 1,3-dibromoadamantane in 70 ml of methanol was irradiated through quartz for 16 hours (no starting material by glc). Analysis showed the products to consist of adamantane (5%), 1-methoxyadamantane (31%), and 1,3-dimethoxyadamantane (64%) by collection and comparison to authentic samples.

Repetition of the experiment showed two intermediate products which disappeared during the course of the reaction. When stopped after 6 hours the products consisted of adamantane (2%), 1-methoxyadamantane (27%), 1-bromoadamantane (17%), 1,3-dimethoxyadamantane (33%), 1-bromo-3-methoxyadamantane (18%), and residual 1,3-dibromoadamantane (3%). (0V-17 125(4)  $32 \rightarrow 200^{\circ}$ , t = 2.0, 5.4, 6.7, 7.4, 8.4, 9.8 minutes).

Again all the products were collected by glc and were identical to authentic samples except for the bromo-ether. mp  $14.5 - 16.0^{\circ}$ 



- <u>MS</u> 244(trace), 165(100), 133(4), 123(4), 109(35)
- <u>IR</u> 1458(m), 1360(w), 1340(m), 1320(m), 1290(m), 1270(w), 1190(m), 1150(w), 1110(s), 1090(s), 1040(s), 960(s), 895(s), 675(s)

<u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - unresolved triplet, 1.21, (2H), H<sub>5</sub>; broad singlet, 1.49, (4H)
H<sub>3</sub>; broad singlet, 1.83, (2H), H<sub>4</sub>; unresolved doublet, 2.06, (4H), H<sub>2</sub>; singlet, 2.31, (2H), H<sub>1</sub>; singlet, 2.98, (3H), -OCH<sub>3</sub>

Analysis - C <sub>11</sub> H <sub>17</sub> BrO		<u> </u>	H
	calculated	53.89	6.99
	found	54.11	7.12

Irradiation of 1,3-Dibromo-5,7-dimethyladamantane



A degassed solution of 300 mg (0.93 mmole) of 1,3-dibromo-5,7dimethyladamantane in 70 ml of methanol was irradiated through quartz for 12 hours (starting material all gone). Workup as before and collection by glc showed the products to consist of 5% 1,3-dimethyladamantane, 34% ',3dimethyl-5-methoxyadamantane and 61% of 1,3-dimethoxy-5,7-dimethyladamantane.

The reaction was repeated and stopped after 6 hours to yield six products. in the following ratios: 1,3-dimethyladamantane (4%), 1,3-dimethyl-5-methoxyadamantane (29%), 1-bromo-3,5-dimethyladamantane (13%), 1,3-dimethoxy-5,7dimethyladamantane (40%), 1-bromo-3,5-dimethyl-7-methoxyadamantane (12%) and residual 1,3-dibromo-5,7-dimethyladamantane (2%) (0V-17 125(4)  $\xrightarrow{32}$  200<sup>o</sup> t = 2.0, 5.5, 6.4, 7.0, 8.1 and 9.2 minutes)

Again all compounds were identical to authentic samples except for the bromo-ether, mp  $28.5 - 29.5^{\circ}$ .



<u>MS</u> - 272(trace), 193(100), 137(65), 121(60), 107(12), 105(15), 97(13), 95(13), 91(20)

<u>IR</u> - 1450(m), 1365(w), 1332(m), 1310(m), 1240(w), 1230(w), 1190(m), 1170(w), 1095(wsh), 1090(mb), 1080(wsh), 965(w), 935(w), 915(w), 865(m)
<u>NMR</u> (CS<sub>2</sub>) - singlet, 0.92, (6H), -CH<sub>3</sub>; singlet, 1.10, (2H), H<sub>2</sub>; singlet, 1.33, (4H), H<sub>3</sub>; singlet, 1.84, (4H), H<sub>4</sub>; singlet, 2.07, (2H), H<sub>1</sub>; singlet, 3.12, (6H), -OCH<sub>3</sub>

<u>Analysis</u> - C <sub>13</sub> H <sub>21</sub> BrO		_ <u>C</u>	. <u>H</u>
	calculated	57.15	7.75
	found	57.02	7.68
	· · · · · · · · · · · · · · · · · · ·		

Irradiation of 1,3,5-Tribromoadamantane



A degassed solution of 150 mg (0.40 mmole) of 1,3,5-tribromoadamantane in 70 ml of methanol was irradiated through quartz for 21 hours (no starting material by glc). Analysis showed the major products to be 1-methoxyadamantane (19%), 1,3-dimethoxyadamantane (50%), and 1,3,5-trimethoxyadamantane (22%) by comparison with authentic samples.

1-Chloro-3-methoxyadamantane



A well degassed solution of 50 mg (0.34 mmole) of 1-bromo-3-chloroadamantane in 70 ml of methanol was irradiated through quartz for 17 hours. Workup as before yielded a light yellow sticky solid which consisted of 1-chloroadamantane (42%) and 1-chloro-3-methoxyadamantane (58%) (mp just below room temperature).

- <u>MS</u> 202(5), 200(15), 171(4), 169(11), 166(13), 165(100), 143(14), 109(40), 93(16), 91(9)
- <u>IR</u> 1448(m), 1340(m), 1320(w), 1298(m), 1192(m), 1150(w), 1110(s), 1090(s), 1044(s), 967(m), 898(s)
- <u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) broad singlet, 1.14, (2H), H<sub>5</sub>; broad singlet, 1.45, (4H), H<sub>3</sub>; singlet, 1.85, (6H), H<sub>2</sub> + H<sub>4</sub>; singlet, 2.18, (2H), H<sub>1</sub>; singlet, 2.93, (3H), -OCH<sub>3</sub>

<u>Analysis</u> -  $C_{11}H_{17}C_{10}$  <u>C</u> <u>H</u> calculated 65.82 8.54 found 65.63 8.43

The same reaction with 1-chloro-3-iodoadamantane in methanol produced the chloroether as the sole product with no evidence for any 1-chloroadamantane. 2-Methoxybicyclo[2.2.1] heptane



A well degassed solution of 520 mg (2.34 mmole) of exo-2-iodonorbornane in 12 ml of methanol was irradiated through quartz for 24 hours. The dark solution was worked up as before to yield a dark yellow oil which was eluted with pentane down a short alumina column to yield 240 mg (81%) of a light yellow liquid (extremely volatile)<sup>158</sup>.

 $\underline{MS}$  - Parent(126)

<u>IR</u> - 1450(m), 1360(m), 1304(w), 1220(w), 1200(w), 1180(w), 1120(w), 1104(s), 1064(m), 982(m), 920(w), 890(w)

<u>NMR</u> (CCl<sub>4</sub>) - multiplets, 0.90 - 1.56, (8H); broad singlet, 2.24, (2H);

broad singlet, 3.08, (1H); singlet, 3.19, (3H)

Irradiation of 1,4-Diiodobicyclo[2.2.1] heptane



A well degassed solution of 250 mg (0.72 mmole) of 1,4-diiodonorbornane in 15 ml of freshly distilled methanol was irradiated through quartz for 24 hours. The dark purple solution was worked up as before to yield a dark yellow oil which consisted of three components by glc in the relative ratio of 19:43:38. The compounds were purified by preparative glc. The first component was shown to be 1-methoxynorbornane.

- <u>MS</u> 127(10), 126(100), 125(34), 111(43), 106(13), 105(13), 97(55), 94(14) <u>IR</u> - 1460(m), 1315(s), 1260(m), 1220(w), 1198(w), 1170(w), 1132(s), 1095(m), 1025(m), 930(w)
- <u>NMR</u> (CCl<sub>4</sub>) multiplets, 0.92 1.80, (11H); broad singlet, 2.04, (1H); singlet, 3.15, (3H)

The major product was shown to be 1,4-dimethoxynorbornane.

 $\underline{MS} = 156(16), 127(100), 125(26), 109(15), 97(23)$ 

- <u>IR</u> 1458(m), 1320(s), 1298(w), 1262(w), 1217(s), 1140(w), 1120(sb), 1030(s), 910(m)
- <u>NMR</u> (CC1<sub>4</sub>) multiplets, 1.28 1.84, (10H); singlet, 3.13, (6H)
- The third component was found to be 1-iodo-4-methoxynorbornane.

MS = 252(trace), 125(100), 109(20), 97(4)

<u>IR</u> - 1480(w), 1443(m), 1308(s), 1277(m), 1198(s), 1140(m), 1120(m), 1037(m), 1024(m), 982(s), 950(w), 870(s)

<u>NMR</u> (CC1<sub>4</sub>) - multiplets, 1.50 - 2.42, (10H); singlet, 3.22, (3H)

Analysis - C.H. OT	· .	С	· · · <b>H</b> ·
<u>Anarysis</u> 8.13			 
	calculated	38.08	5.18
	found	37.78	5.33

When the above reaction was repeated in greater dilution (eg 200 mg of diiodide in 50 ml of methanol) only the mono and diether were observed.

The above reaction was repeated with 250 mg (0.72 mmole) of the diiodide in 12 ml of reagent CH<sub>3</sub>OD and worked up after 22 hours. The same three products were observed and the monoether collected by glc and studied by mass spectrometry for the deuterium content. Calculations (see appendix) indicated a total of 17% deuterium incorporation.

## General Procedure for 02 Photolytic Runs

The adamantyl halides were run as dilute solutions in freshly distilled methanol through pyrex or quartz vessels as before, only this time with oxygen gas being bubbled through the solution during the course of the reaction. The solution was worked up as before (no real difference in the length of the reaction was found) to yield the crude products which were

purified by glc.

Reaction of 1-Haloadamantanes

A solution of 300 mg (1.39 mmole) of 1-bromoadamantane in 70 ml of methanol was irradiated through quartz with  $O_2$  for 16 hours. Workup as before yielded a yellow solid which consisted of 1-methoxyadamantane (69%) and 1-adamantanol (31%), mp 186 - 187° (lit<sup>18</sup> 187 - 188°) <u>IR</u> - 3550(w), 1450(m), 1345(w), 1295(w), 1110(s), 1085(s), 978(m), 930(s) <u>NMR</u> (CS<sub>2</sub>) - singlet, 1.02, (1H), OH; multiplet, 1.64, (12H), $\beta$ + $\beta$ ;

broad singlet, 2.06, (3H), & .

Similarly, a solution of 130 mg (0.5 mmole) of 1-iodoadamantane in 70 -ml of methanol was irradiated through pyrex with  $0_2$  for 3 hours. Workup

as before yielded 1-methoxyadamantane (94%) and 1-adamantanol (6%) identical to authentic materials.

A solution of 215 mg (1.0 mmole) of 1-bromoadamantane in 70 ml of cyclohexane was irradiated through quartz with 0<sub>2</sub> bubbling through the solution for 17 hours. Workup as before yielded a light yellow solid which consisted of 1-adamantanol (32%) and residual 1-bromoadamantane (68%). <u>Reaction of 1-Bromo-3,5-dimethyladamantane</u>



A solution of 350 mg (1.44 mmole) of 1-bromo-3,5-dimethyladamantane in 70 ml of methanol was irradiated through quartz with 0<sub>2</sub> bubbling through the solution for 11 hours. Workup as before yielded a yellow solid containing 1-methoxy-3,5-dimethyladamantane (64%) and 1,3-dimethyladamantan-5-ol (36%), mp (alcohol) 95.5 - 96.5° (1it<sup>159</sup> 97°) <u>MS</u> - 180(49), 165(18), 149(10), 147(20), 123(100), 109(91), 107(35) <u>IR</u> - 3580(w), 1445(s), 1363(w), 1340(m), 1310(m), 1165(m), 1062(s), 1025(s), 975(w), 935(m), 915(m), 882(m)

<u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - singlet, 0.60, (1H), -OH; singlet, 0.78, (6H), -CH<sub>3</sub>; singlet, 0.94, (2H), H<sub>1</sub>: unresolved doublet, 1.13, (4H), H<sub>2</sub>; singlet, 1.23, (4H), H<sub>3</sub>; unresolved doublet, 1.45, (2H), H<sub>5</sub>; multiplet, 2.01, (1H), H<sub>4</sub> Reaction of 1,3-Dibromoadamantane



A solution of 400 mg (1.36 mmole) of 1,3-dibromoadamantane in 70 ml of methanol was irradiated through quartz with 0<sub>2</sub> for 17 hours. Workup as before yielded 5 products in the ratio of 12:6:35:6:41. The first four products were found by comparison to authentic samples to be 1-methoxy-adamantane, 1-adamantanol, 1,3-dimethoxyadamantane and 1-bromo-3-methoxy-adamantane.

The major product was found to be 1-methoxyadamantan-3-ol, mp 61 - 62.5°. <u>MS</u> - 182(34), 164(7), 151(11), 125(100), 109(16), 95(10), 93(11) <u>IR</u> - 3600(w), 1445(m), 1340(m), 1320(w), 1298(m), 1190(m), 1120(s), 1100(w), 1070(s), 995(s), 940(s), 885(m)

<u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - singlet, 1.18, (1H), -OH; unresolved triplet, 1.25, (2H), H<sub>5</sub>; unresolved doublet, 1.47, (4H), H<sub>2</sub> or H<sub>4</sub>; unresolved doublet, 1.54, (4H), H<sub>2</sub> or H<sub>4</sub>; singlet, 1.65, (2H), H<sub>1</sub>; broad singlet, 2.03, (2H), H<sub>3</sub>; singlet, 3.07, (3H), -OCH<sub>3</sub>

<u>High Resolution MS</u> - $C_{11}H_{18}O_2$	calculated	182.1306
	found	182.1308





The procedure of Feiser was followed<sup>160</sup>. A solution of 1.5 g (8.25 mmole) of benzephenone in 50 ml of 2-propanol with 3 drops of glacial acetic acid in a pyrex flask was stopped and allowed to sit exposed to sunlight for three days. The white precipitate was filtered and washed with pentane mp 187 -  $188^{\circ}$  (lit<sup>160</sup> 188 -  $189^{\circ}$ )

<u>IR</u> (nujol) - 3500(w), 1320(mb), 1250(mb), 1152(mb), 1038(m), 1020(m), 950(w), 905(w), 840(mb), 753(s), 738(s), 696(sb)

A degassed solution of 262 mg (1 mmole) of adamantyl iodide and 360 mg (2.0 mmole) of benzophenone in 70 ml of methanol was irradiated through pyrex for 3 hours. Analysis by glc showed the products to consist of adamantane (66%) and 1-methoxyadamantane (34%). Elution with pentane down an alumina column yielded the two adamantane products. Further elution with CHCl<sub>3</sub> yielded residual benzophenone plus a white solid which was shown to be 1,1,2,2-tetraphenyl-1,2-ethandiol by comparison to an authentic sample.

A degassed solution of 215 mg (1 mmole) of 1-bromoadamantane and 360 mg (2 mmole) of benzophenone in 70 ml of methanol was irradiated through pyrex for 20 hours. Glc indicated only residual starting material plus the tetraphenyl diol with no adamantane or adamantyl ether.

The tetraphenyl diol was also produced by irradiation of a benzophenone solution in methanol through pyrex.
#### Quenching Studies

A degassed solution of 262 mg (1 mmole) of 1-iodoadamantane and 1.36 g (20.0 mmole) of a cis-trans mixture of 1,3-pentadiene in 70 ml of methanol was irradiated through pyrex. The reaction was followed by glc and was 50% complete after 5 hours, 80% after 8 hours and 100% after 11 hours. In the absence of the pentadiene the reaction was finished after  $2\frac{1}{2}$  hours. Sensitization Studies

A series of solutions containing 110 mg (0.5 mmole) of 1-bromoadamantane and 3-4 mmole of a triplet sensitizer in 70 ml of methanol were degassed with  $N_2$  and irradiated through pyrex for 12 - 18 hours. In all cases only starting material was present after workup by glc. The sensitizers used were naphthalene, benzene, phenanthrene,  $\alpha$ -chloroanthraquinone, acetophenone, 1-naphthaldehyde and fluorene.

# General Procedure for Photochemical Nitrile Reactions

The desired iodide was dissolved in either acetonitrile or butyronitrile and two drops of water added (the reaction was slow and incomplete if water was absent). The reaction was followed by glc and poured into aqueous sodium bisulfite when starting material had disappeared. To this was added chloroform, the layers separated and the organic phase was washed with aqueous sodium carbonate, three times with water and dried over MgSO<sub>4</sub>. Evaporation yielded the crude amide.

Reaction of 1-Iodoadamantane



a) A solution of 400 mg (1.53 mmole) of 1-iodoadamantane in 13 ml of

acetonitrile (R =  $CH_3^{-}$ ) in a quartz tube was degassed well with N<sub>2</sub> and irradiated for 23 hours. Workup yielded 260 mg (88%) of a light yellow solid. An analytical sample was obtained by preparative glc, mp 145 -146° (lit<sup>22a</sup> 148°)

- <u>MS</u> 193(81), 150(9), 136(100), 94(28)
- <u>IR</u> 3500(w), 1685(s), 1495(s), 1458(m), 1360(m), 1340(w), 1290(m), 1278(m), 1240(w), 1135(w), 1095(w)
- <u>NMR</u> (CDCl<sub>3</sub>) broad singlet, 1.60, (6H), δ ; singlet, 1.69, (3H), -CH<sub>3</sub>; singlet, 1.95, (12H), δ + β; broad singlet, 3.48, (1H), -NH

b) A solution of 400 mg (1.53 mmole) of 1-iodoadamantane in 13 ml of butyronitrate (R =  $CH_3CH_2CH_2$ -) in a quartz tube was irradiated as above for 23 hours. Workup as before yielded a yellow oil which contained some residual solvent. Elution down a short silica gel column with petroleum ether (30-60) yielded the solvent, elution with diethyl ether yielded 350 mg (82%) of a light yellow solid which was recrystallized from methanol to yield white crystals, mp 118 - 119.5° (lit<sup>110</sup> 119 - 120°)

- <u>MS</u> 221(65), 193(69), 164(69), 135(100)
- <u>IR</u> 3500(w), 1690(s), 1500(s), 1457(w), 1358(m), 1342(w), 1304(w), 1290(w), 1277(w), 1202(wb), 1100(wb)

<u>IR</u> (KBr) - 3300(s), 1640(s), 1540(s)

<u>NMR</u> (CDCl<sub>3</sub>) - triplet, J = 7 Hz, 0.92, (3H),  $-CH_3$ ; multiplet, 1.67, (8H),  $-CH_2 + \delta$ ; broad singlet, 2.00, (12H),  $\beta + \delta$ ; triplet, J = 7 Hz, 2.06, (2H),  $-CH_2C$ ; broad singlet, 5.10, (1H), -NH Reaction of 2-lodoadamantane



a) A solution of 200 mg (0.77 mmole) of 2-iodoadamantane in 13 ml of acetonitrile (R = CH<sub>3</sub>-) in a quartz tube was irradiated as before for 10 hours. Workup yielded 140 mg (96%) of a light yellow solid. Preparative glc yielded feathery white crystals, mp 192 - 193<sup>o</sup>.
<u>MS</u> - 193(100), 178(11), 150(16), 136(9), 135(27), 134(49), 92(31)
<u>IR</u> (nearly insoluble in CCl<sub>4</sub>) - 3480(w), 1680(m), 1500(m)
<u>IR</u> (KBr) - 3300(s), 1640(sb), 1550(sb), 1445(m), 1360(m), 1295(m), 1278(m), 1125(m), 960(m)

<u>NMR</u> (CDCl<sub>3</sub>) - multiplets, 1.45 - 2.05, (15H); singlet, 2.00, (3H), -CH<sub>3</sub>; broad doublet, J = 7 Hz, 4.06, (1H), H<; broad singlet, 5.82, (1H), -NH <u>Analysis</u> - C<sub>12</sub>H<sub>19</sub>NO
<u>C</u> H N

calculated	74.56	9.90	7.25
found	74.42	10.05	7.20

b) A solution of 135 mg (0.52 mmole) of 2-iodoadamantane in 14 ml of butyronitrile (R =  $CH_3CH_2CH_2$ -) in a quartz tube was irradiated as before for 15 hours. Workup as before yielded a yellow oil which was eluted with petroleum ether (30-60) down a short silica gel column to yield 90 mg (80%) of a light yellow solid. Preparative glc gave a white solid, mp 145 - 146.5°. <u>MS</u> - 221(100), 206(26), 193(40), 182(23), 150(26), 135(45), 134(35), 119(14) IR - 3470(w), 1680(s), 1495(s), 1468(w), 1448(w), 1190(w), 1120(w), 908(s) IR (KBr) - 3300(m), 1635(s), 1550(s) <u>NMR</u> (CDCl<sub>3</sub>) - triplet, J = 7 Hz, 0.95, (3H), -CH<sub>3</sub>; multiplet, 1.28 - 2.05,

(17H); triplet,	J = 7 Hz, 2.	12 <b>, (</b> 2H)	, CCH <sub>2</sub> ; b	oroad doublet,	J = 7 H	z,
4.05, (1H), H ;	broad multip	let, 5.7	2, (1H),	-NH		
<u>Analysis</u> - C <sub>14</sub> H <sub>23</sub> NO		<u> </u>	<u>H</u>	<u>N</u>		
	calculated	75.97	10.47	6.33		
	found	75.84	10.53	6.28		

1-Acetamido-3-iodoadamantane



A well degassed solution of 300 mg (0.77 mmole) of 1,3-diiodoadamantane in 12 ml of freshly distilled  $CH_3CN$  containing 2 drops of water was irradiated through quartz for 18 hours. Workup as before yielded a sticky brown solid which contained one major peak by glc with a small amount of starting material. The solid was recrystallized four times from  $CCl_4$  to yield a light yellow solid, mp 158.5 - 160°. <u>MS</u> - 319(trace), 192(100), 149(42), 136(42), 94(40) <u>IR</u> (KBr) - 3250(m), 3020(w), 1645(s), 1550(s), 1445(m), 1365(m), 1300(m), 1105(w), 1032(m), 995(w), 975(w), 930(m), 835(m), 760(m) <u>NMR</u> (CS<sub>2</sub>) - singlet, 1.70, (2H), H<sub>5</sub>; singlet, 1.73, (3H), -CH<sub>3</sub>; singlet, 1.98, (6H), H<sub>2</sub> + H<sub>4</sub>, singlet, 2.43, (4H), H<sub>3</sub>; singlet, 2.70, (2H), H<sub>1</sub>

<u>Analysis</u> - C <sub>12</sub> <sup>H</sup> 18 <sup>NOI</sup>		<u> </u>	H	<u>N</u>
	calculated	45.1	6 5.68	4.38
	found	46.14	4 5.87	3.88
High Resolution MS	calcula	ted	319.1877	
	found	-	319.1872	

Irradiation of a solution of the acetamido-iodide in  $CH_3CN$  led to the formation of the 1,3-diamide with no evidence of the monoamide. 1,3-Diacetamidoadamantane



A well degassed solution of 250 mg (0.64 mmole) of 1,3-diiodoadamantane in 50 ml of  $CH_3CN$  containing 2 drops of water was irradiated through quartz for 18 hours. A total of 100 mg (62%) of light brown crystals were filtered from the reaction mixture. The solution was worked up as before to yield a dark brown solid. Glc showed both fractions to consist of the same single peak. Recrystallization from  $CH_3CN$  yielded 120 mg (75%) of white feathery crystals, mp 222 - 224° (lit<sup>22b</sup> 226 - 228°)

<u>MS</u> - 250(67), 207(100), 193(58), 151(14), 150(15), 149(18), 148(20), 136(28), 128(46), 127(22)

<u>IR</u> - 3450(w), 1680(s), 1495(m), 1360(w), 1328(w), 1295(w), 1270(w), 1215(w), 1122(w), 1032(w)

<u>NMR</u> (DMSO-d<sup>6</sup>) - broad singlet, 1.50, (2H),  $\delta$ ; singlet, 1.74, (6H), -CH<sub>3</sub>; broad singlet, 1.84, (8H),  $\beta\delta$ ; multiplet, 2.10, (2H),  $\delta$ ; singlet, 2.15, (2H),  $\beta$ .

Reaction of Exo-2-iodobicyclo[2.2.1] heptane



a) A solution of 400 mg (1.80 mmole) of exo-2-iodonorbornane in 12 ml of acetonitrile (R = CH<sub>3</sub>-) in a quartz tube was irradiated for 23 hours. Workup yielded an orange solid which consisted of nearly equal amounts of

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starting material and product. Low temperature recrystallization from pentane yielded a light yellow solid. Preparative glc gave a white solid, mp 132 - 134° (lit<sup>161</sup> 132 - 133°),

$$\underline{MS}$$
 - 153(100), 138(12), 125(7), 124(23), 110(28), 96(11), 94(100)

<u>IR</u> - 3400(w), 1685(s), 1500(s), 1120(m), 910(s)

<u>NMR</u> (CDCl<sub>3</sub>) - multiplet, 1.10 - 2.00, (8H); singlet, 1.92, (3H), -CH<sub>3</sub>;

broad singlet, 2.23, (2H), bridgeheads; multiplet, 3.70, (1H), Ha; broad singlet, 5.40, (1H), -NH

b) A solution of 500 mg (2.25 mmole) of exo-2-iodonorbornane in 12 ml of butyronitrile ( $R = CH_3CH_2CH_2$ ) in a quartz tube was irradiated for 23 hours to yield an equimixture of product and starting material. Elution with petroleum ether down a silica gel column yielded starting material plus solvent; elution with chloroform yielded the crude amide. Preparative glc yielded a white solid, mp 73.5 - 75°.

<u>MS</u> - 181(100), 166(9), 153(23), 152(27), 137(16), 110(54), 109(25), 94(50) <u>IR</u> - 3400(w), 1680(s), 1490(s), 910(s)

<u>IR</u> (KBr) - 3300(s), 1640(s), 1540(s)

<u>NMR</u> (CDCl<sub>3</sub>) - triplet, J = 7 Hz, 0.80, (3H), -CH<sub>3</sub>; multiplets, 1.05 - 1.90, (10H); triplet, J = 7 Hz, 1.96, (2H), -CCH<sub>2</sub>; broad singlet, 2.11, (2H), bridgeheads; multiplet, 3.59, (1H), Hx; broad singlet, 5.23, (1H), -NH

Analysis - C <sub>11</sub> H <sub>19</sub> NO		<u> </u>	H	<u>N</u>
	calculated	72.88	10.56	7.72
	found	72.78	10.40	7.54

Reaction of 1,4-Diiodobicyclo[2.2.1] heptane



a) A solution of 400 mg (1.15 mmole) of 1,4-diiodonorbornane in 13 ml of acetonitrile in a quartz tube was irradiated for 24 hours. Workup yielded a dark oil which consisted of two products in a 25:75 ratio. Preparative glc gave analytical samples of the two products (5% Carbowax 195<sup>o</sup>, t = 5 and 35 minutes).

The minor product was a feathery white solid which was shown to be the bridgehead amide, mp 158 - 159.5°.

<u>MS</u> - 153(35), 138(2), 125(10), 124(100), 110(12), 96(7), 94(4) <u>IR</u> - 3450(w), 1685(s), 1500(m), 1360(m), 1323(w), 1302(w), 1260(wb), 910(m) <u>IR</u> (KBr) - 3300(m), 1650(s), 1545(s)

<u>NMR</u> (CDC1<sub>3</sub>) - multiplets, 1.20 - 1.90, (10H); singlet, 1.90, (3H), -CH<sub>3</sub>;

broad singlet, 2.13, (1H), bridgehead; broad singlet, 5.86, (1H), -NH <u>Analysis</u> - C<sub>9</sub>H<sub>15</sub>NO <u>C H N</u> calculated 70.72 9.81 9.09 found 70.67 9.80 8.96

The major product, a white solid, was shown to be the iodo-acetamide, mp 96 -  $98^{\circ}$ .

<u>MS</u> - 279(trace), 152(74), 124(4), 110(100)

<u>IR</u> - 3360(w), 1685(s), 1495(s), 1458(w), 1360(m), 1320(m), 1290(m), 1265(m), 1202(m), 985(sb), 910(m), 875(wb),

IR (KBr) - 3300(m), 1635(s), 1550(s)

<u>NMR</u> (CDC1<sub>3</sub>) - multiplets, 1.60 - 2.40, (10H); singlet, 1.90, (3H), -CH<sub>3</sub>; broad singlet, 5.77, (1H), -NH
Analysis - C<sub>0</sub>H<sub>10</sub>NOI

$- {}^{\rm C}9^{\rm H}13^{\rm NOL}$	<u> </u>	<u><u> </u></u>	<u>N</u>
calculated	38.72	5.05	5.01
found	39.00	4.98	4.80

b) A solution of 315 mg (0.91 mmole) of 1,4-diiodonorbornane in 15 ml of butyronitrile (R =  $CH_3CH_2CH_2$ -) in a quartz tube was irradiated for 24 hours. Workup as before yielded a thick oil which contained two components in a 40:60 ratio. Preparative glc yielded the two compounds (5% Carbowax  $220^{\circ}$ , t = 2.5, 17 minutes).

The minor product was shown to be the bridgehead amide, mp 91 - 92.5°. <u>MS</u> - 181(44), 166(3), 153(12), 152(100), 137(4), 110(32), 109(13), 94(12) <u>IR</u> - 3350(w), 1685(s), 1495(s), 1325(m), 1300(w), 1260(w), 1190(w) <u>IR</u> (KBr) - 3300(m), 1640(s), 1550(s) <u>NMR</u> (CDCl<sub>3</sub>) - triplet, J = 7 Hz, 0.93, (3H), -CH<sub>3</sub>; multiplets, 1.20 - 1.90,

(12H); triplet, J = 7 Hz, 2.11, (2H), C-CH<sub>2</sub>; broad singlet, 2.15, (1H), bridgehead; broad singlet, 5.62, (1H), -NH

<u>Analysis</u>	-	<sup>C</sup> 11 <sup>H</sup> 19 <sup>NO</sup>		C	<u> </u>	<u>N</u>
			calculated	72.88	10.56	7.72
			found	72.75	10.57	7.53

The major component was shown to be the iodo-amide, mp 103 - 104.5°. <u>MS</u> - 307(trace), 180(48), 152(4), 110(100) <u>IR</u> - 3350(w), 1685(s), 1495(s), 1325(m), 1285(w), 1210(m), 1000(m) <u>IR</u> (KBr) - 3300(m), 1640(s), 1550(s) <u>NMR</u> (CDCl<sub>3</sub>) - triplet, J = 7 Hz, 0.91, (3H), -CH<sub>3</sub>; multiplets, 1.20 - 2.30, (14H); triplet, J = 7 Hz, 2.10, (2H), -C-CH<sub>2</sub>; broad singlet, 5.52,

(1H), -NH

<u>Analysis</u> - C <sub>11</sub> <sup>H</sup> 18 <sup>NOI</sup>		<u>C</u>	<u>H</u>	<u>N</u>
	calculated	43.01	5.90	4.56
	found	42.73	5.70	4.70
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#### Photochemistry in Halogenated Solvents

A solution of adamantane in a chlorinated solvent was degassed well with  $N_2$  and then irradiated through quartz for 50 hours. No reaction at all was observed when methylene chloride was the solvent, while in chloroform a 30% yield of 1-chloroadamantane and a 2% yield of the 2-chloride was observed. In carbon tetrachloride both mono and dichlorinated products were observed as well as hexachloroethane.

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To avoid the problem of separating secondary monochlorides a series of monohaloadamantanes were used.

The reaction mixture from the irradiation of a solution of 1-chloroadamantane in carbon tetrachloride was poured into aqueous sodium bicarbonate and separated. The organic phase was washed well with water and dried over magnesium sulfate. Evaporation yielded a yellow solid which was eluted down a short silica gel column with petroleum ether (30-60). The first fractions yielded hexachloroethane. The chlorides were washed off with chloroform and rechromatographed down an alumina column with petroleum ether (30-60). Analytical samples were obtained by preparative glc.

The products were found to be 1,3-dichloroadamantane, <u>anti</u>-1,4-dichloroadamantane, <u>syn</u>-1,4-dichloroadamantane, and 1,3,5-trichloroadamantane in order of elution. The bridgehead chlorides were the major products and all four compounds were identical in all respects to authentic samples. Reaction of 1-Bromoadamantane

A degassed solution of 1-bromoadamantane in carbon tetrachloride was irradiated through quartz for 50 yours. Workup and column chromatography as before yielded four major products. - 216 -

The first one was shown to be 1-bromo-3-chloroadamantane, mp 101.5 - 103°.



<u>MS</u> - 248(trace), 171(33), 169(100), 113(4), 111(9), 103(8), 93(10), 91(17) <u>IR</u> - 1450(s), 1338(s), 1318(s), 1284(s), 1100(w), 1024(s), 1006(m), 958(m), 940(w), 840(s), 713(m), 675(m)

<u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - unresolved triplet, 1.05, (2H), H<sub>5</sub>; broad singlet, 1.61, (2H), H<sub>4</sub>; doublet, 1.74, (4H), H<sub>3</sub>; doublet, 1.88,°(4H), H<sub>2</sub>; singlet, 2.55, (2H), H<sub>1</sub>

L		
Analysis - C <sub>10</sub> H <sub>14</sub> BrCl	C	<u>H</u>
calculated	48.14	5.65
found	48,40	5,56



The second and third products were the syn and anti isomers of 1-bromo-4-chloroadamantane which could not be separated.

<u>MS</u> - 248(trace), 205(3), 203(6), 171(32), 169(100), 133(22), 105(9),

93(8), 91(19)

- <u>IR</u> 1445(s), 1342(m), 1285(m), 1260(m), 1100(w), 1025(s), 972(w), 942(m), 922(m), 685(m)
- <u>NMR</u> (CC1<sub>4</sub>) multiplets, 1.80 2.95; singlet, 4.20, (1H), syn; singlet, 4.36, (0.2H), anti





The fourth product was shown to be 1-bromo-3,5-dichloroadamantane, mp 104.5 - 106<sup>o</sup>. <u>MS</u> - 282(trace), 205(33), 203(100), 171(8), 169(16), 167(14), 127(19), 91(22) <u>IR</u> - 1450(s), 1342(w), 1330(w), 1311(s), 1280(m), 1225(w), 1132(w), 1030(s), 960(m), 854(s), 838(m) <u>NMR</u> (CCl<sub>4</sub>) - unresolved doublet, 2.02, (4H), H<sub>3</sub>; unresolved doublet, 2.16, (2H), H<sub>5</sub>; multiplet, 2.36, (1H), H<sub>4</sub>; singlet, 2.42, (2H), H<sub>1</sub>; singlet, 2.56, (4H), H<sub>2</sub>

<u>Analysis</u> - C <sub>10</sub> H <sub>13</sub> BrCl <sub>2</sub>	· .	C	H
	calculated	42.29	4.61
	found	42.20	4.70
• • • • • • • • • • • • • • • • • • • •			

### Reaction of 1-Fluoroadamantane

The same photolytic reaction was done using 1-fluoroadamantane in carbon tetrachloride and the products isolated as before.

The first one off the column was shown to be 1-chloro-3-fluoroadamantane, mp 177 - 178°.



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- <u>MS</u> 190(2), 188(4), 153(100), 123(31), 108(19), 105(24), 97(16) <u>IR</u> - 1448(s), 1348(m), 1340(s), 1320(s), 1295(s), 1150(w), 1105(s), 1078(s), 1037(w), 967(s), 944(m), 920(s), 910(w), 844(m), 684(mb)
- <u>NMR</u> (CC1<sub>4</sub>) unresolved triplet, 1.55, (2H), H<sub>5</sub>; multiplet, 1.81, (4H), H<sub>2</sub>; unresolved doublet, 2.01, (4H), H<sub>3</sub>; doublet, J = 5.5 Hz, 2.23 (2H), H<sub>1</sub>; broad singlet, 2.35, (2H), H<sub>4</sub>
- <u>MMR</u> (<sup>19</sup>F) singlet, -133.0, SCS -5.0 <u>Analysis</u> -  $C_{10}H_{14}FC1$

<u>Analysis</u> -  $C_{10}H_{14}FC1$  <u>C</u><u>H</u> calculated 63.66 7.48 found 63.66 7.69  $CI_{\chi}H$ 



1102(s), 1090(s), 1060(s), 960(s), 925(w), 918(s)

<u>NMR</u> (CC1<sub>4</sub>) - multiplets, 1.45 - 2.00, (8H); multiplets, 2.05 - 2.58, (5H); singlet, 4.09, (1H);

<u>NMR</u>  $({}^{19}F)$  - singlet, -132.4, SCS, -4.4

<u>High Resolution MS</u> -  $C_{10}H_{14}FC1$ 

calculated	188.0767
found	188.0766



The third product was shown to be <u>syn</u>-4-chloro-1-fluoroadamantane, mp 213 - 215.5<sup>o</sup> (sub). <u>MS</u> - 190(12), 188(27), 153(25), 152(100), 110(48), 97(53) <u>IR</u> - 1450(s), 1360(w), 1342(m), 1320(w), 1298(w), 1280(w), 1214(m), 1110(s), 1100(w), 1080(s), 1060(w), 982(s), 964(w), 940(w), 930(s) <u>NMR</u> (CCl<sub>4</sub>) - multiplets, 1.40 - 2.45, (13H); broad singlet, 4.18, (1H) <u>NMR</u> (<sup>19</sup>F) - singlet, -137.2, SCS -9.2 <u>High Resolution MS</u> - C<sub>10</sub>H<sub>14</sub>FC1 calculated 188.0767 found 188.0765

The fourth product was shown to be 1,3-dichloro-5-fluoroadamantane, mp 135.5 - 137°.

- $\underline{MS} = 224(6), 222(12), 189(34), 187(100), 151(8), 131(14), 97(11), 91(8)$
- <u>IR</u> 1444(s), 1342(m), 1318(s), 1282(s), 1230(m), 1130(m), 1092(s), 1014(m), 930(s), 855(s)
- <u>NMR</u> (CCl<sub>4</sub>) triplet, J = 3.5 Hz, 1.80, (2H), H<sub>5</sub>; singlet, 1.93, (4H), H<sub>3</sub>; doublet, J = 5.5 Hz, 2.20, (4H), H<sub>2</sub>; singlet, 2.39, (2H), H<sub>1</sub>;

multiplet, 2.47, (1H), H<sub>4</sub>

<u>NMR</u> (<sup>19</sup>F) - singlet, -136.4, SCS -8.4 <u>Analysis</u> -  $C_{10}H_{13}FC1_2$  <u>C</u> <u>H</u> calculated 53.83 5.87 found 53.50 5.99



# Reaction of 1-Iodoadamantane

In contrast to the other halides, irradiation of a carbon tetrachloride solution of 1-iodoadamantane did not lead to free radical chlorination. After 4 hours the iodide had been consumed yielding a dark purple solution. Workup as before yielded a dark yellow solid shown to consist of mainly 1-chloroadamantane with a small amount of 1,3-dichloroadamantane present.

When all the above reactions were repeated using bromotrichloromethane as the solvent only the bridgehead bromides were formed with no production of any hexachloroethane being observed. There was also no evidence for any chlorination products. From the reaction of 1-fluoroadamantane, two products were observed (in addition to 25% residual starting material).



The major product was shown to be 1-bromo-3-fluoroadamantane, mp 136 - 137°.

- <u>MS</u> 232(trace), 153(100), 133(9), 111(7), 105(5), 99(5), 97(15), 93(13), 91(7)
  <u>IR</u> 1445(s), 1356(m), 1338(s), 1318(s), 1290(s), 1270(w), 1150(w), 1102(s), 1077(s), 962(s), 942(w), 920(s), 678(m)
- <u>NMR</u>  $(C_6H_6)$  unresolved triplet, 1.05, (2H),  $H_5$ ; multiplet, 1.58, (4H),  $H_3$ ; broad singlet, 1.72, (2H),  $H_4$ ; broad singlet, 1.91, (4H),  $H_2$ ; doublet, J = 5.5 Hz, 2.40, (2H),  $H_1$

$\underline{NMR}$ ( <sup>19</sup> F) - singlet, -	-131.6, SCS	-3.6	
<u>Analysis</u> - C <sub>10</sub> H <sub>14</sub> FBr		<u> </u>	H
	calculated	51.52	6.05
	found	51.44	6.17



The minor product was found to be 1,3-dibromo-5-fluoroadamantane, mp 160 - 163.0°. <u>MS</u> - 310(trace), 233(94), 231(100), 187(9), 151(22), 131(7), 111(11), 109(9), 97(9), 91(11) <u>IR</u> - 1450(m), 1350(w), 1318(s), 1282(m), 1230(w), 1092(m), 1010(w), 965(m), 926(s), 710(w) <u>NMR</u> ( $C_6H_6$ ) - multiplet, 1.32, (2H), H<sub>4</sub>; multiplet, 1.47, (1H), H<sub>5</sub>; broad singlet, 1.58, (4H), H<sub>3</sub>; doublet, J = 5.5 Hz, 2.13, (4H), H<sub>2</sub>; singlet, 2.44, (2H), H<sub>1</sub> <u>NMR</u> ( $^{19}$ F) - singlet, -133.2, SCS -5.2 <u>High Resolution MS</u> -  $C_{19}H_{13}FBr_2$  calculated 309.9369 found 309.9351

### Reaction of 1-Chloroadamantane

The photolysis of 1-chloroadamantane in BrCC1<sub>3</sub> produced two main products which were collected by glc. The major product was shown to be 1-bromo-3-chloroadamantane, identical in all respects to that produced by the photolysis of 1-bromoadamantane in carbon tetrachloride.



The minor product was shown to be 1-chloro-3,5-dibromoadamantane, mp 98 -  $102^{\circ}$ .

<u>MS</u> - 328(trace), 251(29), 249(100), 247(77), 169(13), 167(19), 133(8), 132(8), 131(15), 91(25)

<u>IR</u> - 1455(m), 1342(w), 1325(w), 1310(s), 1281(m), 1028(s), 960(m), 850(s), 710(m)

<u>NMR</u> ( $C_6H_6$ ) - singlet, 1.45, (3H),  $H_4 + H_5$ ; unresolved doublet, 1.59, (4H),  $H_3$ ; singlet, 2.27, (4H),  $H_2$ ; singlet, 2.42, (2H),  $H_1$ 

High Resolution MS -  $C_{10}H_{13}Br_2C1$ no parent  $C_{10}H_{13}BrC1$  calculated 248.9869 found 248.9874

### Reaction of 1-Bromoadamantane

Two products were observed from the irradiation of 1-bromoadamantane in BrCC1<sub>3</sub>. These were collected by glc and shown to be 1,3-dibromoadamantane and 1,3,5-tribromoadamantane.

#### Reaction of 1-Iodoadamantane

A well degassed solution of 1-iodoadamantane in BrCCl<sub>3</sub> was irradiated through quartz for 4 hours. The dark purple solution was worked up as before to yield a dark yellow solution which consisted mainly of 1-bromoadamantane with small amounts of 1-chloroadamantane and 1,3-dibromoadamantane.





A well degassed solution of 450 mg (2.47 mmole) of 1,3-dimethyl-5fluoroadamantane in 20 ml of reagent CCl<sub>4</sub> was irradiated through quartz for 12 hours. Purification and removal of hexachloroethane by column chromatography as before yielded the crude products which were purified by glc.

The major product was shown to be 1-chloro-3,5-dimethyl-7-fluoroadamantane,  
mp just below room temperature.  

$$\underline{MS} = 218(11), 216(28), 181(100), 180(30), 167(13), 165(13), 125(87), 111(48), 91(20)$$

$$\underline{IR} = 1445(s), 1365(w), 1358(m), 1238(w), 1180(m), 1038(s), 980(m), 938(w), 915(m), 882(s), 840(w), 675(m)$$

$$\underline{NMR} (C_6H_6) = \text{singlet}, 0.61, (6H), -CH_3; \text{singlet}, 0.87, (2H), H_4; \text{doublet}, J = 5.5 \text{ Hz}, 1.27, (4H), H_2; \text{singlet}, 1.45, (4H), H_3; \text{doublet}, J = 5.5 \text{ Hz}, 2.10, (2H), H_1;$$

$$\underline{NMR} (^{19}\text{F}) = \text{singlet}, -137.0, \text{SCS} = 9.0$$

$$\underline{\text{High Resolution MS}} = C_{12}H_{18}\text{FC1}$$

$$\begin{array}{c} \text{calculated} & 216.1080 \\ \text{found} & 216.1067 \end{array}$$

Two minor products (oils) were also collected by glc but nmr showed them to each contain three different methyl resonances. They were not characterized further.

Reaction of 1,3-Dimethy1-5-fluoroadamantane in BrCC1,



A well degassed solution of 500 mg (2.74 mmole) of 1,3-dimethyl-5fluoroadamantane in 8 ml of  $BrCCl_3$  was irradiated through quartz for 6 hours. Workup as before followed by column chromatography yielded residual starting material (46%) and the brominated species which were collected by glc. The major product was shown to be 1-bromo-3,5-dimethyl-7-fluoroadamantane, mp 31 - 32°.

<u>MS</u> - 262(2), 260(2), 181(100), 167(17), 161(10), 125(45), 121(25), 119(64), 117(62)

Two minor products (oils) were also collected by glc but nmr showed them to contain three different methyl resonances. They were not characterized further.

Reaction of 1-Cyanoadamantane in BrCC1,



A well degassed solution of 500 mg (3.10 mmole) of 1-cyanoadamantane (Aldrich) in 20 ml of BrCCl<sub>3</sub> was irradiated through quartz for 24 hours. Workup as before followed by alumina column chromatography (30-60 petroleum ether) yielded 360 mg (48%) of a light yellow solid. Recrystallization from hexane produced white platelets, mp 128.5 - 130°.

<u>MS</u> - no parent, 160(100), 133(16), 118(13), 104(22), 91(19)

<u>IR</u> - 2240(w), 1445(s), 1370(w), 1357(w), 1340(w), 1335(w), 1320(w), 1300(m),

1238(w), 1220(m), 1100(w), 1090(w), 998(w), 963(s), 942(w), 900(s), 678(m)
<u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - singlet, 1.00, (2H), H<sub>5</sub>; singlet, 1.38, (6H), H<sub>3</sub> + H<sub>4</sub>; singlet,
1.82, (4H), H<sub>2</sub>; singlet, 2.18, (2H), H<sub>1</sub>



1-Cyano-3-fluoroadamantane



To a solution of 130 mg (0.54 mmole) of 1-bromo-3-cyanoadamantane in 20 ml of cyclohexane was added 450 mg (3.56 mmole) of AgF. The solution was stirred under reflux for 2 hours. The solution was then filtered and evaporated to yield a light yellow solid. Elution with 30-60 petroleum ether down an alumina column yielded 86 mg (88%) of a fluffy white solid, mp 180 -  $182.5^{\circ}$ .

<u>MS</u> - 179(44), 160(trace), 152(100), 111(59), 97(33), 93(22), 91(26) <u>IR</u> - 2245(w), 1452(s), 1350(m), 1330(m), 1318(m), 1285(w), 1258(w),

1135(s), 1018(s), 950(w), 940(m), 883(m)

<u>NMR</u> (C<sub>6</sub>H<sub>6</sub>) - multiplet, 0.96, (2H), H<sub>5</sub>; singlet, 1.35, (4H), H<sub>3</sub>; doublet, J = 5.5 Hz, 1.47, (4H), H<sub>2</sub>; broad singlet, 1.58, (2H), H<sub>4</sub>; doublet, J = 5.5 Hz, 1.81, (2H), H<sub>1</sub>

<u>High Resolution MS</u> - $C_{11}H_{14}FN$	calculated	179.1109
	found	179.1113

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Irradiation in Amine Solvents

a) Diethylamine



A degassed solution of 750 mg (2.86 mmole) of 1-iodoadamantane in 70 ml of diethylamine was irradiated through quartz for 2 hours. The greenish yellow solution was washed with aqueous sodium carbonate. Chloroform was added, the layers separated and the organic phase washed with water. After drying the solution was evaporated to yield a light orange solid which was eluted with petroleum ether (30-60) down a short alumina column to yield 310 mg (80%) of a white solid which was shown to be adamantane. Further elution with chloroform yielded a sticky orange solid which was shown to be an adduct of adamantane with solvent.

- MS = 207(26), 192(47), 172(20), 150(100), 135(67), 113(15), 100(50)
- <u>IR</u> 3400(m), 1645(m), 1450(m), 1418(w), 1378(m), 1300(w), 1260(m), 1200(w), 1080(w), 905(w)

<u>NMR</u> (CDCl<sub>3</sub>) - triplet, J = 7 Hz, 0.97, (3H); doublet, J = 7 Hz, 1.14, (3H); unresolved triplet, 1.53, (6H),  $\delta$ ; unresolved doublet, 1.72, (6H),  $\beta$ ; broad singlet, 1.95, (3H),  $\delta$ ; quartet, J = 7 Hz, 2.57, (1H); quartet, J = 7 Hz, 3.03, (2H)

High Resolution MS -  $C_{14}H_{25}N$ calculated207.1986found207.1982

The above reaction was repeated with 500 mg (1.91 mmole) of the adamantyl iodide in 70 ml of diethylamine with  $O_2$  bubbling through the solution. The reaction was worked up as before after 3 hours to yield a light yellow solid.

Collection by glc yielded a white solid identical in all respects to adamantanol as the only product.

The same reaction was repeated with 300 mg (1.15 mmole) of adamantyl iodide plus 350 mg (1.59 mmole) of 3,5-di-t-butyl-4-hydroxytoluene in 70 ml of diethylamine. The solution was degassed well with N<sub>2</sub> and irradiated through quartz. The reaction was followed by glc and was markedly slower than in the absence of the cresol. The iodide was 60% reacted after 4 hours, 80% after 6 hours and 100% after 9 hours. Workup as before yielded a light yellow solid which was shown to consist of the cresol and adamantane with no trace of the free radical adduct.

b) Triethylamine



A degassed solution of 400 mg (1.53 mmole) of 1-iodoadamantane in 70 ml of triethylamine was irradiated through pyrex for 15 minutes. The iodide was all gone and the light greenish solution contained a fluffy white precipitate which was filtered and washed with pentane. The solution was worked up as before and the yellow solid eluted down a short alumina column with pentane to yield 188 mg (92%) of adamantane. The white precipitate was shown to be the hydrogen iodide salt of the solvent.

<u>IR</u> (KBr) - 3000(s), 1460(s), 1420(m), 1390(m), 1360(w), 1184(w), 1162(s), 1062(w), 1034(s), 948(m), 803(m), 750(w)

The above IR was very similar to the HCl and HBr salts of triethylamine from the Sadtler Index.

The above reaction was repeated with 150 mg (0.57 mmole) of adamanty1

iodide with 600 mg (2.72 mmole) of 3,5-di-<u>t</u>-butyl-4-hydroxytoluene in 70 ml of triethylamine. The solution was degassed well with  $N_2$  and irradiated through pyrex as before. This time the reaction was complete after 6 hours. Again, the only products produced were adamantane and the hydrogen iodide salt of the solvent.

c) Morpholine



A degassed solution of 525 mg (2.0 mmole) of adamantyl iodide in 70 ml of morpholine was irradiated through quartz. The starting material was consumed after 1 hour and the reaction worked up to yield a sticky orange solid. This was eluted with petroleum ether (30-60) down an alumina column to yield 122 mg (46%) of adamantane. Further elution with chloroform yielded a light pink solid which was recrystallized from CCl<sub>4</sub>, mp 288 - 289<sup>0</sup> (dec) (lit<sup>162</sup> 292<sup>0</sup>)

<u>IR</u> (KBr) - 3400(m), 2435(w), 1630(m), 1555(m), 1443(m), 1420(m), 1342(w), 1300(m), 1220(m), 1182(w), 1095(s), 1042(m), 895(s), 870(s), 822(w) <u>NMR</u> (CCl<sub>4</sub>) - unresolved doublet, 1.65, (12H),  $\beta \neq \delta$ ; broad singlet, 2.08,

(3H) **%**; multiplet, 2.55, (4H); multiplet, 3.57, (4H)

The above amine was identical to the product produced by the reaction of adamantyl iodide in refluxing morpholine for 60 hours.



A degassed solution of 420 mg (1.60 mmole) of adamantyl iodide in 70 ml of pyrrolidine was irradiated through pyrex for 3 hours. Workup as before yielded a light yellow solid which consisted of only adamantane by glc analysis.

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## APPENDIX

A) Response Factors (glc)

AdH	1.40	2.10
AdOH	1.04	1.65
AdOMe	1.00	1.60
Ad(OMe) <sub>2</sub>		1.00

B) Deuterium Incorporation Studies

1)



non-deut	erated	deuterated	
mass #	Height	mass #	Height
P (126)	118 mm	P' (126)	44 mm
P + 1 (127)	12 mm	(P'+1) (127)	13.5 mm
P + 1 = 10	.2% P	10.2% P' = 4.5	

.: (P' + 1) corrected = 13.5 - 4.5

= 9.0 ... Deuterium incorporation =  $\frac{9.0}{9.0 + 44.0}$  = 17%



 non-deuterated
 deuterated

 Mass #
 Height
 Mass#
 Height

 P (136)
 70 mm
 P'(136)
 35 mm

 P + 1 (137)
 10 mm ' (P' + 1) (137)
 6 mm

 P + 1 = 13.4% P
 13.4% P' = 4.8

 $\therefore$  (P' + 1) corrected = 1.2

: Deuterium incorporation =  $\frac{1.2}{1.2 + 35.0}$  = 3.2%