INTRAMOLECULAR PHOTOCHEMICAL CYCLOADDITION

11205

OF NONCONJUGATED DIENES

BY

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ABSTRACT

The photolysis of isogermacrone (<u>68</u>) has been investigated. Exclusive "straight" cycloaddition occurs to form <u>syn</u> (<u>70</u>) and <u>anti</u> (<u>71</u>) 1,7dimethyl-4-isopropylidene-tricyclo[$5.3.0.0^{2,6}$]decane-3-one. The structures of the photoproducts have been confirmed by an independent synthesis. A mechanism, for the photolysis of <u>68</u>, involving an intermediate 1,4diradical is postulated in order to account for the stereochemistry of the products.

The direct and triplet-sensitized photochemistry of the three geometric isomers of diethyl deca-2,8-diene-1,10-dioate (79 - 81) has been studied. The triplet reaction is one of rapid <u>cis,trans</u> isomerization accompanied by slower 2 + 2 internal cyclization in a "straight" manner to give four of the six possible stereoisomeric diethyl bicyclo[4.2.0]octane-7,8-dicarboxylates (82 - 85). The stereochemistry of these products as well as the triplet nature of the reaction are indicative of a two step mechanism involving 1,4-diradical intermediates. Possible explanations for the direction of initial bond formation in these reactions are also discussed. The direct (singlet) reaction of the deca-2,8-diene-1,10dioates is one of <u>trans</u> to <u>cis</u> isomerization followed by α,β to β,γ double bond migration from the <u>cis</u> isomer; the sole deconjugated product is diethyl <u>trans,trans</u>-deca-3,7-diene-1,10-dioate. A possible explanation for this stereoselectivity is advanced.

Reasons for an investigation of the photolysis of cyclonona-2,6dienone (128) and a scheme for its synthesis are presented.

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DEDICATION

To my wife

Pat

and

To my parents

Rose E. (Stacey) Boire

and

Anthony A. Boire

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INTRODUCTION

A) Background

The need to investigate the photochemistry of organic molecules in solution is both synthetic and mechanistic in nature. In the past ten years, photochemical preparative syntheses of unusual carbocyclic and heterocyclic ring systems have become a respectable and often used method. Usually, these systems are extremely difficult to obtain by conventional modes of synthesis. The syntheses of cubane¹ (Eq 1), the prostanoic acid skeleton² (Eq 2), and pinacols³ (Eq 3) are only a few of the many organic systems which can make use of simple photochemical procedures.





In order to use organic photochemical reactions more fully, an understanding of their mechanisms is important. The first step in any photochemical reaction is the absorption of a quantum of light (E = hv) by a ground state (S₀) molecule (Eq 4). The initially formed electronic

$$s_0 \longrightarrow s_1^{\dagger} Eq 4$$

$$s_1^{\dagger} \longrightarrow s_1^{\dagger} Eq 5$$

species is the vibrationally excited first singlet state (S_1^{\dagger}) which quickly relaxes (Eq 5) especially in solution phase. Excitation to higher singlet states $(S_2, S_3, \text{ etc.})$ is possible with higher energy light, but it is generally accepted that these higher states are too short lived (10^{-12}sec) for any processes to occur except radiationless decay to S_1 .⁴ If only unimolecular processes are possible the excited singlet state has four possible modes of reaction. Fluorescence (Eq 6) and internal conversion (Eq 7) help to depopulate the singlet state in approximately 10^{-8}sec . These radiative and non-radiative deactivations are of little

$$S_1 \longrightarrow S_0 + hv$$
 Fluorescence Eq 6



interest to the organic chemist as no new product (P) is formed. The excited or "hot" ground state that is formed in Eq 7 is capable of rearrangement under low pressures, but usually deactivates quickly to starting material in solution. 3 In order for rearrangement (Eq 8) of the S_1 state or for intersystem crossing (Eq 9) to occur, their rates must compete effectively with those of fluorescence and internal conversion (10^8sec^{-1}) . There are three mechanisms⁴ suggested for the rearrangement of a molecule in the S_1 state to a new product molecule (P). The first one involves a direct rearrangement which produces the excited singlet state of the product, followed by internal conversion to a "hot" ground The second mechanism proposes a continuous rearrangement which state. eventually produces a ground state product. A third possibility, which is not likely to occur in solution phase, is rearrangement from the "hot" ground state of the reactant. The last process of intersystem crossing (Eq 9) produces a vibrationally excited triplet state. This quickly relaxes to T1. The triplet state cannot be populated directly from the ground state because it is a spin forbidden process. Thus its existence depends on the intersystem crossing efficiency and a process called sensitization which will be described later. In a manner analogous to the

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singlet state, the triplet is capable of radiative decay (phosphorescence, Eq 10), nonradiative decay (intersystem crossing, Eq 11) and rearrangement (Eq 12) to a new product (P). The triplet state has a relatively long lifetime $(10-10^{-4}sec)$ and thus has more time in which to undergo



reaction. The mechanism by which the T₁ state goes on to product is a little more complicated than in the singlet case. The direct rearrangement and the "hot" ground state pathways are both possible, but the rearrangement from the triplet state of the starting material to the ground state of the product would involve a discontinuity due to the spin violation process. This is usually the reason that concerted reactions are labeled as singlet state processes and triplet state reactions are considered to proceed <u>via</u> an intermediate. The primary processes in organic photochemical reactions discussed so far are best summarized with the aid of a Jablonski diagram⁵ presented in Fig 1.

Also indicated in Fig 1 is the fact that an electronically excited species can deactivate itself by interacting in a bimolecular fashion. These bimolecular reactions follow the Wigner rules⁵ of spin conservation. Both excited singlet and triplet states are capable of transferring

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their energy to a ground state molecule. In the former case, an excited singlet acceptor and a ground state donor are formed (Eq 13). In the

Fig 1



- A acceptor; D donor
- a excitation
- b vibrational deactivation
- c internal conversion
- d fluorescence
- e intersystem crossing
- f phosphorescence
- g triplet energy transfer from D to A (A is sensitized - D is quenched)

triplet case, a triplet acceptor and a singlet ground state donor are produced (Eq 14). In both of these cases the energy of the donor should

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$$D^1 + A \longrightarrow A^1 + D$$
 Eq 13

$$D^3 + A \longrightarrow A^3 + D$$
 Eq 14

be equal to or greater than that of the acceptor in order that efficient exothermic energy transfer be accomplished. The energy transfer mechanism⁴ is not well understood. One mechanism involves the transfer of energy over relatively long distances <u>via</u> dipolar interactions between donor and acceptor molecules. The other more common mechanism to solution photochemists involves transfer of energy by direct orbital overlap. This generally means collision of donor and acceptor molecules. Both of these processes are predicted to have little effect on the overall geometry of the molecules involved.⁴ However, certain distorted geometries are often proposed in cases where endothermic energy transfer⁶ appears to be occurring.

These bimolecular energy transfer reactions are referred to as sensitization or quenching depending on whether the donor or acceptor molecules are used as reference. Both of these processes are extremely important to the organic photochemist. In order to narrow the topic of bimolecular energy transfer, only triplet state quenching and sensitization will be described. One of the most important aspects of organic

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photochemistry is to determine the multiplicity of a given reaction. In order to do this it becomes imperative that one is able to exclusively populate either the singlet or triplet states of a molecule. Triplet sensitization is capable of putting a molecule into its triplet state without going through its singlet state. Ketones, and in particular aromatic ketones, are extremely useful in this regard. They have almost unit intersystem crossing efficiencies and have high triplet energies³ which are capable of sensitizing a wide variety of unsaturated compounds. In this way, analysis of the direct irradiation versus the sensitized reaction may produce meaningful results as in the case of the irradiation of β , γ unsaturated ketones. Direct⁷ irradiation of <u>1</u> results only in product <u>2</u>



Eq 15



(Eq 15), whereas sensitization⁸ of $\underline{1}$ results only in $\underline{3}$ (Eq 16). This is a good example showing the different reactivities of the singlet and triplet states. Usually, photochemical reactions are not as clear-cut as those mentioned above, and often require detailed kinetic data in order to distinguish the reactivity of the two electronic states. The conditions for sensitization are extremely important. In general, all the light must be absorbed by the sensitizer, and the sensitizer should not undergo any chemical change under the reaction conditions. Common sensitizers^{3,5} are: benzene (E_T = 85 kcal/mole), acetone (E_T = 78 kcal/mole), acetophenone (E_T = 74 kcal/mole), benzophenone (E_T = 69 kcal/mole), and naphthalene (E_T = 61 kcal/mole).

Quenching is essentially the same as sensitization except in the opposite sense. In other words, a compound is added that absorbs no light under the reaction conditions and is capable of accepting triplet energy from an excited molecule. In this case the triplet energy of the quencher must be lower than that of the reactant. Ideally, if any triplet state of the reactant is formed during a photolysis, the quencher will interact with it immediately. Thus if any rearrangement occurs it is proceeding <u>via</u> the singlet state of the reactant. These two techniques are often used indiscriminately as an indication of the multiplicity of a reaction. There are limitations to sensitization and quenching techniques, and if not combined with quantum yield studies and kinetic data, should only be looked upon as qualitative evidence. They can however, be quite convincing as in the case of β,γ -unsaturated ketones (Eq 15 and 16).

In addition to knowing the multiplicity of a reaction, it is important to know the mechanism involved. While a considerable amount of excellent work has been done on the mechanisms of gas and solution phase irradiations, there are still many areas where

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mechanisms are speculative and open to different interpretations and hence many areas that should be investigated. One must not only be able to distinguish between concerted and non-concerted reactions but must be able to consider the possibilities of exciplexes, charge-transfer complexes, transannular interactions, and through-bond interactions.

B) Cycloaddition Reactions

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Cycloaddition reactions⁹ form a large part of the field of organic photochemistry. Even though a considerable amount of work has been done in this area, the results are often stereochemically unpredictable and mechanistically obscure. In general, this class of reactions can be divided into two main groupings: (1) intermolecular and (2) intramolecular.

(1) Intermolecular Photochemical Cycloaddition

In general, intermolecular photochemical cycloaddition occurs when two olefinic moieties add to give a cyclobutane ring (Eq 17). They have

enjoyed the most synthetic use, but paradoxically, simple mechanisms are not available for these reactions. Recently a review¹⁰ has been published on enone annelation which is quite representative of this class of reactions. Usually, substituted enones are photolysed in the presence of excess olefin under conditions where only the enone is absorbing light.

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The excited enone adds to the ground state olefin and, <u>via</u> an undetermined pathway, forms a cyclobutane ring. The dimerization of cyclopentenone¹¹ (Eq 18), the addition of cyclopentenone to cyclopentene¹² (Eq 19), and the addition of cyclohexenone to 1,1-dimethoxyethylene¹³ (Eq 20) are classic



examples of enone annelation. It is generally accepted¹⁰ that it is the triplet state of the enone that is undergoing cycloaddition. Which triplet state, as enones have low lying $n\pi^*$ and $\pi\pi^*$ triplet states, is the reactive species is uncertain, as evidence for either or both has been found. The immediate question now is how the excited enone reacts with ground state olefin to form product. DeMayo has presented the following scheme¹⁰ (Scheme 1) summarizing the postulates to date. Route c involves a

Scheme 1



competitive reactions

concerted formation of product. Due to the complex nature of the products formed (Eq 18 and 20) from enone annelation, this mechanistic route appears to have very little relevance. However, in simpler olefin dimerizations¹⁴ there seems to be concrete evidence for this pathway. Corey found some regiospecificity¹³ in the photolysis of cyclohexenone in isobutylene, vinyl ethers, acrylonitrile, and ketene acetal. He proposed the formation of an excited state charge-transfer complex (exciplex) between excited enone (K^3) and ground state olefin (0) (route a) based on the structure of the product (Eq 21). Cyclohexenone adds to methyl vinyl ether



to form an exciplex <u>4</u>. This exciplex explains the orientation of the substituent in the product. There are, however, many reactions which would be excluded on exciplex theory alone. It would be difficult to explain the equal ratio of head to head and head to tail dimerizations of cyclopentenone (Eq 18). These results tend to favor an interpretation based on the formation of the tetramethylene diradical $[\cdot KO \cdot]^3$. However, rate studies do not indicate the formation of such an intermediate, but require the initial formation of an exciplex (Scheme 1, path a) to account for the observed kinetics.

Other factors, such as the electrophilicity of the excited enone, dipole-dipole interactions, and the possibility of a <u>trans</u> enone intermediate have all been studied and found to play at least a partial role in some reactions. Only when all of these factors are assimilated will a unifying mechanism be possible.

(2) Intramolecular Photochemical Cycloaddition

a) Acyclic

Unlike intermolecular cycloadditions there are two modes of addition open to acyclic dienes. They are able to add in a "straight" (5) manner



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to form bicyclo[n.2.0] systems, or in a "crossed" (<u>6</u>) manner to form bicyclo[n.1.1] systems.¹⁵ <u>A priori</u>, it would appear that either mode of addition is equally likely. However, it can be shown from experimental evidence that the "crossed" versus "straight" nature of cycloaddition depends on the value of n.

Srinivasan studied the mercury sensitized photolysis¹⁶ of a series of non-conjugated dienes at their boiling points under atmospheric pressure. He found that in the case of 1,4 dienes (7, 8, and 9) and 1,6 dienes (12) "straight" addition predominated and for 1,5 dienes (10 and 11) the "crossed" addition mode was most favored (Table 1).

Table 1

Diene

Crossed/Straight



0.10

0.11

0.03



10

2.53

Table 1-cont.



In order to explain his results by a common mechanism, Srinivasan postulated the initial formation of a five membered ring followed by closure of the diradical species thus formed to the observed product (Eq 22-24). This empirical "rule of five" is quite useful and few exceptions are



known.¹⁷ It does, however, disregard the radical and thermodynamic stabilities of the intermediates and products respectively. A better explanation is needed to account for the observed specificity of initial 1,5 bonding.

Liu and Hammond investigated¹⁸ at approximately the same time the photochemistry of substituted 3-methylene-1,5-hexadienes (7_{a-d}) . Irradiat-



ion of $\underline{7a}$ or $\underline{7d}$ in the presence of a sensitizer converts them into only <u>8a</u> and <u>8d</u> respectively. This is another example of exclusive formation of a "crossed" product (Eq 25). In order to investigate the reaction



further they studied the photolysis of $\underline{7b}$ and $\underline{7c}$. The same ratio (5.8 : 1.0) of products was formed irrespective of whether pure $\underline{7b}$ or $\underline{7c}$ was used as starting material (Eq 26). Samples of $\underline{7b}$ and $\underline{7c}$ taken at incomplete conversions showed that they had not lost their geometric purity. Thus it appears that a common intermediate is irreversibly formed. This intermediate

must account for the ratio of products 9 and 10. They suggest that a five



membered ring is formed first. The resulting diradical $(\underline{11})$ is long enough lived to undergo bond rotation and then closure to give the observed



products. The authors give a variety of reasons why the intermediate diradical should be long lived. Firstly, the Wigner hypothesis⁵ indicates

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that the diradical should have triplet character as a result of sensitization and secondly, there should be strain involved in the formation of the cyclobutane ring. In order to explain the unusual stereospecificity in the formation of a five-membered ring, Liu and Hammond suggest that it is probably due to kinetic control of the first step. They rejected radical stability, as there is ample evidence that radical stability increases 19 with substitution. Furthermore, they rejected thermodynamic stability considerations as thermal equilibration studies²⁰ favor cyclohexane over methylcyclopentane. They state that "the preference for formation of fivemembered rings may merely reflect the fact that the carbon atoms that become bonded are, on the average, closer together than those that would have to interact to form a six-membered ring". As added proof for this kinetic control they point out that 5-hexenyl free radicals preferentially form cyclopentylmethyl radicals 21 (Eq 27) even though radical and thermodynamic stability both favor the cyclohexyl free radical. Only when the radical is highly substituted ($R_1 = COOR$, $R_2 = CN$) does cyclohexyl radical formation



predominate.²² Even though this behaviour of 5-hexenyl free radicals is quite general²¹⁻²³ no satisfactory explanation has yet been given. Liu and Hammond's intermediate (<u>11</u>) has drawn the interest of K. Fukui,²⁴ He calculated the energies of the electronic states of two model intermediates (<u>11a</u> and <u>11b</u>) based on structure <u>11</u>. The first model (<u>11a</u>) has carbons C_1 , C_2 , C_3 , C_4 , C_5 , and C_6 all in one plane while the second



model (11b) has the C_4 , C_7 axis perpendicular to a common plane shared by carbons C_1 , C_2 , C_3 , C_5 , and C_6 . Model <u>11b</u> was shown by extended Huckel molecular orbital calculations to be of lower energy than model <u>11a</u> in both the ground and excited state. Fukui stated that <u>11a</u> was most likely the initial species formed followed by the "true" intermediate <u>11b</u>. Fukui, however, does not indicate the reason for the preference of 1,5 bonding in this system. His major concern is with the fate of the intermediate once it is formed and not why it is formed.

The triplet nature of these intramolecular cycloadditions has so far been taken for granted as a result of the use of triplet sensitizers. In order to confirm the idea that the triplet state is responsible for this phenomenom, the direct²⁵ (Eq 28) and sensitized²⁶ (Eq 29) irradiation of myrcene (<u>12</u>) has been done. The small amount of "crossed" product formed under direct photolysis conditions probably results from a limited amount of intersystem crossing of the myrcene singlet.



Another diene system which has been investigated is β -farnesene (<u>13</u>). It was photolysed²⁷ under direct (Eq 30) and sensitized (Eq 31) conditions by White and Gupta. As in the case of myrcene the direct and sensitized irradiation of β -farnesene yields different products indicating that



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the "crossed" cycloadditions are primarily originating from the triplet state of β -farnesene and that the low yield of "crossed" products from the direct irradiation is a good indication of the intersystem crossing efficiency of the β -farnesene singlet state. It is worthwhile to note that "straight" additon occurs to some extent in β -farnesene under direct irradiation conditions.

White and Gupta do not feel that kinetic control of the first step based on steric reasons is sufficient to explain the preference for 1,5 bonding. They reason that since the reaction is essentially quantitative, the kinetic argument would "necessitate a highly oriented ground state of the substrate". In order to explain the observed specificity they have postulated an "oriented complex (<u>16</u>) of excited diene and ground state olefin" in much the same manner as Corey's explanation for the observed specificity in cyclohexenone annelation.¹³ The excited diene moiety can



be considered to have molecular orbitals similar to butadiene. Thus it will have two electrons in the lowest bonding orbital ψ_1 , one in the second bonding orbital ψ_2 , and one in the lowest antibonding level ψ_3 . The correlation diagram (Fig 2) has the electron in ψ_2 of the diene interacting with the bonding orbital ψ_1 of the olefin molety and the electron



in ψ_3 of the diene interacting with the antibonding level ψ_2 of the olefin. Although not specifically stated in the above description of the complex, its geometry is suggested to be of a one to one fashion as indicated in structure <u>16</u>. All other combinations lead to rings with greater than six carbon atoms and are thus less stable on thermodynamic grounds. Then White and Gupta further suggest that "subsequent bond formation from the complex may be determined by radical stabilities, at least where such bond formation proceeds stepwise or unsymmetrically so that the collapse" of the complex leads to <u>17</u>. Such an argument rationalizes cycloaddition and indicates a preference for "crossed" over "straight" cycloaddition at least in the case of β -farnesene itself.

Appropriate substituents are often used in order to give a nonconjugated diene an ultraviolet absorption in a region easily accessible to conventional light sources. We have already seen the use of the butadiene moiety and now it will be valuable to describe the use of the carbonyl as an activating group.

One of the earliest intramolecular photochemical cycloadditions was done by Ciamician and Silber²⁸ in 1908 followed by Büchi and Goldman²⁹ in 1957. In this experiment carvone (<u>18</u>) was subjected to California sunlight in a Pyrex vessel for 6.5 months. Carvone-camphor (19) was the



only product isolated besides polymer. Another more recent example³⁰ is the photolysis of 1,5-hexadiene-3-one ($\underline{20}$) by Scerbo (Eq 34). "Crossed" product $\underline{21}$ is the only product observed. Both of these 1,5 dienes (18



and $\underline{20}$) exhibit their preference for "crossed" addition. While quenching and sensitization work has not been done on these systems it is generally accepted that they are proceeding <u>via</u> an excited triplet state. Brown^{31,32} in his attempt to synthesize either the copaene or bourbonene skeleton, photolysed the following 1,6 dienes (Eq 35). He



Eq 35

obtained identical results under both direct and sensitized irradiations. Again the empirical "rule of five" seems to hold as "straight" cycloadded products are formed. Brown suggests that it is probably the triplet state that is reacting and that the triplet of one olefin (24) is attacking the



ground state of the other to form a five-membered ring (25). Besides

obeying the "rule of five" Brown feels that increased conjugation in diradical 25 increases its stability.

A notable exception to the "rule of five" was observed by Meinwald³³ in his photolysis of 1,8-divinylnaphthalene (26) and 1,8-distyrylnaphthalene (27). Photolysis of a 0.002 M solution of 26 in cyclohexane gave an 80 -90% yield of 28 and 29 in a ratio of 10 : 1 respectively (Eq 36).



Similarly, photolysis of a 0.001 M solution of <u>27</u> in ether yielded 40% and 38% of "crossed" products <u>30</u> and <u>31</u> and 5% of "straight" cycloaddition product 32 (Eq 37). These results are quite surprising as "crossed"



cycloaddtion has only been observed as a major pathway in 1,5 dienes. Meinwald explains this unusual specificity on the stabilities of the ground state conformations of <u>26</u> and <u>27</u> (<u>33</u> and <u>34</u>) Conformation <u>33</u> is the most favorable in the ground state and it is from this conformation



that "crossed" cycloaddition occurs. "Straight" cycloaddition products arise from the less preferred conformer 34.

In 1963 Cookson <u>et al</u>. studied the photolysis of citral³⁴ (Eq 38) (a 1 : 1 mixture of <u>cis</u> and <u>trans</u> isomers). Although the major product is not a cycloadded one, the minor product, photocitral B (<u>35</u>) is formed in an analogous manner to those previously mentioned. Both products can



be rationalized on the basis of initial 1,5 bonding (<u>36</u>). Photocitral A (<u>37</u>) can then be formed by 1,4 hydrogen migration and photocitral B by bond formation. Cookson felt that the reason for initial bond formation could be traced to a charge-transfer complex of a pure localized n, π^* transition of the enone with the antibonding π^* orbital of the unconjugated double bond. This charge-transfer complex then overlaps both the oxygen

p -orbital and the enone π^* orbital. Evidence for this lies in the fact that the extinction coefficient for citral is 72 whereas that for β -methacrolein is 25. This is almost a three-fold enhancement.

Later in 1968 Cookson discussed in his Tilden lecture³⁵ to the Chemical Society the various reactivities of the different electronic states of diallyl and its derivatives. Compound <u>38</u> best describes the unique behaviour of the ground (Eq 39), excited singlet (Eq 40), and excited triplet (Eq 41) states. The first two reactions are the familiar



Cope rearrangement (3,3-sigmatropic shift) and the 1,3-sigmatropic shift respectively. Both are well documented.^{37,36} The triplet state is again responsible for cycloaddition and proceeds in the manner predicted by initial 1,5 bonding. This specific electronic state behaviour prompted Cookson to construct an energy level scheme (Fig 3) for diallyl utilizing the four orbitals of the dienes and the two sigma orbitals of the central

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3,4 sigma bond. The levels at the left are uncoupled as they would be in an isolated system. In the middle, the 3,4 sigma bond is in a plane at right angles to the plane of both double bonds. The sigma bond then effectively splits the levels of the π and π * states. Cookson felt that the levels (ψ_2 and ψ_3 ; ψ_4 and ψ_5) could be reversed as this was only a zero order approximation.





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This scheme does, however, predict that diallyl will have a long wavelength absorption, as this type of interaction brings the highest occupied molecular orbital and the lowest unoccupied molecular orbital closer together. This prediction, he claims, is supported by the ultraviolet absorption of molecules possessing the necessary geometry. On the right (Fig 3) Cookson has drawn the molecular orbitals by increasing the number of nodes from zero to five. He points out that the highest occupied molecular orbital π_s explains the observed Cope rearrangement in the thermolysis of diallyls. He did not, however, extend this argument to include 1,3 signatropic shifts or cycloadditions.

Acyclic photochemical cycloadditions of 1,4- 1,5- and 1,6 dienes have been discussed and it appears as if they all have two properties in common. They obey the "rule of five" and they are all triplet state reactions. With this in mind it will now be necessary to investigate cyclic systems to see if they behave in an analogous manner.

b) Cyclic

Cyclic nonconjugated dienes are also capable of adding in a "crossed" or "straight" manner (Eq 42). Much less work has been done in this area



and as a result, this discussion will be as complete as possible. Since the question of "crossed" versus "straight" cycloaddition is of immediate importance, this discussion will not be concerned with non-conjugated dienes which are constrained geometrically to add in a specific manner. The largest group of such compounds can be illustrated by Eq 43. These



dienes react via the triplet state and usually produce caged ring systems 38 by adding in a "straight" manner.

In general, cyclic 1,3 dienes close photochemically to give cyclobutenes rather than bicyclobutanes. Since the intersystem crossing efficiency of dienes is low, presumably these reactions are proceeding <u>via</u> the excited singlet state. 1,3-Cycloheptadiene³⁹ closes in a



disrotatory fashion to give bicyclo[3.2.0]-6-heptene (Eq 44). The behaviour of 1,3 dienes under irradiation conditions may be best described as electrocyclic reactions.

Acyclic 1,4 dienes usually undergo a di- π -methane rearrangement⁴⁰ as
the major reaction pathway. In contrast to this, the results of Moon and $Ganz^{41}$ concerning the photolysis of 1,4-cyclooctadiene (39) are quite unique. Under direct irradiating conditions they obtained a quantitative yield of <u>syn</u> tricyclooctane (40). The excited species reacting is probably the singlet state. <u>A priori</u>, it could be said that



<u>40</u> could arise <u>via</u> initial 1,5 bond formation but this does not explain the geometry of the final product unless kinetic closure of the diradical is proposed. It has been shown that <u>40</u> is converted into its <u>anti</u> isomer <u>41</u> (Eq 45) under thermolysis conditions. Thus the mechanism of this photolysis would best be described as an allowed ${}^{42}\pi^2_s + \pi^2_s$ cycloaddition.

Of the 1,5 cyclic cycloadditions, none have been studied as extensively as <u>cis,cis</u>-1,5-cyclooctadiene (<u>42</u>). In 1964 Srinivasan first published his results⁴³ on the gas and solution phase photolysis of 1,5-cyclooctadiene and its copper chloride complex (<u>44</u>). In the solution phase he was able to determine that the uncomplexed cyclooctadiene was the principle absorber of the light. This was based on the optical density studies of

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and uncomplexed forms of cyclooctadiene into <u>43</u>. Based on this and deuterium labeling studies⁴⁴ Srinivasan postulated an intramolecular mechanism in which <u>42</u> absorbs the light, bonds in a 1,5 manner, complexes with copper chloride, and then closes to product (Scheme 2). This scheme shows <u>42</u> (as opposed to the <u>cis,trans</u> and <u>trans,trans</u> isomers of cyclo-



the components of the photochemical transformation of the complexed

Scheme 2 - cont.



octadiene) as the immediate precursor of product 43.

In 1967 Cope and Whitesides synthesized the <u>cis,trans</u>⁴⁵ and <u>trans</u>, <u>trans</u>⁴⁶ isomers of 1,5-cyclooctadiene (45 and 46 respectively). They investigated the photolysis of these isomers in order to shed light on the irradiations of 42 and 44. In 1969 they published a full paper⁴⁷ that pointed to the fact that the major amount of 43 formed comes from the <u>cis,trans</u> (45) isomer and hints at the possible intermediacy of the <u>trans</u>, <u>trans</u> (46) isomer (See Table 2 and Scheme 3). Unlike Srinivasan, they photolysed 44 in pentane which results in a heterogeneous mixture. On the

Table 2

Substrate	Irradiation time (hrs)	42(%)	<u>45</u> (%)	<u>46</u> (%)	<u>43</u> (%)
<u>42</u> ^p	24	100	0	0	0
<u>42</u> ^b	72	Major	Trace	0	0
<u>44</u> ^p	3	93	4	<1	3
<u>44</u> P	24	62	13	∿1	19
<u>44</u> ^p	48	28	17	∿1	43
<u>45</u> ^P	2	19	0	0	0
<u>45</u> ^b	20	Major	Minor	0	Trace
<u>47</u> ^P	48	32	∿20	∿1	12
<u>46</u> ^p	1	0	0	0	70

p - photolysis done in pentane
b - photolysis done in benzene

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basis of the qualitative observation that a significant fraction of the $\underline{cis}, \underline{cis}$ isomer present in the pentane solution of the complex is free in solution, and on the basis of the similarity between their system and that of Srinivasan's, they assumed that $\underline{42}$ is the primary light absorbing species in the photolysis of a pentane suspension of $\underline{44}$. Thus based on this assumption and on the data in Table 2 the following mechanistic pathways are suggested for the photolysis of $\underline{44}$ (Scheme 3). This scheme

Scheme 3



presents the <u>cis,trans</u> copper chloride complex $\underline{47}$ and $\underline{46}$ as the immediate precursors of $\underline{43}$. They present several reasons why they discard

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the possibility of 42 as the reactive species responsible for cycloaddition. Neither direct nor sensitized photolysis of 42 in the absence of copper chloride yields detectable quantities of 43. Furthermore, the appearance of 45 and 46 under the photolysis conditions (photolysis of 44) and the fact that these in turn can be photolysed to 43 (Table 2) strongly suggest that these are intermediates. Secondly, the relative yields of 45 and 43 show that the formation of 43 depends on the concentration of this diene in solution. This suggests that at least part of the cycloaddition is occurring from the cis, trans isomer (45). The high steady state concentration of 45 during the latter stages of the photolysis combined with the relatively high efficiency with which it is converted into tricyclooctane (43) in the presence of copper chloride indicates that a major portion comes from 45. Finally, photolysis of 46 gives 43 cleanly (70%) and photolysis of 47 yields the trans, trans isomer, and despite its consistently low concentration, could give rise to a significant amount of 43.

The authors feel that the intriguing possibility of the <u>trans,trans</u> isomer (<u>46</u>) as a major contributor exists if one can assume that the extinction coefficient of the complexes are in the same ratio as that of the dienes. In such a case one would have "at one extreme of interpretation the rates of formation of <u>43</u> from <u>45</u> and <u>46</u> precursors should be approximately equal; at the other extreme the major fraction of <u>43</u> might be formed from the <u>trans,trans</u> diene". If this were so, a simple mechanism of a concerted $\pi_s^2 + \pi_s^2$ cycloaddition is conceivable from the



Eq 48

twisted conformation (48) of trans, trans-1, 5-cyclooctadiene (Eq 48).

A compound which could conceivably add in a 1,5 manner to give either "straight" or "crossed" addition would be of considerable interest in order to observe which manner of cycloaddition prevails. One such series of compounds would be the 1,5-cyclononadienes. In 1965 Sutherland photolysed⁴⁸ byssochlamic acid to give a single cycloadded product (Eq 49).



The product, however, was not completely identified and its structureproof rests solely on its thermal stability.

Not until 1968 did anyone investigate the photochemistry of nonconjugated 1,6-cyclodecadienes. Based on the empirical rule of 1,5bonding these can be predicted to add in a "straight" manner. Late in 1968 and early in 1969 three separate papers dealt with the photochemistry of <u>cis,cis</u>-cyclodeca-3,8-diene-1,6-dione. 49,50,51 Scheffer and Lungle⁵⁰

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established that the <u>cis,cis</u> isomer photolyses to the <u>cis,trans</u> isomer and that this is the immediate precursor of the anti "straight" product (Eq 50).



A concerted reaction of the <u>cis</u>, <u>trans</u> isomer to the observed product is not possible and thus the authors suggest a diradical mechanism (Eq 51)



involving 1,5 bonding with subsequent bond rotation and closure to form <u>49</u>. Exclusive formation of the <u>anti</u> isomer is explained on the basis of unfavorable steric interactions in the formation of the <u>syn</u> isomer. Here again the possibility of a <u>trans,trans</u> intermediate is conceivable as the final product could then be obtained <u>via</u> a concerted $\pi_s^2 + \pi_s^2$ cycloaddition.⁴² Attempts to isolate this intermediate under various conditions, however, have not produced positive results.⁵² The multiplicity of the reaction is probably the triplet state as it has been observed that the reaction proceeds in the same manner under sensitization conditions.⁵²

A less specific cyclization 53 was observed by Heathcock in his

attempt to enter the copaene ring system <u>via</u> a cyclodecadienone (50). Photolysis of <u>50</u> (double bond isomers of unknown geometry) in ether led to both "straight" (<u>51</u> and <u>52</u>) and "crossed" (<u>53</u>) cycloadded products in



+

Eq 52

a 35 : 22 ratio respectively. These results are quite unique as a significant amount of product (53) arises via initial 1,6 bonding.

Germacrene D (<u>54</u>), a naturally occurring sesquiterpene was photolysed⁵⁵ by Yoshihara <u>et al</u>. This compound is potentially a precursor of the bourbonene or copaene systems depending on whether the cycloaddition proceeds



in a "straight" or "crossed" manner respectively. Irradiating <u>54</u> under direct conditions led mainly to $(-)-\beta$ -bourbonene (55) and minor amounts

of α -bourbonene and β -copaene (Eq 53). Possibly, more copaene would have been formed had the photolysis been done under triplet conditions.⁵⁶ In order to explain the transannular interactions (uv max = 259 nm, ϵ 4500) between the two double bonds, Yoshihara suggests that germacrene D prefers the conformation (56) in which the two double bonds in the ring



are situated parallel and face to face with each other. The three substituents are orientated in the same direction β to the ring. It is from conformation <u>56</u> that Yoshihara explains his photolysis and thermolysis results of germacrene D.

A closely related system is the photolysis⁵⁷ of isabelin (Eq 54). Here we have a 1,5 diene which adds in a "straight" manner but careful analysis of molecular models indicates that the resulting product derived



from "crossed" cycloaddition would be severely strained due to the presence

of the lactone ring.

Sondheimer has reported the photocycloaddition of the largest cyclic diene (58) system. ⁵⁸ The addition proceeds readily on exposure of 58 to sunlight and can be looked upon as a concerted photochemical $\pi_s^2 + \pi_s^2$



cycloaddition. The structure proof of product <u>59</u>, however, is not unequivocal and no multiplicity studies were carried out.

As can be seen from this survey, very little has been accomplished in understanding the mechanisms of cyclic photochemical cycloadditions of non-conjugated dienes. There remains much to be done in this area.

C) Photodeconjugation

 α,β -Unsaturated carbonyl compounds having a γ hydrogen atom are capable, under photolysis conditions, of the migration of the double bond to the β,γ position. While this phenomenon has been observed in acids⁵⁹ ketones^{60,61} and esters,⁶²⁻⁶⁵ only the latter appears to have been studied to any extent.

In 1968, Barltrop and Wills⁶² sought to find a mechanism which would explain deconjugation. Irradiation of the <u>trans</u> compound <u>60</u> under direct conditions led to a rapid interconversion of cis and trans isomers (Eq 56). This was followed by the formation of the β,γ isomer (<u>62</u>). Photolysis of the <u>cis</u> isomer was almost identical except that no induction period for the formation of 62 was observed. Irradiation under triplet conditions



(benzophenone, acetophenone, and acetone) led to <u>cis,trans</u> isomerization but no photodeconjugation was observed. Barltrop feels that it is the n,π^* singlet that is responsible for deconjugation⁶²⁻⁶⁴ whereas it is probably the n,π^* triplet state doing the <u>cis</u> to <u>trans</u> isomerization. He proposes an intramolecular γ hydrogen abstraction by the oxygen to form a dienol (<u>63</u>) which ketonizes to form the observed product (Scheme 4).

Scheme 4



This mechanism is supported by the fact that the double bond must be in the <u>cis</u> configuration in order for deconjugation to occur. The mechanism is further supported by the fact that when ethyl crotonate is photolysed in methanol-OD the products contain at least 97% of one deuterium at the carbon atom adjacent to the ester group. There is also a solvent effect in which the reaction proceeds faster in alcoholic solvents. This may either be an effect on the quantum efficiency of the intramolecular hydrogen abstraction leading to the dienol or the ease of ketonization of the dienol to the β,γ isomer.

At the same time Jorgenson⁶³ confirmed these results by studying the photolysis of <u>64</u>. Only <u>cis</u> to <u>trans</u> isomerization was observed under

Scheme 5



sensitized conditions but under direct irradiation conditions <u>66</u> and <u>67</u> were also formed (Scheme 5). Jorgenson felt that <u>66</u> (deconjugation) was coming from the singlet state of the <u>cis</u> isomer, whereas <u>67</u> was coming from the singlet state of the <u>trans</u> isomer. If <u>65</u> is photolysed in methanol-OD both <u>66</u> and <u>67</u> are formed possessing one deuterium at the

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 α carbon. This she feels supports the dienol intermediate formed <u>via</u> an intramolecular hydrogen transfer (Scheme 4).

Further support for the dienol intermediate in photodeconjugations comes from the work⁶¹ of Noyori <u>et al</u>. on the photolysis of an α , β unsaturated ketone (Eq 57). Dienols <u>65</u> and <u>66</u> were formed in 80% yield



Eq 57

in a ratio of 5 : 1 respectively. Heating the dienol mixture at 100° for 2 hr afforded deconjugated product (<u>67</u>) and starting material (<u>64</u>) in an 83 : 17 ratio respectively.

Early in 1968 Rando and Doering studied the photodeconjugation of a series of substituted α , β -unsaturated esters and acids (Eq 58).⁵⁹ They

$$\begin{array}{c} R_{1} & 0 \\ R_{2} & CH-CH=CH-C-OR(H) \end{array} \xrightarrow{hv} \\ R_{2} & R_{2} \end{array} \begin{array}{c} R_{1} & 0 \\ R_{2} & C=CH-CH_{2}-C-OR(H) \end{array}$$
 Eq 58

observed, in the case of the acids $(R_1 = n-C_6H_{13}, n-C_7H_{15}, and n-C_{12}H_{25};$ $R_2 = H$), that both <u>cis</u> and <u>trans</u> β , γ -unsaturated products were formed. A <u>trans</u> to <u>cis</u> ratio of 2 : 1 was observed for these reactions.

RESULTS AND DISCUSSION

A) Isogermacrone

(1) Objectives and Choice of Starting Material

Before 1969 the photochemistry of nonconjugated medium-sized ring dienes was essentially an untouched area of research. With the exception of some extensive work done on 1,5-cyclooctadiene $^{42-47}$ and 3,8-cyclodecadiene-1,6-dione $^{49-51}$ only two other compounds 41,53 were photolysed in which the final products were characterized. Thus a further investigation in this area promised to be both interesting and useful.

The choice of a starting material was based on three properties which it must possess: 1) a nonconjugated medium ring cyclic diene, 2) an easily accessible ultraviolet region, and 3) easy availability. Isogermacrone (68) fulfils all these requirements. It has a basic



1,6-cyclodecadiene skeleton, an easily accessible ultraviolet region (uv max 334 nm, log ε 1.923)⁶⁵ and can be prepared in one step from the naturally occurring sesquiterpenone germacrone (<u>69</u>).⁶⁶ Generous samples of germacrone were received from Dr. M. Suchý, Czechoslovak Academy of Science, and Fritzsche Brothers, Inc., New York, N.Y. Germacrone was converted to isogermacrone under basic conditions in reasonable yields. A solution of germacrone in 0.5 N alcoholic potassium hydroxide was refluxed for four hours (Eq 59). This gave after conventional workup



procedures, followed by column chromatrography, pure crystals of isogermacrone, mp 48° - 50° (lit.⁶⁶ mp 51° - 52°). The geometry of the C_3 , C_4 and C_7 , C_8 double bonds in germacrone have been established by nmr observations⁶⁷ to be <u>trans</u> with respect to the cyclodecane ring. However, in isogermacrone while the geometry of the C_2 , C_3 double bond is probably <u>trans</u> only the <u>trans</u> configuration of the C_7 , C_8 double bond is known with certainty.⁶⁷ Isogermacrone, prepared by the above method, is a single isomer as indicated by various tlc and vpc experiments. The spectral data (mass spectrum, ir, and nmr) are in complete agreement with those reported by Ohloff.⁶⁶

(2) Photolysis of Isogermacrone

Photolysis of a 0.1% benzene solution of isogermacrone⁶⁸ under the conditions indicated (Eq 60) led to the formation of seven new products <u>A</u> - <u>G</u> in the following percentages: <u>A</u>, 0.5%; <u>B</u>, 4.5%; <u>C</u>, 2.4%; <u>D</u>, 48.4%;

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<u>E</u>, 29.5%; <u>F</u>, 5.2%; and <u>G</u>, 9.4%. Photoproducts <u>D</u> and <u>E</u>, the major products (78%), were isolated and purified by preparative vpc. Compounds



<u>A</u>, <u>B</u>, and <u>C</u> were found to be too volatile to permit isolation. Compounds <u>F</u> and <u>G</u> were collected in sufficient amounts by preparative vpc to obtain crude spectral data.

(3) Structure Proof of Photoproducts D and E

Spectral data (ir and nmr) of <u>D</u> and <u>E</u> indicated the absence of any vinyl hydrogens and the presence of a ketone and an isopropylidene group. Mass spectra and elemental analyses confirmed their isomeric relationship with starting material. On the basis of this preliminary evidence it was concluded that cycloaddition had taken place between the C_2 , C_3 and the C_7 , C_8 double bonds. There are two possible modes of cycloaddition available to isogermacrone. "Straight" bonding, derived from initial 1,5bonding, produces two possible isomers <u>70</u> and <u>71</u>. "Crossed" bonding, derived from initial 1,6 bonding gives only the symmetrical structure <u>72</u>. The possibility of structure <u>72</u> was discounted on the basis of spectral evidence (mass spectrum, ir, and nmr). The mass spectra of <u>D</u> and <u>E</u> showed large peaks at m/e 96 and at m/e 122 corresponding to cleavage of the cyclobutane ring in structures <u>70</u> and <u>71</u>. Furthermore, there is no common fragmentation pattern between the mass spectra of <u>D</u> and <u>E</u>, and that of



ylangene and copaene;⁶⁹ the latter two have the basic tricyclo[5.3.0.0]decane skeleton as in $\underline{72}$.

The infrared spectra of <u>D</u> and <u>E</u>, which were very similar, showed strong absorptions at 5.88 μ (carbonyl) and at 6.14 μ (isopropylidene). The peak heights of these absorptions are approximately equal and can be attributed to a five-membered ring structure as present in structures <u>70</u> and <u>71</u> (See Fig 4).⁷⁰ In structure <u>72</u> the carbonyl absorption would

<u>Fig 4</u>



(a - Intensity of infrared C=O stretch/Intensity of infrared C=C stretch) be expected on the basis of the data in Fig 4 to be around four times more intense than the isopropylidene stretch. Further confirmation of a five-membered ring structure for photoproducts <u>D</u> and <u>E</u>, comes from the proximity of their carbonyl absorptions of 5.88 μ to 5.87 μ instead of to 5.93 μ which is associated with a six-membered ring structure (Fig4).

The nmr spectra of <u>D</u> and <u>E</u> are generally featureless with the exception of the C_{11} and C_{12} methyl singlets. In both <u>D</u> and <u>E</u> these are nonequivalent which is not compatible with the symmetrical "crossed" product <u>72</u>. In the <u>syn</u> structure (<u>70</u>) the C_{11} and C_{12} methyl groups are relatively far from the effects of the carbonyl as determined by molecular model examination. However, in structure <u>71</u> both the C_{11} and the C_{12} methyl groups should be significantly shielded⁷¹ by the anisotropic effect of the carbonyl. On the basis of this observation <u>D</u> [partial nmr (CDCl₃) τ 8.81 (s, 3, C_{12} -CH₃), and 8.92 (s, 3, C_{11} -CH₃)] and <u>E</u> [partial nmr (CDCl₃) τ 9.10 (s, 3, C_{12} -CH₃), and 9.17 (s, 3, C_{11} -CH₃)] were assigned structures <u>70</u> and <u>71</u> respectively. In both cases the downfield methyl signal was assigned to the more remote C_{12} methyl group based on a similar argument of carbonyl shielding.

Unequivocal proof of structure was derived from an independant synthesis of $\underline{70}$ and $\underline{71}$. Use was made of the well known photochemical addition of enones to alkenes (enone annelation).¹⁰ In this case



Eq 61

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cyclopentenone was photolysed in an excess of 1,2-dimethylcyclopentene to give a 5 : 3 mixture of photoadducts 73 and 74 respectively (Eq 61). The gross structures of 73 and 74 were verified by mass spectra, ir, and nmr. The nmr also supplied the information needed in assigning the syn or anti configuration. The major product [partial nmr (CDC13) τ 8.55 (s, 3, C_{12}^{-CH}), and 8.93 (s, 3, C_{11}^{-CH})] and the minor product [partial nmr (CDC1₃) τ 8.99 (s, 3, C₁₂-CH₃), and 9.11 (s, 3, C₁₁-CH₃)] were assigned the structures of 73 and 74 respectively. Similarly, based on the argument of the shielding influence of the carbonyl, the downfield singlet was assigned to the more remote C_{12} methyl group.

Two approaches were taken in order to extablish the structures of photoproducts D and E as 70 and 71 respectively. The first of these involved the sodium amide alkylation of $\underline{73}$ and $\underline{74}$ with isopropyl bromide. The products of these were then compared to the hydrogenation products of \underline{D} and \underline{E} (Fig 5). While the spectral data (ir, nmr, and mass spectra)

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Fig 5 H₂-PtO₂ ethyl acetate D

E

73 bromide 75 H2-Pt02 74 sopropyl

showed the products obtained from each method to be quite similar, there were enough differences to warrant further evidence. These slight differences could arise from the fact that the isopropyl group is capable of existing in either the <u>endo</u> or <u>exo</u> position. Undoubtably <u>75</u> and <u>76</u> synthesized by the above procedures are a mixture of these two stereoisomers.

The second attempt involved the direct synthesis of $\underline{70}$ and $\underline{71}$. Adducts $\underline{73}$ and $\underline{74}$ were condensed with acetone in the presence of excess sodium ethoxide.⁷² Compounds $\underline{70}$ and $\underline{71}$ prepared in this manner from



<u>73</u> and <u>74</u> respectively were identical (ir, nmr, mass spectra, vpc retention times) to photoproducts <u>D</u> and <u>E</u> isolated from the photolysis of isogermacrone.

(4) Mechanistic Implications

The major products derived from the photolysis of isogermacrone can be formally explained as arising from initial 1,5 bonding of the nonconjugated diene moiety. "Crossed" addition which would involve initial 1,6 bonding does not occur as the crude spectral properties of the minor products (\underline{F} and \underline{G}) indicate unsymmetrical type products incompatible with the symmetrical "crossed" compound 72.

The possibility of photoproducts <u>70</u> and <u>71</u> arising <u>via</u> a concerted $\pi_s^2 + \pi_s^2$ cycloaddition offers no explanation for the formation of both <u>syn</u> and <u>anti</u> tricyclodecanes. As there is no evidence of any geometric isomers of <u>68</u> forming during the photolysis, a concerted pathway appears very unlikely. The formation of both possible "straight" cycloadducts could be interpreted as indicating a two-step mechanism involving a diradical intermediate (<u>77</u> or <u>78</u>) which is capable of closing in two different

Scheme 6



ways to yield the observed products <u>70</u> and <u>71</u> (Scheme 6). Presumably, based on known radical stabilities, diradical <u>78</u> would be the most likely intermediate energetically. The preference for formation of 70 could then be explained on the basis of less steric hindrance in its formation. Molecular models support the idea that the two methyl groups in a <u>syn</u> relationship to the cyclopentenone ring involves more steric interactions than the methylene groups of the cyclopentane ring in a similar <u>syn</u> relationship. It appears likely that both methyl groups are needed to affect the product distribution. Heathcock and Badger find a 10 : 1 ratio of <u>anti</u> to <u>syn</u> products in the photolysis⁵³ of 6-methyl-1,6-cyclodecadien-3-one (Eq 52). Further evidence for the influence of the two methyl groups on product formation comes from the 5 : 3 ratio of <u>syn</u> to <u>anti</u> products formed in the photoaddition of 1,2-dimethylcyclopentene to cyclopentenone (Eq 61).

This exclusive "straight" cycloaddition for cyclic 1,6-dienes is in accord with those reported. 50,51,54,55 The major exception to this is worthy of note. Heathcock and Badger photolysed 6-methyl-1,6-cyclodecadien-3-one (Eq 52) which is structurally similar to isogermacrone. In ether 53 they obtained a mixture of 51 (32%), 52 (3%), and 53 (22%). In hexane 54 solution they obtained a 51 to 53 ratio of 2 : 1. However, under the same photolysis conditions cyclodecadienone 50 yields a 51 : 53 ratio of 9 : 1. This result strongly indicates a triplet precursor for "crossed" product 53. This seems to be in accord with multiplicity results obtained for "crossed" product formation in the photolysis of 1,5 dienes. 26,27 However it cannot be concluded on the basis of this data that the triplet excited state is not responsible for "straight" cycloaddition products 51 and 52. There is ample evidence especially in 1,6 and 1,7 dienes that the triplet state is the excited state responsible for "straight" cycloaddition.^{52,15} Unfortunately the photolysis of isogermacrone cannot shed any light on this problem as the excited state species responsible for exclusive "straight" addition is at present unknown.

(5) Conclusion

It is evident that more work in the area of the photochemistry of cyclic nonconjugated dienes is necessary. Many factors concerning the nature of the cycloaddition are still in doubt. Why does compound <u>50</u> give a reasonable yield of "crossed" product? Why do all other cyclic 1,6 dienes give only "straight" addition products?⁵⁵ Are the "straight" and "crossed" products coming from the same excited species? These are only a few of the questions that still have to be answered. Two things however, remain fairly certain: Cyclic 1,6 dienes in general prefer to cycloadd by initial 1,5 bonding and give products indicative of a two-step mechanism.

B) Acyclic Diene-diesters

(1) Introduction

a) Background and Objectives

Acyclic non-conjugated dienes are capable of photochemically cycloadding to form bicyclo[n.2.0] or bicyclo[n.1.1] systems, where n is the number of carbon atoms between the double bonds.¹⁵ The "rule of five"¹⁶ predicts "straight" bonding for systems with n = 1 and 3, and "crossed" bonding for systems with n = 2 (Eq 62). Experimental results in general support these predictions quite well.⁹ Up until 1969, when the



present project was begun, no acyclic diene system with n = 4 (i.e., a 1,7-diene) had been studied. By investigating the photochemistry of acyclic dienes with n = 4 and greater, the "rule of five" will be inapplicable as initial 1,5 bonding will be impossible. Other factors such as the distance between the olefin moieties, and the stabilities of the rings formed may be more important as n is increased. In diene systems with n = 5 or greater, however, molecular models indicate that there may be no distinction between a "crossed" or "straight" cycloaddition mechanism. If n is sufficiently large it would be impossible to determine whether a bicyclo[n.1.1] system was formed <u>via</u> "crossed" or "straight" bonding (Eq 63). In these cases, the olefin moieties would have to be looked



upon as isolated double bonds. With n = 4 there are too many non-bonding interactions for a "straight" cycloaddition mechanism for the formation of a bicyclo[n.1.1] system. Thus a 1,7 diene would make an ideal starting material for the investigation of acyclic photochemical cycloadditions where the "rule of five" is inapplicable. The compounds chosen for this investigation were the geometric isomers of diethyl-2,8-decadiene-1,10dioate (79, 80, and 81).



b) Source of Starting Material

Diene-diester <u>79</u> has an easily accessible n, π^* ultraviolet absorption (uv max 241 (ϵ 410) nm) region⁷³ and can be easily prepared by known literature procedures.^{74,75} Sebacic acid (1,10-decanedioic acid) was converted into its diacid chloride (Scheme 7) by heating at 90[°] in a slight excess of thionyl chloride. The diacid chloride was photobrominated by the dropwise addition of bromine in the presence of light. The resulting



mixture was esterified with absolute alcohol (Scheme 7).⁷⁴ The dibromodiester was then converted to <u>79</u> by refluxing in dimethyl formamide.⁷⁵ Diene-diester <u>79</u>, bp 104^o at 0.02 mm (lit.⁷⁵ bp 127^o at 0.28 mm) was characterized by its spectral properties which will be discussed later. A small amount of the <u>cis,trans</u> isomer <u>80</u> was also obtained by the above method but it was found more practical to synthesize this isomer and isomer 81 by photochemical means.

(2) Irradiation in the Presence of Triplet Energy Sensitizers

a) Photolysis of 79, 80, and 81

Scheme 7

Diethyl trans, trans-deca-2,8-diene-1,10-dioate (79) (5 mmol in 400 ml

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of acetone) was photolysed⁷⁶ under Corex optics using acetone ($E_T = 78$ kcal/mole) as a triplet energy sensitizer and solvent (Scheme 8). Under these conditions greater than 98% of the light was absorbed by the acetone (See Experimental). The course of the reaction was followed by analytical vpc. Initially, an equilibrium mixture of the geometric isomers

Scheme 8



79, 80, and 81 was observed and after extended photolysis only photoproducts

<u>82</u> (42%), <u>83</u> (15%), <u>84</u> (36%), and <u>85</u> (7%) remained. The equilibrium ratio of <u>79</u> : <u>80</u> : <u>81</u> remained constant at 3.8 : 3.5 : 1.0 throughout the photolysis (from 6% to 94% conversion to the final product mixture). A similar equilibrium mixture of <u>79</u> - <u>81</u> was formed using acetophenone ($E_T = 74 \text{ kcal/mole}$) as sensitizer (benzene solvent, Pyrex filter). Continued irradiation similarly gave <u>82</u> (45%), <u>83</u> (16%), <u>84</u> (31%), and <u>85</u> (8%). Benzophenone was also found to sensitize cyclization but naphthalene failed to produce any change in 79 during irradiation.

Diene-diesters <u>80</u> and <u>81</u> were isolated by preparative vpc. Their characterization will be described in the section concerning the direct irradiation of the diene-diesters <u>79</u> and <u>80</u>. Diene-diester <u>80</u> was photolysed in the presence of acetone and gave an identical equilibrium mixture of <u>79</u> - <u>81</u> as in the sensitized irradiation of <u>79</u> (Scheme 8). Continued irradiation gave photoproducts <u>82</u> - <u>85</u> in the following yields: 82 (44%), 83 (18%), 84 (31%), and 85 (7%).

Diene-diester <u>81</u> similarly, upon acetone sensitization, gave a mixture of <u>79</u> - <u>81</u> (Scheme 8). However, an equilibrium mixture was never obtained and continued irradiation gave photoproducts <u>82</u> - <u>85</u> in slightly different percentages: <u>82</u> (26%), <u>83</u> (17%), <u>84</u> (49%), and <u>85</u> (8%).

b) Characterization of Photoproducts 82, 83, 84, and 85

The gross structures of $\underline{82} - \underline{85}$ were indicated by mass spectral parent peaks at m/e 254. Nmr spectra indicated the absence of vinyl hydrogens and the ir spectra showed the presence of a saturated ester carbonyl. In order to determine the specific structures of the photoproducts <u>82</u>, <u>83</u>, and <u>84</u> their independent systhesis was undertaken. By the method of de Mayo,⁷⁷ diethyl maleate was photolysed in the presence of an excess of cyclohexene (Eq 64). The photoadducts corresponding in vpc



retention times to <u>82</u>, <u>83</u>, and <u>84</u> were collected by preparative vpc and found to have identical spectral properties to <u>82</u>, <u>83</u>, and <u>84</u> formed in the sensitized photolysis of <u>79</u> - <u>81</u>. Additional support for structures <u>82</u>, <u>83</u>, and <u>84</u> came from their hydrolysis to the known dicarboxylic acids.^{77,78} The hydrolysis of <u>82</u> gave <u>trans,anti,trans-bicyclo[4.2.0]octane-7,8-</u> dicarboxylic acid, mp 180°-182° (lit.⁷⁷ mp 181°-182°)(Eq 65). Similarly, <u>83</u> afforded <u>cis,trans-bicyclo[4.2.0]octane-7,8-</u>dicarboxylic acid, mp 197°-





198° (lit.⁷⁷ mp 199°-200°) (Eq 66), and <u>84</u> gave <u>cis</u>,<u>anti</u>,<u>cis</u>-bicyclo[4.2.0]octane-7,8-dicarboxyxlic acid, mp 170°-172° (lit.⁷⁷ mp 174°-176°) (Eq 67).

Eq 67

c) Thermodynamic Stabilities of Photoproducts 82 - 85

In order to establish the structure proposed for photoproduct $\underline{85}$ which could not be obtained completely free of isomer 5, it was necessary to utilize the results of base catalysed epimerization experiments. It has been reported⁷⁸ that the <u>dimethyl</u> esters analogous to photoproducts $\underline{82}$ and $\underline{85}$ epimerize under basic conditions to a mixture of the two with <u>dimethyl</u> ester $\underline{82}$ being favored. A 50 : 50 mixture of $\underline{83}$ and $\underline{85}$ was subjected to a catalytic amount of sodium ethoxide in absolute alcohol in a sealed vial for 12 hrs at $\underline{80}^{\circ}$. Four products, corresponding in vpc retention times to $\underline{82}$, $\underline{83}$, $\underline{84}$, and $\underline{85}$ were formed (Eq 68). The ratios of $\underline{82}$: $\underline{85}$ and $\underline{83}$: $\underline{84}$ were 90 : 10 and $\underline{85}$: 15 respectively. Compounds $\underline{82}$



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and 84 prepared in this manner were identical (ir, nmr) to those previously observed. Photoproduct 82 under similar basic conditions gave an 87 : 10 : 3 ratio of three products (Eq 69). The first was shown to be starting material 82 (vpc retention time, ir, nmr) and the second to be isomer 85 (vpc retention time and ir). The third product was not isolated. Under identical conditions 84 gave an 86 : 14 ratio of two products (Eq 70). These were shown by spectral data (ir and nmr) and vpc retention times to be compounds 83 and 84 respectively. These results from the base catalysed epimerization of 82 (Eq 69) and 84 (Eq 70) clearly indicate that in the epimerization of the 50 : 50 mixture of 83 and 85 (Eq 68) products 83 and 84 are produced from compound 83 and compounds 82 and 85 are coming from compound 85. These conclusions confirm the structure proposed for photoproduct 85. These results also established 82 and 83 as the most thermodynamically stable isomers in the trans and cis series respectively. Additional support for these stability results came from the thermolysis of photoproducts 82, 83, and 84. Diester 84 was heated in a sealed tube

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at 250°. After 28 hrs there was no change in the $\underline{83}$: $\underline{84}$ ratio of 81 : 19 (Eq 71). Both products were characterized by their spectral



properties (ir, nmr) and vpc retention times. These were the only two products with the exception of diethyl maleate and cyclohexene (based on vpc retention times) present in less than 1%. Diester <u>83</u> under identical conditions gave a mixture of <u>83</u> (82%) and <u>84</u> (18%) after 62 hrs (Eq 72). Diester <u>82</u> initially appeared to give the same products as in its base catalysed epimerization (Eq 69) but after 88 hrs gave 5 products in the ratio of 1.1 : 1.0 : 3.3 : 1.6 : 1.2 (Eq 73). The first of these was diester 82 (vpc retention time and nmr). The others were not identified.

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(3) Discussion of Sensitized Photolyses of 79, 80, and 81

a) Possible Mechanisms

The equilibrium mixture of dienes <u>79</u>, <u>80</u>, and <u>81</u> formed in the sensitized (acetone, acetophenone) photolysis of compounds <u>79</u> and <u>80</u> indicate a <u>cis,trans</u> isomerization that is faster than cycloaddition. In the case of the photolysis of diene-diester <u>81</u>, an equilibrium mixture of <u>79</u> - <u>81</u> is not reached as cycloaddition appears to be at least competitive with <u>cis</u> to <u>trans</u> isomerization. Thus if the geometry of the double bonds affects the products formed, then one would intuitively expect a different ratio of photoproducts in the photolysis of <u>81</u>. This is in fact shown to be true experimentally.

There are two general types of mechanisms usually postulated for photochemical reactions. The first involves a symmetry allowed process⁴² resulting in the stereospecific formation of products <u>via</u> a concerted mechanism. The second involves a two or more step process having distinct intermediates. The intermediate may be diradical or ionic, and product formation is often non-stereospecific. In order to determine what one might expect from these two types of mechanisms it would be helpful to predict the products from a simple 2 + 2 cycloaddition of two <u>cis</u>-1,2 disubstituted ethylenes. In the concerted cycloaddition¹⁴ (Eq 74) one would expect only products <u>86</u> and <u>87</u>. The relative yields of these products may or may not be in line with their thermodynamic stabilities. More important is the steric hindrance involved in the geometry of approach of the two olefins. In the stepwise mechanism (Eq 75) one would expect the same products <u>86</u> and <u>87</u> plus the other four possible isomers

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<u>88</u>, <u>89</u>, <u>90</u>, and <u>91</u>. If the intermediates are sufficiently long lived the products are usually formed in amounts corresponding to their thermodynamic stabilities. Sometimes kinetic control^{18,79} in the formation of the intermediate or of the product may be an important factor in these reactions. Sometimes both concerted and stepwise mechanisms are operative in the same reaction⁸⁰ and detailed kinetic data is usually necessary to determine how large a part each mechanism contributes.

In the cases of diene-diesters <u>79</u>, <u>80</u>, and <u>81</u> each are capable of photochemically cycloadding in a $\pi_s^2 + \pi_s^2$ fashion to give two products. Since the olefins are in a relatively small acyclic chain, $\pi_a^2 + \pi_a^2$ cycloaddition appears to be sterically unlikely. Diene-diester <u>79</u> is capable of giving in a concerted fashion cycloadded products <u>82</u> and <u>84</u>. Similarly, <u>80</u> and <u>81</u>







can concertedly give rise to photoadducts <u>83</u> and <u>85</u> (Eq 77), and <u>92</u> and <u>93</u> (Eq 78) respectively. If this were the only mechanism operative one would expect a 46% yield of <u>82</u> + <u>84</u>, a 42% yield of <u>83</u> + <u>85</u>, and a 12% yield of <u>92</u> and <u>93</u>. These are based on the percentages of dienes <u>79</u>, <u>80</u>, and <u>81</u> present throughout the photolysis of <u>79</u> and <u>80</u>. In actual fact, however, in the photolysis of <u>79</u> and <u>80</u>, 78% of <u>82</u> + <u>84</u> and 22% of <u>83</u> + <u>85</u> are formed. No <u>92</u> or <u>93</u> is ever found to be present even when pure <u>81</u> is used as starting material. In this latter case an equilibrium mixture

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of $\underline{79} - \underline{81}$ was never achieved and thus a similar prediction of product distributions is impossible. Experimental evidence thus points away from a concerted mechanism.

In the case of a diradical or ionic mechanism there should be one intermediate for the formation of <u>trans</u> fused products <u>82</u> and <u>85</u> (<u>94</u>), and another intermediate for the formation of cis fused products 83 and



<u>84</u> (95). The formation of <u>94</u> and <u>95</u> from the photolysis of <u>79</u> and <u>80</u> is probably statistical in nature as equal amounts of <u>cis</u> and <u>trans</u> fused products are formed. Intermediate <u>94</u> can exist in two different conformations (i.e., the e,e and a,a conformation). Since bonding is only possible from the e,e conformation only this will be considered in the following discussion. The e,a and the a,e conformations of intermediate <u>95</u> are degenerate and thus only one of them need be considered. Theoretically <u>94</u> can give rise to photoproducts <u>82</u>, <u>85</u>, and <u>93</u> while intermediate <u>95</u> can bond to give <u>83</u>, <u>84</u>, and <u>92</u>. Each of these possibilities will be considered separately.

Intermediate <u>94</u> may be regarded as a vibrationally deactivated⁸¹ triplet 1,4 diradical which spin inverts to the singlet excited state and then bonds to form trans fused bicyclo[4.2.0]octane systems. As the
radicals approach each other for bonding (i.e., approaching the transition state), non-bonded interactions are encountered between C_1 and C_4 (α, δ interaction), between C_{10} and C_7 (α, δ), and between C_1 and C_{10} (α, α interaction). These interactions (Scheme 9) are expected to determine





the relative amounts of the three possible <u>trans</u> fused bicyclo[4.2.0]octanes which are formed. Formation of photoproduct <u>82</u> involves no adverse α, δ or α, α interactions and would be expected to be formed in greater amounts than isomers <u>85</u> or <u>93</u>. Closure of <u>94</u> to give both <u>85</u> and <u>93</u> involves two steric interactions (α, δ and α, α) (Scheme 9) and the effect of this on their relative distribution should depend on the magnitudes of the α, δ and α, α interactions as the transition state is approached in each case. Previous work on the photolysis⁷⁹ of the geometric isomers of dimethyl-2,7-nonadiene-1,9-dioate indicate that α , δ effects are stronger than α , α effects as the 2,8 bond begins to form (Eq 79). Photoproduct 98 whose formation from intermediate diradical 97



involves one α, α interaction, is favored by a factor of three over photoproduct <u>99</u>, whose formation involves one α, δ interaction. These results tend to support the experimentally observed formation of photoproduct <u>85</u> (one α, δ and one α, α interaction) in preference to isomer <u>93</u> (two α, δ interactions). Photoproducts <u>82</u> and <u>85</u> are formed in a ratio of 6 : 1 and none of isomer <u>93</u> was detected. Fortuitously, the product ratio is also in line with the relative thermodynamic stabilities of the various photoproducts. Base catalysed epimerizations of <u>82</u> (Eq 69) and <u>85</u> (Eq 68), which only involve avoidance of α, α interactions, both give an <u>82</u> to <u>85</u> ratio of approximately 9 : 1.

Intermediate <u>95</u> which is the immediate precursor of the <u>cis</u> fused bicyclo[4.2.0]octanes, can also be looked upon as a vibrationally relaxed⁸¹ triplet 1,4 diradical which spin inverts to the singlet state and then bonds. The same type of non-bonded interactions (α , δ and α , α) are involved in the transition state as the diradical starts to bond (Scheme 10). Formation of photoproduct <u>83</u> involves one α , δ interaction while the formation of isomer 84 involves one α , α interaction. This is very similar

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to the formation of <u>99</u> and <u>98</u> respectively in Eq 79. On this basis, formation of photoproduct 84 would be expected to be favored over formation

Scheme 10



of isomer <u>83</u>. This was found to be true experimentally as the <u>84</u> : <u>83</u> ratio in the photolysis of <u>79</u> and <u>80</u> was approximately 2 : 1. Formation of isomer <u>92</u> involves two α, δ and one α, α interaction, and thus the activation energy for its formation would be expected to be quite high relative to the formation of <u>83</u> and <u>84</u>. Experimentally, no <u>92</u> is observed. The product ratio in the formation of the <u>cis</u> fused series is not in line with the thermodynamic stabilities of the products. On treatment of <u>83</u> or <u>84</u> under base catalysed epimerization conditions or under thermolysis conditions the α, α interactions are avoided and the <u>83</u> : <u>84</u> ratio becomes approximately 17 : 3.

It is interesting to note that the mixed cycloadditions of diethyl

and <u>dimethyl</u> maleate to cyclohexene are not governed by the same factors as in the photolyses of <u>79</u> and <u>80</u> and thus different product ratios are observed (Eq 80). In these cases the α, α interactions are far more important than α, δ interactions in the closure of diradical species <u>100</u>. The reason for the increased effect of the α, α interaction stems from the fact that the C₂, C₉ bond is already formed and thus the C₁ and C₁₀ groups



R = Me or Et



feel each other (α, α) more than the C₇ and C₁₀ carbons as the C₈, C₉ carbons begin to bond. This explains the preference for <u>trans</u> carboethoxy groups in both <u>cis</u> and <u>trans</u> fused bicyclo[4.2.0]octane systems (Eq 80). The preference for <u>cis</u> fused bicyclo[4.2.0]octane products (R = Et, 72% <u>cis</u>; R = Me, 82% <u>cis</u>) can be attributed to the relative stabilities of <u>cis</u> and <u>trans</u> fused bicyclo[4.2.0]octane systems.⁸²

These arguments based on a kinetic closure of diradical <u>94</u> and <u>95</u> explain the relative amounts of products <u>82</u> - <u>85</u> formed in the sensitized photolysis of diene-diesters $\underline{79}$ and $\underline{80}$.

Up until now, the photolysis of diene-diester 81 has been ignored for the most part. This is mainly the result of the anomalous product ratio that is observed when pure 81 is used as a starting material. The major difference involves the preference for formation of cis-bicyclo-Instead [4.2.0]octane systems over the corresponding trans fused systems. of a cis/trans ratio of almost unity the photolysis of 81 produces a ratio of almost 2 : 1. This change is mainly brought about by the increase of photoproduct 84 and the decrease of photoproduct 82. In order to explain these results in a satisfactory manner it would be necessary to propose a unique mechanism for the cycloaddition from the cis, cis isomer In the photolyses of 79 and 80, isomer 81 is only present to a maximum 81. of 12% and thus responsible for 12% of the final product mixture. Thus it is not too far wrong to consider the photolyses 79 and 80 as being separate from the photolysis of 81. However, in the photolysis of pure 81 an equilibrium mixture of diene-diesters is never reached and 81 is always present as a major component in the $\underline{79} - \underline{81}$ mixture. Since the product ratios are in the same direction as observed in the photolyses of 79 and 80 (i.e., 82 and 84 are formed in greater amounts than 85 and 83 respectively), then it would seem likely that initial bond formation is the differing factor operating. A ground state complex such as that shown in 101 would favor the formation of 95 and hence lead to more cis fused products. It is also conceivable that an excited state complex of similar geometry could be formed in the photolysis of the cis, cis isomer



<u>81</u>. This argument, based on exciplex formation, is analogous to Corey's explanation¹³ for the stereospecific photocycloaddition of cyclohexenone to methoxy ethylene (Eq 21) and White's reasoning²⁷ for the direction of photocycloaddition in β -farnesene (Eq 30). While such a complex (<u>101</u>) explains the results, the reason for such a complex is unclear. Molecular model investigation does not indicate any obvious preference for a conformation such as that in <u>101</u> over a complex such as that in <u>102</u> which would lead to the <u>trans</u> intermediate <u>94</u>. As can be seen, a simple explanation for the preference for <u>cis</u> fusion in the photolysis of diene-diester <u>81</u> is not available at present. It is still fairly certain however that the photolysis of <u>81</u> is proceeding <u>via</u> a triplet diradical intermediate as is the case for the photolyses of <u>79</u> and <u>80</u>.

b) Initial Bond Formation

There have been many attempts to explain the selectivity of the initial bonding step in photochemical cycloadditions of acyclic and cyclic non-conjugated dienes. Each of these explanations possesses certain merits in individual examples, but usually cannot be extended to other systems. The most widely used guide to these cycloadditions is that a five membered ring is formed first. This was proposed by Srinivasan and Carlough¹⁶ and is better known as the "rule of five". While this mnemonic does indicate the direction of cycloaddition in 1,4- 1,5- and 1,6 dienes, it is inapplicable in the case of 1,7 dienes. Furthermore, it is strictly empirical and does not indicate why five membered ring formation should be preferred.

An often used explanation for the direction of cycloaddition is based on the supposition that initial bond formation occurs in such a way as to produce the most stable diradical intermediate. At first glance it could be argued that the photolyses of diene-diesters <u>79</u>, <u>80</u>, and <u>81</u> are best described in this manner. Intermediate <u>103</u> (mixture of <u>94</u> and <u>95</u>) would be expected to be more stable due to the influence of the carboethoxy groups³² than intermediates <u>104</u> or <u>105</u> (Eq 81). There are two



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factors which mitigate against this radical stability argument. Recently, the importance of the stabilizing influence of the carbonyl group on an α radical (103) has been cast in doubt by the work of King, Golden, and Benson.⁸³ Thermal studies on the bromination of acetone indicate that there is no stabilization in the acetonyl radical (106). This indicates



that structure <u>107</u> does not contribute toward the stability of <u>106</u>. There is a stabilization energy of 2.7 kcal/mole in going from the acetonyl to the methyl acetonyl radical but this change is in line with the stabilization gained in going from a primary to a secondary radical.¹⁹ These studies indicate that there should be very little difference among the stabilities of the diradicals <u>103</u>, <u>104</u>, and <u>105</u>. Secondly, while a few photochemical cycloadditions (e.g., myrcene (Eq 29) and isogermacrone(Scheme 6)) proceed through the formation of their most stable diradical intermediates most cyclizations do not. This is especially so in the case of 1,5 dienes (Eq 82).



Other systems such as cyclooctadiene (Scheme 2) and cyclodeca-3,8-diene-1,6-dione (Eq 51) are capable of initial bond formation to give two diradicals which do not differ significantly in stability and yet in the case of cyclooctadiene only "crossed" cycloaddition occurs while "straight" cyclization occurs exclusively for cyclodeca-3,8-diene-1,6dione. The above observations tend to rule out the validity of using radical stability to explain the direction of cycloaddition in the photolyses of the geometric isomers of diethyl 2,8-decadiene-1,10-dioate (79 - 81).

Another possible explanation for the direction of initial bond formation in the photolyses of <u>79</u>, <u>80</u>, and <u>81</u> may be obtained by observing the mode of addition of the triplet state of an α , β -unsaturated carbonyl species to an olefin. Initial excitation followed by delocalization produces an intermediate diradical species which possesses a radical centre on C₃ (Eq 83 - 85) and a radical centre on the carbonyl oxygen.⁸⁴ The radical centre at C₃ is now capable of adding intramolecularly to the ground state olefin. Initial bonding by the β carbon (C₃) of a photochemically excited α , β -unsaturated carbonyl species has been recently



Eq 83



established by the work of Dilling⁸⁵ on the mixed cycloaddition of cyclopentenone to 1,2-dichloroethylene. Experimentally, 90,79,76 the radical centre on C₃ in diradicals <u>109</u>, <u>110</u>, and <u>111</u> cyclize at the olefin centre via path <u>b</u> (five membered ring formation), path <u>a</u> (five membered ring formation), and path a (six membered ring formation) respectively.

These cyclizations (i.e., <u>via</u> path <u>a</u> or <u>b</u>) can be compared to the ground state intramolecular addition of a free radical to an olefinic centre (Scheme 11). When n (the number of carbon atoms separating the free radical centre from the olefin centre in <u>112</u>) is equal to 2, Julia⁸⁶ states that there is relatively poor overlap between the free radical centre and the olefin centre in both path <u>a</u> and path <u>b</u> cyclizations. Experimentally, this is supported by the fact that cyclization of 4-pentenyl free radicals (n = 2) is only a minor reaction⁸⁷⁻⁸⁹ pathway compared to competitive intermolecular reactions. When cyclization does



occur^{87,88} exclusive five membered ring formation (path <u>b</u>) is observed (Table 3). Classically, preferential path <u>b</u> cyclization can be rationalized on the basis of the relative radical and thermodynamic stabilities of the species involved in path <u>a</u> and path <u>b</u> cyclizations (Scheme 11). These results for 4-pentenyl free radicals closely parallel those of the photochemical intramolecular addition of <u>109</u> (Eq 83). Photochemically, only five membered ring formation⁹⁰ (i.e., "crossed" cycloaddition, path <u>b</u>) is observed.

When n = 4, molecular model investigations^{86,89} indicate good overlap of orbitals for path <u>a</u> and poor overlap for path <u>b</u>. This indicates that six membered ring formation (path <u>a</u>) should be favored over seven membered ring formation (path <u>b</u>). Furthermore, thermodynamic stability of the six membered ring and probability factors governing the cyclization of the radical both tend to favor path <u>a</u>. Experimentally, 6-heptenyl free radicals cyclize intramolecularly to give preferentially six membered ring formation (path <u>a</u>).^{86,89} The photochemical analogue of this cyclization (i.e., cyclization of <u>111</u>) gives products indicative of an exclusive path <u>a</u> mechanism ("straight" cycloaddition).⁷⁶

The cyclization of 5-hexenyl free radicals (n = 3) does not present as simple a picture as when n = 2 or 4 (Table 3). Here molecular models \underline{Table} 3

<u>n</u>	X	<u>Y</u>	<u>R</u> 1	<u>R</u> 2	<u>Path</u> <u>a</u> (%)	Path $b(\%)$	<u>Ref</u> .
1	Н	Н	н	Н	0	0	88
2	Н	H ·	H	Н	0	14	88
2	CN	COOEt	н	Me	0	30	87
2	CN	COOEt	Н	Н	0	0	87
2	н	H	Н	Н	0	0	89
3	н	н	Н	H	43	0.	89
3	н	н	н	Н	84	8	88
3	н	н	н	Н	90	3	23
3	CN	COOEt	н	Н	16	84	86
3	Н	COOEt	Н	Н	44	56	86
4	H	н	н	н	49	trace	88
4	CN	COOEt	н	н	34	0	86

indicate good overlap^{86,89} of the free radical with both centres of the olefin moiety. Based on the thermodynamic stabilities of the products formed (cyclohexane vs. methylcyclopentane) and on the radical stabilities of the intermediates (cyclohexyl radical vs. the cyclopentylmethyl radical) one would expect six membered ring formation to predominate (path <u>b</u>). Experimentally, however, just the opposite has been found to be true. The

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work of Brace²¹ on the treatment of 1,6-heptadiene with iodoperfluoropropane ($R_{\rm F}I$) leads exclusively to cyclopentane formation (Eq 86). He offers no explanation for the generality of these reactions. Walling⁸⁹ has found that the reaction between 5-hexenyl mercaptan and triethyl phosphite results in preferential methylcyclopentane formation (Eq 87).



Only when he raises the temperature of the reaction from 60° to 120° does he find any cyclohexane formation. He comments on the fact that there is little difference in the steric requirement for closure at C₅ (path <u>a</u>) or at C₆ (path <u>b</u>) and indicates that formation of methylcyclopentane is probably kinetic in nature. Further evidence for this similiar, unique behaviour of 5-hexenyl free radicals comes from the work of Pines⁸⁸ on the treatment of 1-phenyl-6-hexene with di-t-butylperoxide. Here (Eq 88) some cyclohexane formation occurs but it is very minor compared to the amount of methylcyclopentane formed. If, as indicated in the above examples (Eq 86 - 88), the free radical cyclizes kinetically then the formation of the cyclohexyl and the cyclopentylmethyl radical must be irreversible. This has been shown to be true as the thermal decomposition of di(cyclohexyl-formyl) peroxide and di(cyclopentyl-acetyl) peroxide give only cyclohexane and methyl cyclopentane respectively.²³ There are several examples, when the free radical is highly stabilized, that six membered ring formation is preferred (Scheme 12).^{22,86,91} These results

Scheme 12



X = CN, Y = COOEt or X = Y = COOEt

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have been explained by Julia to be due to the reversible formation of the cyclohexenyl and cyclopentylmethyl radicals, followed by irreversible product formation (Scheme 12).⁹¹ Such an explanation would tend to favor the most thermodynamically stable product (i.e., cyclohexane formation, path b). Thus thermodynamic control replaces kinetic control when the free radical is stabilized. In order to support his scheme for the reversible path a and path b cyclizations (Scheme 12), Julia thermolysed the appropriately substituted ($R_1 = CN$ and $R_2 = COOEt - Scheme 12$) tertiarybutyl cyclohexyl performate and tertiary-butyl cyclopentyl peracetate, and found that they both gave mixtures of cyclohexane and methyl cyclopentane The similarity between the cyclization of 5-hexenyl free products. radicals and photocyclization of the 1,6 dienes 96 probably lies in the kinetic closure to form a five membered ring via path a. It has been shown by Liu and Hammond¹⁸ that their intermediate diradical (11) is formed irreversibly. There is no reason to expect that the cyclization of 110 (Eq 84) would be reversible. Experimentally 110 (photochemically excited 96) cyclizes exclusively via path a to form "straight" addition products.⁷⁹

It can be concluded that both ground state and photochemical intramolecular cyclizations of alkenyl free radicals <u>112</u> (n = 2 and 4) proceed in a manner expected on the basis of the radical and thermodynamic stabilities of the species involved. However, five membered ring formation in the cyclization of 5-hexenyl free radicals (n = 3, <u>112</u>) and in the analogous photochemical cyclizations (Eq 84) is proceeding <u>via</u> a kinetic closure. The reason for such a closure is not immediately clear but it has been suggested⁹¹ that entropy factors may play a major part. A final highly speculative explanation for the direction of initial bond formation in photochemical cycloadditions is based on the possibility that the first step is controlled by the symmetry of the highest occupied molecular orbital. If a $\pi_s^2 + \pi_s^2$ geometry of approach of the olefins is assumed then the mixing of their bonding ($\pi_1 \pm \pi_2$) and antibonding ($\pi_1^* \pm \pi_2^*$) orbitals (Fig 5) will produce a set of four new non-degenerate molecular orbitals. If excitation occurs, the highest occupied molecular orbital (ψ_3) predicts that the first step should proceed in a "straight"



manner. Such a molecular orbital approach explains the direction of cycloaddition in 1,4- 1,6- and 1,7- dienes but fails to explain "crossed" cycloaddition in 1,5 dienes (Eq 89). If the orbitals of the 3,4 sigma bond in 1,5 dienes were mixed with the four molecular orbitals $\psi_1 - \psi_4$



derived above then a possible crossing of the energy levels of ψ_1 and ψ_2 , and ψ_3 and ψ_4 may occur. Cookson (See Introduction) has done a similar mixing of the central sigma bond in order to explain the Cope rearrangement of 1,5 dienes.³⁵ If the mixing of the sigma bond is sufficiently large and level changing does occur then the highest occupied molecular orbital in the excited state is ψ_4 (See Fig 3) and this predicts that



"crossed" initial bonding should occur. These ideas of through-bond coupling are not unique as Hoffmann⁹² has published a paper dealing with this topic specifically. The application of through-bond coupling to 1,5 dienes, however, is very speculative and many factors such as different geometries of approach in the transition state, non-coplanarity of the sigma and pi systems and steric interactions probably render such an explanation inconclusive. It is hoped that future studies in photoelectron spectroscopy will be able to determine the extent of through-bond interactions on the direction of photocycloaddition of 1,5 dienes.

(4) Direct Irradiation of Compounds 79, 80, and 115

a) Photolysis of 79

Photolysis of $\underline{79}$ in either methanol or hexane under Corex optics led to a complex mixture of photoproducts $\underline{79}$, $\underline{80}$, $\underline{81}$, $\underline{115}$, $\underline{116}$, and $\underline{117}$. Continued irradiation led exclusively to the formation of $\underline{117}$. As indicated by analytical vpc, photoproducts $\underline{80}$, $\underline{81}$, $\underline{115}$, and $\underline{116}$ build up initially and then disappear in accordance with Scheme 13. Compound $\underline{79}$ decreases throughout and photoproduct $\underline{117}$ increases throughout. Vpc

Scheme 13



indicates an obvious induction period for the formation of $\underline{117}$ and a less obvious one for $\underline{115}$ and $\underline{116}$.

b) Characterization of Photoproducts 79 - 81 and 115 - 117

Characterization of the photoproducts was made on the basis of their nmr and ir spectra as given in Table 4. The geometries of the various double bonds were indicated by characteristic double bond ir stretches at 10.04 - 10.27 μ (trans double bond CH out of plane deformation) and 11.93 - 12.04 μ (cis double bond CH out of plane deformation), while the positions of the double bonds could be determined by the infrared carbonyl stretching frequencies of 5.74 - 5.79 μ (β , γ -unsaturated ester) and 5.81 -5.83 μ (α , β -unsaturated ester). Furthermore the geometry of the double

Table 4

Compound	Double Bond Position and Geometry	C <u>H</u> =C <u>H</u> Coupling Constants (Hz)	IR Double Bond C-H Rock (µ)	IR C=O (µ)
79	$trans-\alpha, \beta$	15.5	10.15	5.81
	trans- α , β	15.5	10.15	5.81
80	$\underline{trans}-\alpha,\beta$	15.5	10.04	5.81
	<u>cis</u> -α,β	11.5	11.97	5.81
<u>81</u>	<u>cis</u> -α,β	11.6	12.04	5.82
	<u>cis</u> -α,β	11.6	12.04	5.82
115	trans- α , β	15.4	10.18	5.82
	$trans-\beta,\gamma$	mult	10.18	5.79
116	<u>cis</u> -α,β	11.5	11.93	5.83
	<u>trans</u> - β , γ	mult	10.14	5.79
117	trans- β , γ	mult	10.27	5.74
	trans-β,γ	mult	10.27	5.74

bonds in the case of the α , β -unsaturated esters was indicated clearly by nmr. The β proton always appeared as a doublet of triplets with a coupling constant of 15.5 Hz (trans double bond) or 11.5 Hz (cis double bond). The α vinyl hydrogen appeared as a doublet with small allylic (1.5 Hz) coupling The vinyl hydrogens of the β , γ -unsaturated double bonds were complex multiplets and a shift reagent was used in order to determine the geometry of the double bonds in <u>117</u>. The use of tris(dipivalomethanato)europium⁹³ in a CCl₄ solution of <u>117</u> caused the equivalent C₃ and C₈ vinyl hydrogens to appear as two distinct triplets with a typical trans vinyl coupling constant of 15.7 Hz. This value could also be obtained from the broad doublet responsible for the C₄ and C₇ vinyl hydrogens. These assignments were supported by decoupling experiments (See Experimental).

Further proof of structure for photoproduct <u>80</u> came from an independent synthesis⁷⁵ while the structure of <u>117</u> was verified by hydrolysis to the known⁹⁴ <u>trans,trans-deca-3,8-diene-1,10-dicarboxylic acid which was identical</u> to an authentic sample.⁹⁵ We thank Dr. Chiusoli for a generous sample of trans,trans-deca-3,8-diene-1,10-dicarboxylic acid.

Finally, analytical analyses were obtained on the unknown compounds <u>81</u>, <u>115</u>, and <u>116</u> which supported their isomeric structures. Mass spectral fragmentation patterns of the photoproducts are in agreement with the structures presented in Scheme 13.

c) The Photolysis of 80 and 115

Scheme 13 was further supported by the direct photolysis of <u>80</u> and <u>115</u>. Diene-diester <u>80</u> led to photoproducts <u>81</u>, <u>115</u>, <u>116</u>, and <u>117</u> with <u>117</u> being the sole product after extended irradiation. At no time was the appearance of <u>79</u> observed. On photolysis, <u>trans,trans-diester 115</u> initially gave compound <u>116</u>, and after an observable induction period, compound <u>117</u>. Compound <u>117</u> was the only product after continued photolysis. At no time in the photolysis of 115 were compounds $\underline{79} - \underline{81}$ observed.

d) Quenching Studies

Photolysis of <u>79</u> (0.001 moles) in hexane in the presence of varying amounts of piperylene (0.005 moles, 0.05 moles, and 0.2 moles) led to a mixture of products in accord with Scheme 13. The time for the photolyses was, however, greatly affected. The larger the amount of piperylene present the longer it took for deconjugation to occur.

(5) Discussion of the Direct Irradiation of Compounds 79, 80, and 115

Photodeconjugation of an α , β -unsaturated ester to the corresponding β , γ -unsaturated ester is a fairly well documented reaction (See Introduction). The most generally accepted mechanism involves <u>trans</u> to <u>cis</u> isomerization followed by γ hydrogen abstraction by the n, π * excited singlet state of the ester carbonyl. The resulting diradical forms a dienol which can ketonize to give the observed β , γ isomer.

The intermediacy of the <u>cis</u> olefin in the photodeconjugation of <u>79</u> is, in general, indicated by Scheme 13 and in particular, by the photolysis of <u>115</u>. Direct irradiation of <u>115</u> gives at first <u>116</u> and then after an induction period deconjugated product <u>117</u>. These results indicate that the <u>cis</u> (α,β) , <u>trans</u> (β,γ) isomer <u>116</u> and not the <u>trans</u> (α,β) , trans (β,γ) isomer <u>115</u> is the immediate precursor of <u>117</u>. The excited state responsible for the deconjugation observed in the irradiation of <u>79</u>, <u>80</u>, and <u>115</u> is the n, π * singlet state. ^{62,64} The assignment of the excited state is supported by photolysis experiments under Corex optics where only the n, π^* absorption band of the α , β -unsaturated ester is absorbing light. The multiplicity is supported by the sensitization ⁷⁶ and quenching studies. Triplet sensitization failed to give any deconjugation. Under these conditions only cycloadded product formation was observed. Quenching experiments with piperylene failed to prevent photodeconjugation from occurring. With larger amounts of piperylene present the rate of the deconjugation was slower but this could be due to a slower rate of <u>trans to cis</u> isomerization. The rate of photodeconjugation is faster than <u>cis to trans</u> isomerization as no <u>79</u> is observed in the direct irradiation of 80.

Unique to this system is the fact that only the di- β , γ -<u>trans,trans</u> isomer <u>117</u> is formed in the deconjugation of <u>79</u>, <u>80</u>, and <u>115</u>. Other authors have found a much less preference for the formation of the <u>trans</u> β , γ isomer (See Introduction).⁵⁹ These results may be explained by the mechanism presented in Scheme 14. <u>Trans</u> to <u>cis</u> isomerization of <u>79</u>

Scheme 14



followed by γ hydrogen abstraction by the half-filled n-orbital on oxygen in the n, π * singlet state (<u>118</u>) leads initially to a species <u>119</u>. This could then undergo rotation about the β , γ -carbon carbon bond to give either the <u>cis</u> (<u>120</u>) or the <u>trans</u> (<u>121</u>) dienol. The latter would be the most favored on steric grounds. This is supported experimentally as only the trans deconjugated product is observed.

These results point out the possible synthetic utility of such a deconjugation process. Almost any di- β , γ -unsaturated ester of specified chain length and known geometry can be prepared in this manner.

(6) Conclusion

Like β , γ -unsaturated ketones, the photolysis of acyclic 1,7 dienediesters (<u>79</u>, <u>80</u>, and <u>81</u>) show unique properties under direct and sensitized conditions. In the presence of triplet sensitizers 1,7dienes cycloadd in a "straight" manner to give a mixture of <u>cis</u> and <u>trans</u> fused bicyclo[4.2.0]octanes. Under direct irradiation, photodeconjugation occurs to give exclusively the trans, trans isomer 117.

<u>C)</u> Cyclonona-2,6-dienone

A literature survey of the photochemistry of cyclic non-conjugated dienes (See Introduction) quickly demonstrates the tendency of the dienes to give cycloaddition products indicative of initial five-membered ring formation. 1,5-Cyclooctadiene (Scheme 2) and isogermacrone (Scheme 6) are typical examples of 1,5- and 1,6 dienes respectively, which photochemically cycloadd in this manner. Perhaps due to synthetic difficulties, homologous cyclic dienes (i.e., 1,4-cycloheptadiene; 1,5-cyclononadiene; 1,6-cycloundecadiene; etc.) have received very little attention.^{48,58} Of these cyclic dienes, 1,5-cyclononadiene (122) possesses the unique property of being able to photochemically cycloadd <u>via</u> initial five-membered ring formation to give both "straight" and "crossed" addition products (Scheme 15).

Scheme 15



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The photochemistry of <u>122</u> could shed some light on the mechanism of cycloaddition in non-conjugated dienes depending on whether "straight" or "crossed" product formation predominated.

Based on this unusual property of cyclononadiene it was decided that such a skeleton would become the basis of a photochemical investigation. Compound <u>122</u> is in itself a poor choice for such an investigation as its ultraviolet absorption region is not easily accessible by conventional light sources. It was decided then that 2-bromo-cyclonona-2,6-dienone (<u>126</u>), and cyclonona-2,6-dieneone (<u>128</u>) would make good starting materials. These choices were based on a possible synthetic scheme (Scheme 16) and on the



fact that the carbonyl has an easily accessible ultraviolet absorption region. Scheme 16 outlines the synthetic approach taken to obtain ketones 126 and 128. Cyclooctadiene was converted to 9,9-dibromo-bicyclo-[6.1.0]non-4-ene (123) by the method of Skattebøl. 99 Compound 123 was then subjected to a Ag^+ assisted acetolysis by stirring it in a solution of silver acetate in acetic acid for two days. This results in the stereospecific¹⁰⁰ formation of 2-bromo-3-acetoxy-<u>cis,trans</u>-cyclonona-1,6diene (124) This was easily converted to the alcohol (125) by alkaline hydrolysis of the acetoxy group. Many attempts to oxidize alcohol 125 with various oxidizing reagents (e.g., Jones, ¹⁰² Browns, ¹⁰³ Collins Cornforth, 105 AgO, and MnO₂¹⁰⁶) to the corresponding ketone proved fruitless. Equimolar mixtures of oxidizing reagent and alcohol usually returned starting material unreacted, while excesses of reagents produced inseparable complex mixtures of products. The failure of the oxidation of 125 could be due to the influence of the bromine group. In order to test this hypothesis the removal of the bromine was carried out by stirring alcohol <u>125</u> in an excess of sodium in liquid ammonia.¹⁰¹ This gave in good yield trans, cis-2, 6-dienol (127). Several attempts (MnO2, Browns oxidation, and Collins oxidation) at oxidizing 127 to the corresponding ketone also failed. Some encouraging results have been obtained with the use of Jones reagent although the yield of product suspected to be ketone 128 is quite low (<10%). Work at characterizing this product and at improving its yield is presently underway.

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EXPERIMENTAL

A) General Procedures

Infrared (ir) spectra were obtained, unless otherwise stated, on neat liquid samples between sodium chloride plates with a Perkin-Elmer 137 spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded by Miss P. Watson and Mr. R. Burton on the following spectrophotometers: Varian Model A-60, T-60, and HA-100, and Jeolco C-60H. In all cases tetramethylsilane was used as an internal standard. Mass spectra were obtained on a direct inlet AEI MS-9 instrument at 70 eV, and ultraviolet spectra were recorded on a Unicam SP-820 spectrophotometer. Melting points were taken on either a Thomas-Hoover (TH) capillary apparatus or a Fisher-Johns (FJ) melting point block and are corrected unless otherwise indicated. Elemental analyses were performed by the departmental microanalyst, Mr. P. Borda. Vapour phase chromatography (vpc) was carried out on either a Varian-Aerograph 90-P3 or a Varian Aerograph Autoprep Model A700. Both were connected to Honeywell Electronik 15 strip chart recorders. The carrier gas in all cases was helium. The following analytical (A -5' x 1/4'') and preparative (P - 20' x 3/8'') columns were used: 20% SE-30 on 60/80 Chromosorb W A/W DMCS, (column A-1); 20% DEGS 60/80 Chromosorb W, (column A-2); 10% Carbowax 60/80 Chromosorb W, (column A-3); 10% FFAP 60/80 Chromosorb W, (column A-4); 30% SE-30 45/60 Chromosorb W, (column P-1); 30% DEGS 45/60 Chromosorb W, (column P-2); and 30% Carbowax 45/60 Chromosorb W, (column P-3). The column temperature (^OC) and the helium flow rate (ml/min) are given in parenthesis after the column stated.

Thin layer chromotography (tlc) was carried out on plates coated with E. Merck and Co. Silica Gel G. Grace (activated) Silica Gel was used for column chromotography. Large scale photolyses (internal) were carried out in a water-cooled Quartz immersion well apparatus. Small scale photolyses (external) were performed by placing the solution to be photolysed in a 50 ml Quartz tube and strapping this to the outside of the water-cooled immersion well. In either case, a Hanovia 450 W type L lamp with a Pyrex, Corex, or Vycor filter was used. All solvents were distilled, the methanol being distilled from a solution of sodium methoxide and dimethyl phthalate.⁹⁶ All organic reagents used were reagent grade unless otherwise indicated. Photolysis solutions were degassed prior to irradiation with Canadian Liquid Air argon or L grade nitrogen.

B) Isogermacrone

<u>Source of Germacrone (68).</u> The author is indebted to Dr. M. Suchý, Czechoslovak Academy of Science, and to Fritzsche Brothers, Inc., New York, N.Y. for generous samples of <u>68</u>. In the latter case, it was necessary to isolate germacrone from Zdravetz oil. The contents from a one ounce bottle of zdravetz oil were filtered to yield 2.2 g of crude yellow crystals, mp $50^{\circ}-53^{\circ}$ uncor. One recrystallization from methanol (15 ml) yielded 1.9 g of needle-like white crystals of <u>68</u>, mp $55^{\circ}-55.5^{\circ}$ uncor (lit.⁶⁶ $55.5^{\circ}-56^{\circ}$). A small amount of triacontaine,⁶⁶ mp 66° was present as an impurity and could be effectively removed by elution on Silica Gel with hexane. Germacrone isolated in this manner had the following spectral characteristics: uv max (MeOH) 246 nm; ir (CHCl₂)

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5.97 (C=O), and sh 6.02 (C=C) μ ; nmr (CCl₄) τ 4.45-5.00 (m, 2, C₄ and C₈ vinyl <u>H</u>), 6.55-7.33 (m, 4, C₂ and C₉ C<u>H</u>₂), 7.88 (broad s, 4, C₅ and C₆ C<u>H</u>₂), 8.23 (s, 3, C₁₄ C<u>H</u>₃), 8.30 (s, 3, C₁₅ C<u>H</u>₃), 8.42 (s, 3, C₁₁ C<u>H</u>₃), and 8.60 (s, 3, C₁₂ C<u>H</u>₃). These spectra are in full agreement with those reported by V. G. Ohloff.⁶⁶

Synthesis of Isogermacrone.⁶⁶ A solution of germacrone (1.92 g, 0.0088 mole) in 50 ml of ethanolic 0.5 N potassium hydroxide was refluxed under nitrogen for 4 hrs. After this period, tlc (10% ether-benzene) indicated the presence of starting material and one new product; the latter being the most intense spot under iodine development. The solvent was removed in vacuo and the residue neutralized with 5% aqueous hydrochloric The mixture was then extracted with chloroform $(3 \times 50 \text{ ml})$. acid. The combined chloroform extracts were washed with water (2 x 50 ml) and dried (sodium sulfate). The chloroform was removed in vacuo to yield approximately 2 g of clear oil. Vpc column A-1 (200°, 60 m1/min) indicated the presence of four products, isogermacrone being the major one. Purification by column chromatography afforded 0.550 g of 60-80% pure isogermacrone (benzene as eluant), and 1.30 g of 90-95% pure isogermacrone (5% ether-benzene as eluant). Purity of chromatography fractions was determined by vpc column A-1 (200°, 60 ml/min). Crystallization of the clear oil, obtained from column chromatography, from methanol gave white crystals, mp 48° -50° uncor (lit.⁶⁶ 51°-52°). Isogermacrone exhibited the following spectral characteristics: uv max (hexane) 203, 252, and 330 nm; ir (CHCl₃) 6.00 (C=0), and 6.14 (C=C) μ ; nmr (CDCl₃) τ 3.99 (s, 1, C₂) vinyl <u>H</u>), 4.82 (t, 1, C₈ vinyl <u>H</u>), 6.82-7.20 (m, 2, C₉ C<u>H</u>₂), 7.40-8.60

(m, 6, C_4 , C_5 , and C_6 CH₂), 8.19 (d, 3, C_{14} CH₃), 8.32 (m, 6, C_{11} and C_{15} CH₃), and 8.48 (s, 3, C_{12} CH₃). These spectral characteristics are in full agreement with those previously reported for isogermacrone.⁶⁶

<u>Photolysis of Isogermacrone (69)</u>. A solution of <u>69</u> (0.454 g, 0.00208 mole) in 500 ml of benzene was photolysed internally through a Pyrex filter for 55 min. Tlc (10% ether-benzene) indicated the disappearance of starting material. Removal of the benzene <u>in vacuo</u> gave a quantitative recovery of yellow oil. Vpc column P-1 (200°, 60 ml/min) showed that the crude photolysis mixture contained seven products (<u>A</u> - <u>G</u>). Their retention times were as follows (compd, ret time, rel amount): <u>A</u>, 2.9 min, 1.00; <u>B</u>, 13.4 min, 9.07; <u>C</u>, 58.3 min, 4.86; <u>D</u>, 79.5 min, 96.8; <u>E</u>, 86 min, 59.0; <u>F</u>, 96 min, 10.47; <u>G</u>, 122 min, 18.81. Retention times were taken relative to the air peak. The major products at retention times 79.5 min (<u>70</u>, <u>D</u>) and 86 min (<u>71</u>, <u>E</u>) accounted for 78% of the total product mixture. Nmr (CDCl₃) of this crude mixture indicated the absence of vinyl hydrogens.

<u>Isolation of Photoproducts 70 and 71.</u> The above photomixture was subjected to preparative vpc column P-1 (200°, 60 ml/min). Photoproducts <u>70</u> and <u>71</u> were collected in this manner and found to be colorless liquids.

Photoproduct <u>70</u> exhibited the following spectral characteristics: ir (CHCl₃) 5.88 (C=O), and 6.14 (C=C) μ ; nmr (CDCl₃) τ 7.25-7.61 (broad m, 4), 7.78 (broad t, 3), 8.17 (broad s, 3), 7.92-9.0 (broad m, 6) 8.81 (s, 3, C₇-CH₃), and 8.92 (s, 3, C₁-CH₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 218(63), 207(37), 123(37), 122(50), 96(67), 91(37), 81(100), 79(57), 77(40), 68(63), and 67(47). <u>Anal</u>. Calcd for C₁₅H₂₂O: C, 82,51; H, 10.16. Found: C, 82.39; H, 10.21.

Photoproduct $\underline{71}$ had the following spectral properties: ir (CHCl₃) 5.88 (C=O), and 6.13 (C=C) μ ; nmr (CDCl₃) τ 7.18-7.97 (broad m, 6), 7.97-9.0 (broad m, 7), 8.12 (broad s, 3), 9.10 (s, 3, C₇-CH₃), 9.17 (s, 3, C₁-CH₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 218(12), 123(21), 122(52), 96(99), 95(80), 91(20), 81(100), 79(24), 77(20), 68(14), and 67(17).

<u>Anal.</u> Calcd for C₁₅H₂₂O: C, 82.51; H, 10.16. Found: C, 82.31; H, 9.98.

<u>Isolation of Photoproducts F and G</u>. Although present in small amounts, sufficient quantities of <u>F</u> and <u>G</u> needed for crude spectral analyses were obtained by preparative vpc (column P-1, 200°, 60 ml/min) separation of an isogermacrone photolysis mixture.

Photoproduct <u>F</u> collected in this manner gave the following spectral characteristics: ir (CHCl₃) 5.95 (C=O), and 6.16 (C=C) μ ; nmr (CDCl₃) τ 7.00-9.30 (featureless broad multiplet with large multiplet centres at τ 7.80(1), 8.25(3) and 8.90(2).

Photoproduct <u>G</u> collected under identical conditions showed the following spectral properties: ir (CHCl₃) 5.90 (C=0), 6.13 (C=C) μ ; nmr (CDCl₃) τ 6.6-9.4 (broad multiplet with broad singlets centred at τ 7.80(2), 8.17(2), 8.27(2), 9.13(1) and 9.25(1); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 218(100), 203(38), 175(27), 161(23), 147(32), 121(44), 119(32), 105(32), 96(47), 93(51), 91(66), 79(64), 77(44), 68(67), and 67(53). <u>Hydrogenation of Photoproduct 70 and 71</u>. A solution of <u>70</u> (.200 g, 0.00092 mole) in 15 ml ethyl acetate was hydrogenated over 8 mg of Adams Catalyst for 5 hrs. Filtration through Celite and removal of solvent <u>in vacuo</u> afforded 0.154 g of clear oil. Vpc column A-4 (165°, 60 ml/min) indicated that the product was 90% pure. This was further purified by collection on the same column. Hydrogenated <u>13</u> gave the following spectral characteristics: ir (CHCl₃) 5.82 (C=0) μ ; nmr (CDCl₃) τ 7.3-8.65 (featureless broad m, 10), 8.65-9.3 (featureless multiplet, 14); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 220(26), 178(25), 121(54), 122(32), 109(50), 107(39), 96(84), 95(61), 93(44), 81(100), 79(36), and 68(27).

<u>Anal</u>.Calcd for C₁₅H₂₄O: C, 81.73; H, 11.00. Found: C, 81.36; H, 11.18.

In an analogous manner $\underline{71}$ (50 mg, 0.227 mmoles) was hydrogenated to give 40 mg of crude product. Vpc column A-1 indicated that at least 80% of the mixture was one product. The following spectral characteristics were taken on this crude mixture: ir (CHCl₃) 5.82 (C=0) μ ; mass spectrum (purified by vpc collection) (70 eV) <u>m/e</u> (rel intensity) 220(7), 178(22), 136(19), 121(26), 109(21), 107(24), 96(90), 95(37), 93(27), 81(100), 79(29), and 68(25).

Synthesis of syn (73) and anti (74) 1,7-Dimethyltricyclo decane-<u>3-one.</u>⁹⁷ A solution of 1,2-dimethyl cyclopentene (Chemical Samples, 99% pure) (22.43 g, 0.233 mole) in absolute ether (175 ml) was photolysed through Corex for 8 hours. Cyclopentenone (Aldrich Chemical Co.) (13.00 g, 0.158 mole) was added dropwise to this solution at various times throughout the photolysis. The photolysis was followed by vpc column A-1 (150°, 60 ml/min). The ether and the majority of the starting materials were removed <u>in vacuo</u> to give 15.92 g of a yellow-orange liquid. According to column A-1, 57% of the crude product mixture was <u>73</u> and <u>74</u> in a 5:3 ratio respectively. The two desired products were isolated and purified by preparative vpc column P-3 (210°, 60 ml/min).

The following spectral properties were obtained for <u>73</u>: ir (CHCl₃) 5.83 (C=O) μ ; nmr (CDCl₃) τ 6.33 (s, 1, C₂ C<u>H</u>), 7.30-9.00 (broad m, 11, C₄, C₅, C₈, C₉, C₁₀ C<u>H</u>₂ and C₆ C<u>H</u>), 8.85 (s, 3, C₁₂-CH₃), and 8.93 (s, 3, C₁₁-CH₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 178(24), 121(30), 109(26), 107(30), 96(65), 95(36), 93(38), 91(37), 81(100), and 79(40).

<u>Anal</u>. Calcd for C₁₂H₁₈O: C, 80.81; H, 10.12. Found: C, 80.84; H, 10.25.

Photoproduct <u>74</u> exhibited the following spectral properties: ir (CHCl₃) 5.83 (C=0) μ ; nmr (CDCl₃) τ 6.38 (s, 1, C₂ CH), 7.45-8.05 (m, 5, C₄, C₅ CH₂ and C₆ CH), 8.05-8.80 (m, 6, C₈, C₉ and C₁₀ CH₂), 8.99 (s, 3, C₁₂-CH₃), and 9.11 (s, 3, C₁₁-CH₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 178(24), 136(20), 121(20), 107(18), 96(72), 95(27), 93(20), 81(100), and 79(24).

<u>Anal</u>. Calcd for C₁₂H₁₈O: C, 80.81; H, 10.12. Found: C, 80.59; H, 9.99.

<u>Condensation of syn-1,7-Dimethyltricyco[5.3.0.0^{2,6}]decane-3-one</u> (73) with Acetone.⁷² A solution of 73 (0.088 g, 0.00049 mole), acetone (0.440 g, 0.0076 mole), and sodium metal (0.0644 g, 0.0028 mole) in absolute ethanol (15 ml) was refluxed under nitrogen with stirring for four hrs. After this period, tlc (10% ether-benzene) indicated the disappearance of starting material and the formation of a single product. The solution was neutralized with dilute aqueous hydrochloric acid. The ethanol was removed <u>in vacuo</u> and the residue was taken up in 10 ml of ether and 10 ml of water. The layers were separated and the aqueous layer was extracted with ether (1 x 10 ml). The ether extracts were combined, washed with water (1 x 10 ml), and dried (Na_2SO_4). The ether was removed <u>in vacuo</u> to yield 0.095 g of yellow oil. Vpc column A-3 (170°, 40 ml/min) indicated that 95% of this oil was compound <u>70</u>. Purification by vpc (column A-3) afforded <u>70</u> which was identical (nmr, ir, mass spectrum) to <u>70</u> obtained in the photolysis of isogermacrone.

<u>Condensation of anti-1,7-Dimethyltricyclo[5.3.0.0^{2,6}]decane-3-one⁷²</u> (74) with Acetone. In a similar manner 74 (0.131 g, 0.00074 mole) was condensed with acetone (1.4 g, 0.0242 mole) in an ethanolic solution (15 ml) containing sodium metal (0.0856 g, 0.00372 mole). Workup in the usual manner yielded 0.170 g of yellow oil. Vpc column A-3 (170°, 40 ml/min) indicated that 88% of the oil was compound 71. Purification by vpc yielded pure 71 which was indistinguishable (nmr, ir, mass spectrum) from 71 isolated in the photolysis of isogermacrone.

C) ACYCLIC DIENE-DIESTER

Preparation of Diethyl trans,trans-deca-2,8-diene-1,10-dioate.^{74,75} A mixture of 1,10-decanedioic acid (Eastman Organic Chemicals, technical grade) (120 g, 0.59 mole) and thionyl chloride (BDH) (171 g, 1.43 mole) in a flame dried three-necked 1 litre round bottom flask fitted with a

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condenser and drying tube was refluxed at 90° for 2 hrs. Heating was discontinued, and bromine (AnalaR) (229 g, 1.43 mole) was added dropwise to the clear yellow solution.⁷⁴ During the addition the complete apparatus was irradiated with a 275W sun lamp. After the addition was complete (1 hr), the dark brown solution was heated in the dark between 90 and 100° for 5 hrs. The solution was then cooled to 0° and absolute ethanol (165 ml) was added dropwise followed by a solution of sodium bicarbonate (25.84 g, 0.308 mole) in 205 ml of water. Chloroform (200 ml) was added and the two layers were separated. The aqueous layer was extracted with chloroform (2 x 100 ml). The combined chloroform extracts were washed with saturated sodium bicarbonate solution (2 x 200 ml), water (2 x 200 ml) and saturated sodium bicarbonate solution (2 x 200 ml), decolorized (Norit), and dried (MgSO4). The chloroform was removed in vacuo to yield 210 g of a light yellow liquid. The following spectral data confirmed this liquid to be diethyl-2,8-dibromodecane-1,10-dioate: ir (neat) 5.78 (C=0) μ ; nmr (CC1₄) τ 5.78 (q, 4, COOCH₂CH₃), 4.00 (t, 2, J_{2,3} = 7.2 Hz, CHBr-COOEt), 8.00 (m, 4, CH2CHBr-COOEt), and 8.70 (m, 8, C4, C5, C6, and C7 CH2). The crude yellow oil (210 g, 0.504 mole) was refluxed in dimethyl formamide (420 ml) for 4 hrs.⁷⁵ The solution was cooled and to it were added 800 ml of water and 300 ml of ether. The mixture was then separated. The aqueous layer was extracted with ether $(2 \times 100 \text{ ml})$ and the ether extracts were combined. These were washed with water (2 x 200 ml) and saturated sodium chloride solution (2 x 200 ml), decolorized (Norit), and dried (MgSO $_4$). The ether was removed in vacuo to give 124 g (97%) of an orange liquid. Vpc column

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A-2 (170°, 120 ml/min) indicated that 60% of the crude product mixture was <u>79</u> and that 20% of it was the <u>cis,trans</u> isomer <u>80</u>. Distillation through a Vigreux column resulted in a colorless liquid, bp 104° at 0.02 mm (reported⁷⁵ bp 127° at 0.28 mm). Further distillations were necessary to completely separate <u>79</u> from the product mixture. Compound <u>79</u> prepared in this manner showed the following spectral data: uv max (hexane) 207 nm (ε 23,000), and sh 241 nm (ε 410); ir (neat) 5.81 (C=0), 6.06, and 10.15 µ; nmr (CC1₄) τ 3.06 (d of t, 2, J_{2,3} = J_{8,9} = 15.5 Hz, J_{3,4} = J_{7,8} = 6.8 Hz, <u>trans</u> CH=CH-COOEt), 4.22 (d, 2, J_{2,3} = J_{8,9} = 15.5 Hz, <u>trans</u> CH=CH-COOEt), 5.85 (q, 4, COOCH₂CH₃), 7.78 (broad d, 4, J_{3,4} = J_{7,8} = 6.8 Hz, C₄ and C₇ CH₂), 8.50 (m, 4, C₅ and C₆ CH₂), and 8.73 (t, 6, COOCH₂CH₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 254(9), 209(24), 208(23), 182(28), 181(70), 163(57), 16237), 152(14), 140(24), 135(97), 134(75), 108(26), 107(100), 106(45), 93(30), 89(29), 81(66), 79(51), 68(47), and 67(58).

<u>Direct Photolysis of Diethyl trans,trans-deca-2,8-diene-1,10-</u> <u>dioate (79)</u>. This photolysis could be carried out in either methanol or hexane with no observed differences; the following description is typical. Diene-diester <u>79</u> (2.54 g, 10 mmole) in 1 1. of methanol was irradiated through Vycor and the course of the reaction followed by analytical vapour phase chromatography using column A-2 (170°, 120 ml/min). Five new peaks in addition to starting material were observed corresponding to photoproducts <u>80</u>, <u>81</u>, <u>115</u>, <u>116</u> and <u>117</u> the latter being the ultimate sole product after 2.5 hrs of irradiation.⁹⁸ The retention times were as follows (ret time, compound): 10.5 min, <u>81</u>; 11.7 min, <u>116</u>; 12.9 min, <u>117</u>; 16.2 min, <u>80</u>; 17.5 min, <u>115</u>; and 28.2 min, 79.

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Isolation and Identification of Photoproducts 80, 81, 115, 116, and 117. Irradiation as above for 90 min led to near-maximum amounts of photoproducts 80, 81, 115 and 116. These products were separated and isolated by vpc column P-2 (175°, 200 ml/min). Photoisomer 117 was isolated by preparative vpc column P-1 (200°, 60 ml/min) of the final (2.5 hr) photolysis mixture. All the products were colorless liquids.

The structure of <u>80</u> was deduced to be diethyl <u>cis,trans</u>-deca-2,8diene-1,10-dioate from the following data: uv max (isooctane) 208 nm (ε 22,000), and sh 241 nm (ε 425); ir (neat) 5.81 (C=0), 6.07, 10.04, and 11.97 μ ; nmr (CCl₄) τ 3.20 (d of t, 1, J_{8,9} = 15.5 Hz, J_{7,8} = 6.8 Hz, <u>trans</u> CH=CH-COOEt), 3.92 (d of t, 1, J_{2,3} = 11.5 Hz, J_{3,4} = 7.3 Hz, <u>cis</u> CH=CH-COOEt), 4.32 (d, 1, J_{8,9} = 15.5 Hz, <u>trans</u> CH=CH-COOEt), 4.36 (d, 1, J_{2,3} = 11.5 Hz, <u>cis</u> CH=CH-COOEt), 5.94 (q, 4, COOCH₂CH₃), 7.37 (broad d, 2, J_{3,4} = 7.3 Hz, C₄ CH₂), 7.80 (broad d, 2, J_{7,8} = 6.8 Hz, C₇ CH₂), 8.52 (m, 4, C₅ and C₆ CH₂), and 8.76 (t, 6, COOCH₂CH₃); mass spectrum parent (70 eV) <u>m/e</u> 254. Photoproduct <u>2</u> was identical to an independently prepared sample of diethyl <u>cis,trans</u>-deca-2,8diene-1,10-dioate.⁷⁵

Photoisomer <u>81</u> was shown to be diethyl <u>cis,cis</u>-deca-2,8-diene-1,10-dioate from the following: ir (neat) 5.82 (C=0), 6.07, and 12.04 μ ; nmr (CC1₄) τ 3.91 (d of t, 2, J_{2,3} = J_{8,9} = 11.6 Hz, J_{3,4} = J_{7,8} = 7.3 Hz, <u>cis</u> CH=CH-COOEt), 4.38 (d, 2, J_{2,3} = J_{8,9} = 11.6 Hz, <u>cis</u> CH=CH-COOEt), 5.95 (q, 4, COOCH₂CH₃), 7.37 (broad d, 4, J_{3,4} = J_{7,8} = 7.3 Hz, C₄ and C₇ CH₂), 8.53 (m, 4, C₅ and C₆ CH₂), and 8.78 (t, 6, COOCH₂CH₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 254(2), 209(10), 181(14), 173(16), 149(36), 135(19), 107(15), 95(17), 91(30), 81(100), and 67(21). <u>Anal</u>. Calcd for C₁₄H₂₂O₄: C, 66.12; H, 8.72. Found: C, 65.94; H, 8.59.

Photoisomer <u>115</u> was shown to have the structure diethyl <u>trans, trans</u>deca-3,8-diene-1,10-dioate from the following data: ir (neat) 5.79 (C=0), 5.82 (C=0), 6.07, and 10.18 μ ; nmr (CC1₄) τ 3.18 (d of t, 1, J_{8,9} = 15.4 Hz, J_{7,8} = 6.8 Hz, <u>trans</u> CH=CH-COOEt), 4.32 (d, 1, J_{8,9} = 15.4 Hz, <u>trans</u> CH=CH-COOEt), 4.50 (m, 2, CH=CH), 5.90 (q, 2, COOCH₂CH₃), 5.92 (q, 2, COOCH₂CH₃), 7.07 (m, 2, C₂ CH₂), 7.85 (m, 4, C₅ and C₇ CH₂), 8.38 (m, 2, C₆ CH₂), and 8.70 (t, 6, COOCH₂CH₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 254(2.5), 209(15), 208(14), 179(18), 163(19), 162(22), 140(34), 135(58), 134(50), 114(58), 107(62), 99(30), 93(43), 86(45), 81(79), 79(41), 68(76), and 67(100).

<u>Anal</u>. Calcd for C₁₄H₂₂O₄: C, 66.12; H, 8.72. Found: C, 65.94; H, 8.80.

Photoproduct <u>116</u> was proved to be diethyl deca-<u>trans</u>-3-<u>cis</u>-8diene-1,10-dioate from the following: ir (neat) 5.79 (C=0), 5.83 (C=0), 6.12, 10.14, and 11.93 μ ; nmr (CC1₄) τ 3.91 (d of t, 1, J_{8,9} = 11.5 Hz, J_{7,8} = 7.2 Hz, <u>cis</u> CH=CH-COOEt), 4.37 (d, 1, J_{8,9} = 11.5 Hz, <u>cis</u> CH=CH-COOEt), 4.53 (m, 2, CH=CH), 5.95 (q, 2, COOCH₂CH₃), 5.97 (q, 2, COOCH₂CH₃), 7.09 (m, 2, C₂ CH₂), 7.38 (broad d, 2, J_{7,8} = 7.2 Hz, C₇ CH₂), 7.93 (m, 2, C₅ CH₂), 8.43 (m, 2, C₆ CH₂), 8.75 and 8.78 (t, 6, COOCH₂CH₃); mass spectrum parent (70 eV) <u>m/e</u> 254.

<u>Anal</u>.Calcd for C₁₄H₂₂O₄: C, 66.12; H, 8.72. Found: C, 66.14; H, 8.55.

Compound <u>117</u> was identified as diethyl <u>trans</u>,<u>trans</u>-deca-3,7-diene-1,10-dioate on the basis of the following information: uv max (hexane) 208 nm (ε 1300); ir (neat) 5.74 (C=0), and 10.27 μ ; nmr (CC1₄) τ 4.45 (m, 4, C<u>H</u>=C<u>H</u>), 5.87 (q, 4, COOC<u>H</u>₂CH₃), 6.97 (m, 4, C₂ and C₉ CH₂), 7.87 (broad s, 4, C₅ and C₆ CH₂), and 8.73 (t, 6, COOCH₂C<u>H₃</u>), mass spectrum (70 eV) <u>m/e</u> (rel intensity) 254(21), 209(57), 208(50), 181(69), 179(50), 162(35), 135(91), 134(53), 127(67), 108(59), 107(78), 99(53), 93(78), 91(60), 85(72), 81(83), 79(100), and 67(86).

The nmr (HA-100) of a CCl₄ solution containing 70 mg of <u>117</u> plus 30 mg of Eu(DPM)₃⁹³ showed the following signals attributable to the vinyl hydrogens at C₃ and C₈: τ 3.30 (d of t, 2, J_{3,4} = J_{7,8} = 15.7 Hz, J_{2,3} = J_{8,9} = 6.8 Hz, <u>trans</u> CH=CH-CH₂-COOEt). The C₄ and C₇ vinyls appeared as: τ 3.68 (broad d, 2, J_{3,4} = J_{7,8} = 15.7 Hz, <u>trans</u> C<u>H</u>=CH-CH₂-COOEt). Irradiation at C₂ and C₉ caused the C₃ and C₈ vinyl hydrogens to appear as a doublet, J = 15.5 Hz. Irradiation at C₅ and C₆ caused sharpening of the C₄ and C₇ doublet.

A 60% aqueous dioxane solution of <u>117</u> (150 mg) containing 0.3 ml of conc HCl was refluxed under nitrogen for 22 hrs. Removal of the solvent <u>in vacuo</u> afforded a wet white solid residue which was recrystallized from water, filtered, and dried over P_2O_5 <u>in vacuo</u> to yield 35 mg of yellow crystals. Norit decolorization followed by a further recrystallization from water afforded 25 mg of pure <u>trans,trans</u>deca-3,7-diene-1,10-dioic acid, mp 118°-120° (1it.⁹⁵ 118°-120°). ir (KBr) 3.56 (OH), 5.91 (C=O), and 10.37 µ; nmr (DMSO d₆) τ 4.47 (m, 4, C<u>H=CH</u>), 7.03 (m, 4, C₂ and C₉ CH₂), and 7.90 (s, 4, C₅ and C₆ CH₂). This material was identical (mixed mp, ir, and nmr) to an authentic sample.⁹⁵ <u>Anal</u>. Calcd for C₁₀H₁₄O₄: C, 60.59; H, 7.12. Found: C, 60.63; H, 7.21.

<u>Direct Photolysis of Diethyl cis,trans-deca-2,8-diene-1,10-</u> <u>dioate (80)</u>. Compound <u>80</u> (211 mg) in 200 ml of hexane was irradiated through a Vycor filter and the course of the reaction followed by vpc column A-2 (160°, 180 ml/min). Peaks attributable to photoproducts <u>81, 115, and 116 grew and then diminished while the peak due to 80</u> steadily decreased and that due to <u>117</u> steadily increased. After 30 min, <u>117</u> was the only product detectable by vpc.⁹⁸ A peak corresponding to <u>79</u> was not observed at any time during the photolysis. A preparative vpc-collected (column P-1, 200°, 60 ml/min) sample of <u>117</u> from this run was identical to previous samples.

Direct Photolysis of Diethyl trans, trans-deca-3,8-diene-1,10dioate (115). Compound 115 (62 mg) in 45 ml of hexane was photolysed externally through Corex and the reaction followed by vpc column A-2 (159°, 150 ml/min). For the first hour the disappearance of 115 and the appearance of 116 was observed. At this point a peak corresponding to 117 appeared, until after 2.15 hrs there were approximately equal amounts of 115, 116 and 117. After 3.6 hrs, 117 was the sole product (> 95%) detectable by vpc. At no point during the photolysis were peaks corresponding to isomers 79, 80 or 81 observed. A sample of 117 from this run, collected by preparative vpc (column P-1, 200°, 60 ml/min) was identical to previous samples.

Acetone-Sensitized Photolysis of Diethyl trans, trans-deca-2,8diene-1,10-dioate (79). Diene-diester 79 (1.27 g, 5 mmole) in 400 ml of acetone was irradiated through Corex (λ > 260 nm) and the course of the reaction followed by analytical vpc using column A-2 (170°, 120 ml/min). The percentage of the incident irradiation absorbed by the acetone at various wavelengths was calculated using the relation: % light absorbed by sensitizer = $C_S \varepsilon_S/C_S \varepsilon_S + C_D \varepsilon_D$ in which S refers to the sensitizer (acetone), D is the substrate being sensitized (diene-diester), C is the molar concentration, and ε is the extinction coefficient at the wavelength in question. The calculated percentages are as follows (wavelength, %): 255 nm, 97.7%; 260 nm, 98.7%; 265 nm, 99.2%. After 40 min a photostationary state mixture of products <u>79</u>, <u>80</u>, and <u>81</u> (94%) was formed in the ratio of 3.8 : 3.5 : 1.0. These products were isolated by column P-2 (170°, 200 ml/min) and identified by ir, nmr, and vpc retention time.

In a separate experiment, 0.51 g (2 mmole) of <u>79</u> in 500 ml of acetone was irradiated through Corex until vpc column A-2 indicated the presence of products <u>82</u> - <u>85</u> and the disappearance of geometric isomers <u>79</u> - <u>80</u> (8.5 hrs). The <u>79</u> : <u>80</u> : <u>81</u> ratio remained constant at 3.8 : 3.5 : 1.0 during the transformation into cyclized products <u>82</u> - <u>85</u>. Compounds <u>82</u> - <u>85</u> had the following retention times on column A-2 (150°, 200 ml/min): 11.8 min, <u>82</u>; 15.1 min, <u>83</u>; 16.2 min, <u>85</u>; and 19.7 min, <u>84</u>. The products were formed in the following relative amounts (average of three runs): <u>82</u> (42%), <u>83</u> (15%), <u>84</u> (36%), and <u>85</u> (7%); further irradiation led to loss of yield and eventual loss of any isolable products.

Isolation and Identification of Cyclized Products 82 - 85. The crude photolysate from above (525 mg) was subjected to preparative vpc on column P-2 (165°, 200 ml/min) and the isolated products <u>82</u> - <u>85</u> further purified by Kugelrohr distillation; all were colorless liquids. On

larger scale photolyses the crude photolysate was initially purified by elution on silica gel with 10% ether-benzene. This effectively removed any acetone by-products and any polymers which may have formed. The purified photolysate was then subjected to vpc separation as described above.

Photoproduct 82 had the following spectral characteristics: ir (neat) 5.97 (C=0) μ ; nmr (CCl₄) τ 5.88 (q, 4, COOCH₂CH₃), 6.80 (d, J = 9.5 Hz, 2, CH-COOEt), 7.57 (m, 2, CH-CH-COOEt), 8.43 (m, 8, cyclohexane ring CH₂), and 8.70 (t, 6, COOCH₂CH₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 255(.67), 254(.80), 225(1.1), 210(2.5), 209(17), 208(4.2), 182(13), 181(100), 180(4.6), 173(4.1), 153(5.1), 145(3.5), 136(5.9), 135(45), 134(4.8), 127(9.5), 117(5.2), 105(4.5), 107(19), 99(7.9), 93(6.3), 91(6.0), 81(8.7), 79(17), 77(5.7), and 67(14).

Photoproduct <u>83</u> exhibited the following spectral data: ir (neat) 5.79 (C=0) μ ; nmr (CCl₄) τ 5.88 (q, 4, COOC<u>H</u>₂CH₃), 6.80 (d, J = 9.5 Hz, 2, C<u>H</u>-COOEt), 7.57 (m, 2, C<u>H</u>-CH-COOEt), 8.43 (m, 8, cyclohexane ring CH₂), and 8.70 (t, 6, COOCH₂C<u>H</u>₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 254(6), 209(20), 208(9.5), 181(31), 182(11), 173(54), 149(30), 145(21), 135(35), 134(11), 127(34), 117(15), 107(25), 99(19), 96(16), 93(14), 91(20), 81(100), 79(30), 77(20), and 67(29).

Photoisomer <u>84</u> had the following spectral characteristics: ir (neat) 5.78 (C=0) μ ; nmr (CCl₄) τ 5.95 (q, 4, COOC<u>H</u>₂CH₃), 7.05 (m, 2, C<u>H</u>-COOEt), 7.34 (m, 2, C<u>H</u>-CH-COOEt), 8.52 (m, 8, cyclohexane ring CH₂), and 8.80 (t, 6, COOCH₂C<u>H</u>₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 255(2.3), 254(2.6), 209(45), 208(31), 182(14), 181(100), 180(15), 173(9), 153(13), 136(9), 135(72), 134(13), 127(23), 117(13), 107(31), 105(12), 99(35), 93(15), 81(20), 79(49), 77(18), and 67(40).

Photoproduct <u>85</u> could not be obtained free of isomer <u>83</u> due to their similar vpc retention times. Spectra of <u>85</u> slightly contaminated with <u>83</u> were in accord with the structure proposed: ir (neat) 5.80 (C=O) μ ; nmr (CCl₄) τ 5.90 (q, 2, COOC<u>H</u>₂CH₃), 5.93 (q, 2, COOC<u>H</u>₂CH₃), 6.40-9.00 (m, 12, C<u>H</u>-C<u>H</u>-(C<u>H</u>₂)₄-C<u>H</u>-C<u>H</u>), 8.72 and 8.73 (t, 6, COOCH₂C<u>H</u>₃); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 254(1.6), 225(1.1), 210(6.1), 209(38), 208(10), 182(13), 181(100), 180(7.4), 173(6.8), 153(5.8), 136(6.3), 135(50), 134(5.8), 127(15), 117(4.5), 107(15), 99(12), 93(7.1), 91(5.8), 81(12), 79(13), and 67(14). The structure of <u>85</u> was proved by sodium ethoxide-catalyzed epimerization (<u>vide infra</u>) to the more stable <u>trans</u>-fused isomer <u>82</u> in direct analogy to results obtained with the corresponding <u>dimethy1</u> esters.⁷⁸

The structures of photoproducts $\underline{82} - \underline{84}$ were proved by direct comparison (retention time, ir, and nmr) with authentic samples obtained by the photoaddition of diethyl maleate to cyclohexene.⁷⁷ A solution of diethyl maleate (26.6 g, 0.155 mole) in cyclohexene (200 ml, 162 g, 1.98 mole) was irradiated through Vycor for 9 hrs. Removal of the cyclohexene <u>in vacuo</u> afforded 32.5 g of crude product mixture. This yellow oil was distilled (0.05 mm) and then subjected to preparative vpc column P-2 (163°, 120 ml/min). Four peaks corresponding in retention times to <u>82</u> - <u>85</u> were collected. Three of these proved to be identical (retention times, ir, and nmr) to <u>82</u>, <u>83</u>, and <u>84</u>. The remaining compound corresponding in retention time to <u>85</u> was found to be unsaturated. Further evidence for the structures of <u>82</u>, <u>83</u> and <u>84</u> came from their hydrolyses to the known dicarboxylic acids. In general one mmole of diester was refluxed in 5 ml of aqueous 2 N NaOH under nitrogen for 2 hrs. The solution was acidified (aqueous HCl) to litmus, cooled, and centrifuged. The white solid was washed twice with cold water.

<u>trans, anti, trans</u>-Bicyclo[4.2.0]octane-7,8-dicarboxylic acid obtained from the hydrolysis of <u>82</u> was recrystallized once from ethyl acetate-petroleum ether to give the pure diacid, mp 180°-182° (lit.⁷⁷ 181°-182°); nmr (DMSO-d₆) τ 7.17 (m, 2, CH-COOH), 8.53 (m, 10, -CH-(CH₂)₄-CH).

Similarly <u>83</u> afforded, after two recrystallizations from 20% acetonebenzene, pure <u>cis,trans</u>-bicyclo[4.2.0]octane-7,8-dicarboxylic acid, mp 197°-198° (lit.⁷⁷ mp 199°-200°); nmr (acetone d₆) τ 6.70 (d, 2, CHCOOH), 7.47 (m, 2, CH-CH-COOH), and 8.43 (m, 8, cyclohexane ring CH₂).

Hydrolysis of <u>84</u> gave <u>cis,anti,cis</u>-bicyclo[4.2.0]octane-7,8dicarboxylic acid. Three recrystallizations from ethyl acetate-petroleum ether gave a mp of 170°-172° (lit.⁷⁷ 174°-176°); nmr (acetone d_6) τ 6.87 (m, 2, C<u>H</u>-COOH), 7.30 (m, 2, C<u>H</u>-CH-COOH), and 8.43 (m, 8, cyclohexane ring CH₂).

<u>Acetone-Sensitized Photolysis of Diethyl-cis,trans-deca-2,8-diene-</u> <u>1,10-dioate (80)</u>. Diene-diester <u>80</u> (0.16 g, 0.63 mmole) in 200 ml of acetone was irradiated through Corex to give an initial 3.8 : 3.5 : 1.0 mixture of products <u>79, 80</u>, and <u>81</u> respectively. Further photolysis (2.8 hrs) caused the disappearance of geometric isomers <u>79 - 81</u> with the concommitant formation of cyclized products <u>82 - 85</u> in the following relative amounts: <u>82</u> (44%), 83 (18%), 84 (31%), and <u>85</u> (7%). These photoproducts were identical in vpc retention times and spectral characteristics to those previously observed.

Acetone-Sensitized Photolysis of Diethyl-cis, cis-deca-2, 8-diene-1,10-dioate (81). Diene-diester 81 (89 mg, 0.35 mmole) in 50 ml of acetone was irradiated externally through Corex until only photoproducts 82 - 85 were present (5.5 hrs). Removal of the acetone yielded 0.144 g of yellow oil. The products were separated by preparative vpc column P-2 (170°, 150 ml/min) and were identical in all respects to those obtained in the photolysis of 79 and 80. The initially formed geometric isomers never reached an equilibrium state as in the photolysis of 79 and 80, and the final 82 - 85 photostationary state mixture differed as follows: 82 (26%), 83 (17%), 84 (49%), and 85 (8%).

Acetophenone-Sensitized Photolysis of 79. trans,trans-Diene-diester 79 (0.254 g, 1 mmole) and acetophenone (0.240 g, 2 mmole) in 200 ml of benzene were irradiated through Pyrex and the reaction followed carefully by column A-2 (168°, 200 ml/min). Initially the ratios of 79, 80, and 81 were identical to those found in the acetone-sensitized photolysis of 79 and 80. After 24 hrs, only products 82 - 85 remained in the following relative amounts (obtained from column P-2, 170°, 180 ml/min): 82 (45%), 83 (16%), 84 (31%), and 85 (8%). The photoproducts were identified by their vpc retention times and ir spectra which were identical to previously isolated samples. Benzophenone was also found to sensitize the cycloaddition, but because of its retention time, the ratios of $\underline{82} - \underline{85}$ could not be obtained. Naphthalene failed to sensitize the photocycloaddition. <u>Base-Catalyzed Epimerization of Cyclized Products 82 - 85</u>. Diethyl <u>trans, anti, trans</u>-bicyclo[4.2.0]octane-7,8-dicarboxylate (82) (0.052 g, 0.21 mmole) and sodium (5 mg) in 1.5 ml of abs ethanol were sealed in a vial and heated for 12 hrs at 80°. The ethanol was removed <u>in vacuo</u>, water added, and the mixture acidified (aqueous HCl) to litmus. The aqueous layer was extracted with chloroform (5 x 2 ml). The combined chloroform extracts were washed with water (1 x 4 ml) and dried (MgSO₄). The chloroform was removed <u>in vacuo</u> to yield 0.036 g of oil. Analytical vpc column A-2 (168°, 200 ml/min) indicated the presence of three products in the ratio 87 : 10 : 3. The first of these was identical to starting material (vpc, ir, nmr), and the second was shown to be stereoisomer <u>85</u> by vpc retention time and ir. The third product, present in minute quantities, was not isolated.

<u>cis,anti,cis</u>-Diester <u>84</u> (0.068 g, 0.28 mmole) under identical conditions gave 0.054 g of oil. Column A-2 (168°, 200 ml/min) showed two products in an 86 : 14 ratio. Spectral data and vpc retention times proved the major product to be photoproduct <u>83</u> and the minor product to be 84.

A 50 : 50 mixture of isomers <u>83</u> and <u>85</u> (0.047 g, 0.19 mmole) gave four products corresponding in retention times to <u>82</u>, <u>83</u>, <u>84</u>, and <u>85</u> after being subjected to the basic conditions previously described. The ratios of <u>82</u> : <u>85</u> and <u>83</u> : <u>84</u> were 90 : 10 and 85 : 15 respectively. Compounds <u>82</u> and <u>84</u> prepared in this manner had identical spectral properties to those previously observed.

Thermolysis of Diesters 82, 83, and 84. Diester 84 (0.030 g, 0.11 mmole) was heated in a sealed tube at 250° for 88 hrs. Vpc column

A-2 (168°, 100 ml/min) indicated that the diester slowly thermolysed to diester <u>83</u>. After 28 hrs, no further change in the <u>83</u> : <u>84</u> ratio was observed. This ratio consisted of 81% <u>83</u> and 19% <u>84</u>; the identity of both was authenticated by vpc and ir. With the exception of two low retention time products (diethyl maleate and cyclohexene on the basis of retention times, sum < 1%), these were the only two products observed.

Diester $\underline{83}$ (0.030 g, 0.11 mmole) under identical conditions gave a mixture of 83 (82%) and 84 (18%) after 62 hrs.

Diester <u>82</u> initially appeared to give the same products as in its base-catalyzed epimerization, but upon increased thermolysis times (88 hrs), <u>82</u> was converted to a mixture of five products in the ratio of 1.1 : 1.0 : 3.3 : 1.6 : 1.2. The first of these is diester <u>82</u>. The remaining products were not identified.

D) CYCLONONA-2,6-DIENONE

Synthesis of 9,9-Dibromobicyclo[6.1.0]non-4-ene (123).⁹⁹ Dry t-BuOH (1 1.) was poured into a flame dried 2 1. 3-necked flask, fitted with an overhead mechanical stirrer, a nitrogen inlet, and a condenser equipped with a drying tube. Potassium metal (50 g, 1.28 mole) was added with stirring to the t-BuOH. Refluxing proved necessary to completely react last traces of potassium. The clear pale yellow solution was then distilled to remove the t-BuOH at a pot temperature of 90°C. When the potassium t-butoxide came out of solution, 200 mls of pentane were added and then removed by distillation. This was repeated six times. Heating was discontinued and an additional 300 mls

of pentane were added. This white suspension of potassium t-butoxide in pentane was cooled in a salt-ice bath. To this cooled suspension was added cyclooctadiene (107 g, 1.0 moles). Then, with stirring, a pentane (200 ml) solution of bromoform (253 g, 1.0 mole) was added dropwise over a period of 5 hrs. The mixture was then stirred overnight at room temperature. It was then poured into 800 mls of water and filtered to give 63.5 g of 9,9,10,10-tetrabromotricycl0[7.1.0.0 1,8]decane, mp 179°-182° uncor (lit. ⁹⁹ mp 174°-180°). The filtrate was separated into an aqueous layer and a pentane layer. The aqueous layer was extracted once with ether (200 mls). This was then combined with the pentane layer and washed with water (6 x 200 ml), saturated sodium chloride solution (2 x 200 ml), dried (MgSO₄) and removed <u>in vacuo</u> to give 181.4 g of a clear dark orange-red liquid, bp 51.5°-52.5° at 0.008 mm. Tlc (20% benzene-pentane) indicated the presence of only one product. Compound 123 showed the following spectral characteristics: ir (neat) 3.46, 6.74, and 6.69 $\mu;$ nmr (CCl_1) τ 4.47 (broad s, 2, CH=CH), 7.30-8.53 (m, 10, C_1 and C_8 CH and C_2 , C_3 , C_6 , and C_7 CH_2).

Synthesis of 2-Bromo-3-acetoxy-trans, cis_cyclonona-1,6-diene (124). 100 An acetic acid (675 ml) of compound <u>123</u> (142 g, 0.507 mole) and AgOAc (87 g, 0.52 mole) was stirred at room temperature under nitrogen for 48 hrs. After this period the mixture was filtered to remove the precipitated AgBr formed, and diluted with 400 ml of water and 400 ml of ether. The layers were separated and the aqueous layer was extracted with ether (2 x 400 ml). The combined ether extracts were washed with water (5 x 400 ml), saturated aqueous NaHCO₃ solution (5 x 400 ml), water (2 x 400 ml) and saturated NaCl solution (2 x 100 ml). The ether was dried (MgSO₄) and removed <u>in vacuo</u> to give 112 g of light yellow liquid. Tlc (benzene) indicated that all the starting material (<u>123</u>) was gone and only the acetate (<u>124</u>) was present. Compound <u>124</u> was found to possess the following spectral properties: ir (neat) 5.77 (C=O) and 6.08 (HC=CBr) μ ; nmr (CCl₄) τ 4.00 (t, 1, CH=CHBr), 4.67 (m, 2, CH=CH), 4.97 (m, 1, CHOAc), 7.97 (s, 3, OCOCH₃), and 7.53-8.53 (m, 8, C₄, C₅, C₈, and C₉ CH₂).

Synthesis of 2-Bromo-3-hydroxy-trans, cis-cyclonona-1,6-diene (125).¹⁰⁰ A solution of 124 (112 g, 0.432 mole) and sodium hydroxide (18 g, 0.450 mole) in 700 ml of methanol was stirred at room temperature under nitrogen for 6 hrs. After this period tlc (10% etherbenzene) indicated the absence of starting material and the appearance of one new product. The methanol was removed in vacuo, water added, and the mixture extracted with 200 ml of ether. The aqueous layer was neutralized and extracted with ether (200 ml). The combined ether extracts were washed with water (2 x 200 ml) and saturated sodium chloride solution (2 x 200 ml), and dried (MgSO,). The ether was removed in vacuo to give 85 g of a wet yellow solid. This was recrystallized from ether-hexane, after treatment with Norit, to give 49.5 g of white crystals, mp 80°-83°. A second recrystallization raised the mp to 88.5°-89°. Compound 125 gave the following spectral data: ir (CHCl₃) 2.94 (OH) and 6.12 (C=C) $\mu;$ nmr (CCl₄) τ 4.20 (t, 1, CH=CHBr), 4.70 (m, 2, CH=CH), 6.03 (m, 1, CHOH), and 7.50-8.70 (m, 9, C_4 , C_5 , C_8 , and C_9 CH₂ and C_3 OH).

Synthesis of trans, cis-Cyclonona-2, 6-dienol (127).¹⁰¹ A solution of <u>125</u> (6 g, 0.0276 mole) in ether (200 ml) was added dropwise over a

period of 20 min to a stirred, refluxing solution of sodium (11.3 g, 0.492 mole) in liquid NH₃ (200 ml). The mixture was stirred for an additional 40 min. Ammonium chloride (30 g, 0.561 mole) was added followed by 200 ml water. The layers were separated and the aqueous layer was extracted with ether (2 x 100 ml). The combined ether extracts were washed with water (4 x 100 ml) and dried (MgSO₄). The ether was removed <u>in vacuo</u> to give 3.181 g (85%) of a colorless liquid. Tlc (20% ether-benzene) indicates that there is only one new product present. After Kugelrohr distillation compound <u>127</u> gave the following spectral data: ir (neat) 2.97 (OH), 6.03 (C=C) μ ; nmr (CCl₄) τ 4.14-5.12 (m, 4, CH=CH), 5.80-6.18 (m, 1, CHOH), 6.76 (s, 1, C₁ OH), and 7.56-8.84 (m, 8, C₄, C₅, C₈ and C₉ CH₂).

<u>Anal</u>. Calcd for C₉H₁₄O: C, 78.28; H, 10.14. Found: C, 78.19; H, 10.04.

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