

A PROPOSED STUDY OF THE CYCLOPENTADIENYL ANION  
USING CARBON-14 AS A TRACER.

by

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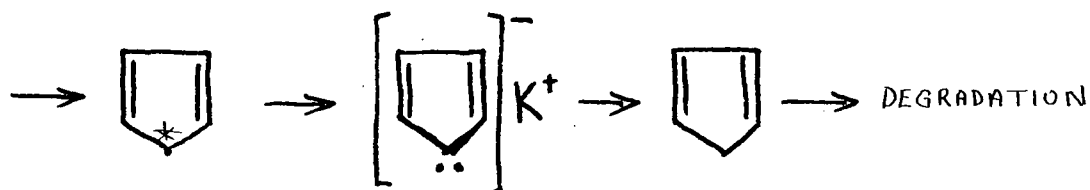
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### ABSTRACT

It is thought that some information about the bond structure in the cyclopentadienyl anion can be provided by synthesizing cyclopentadiene-5- $C^{14}$ , making the cyclopentadienyl anion (as the potassium salt), and degrading the cyclopentadiene regenerated from this anion for the determination of the distribution of carbon-14:



A method for the synthesis of cyclopentadiene, starting from formaldehyde, has been shown. The potassium cyclopentadienyl salt was then made. The cyclopentadiene regenerated from this salt was completely degraded. Repetition of this work, using formaldehyde- $C^{14}$  would give the desired cyclopentadiene-5- $C^{14}$ , etc.

Using carbon-14, the precursor to cyclopentadiene-5- $C^{14}$  was made, but the synthesis of cyclopentadiene-5- $C^{14}$  could not be carried out in the available time.

### ACKNOWLEDGMENT

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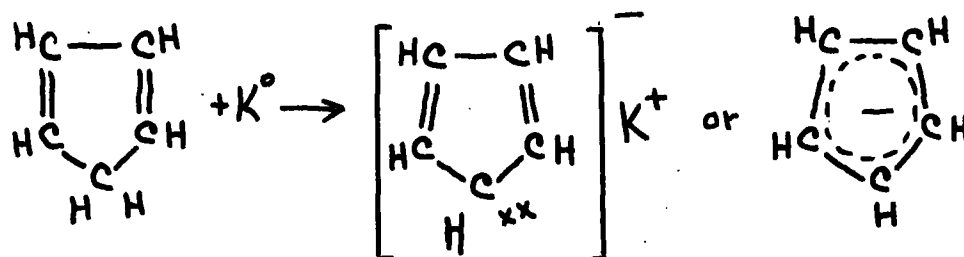
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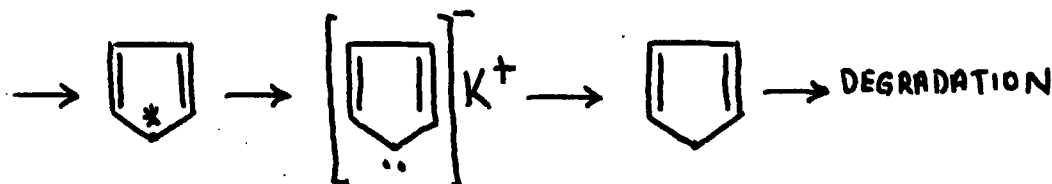
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# GENERAL INTRODUCTION

The object of this work is a proposed study of the bond-structure of the cyclopentadienyl anion. The present theory of "aromatic character" ascribes the stability of aromatic compounds, of which the cyclopentadienyl anion is a member, to those unsaturated conjugated cyclic systems having six resonating  $\pi$ -electrons. In the cyclopentadienyl anion, these conditions are fulfilled by utilizing the two electrons which formerly held a carbon-hydrogen bond together in the methylene group of cyclopentadiene:



However, experimental verification of these predications is incomplete. It is thought that this verification, or otherwise, can be obtained in the case of the cyclopentadienyl anion, by the use of carbon-14 as a tracer. This can be done by synthesizing cyclopentadiene-5- $C^{14}$ , making the potassium anion, and then regenerating cyclopentadiene from this latter salt:



If the anion is aromatic according to our present definition of aromaticity, then the carbon-14 in the regenerated cyclopentadiene will be distributed equally on every carbon atom. If the negative charge remains on the former methylene group, the original cyclopentadiene-5-C<sup>14</sup> will be regenerated, etc.

The aim in the present work was to find a suitable hypothetical synthesis for cyclopentadiene-5-C<sup>14</sup>, and a method for the regeneration of cyclopentadiene from its potassium salt. This was done. To familiarize oneself with the reaction procedures and to learn the over-all yield, a complete synthesis, formation of the potassium salt, regeneration, and a complete degradation of cyclopentadiene were effected. Time permitting, the above work was to be repeated as far as possible, using carbon-14. Cyclopentane-1,2-diol-5-C<sup>14</sup> (cis-trans) was synthesized, but the dehydration of it to cyclopentadiene could not be repeated.

## HISTORICAL INTRODUCTION

### (A) GENERAL

Aromatic compounds were so classified originally because of their odor. Today aromaticity or aromatic character infers a much different meaning. Although there is much disagreement on the definition of aromaticity, very briefly it may be associated with cyclic compounds possessing the following properties:

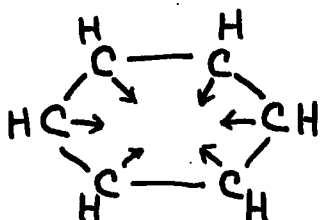
- (1) A very stable nucleus of carbon atoms

- (2) A particularly resistant type of unsaturation towards the formation of additional products
- (3) A tendency to undergo substitution reactions
- (4) Acidic enolic derivatives with little tendency to form the "keto form"
- (5) A tendency to form quinone and diazonium salts
- (6) Halide derivatives which are very inert
- (7) A pronounced tendency towards their formation.

Benzene and its derivatives of course provide the classical example of illustrating these properties.

Chemists elucidating the properties and structures of these aromatic compounds have come up with many theories. One school of thought, due to Armstrong, von Baeyer and Bamberger, suggested that aromatic character was due to the symmetrical arrangement of conjugated linkages in these cyclic compounds.

Independently, Armstrong (3) in 1887 and von Baeyer (4) in 1888 provided for benzene a symbol based on the 24-affinities of the six carbon atoms. Of these 24-affinities, 12 are engaged in the formation of the six-carbon ring and six retaining the six hydrogen atoms, while the remaining six react upon each other--"acting towards a centre as it were"--so that the "Affinity" may be said to be uniformly and symmetrically distributed (3):



Bamberger (6), in 1891-1893, suggested that the six valences unnecessary for the formation of benzene "saturated each other". Rings not having six such valences could not attain the same stability. Bamberger extended his hexacentric argument to unsaturated heterocyclics by utilizing the salt forming valences of the hetero-atoms:



Pyridine

Pyrrole

Thiophene

Pyrazole(Imidazole)

Furan

Thiele (53) in 1899, considered that each carbon atom of a double-bond to possess a partial valence, and that in a diene these partial valences neutralize each other with the resulting accumulation of residual energy at the ends of the conjugated system (to explain 1,4-additions):

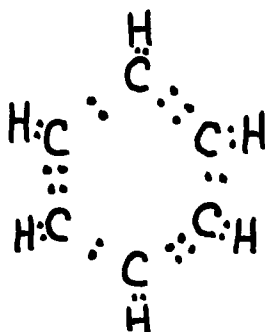


Applying this argument to ~~the~~ Kekules cyclohexatriene formula for benzene with its closed conjugated system, three inactive double bonds alternating with the original deactivated double bonds are formed, resulting in six nearly equivalent inert linkages:

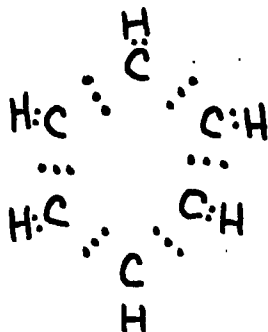




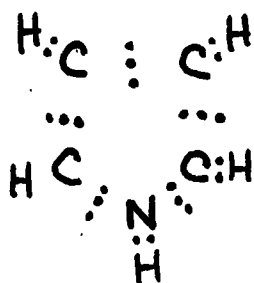
In the nineteenth century, the valence bond was represented by a line drawn between the symbols of two chemical elements, the nature of the bond being unknown. Following the discovery of the electron in 1897, electrons instead of the former lines soon appeared as the link between atoms in chemical compounds. However, it was not until 1916, <sup>that</sup> when G. N. Lewis (40) formulated the basis of the modern electronic theory of valence. And so electronic formulae for benzene soon appeared in the literature:



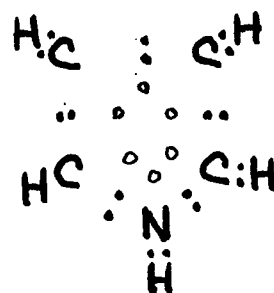
The first alternative formulation for benzene, where all the nuclear carbon atoms are connected by three electrons, was suggested by Kauffmann(37), and drawn by Kermac and Robinson (39):



Later, Armit and Robinson (2) suggested that the "aromatic sextet" in the benzoid group infers marked stability and postulated that groups of two or four electrons also occur, for example, in acids and cyclopentadiene. Gross and Ingold (28) extended Bamberger's theory by assigning electronic structures to the aromatic hetero-cyclic compounds:



Pyrrole - (a)



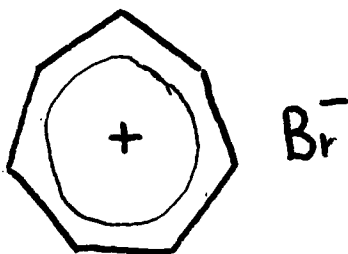
Pyrrole - (b)

The second formula (b), again gives rise to the aromatic sextet.

The aromatic sextet theory has received much attention since Hückel(39) in 1931 invented the quantum mechanical foundation in which he ascribes that aromatic character with its relative stability, originates from those conjugated unsaturated cycles containing six  $\pi$ - electrons.

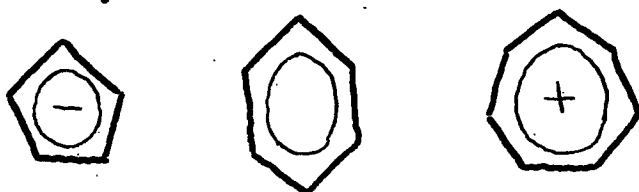
The first attempts to test this aromatic sextet theory were by Willstatter on the non-existent cyclobutadiene (63) and cyclo-octatetraene(62,69), which theoretically are non-aromatic molecules. Cyclobutadiene still has not been synthesized and would, in any case, have a large obscuring angular strain. Cyclo-octatetraene, although synthesized, has a non-planer structure and so is <sup>not</sup> ~~impertinent~~ to the theory(38). Theoretical predictions concerning the five and seven-membered rings are definite (26,34,59):  $(\text{CH})_5^-$  should be more stable than  $(\text{CH})_7^-$ , and  $(\text{CH})_7^+$  should be more stable than  $(\text{CH})_5^+$ . The positive ion  $(\text{CH})_5^+$  has never been prepared; but from the failure of cyclopentadienone to exist as contrasted with the stability and basicity of cycloheptatrienone, it can be inferred that the  $(\text{CH})_7^+$  ion is much more stable than the  $(\text{CH})_5^+$  ion (15,20).

In 1954, Doering and Knox synthesized the cycloheptatrienylium (tropylium) ion (21):



From its properties it appears that resonance stabilization in the cyclic ion is large enough to overcome the normal tendency of the carbon-bromine bond to be covalent. Thus we have another new aromatic system in which large resonance energy originates from the cyclic nature of the system.

In summary the present "aromatic sextet" theory predicts that the cyclopentadienyl ion, benzene and the cycloheptatrienylium ion

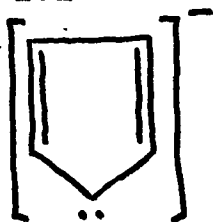


constitute a triad possessing aromatic resonance energy and hence remarkable stability.

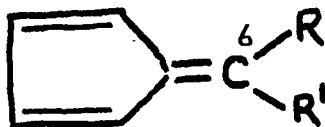
#### (B) THE CYCLOPENTADIENYL ANION

The resonance energy of cyclopentadiene, calculated from the heat of hydrogenation, is only about 3 kcal/mole (5). But cyclopentadiene possesses an active methylene group, and has an exceptionally high acidity for a hydrocarbon, as

potassium t-butoxide ( $pK_a$  19) converts cyclopentadiene quantitatively into its potassium salt(49). This shows that the negatively charged ion



is very stable, although very reactive chemically. The reason given by Goss and Ingold (28) in 1928, was that this ion had six  $\pi$ -electrons distributed over five equivalent CH groups, thus constituting a stable aromatic system similar to benzene. The resonance energy of the ion has been calculated to be about 42 kcal./mole, and apparently is in harmony with the observed stability (48). The tendency of the cyclopentadiene system to accept an electron and thus achieve aromatic stability is also shown by the fulvenes.



Dimethylfulven ( $R=R^1=Me$ ) has a dipole moment of 1.44D, the ring being negative and the carbon atom-6 positive(60). This indicates the electron attracting nature of the ring which tends to acquire a stable sextet of electrons. The recently prepared diazocyclopentadiene (19)



is a very stable molecule. It is suggested that the molecule is a resonance hybrid of the two following structures:



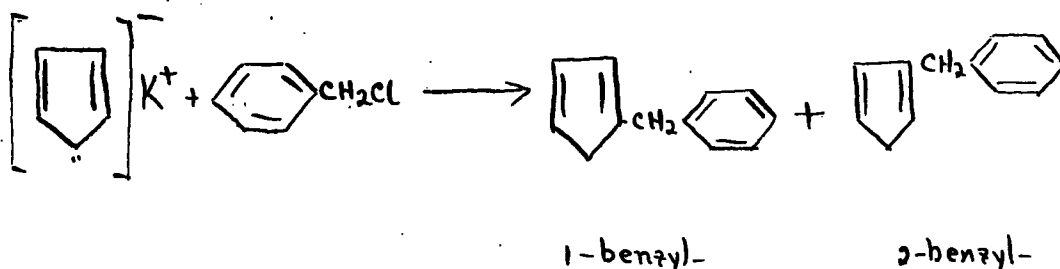
The form in which the ring accommodates the negative charge probably contributes most to the hybrid.

The aromatic character of the cyclopentadienium ring is best illustrated by dicyclopentadienyl iron (5):



This compound is insoluble in, and does not react with water, sodium hydroxide, or conc. hydrochloric acid. It is not decomposed at 470°. The exact nature of the Fe-C bonds is not known. Regarding the cyclopentadienyl rings, infrared spectrum indicates only one type of C-H bond, and X-ray evidence indicates that the five-membered rings are planar, and symmetrical, the C-C distances being about 1.4 Å. Dicyclopentadienyl iron does not react with maleic anhydride, cannot be catalytically hydrogenated, and undergoes the Friedel-Crafts reaction. Because of these typically aromatic characteristics, the compound has been named ferrocene.

The only experimental work on the structure of the cyclopentadienyl anion seems to be that by Alder and Holzrichter (1), who treated the potassium salt of cyclopentadiene with benzyl chloride and obtained both benzyl- and dibenzylcyclopentadienes and their dimers. From these products only the 1- and 2-benzyl cyclopentadienes were found.



Strangely, the 5-benzyl derivative was not formed. This work is limited in that one does not know whether or not the depolymerization of dicyclopentadiene derivatives involves tautomeric changes. Besides the fact that the 5-benzyl derivative did not form, the authors could not add any information to the structure of the cyclopentadienyl anion.

### DISCUSSION

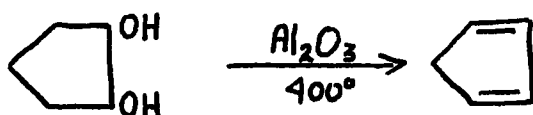
#### (A) SYNTHESIS OF CYCLOPENTADIENE

The immediate precursor to cyclopentadiene, labelled in the methylene group with carbon-14



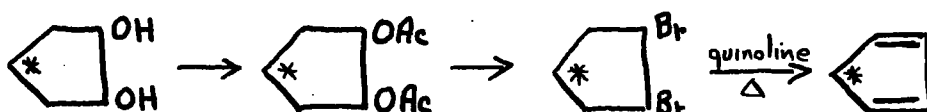
was chosen to be (cis-trans)cyclopentane-1-diol-4- $C^{14}$  since it was shown in the present work that cyclopentadiene could

be prepared from trans-cyclopentane-1,2-diol in a yield of 20%:



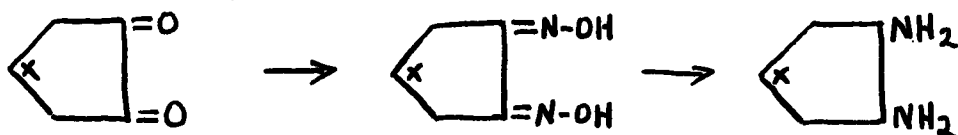
Whether the dehydration does proceed as shown above can only be determined by an actual dehydration attempt of (cis-trans) cyclopentane-1,2-diol-4- $C^{14}$  followed by degradation of the cyclopentadiene obtained to ascertain the location of  $C^{14}$  in the ring.

If the dehydration, as shown in the preceding paragraph, was not successful, we still have two other possibilities of obtaining cyclopentadiene from (cis-trans) cyclopentane-1,2-diol-4- $C^{14}$ , or from its precursor, 1,2-cyclopentadione-4- $C^{14}$ . One possibility would be a dehydrohalogenation of 1,2-dibromocyclopentane-4- $C^{14}$  according to the following scheme:

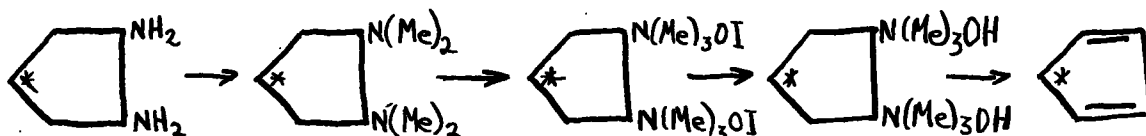


The diacetate of cyclopentane-1,2diol has been prepared (41), and the two remaining steps are similar to the successful preparation of 1,3-cyclohexadiene (65). Furthermore, a similar preparation has been successful in the preparation of cycloheptatriene by Willstatter (61).

The second possibility would be the preparation of the dioxime and then the diamine from 1,2-cyclopentadione-4- $C^{14}$ , which has been realized by Jaeger and Blumendal (35):

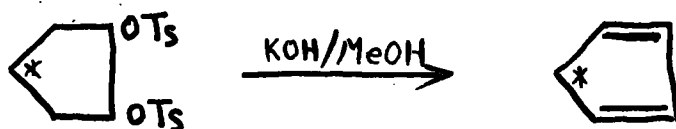


From the diamine, a Hoffmann degradation could be attempted



as in the attempted synthesis of cyclobutadiene by Buchman and his collaborators (10) or the famous synthesis of cyclo-octatetraene by Willstatter and co-workers (62,64), and more recently by Cope and Overberger (12).

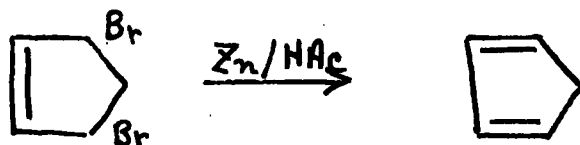
Besides the cleavage of dicyclopentadiene, there seem to be only three reported reactions which lead to cyclopentadiene. Only one of these methods would be useful in this present work, namely, the hydrolysis of the di-*p*-toluene-sulphonate of cyclopentane-1,2-diol according to Owen and Smith(44).



The yield of cyclopentadiene was not recorded by Owen and Smith. However, in two attempts to repeat the work of these authors, no cyclopentadiene could be detected.

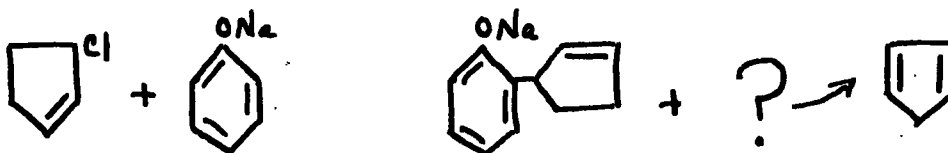


Thiele in 1901 obtained cyclopentadiene by the reduction of 2,4-dibromo cyclopentene with zinc dust in glacial acetic acid (55):



Thiele did not mention the yield, but from his description of the reaction, the yield of cyclopentadiene seemed considerable. However 2,4-dibromo-cyclopentene is made from cyclopentadiene, and to synthesize 2,4-dibromo-1-cyclopentene-3- $\text{Cl}^{14}$  seems a very formidable, if not impossible, task.

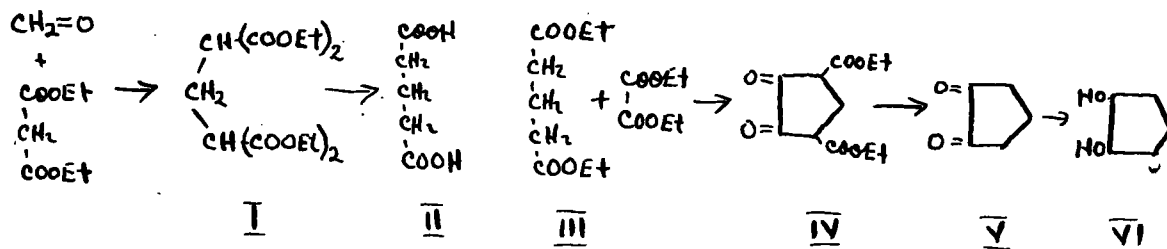
Finally, Braun and Kuhn have reported that, during the preparation of o-cyclopentenylphenol, by condensing sodium phenolate and 2-cyclopentenyl,(8),



an alkali-insoluble portion of the product was obtained. This latter oil, with a boiling point of 110-200° at 12 mm., evolved a distinct odor of cyclopentadiene. It would seem that this reaction is not very suitable for the preparation of cyclopentadiene labelled in the 5- position.

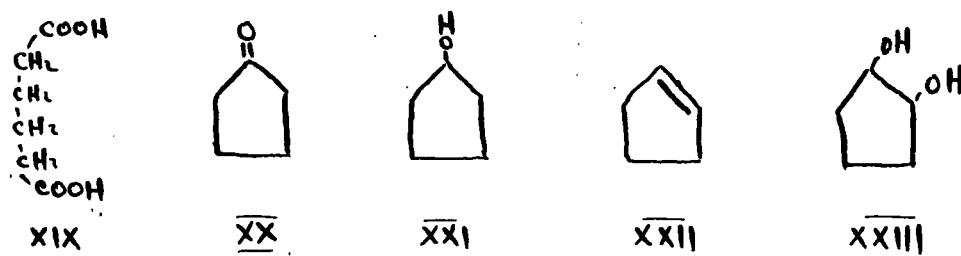
(B) SYNTHETIC AND DEGRADATIVE PROCEDURES

The preliminary synthetic procedures listed below were done with a view to perfecting a route for the formation of cyclopentadiene-5-C<sup>14</sup>:



The synthesis of cyclopentadiene started from formaldehyde, as eventually the carbon-14 could then be introduced in the form of formaldehyde-C<sup>14</sup>.

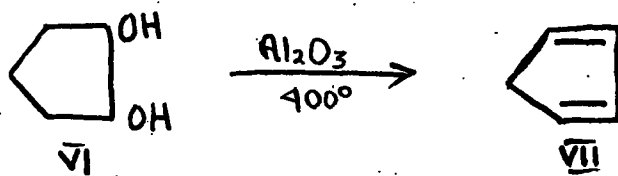
Thus tetraethyl propane-1,1,3,3-tetracarboxylate (I) was prepared from the condensation of formaldehyde and diethyl malonate and hydrolyzed to glutaric acid (II). This glutaric acid was then esterified to diethyl glutarate (III). A Dieckmann condensation of the latter with diethyl oxalate gave 3,5-dicarboethoxycyclopentadione-1,2 (IV), which on hydrolysis afforded cyclopentadione-1,2 (V). Hydrogenation of (V) over platinum oxide gave apparently an isomeric mixture of (cis-trans) cyclopentane-1,2-diols (VI). As this latter product could not be characterized by ordinary means, authentic trans-cyclopentane-1,2-diol (XXIII) was synthesized, starting from adipic acid as in the following sequence:



Cyclopentanone(XX), prepared by heating adipic acid(XIX) with barium hydroxide, was converted to cyclopentanol(XXI) with lithium aluminum hydride. Dehydration of the latter alcohol with 85% ortho-phosphoric acid gave cyclopentene(XXII), which in turn was trans-esterified with performic acid and hydrolyzed to give trans-cyclopentane-1,2-diol(XXIII). The over-all yield from adipic acid was 19.5%.

After the trans-cyclopentane-1,2-diol was characterized, an infra red spectrum was taken of it, and also of the cyclopentane-1,2-diol obtained by hydrogenation of cyclopentadione-1, 2(V). The infrared absorption curves obtained for these two alcohols, as 3% solutions in chloroform, were superimposable except for one extra slight peak in the "finger-print" region for the diol(VI) from the hydrogenation of V. (Fig. 1, p. 37)

Cyclopentadiene(VII), in a yield of 20%, was prepared by passing trans-cyclopentane-1,2-diol over alumina pellets at 400°:

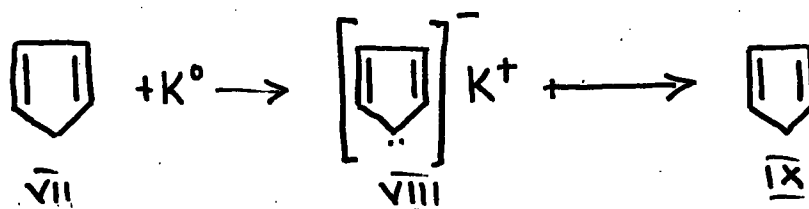


The cyclopentadiene produced, besides its very characteristic odor, was characterized as the maleic anhydride adduct. The preparation of cyclopentadiene by this method is not listed in the literature.

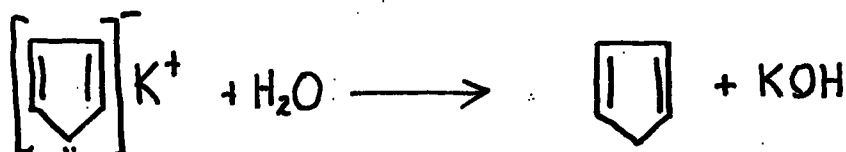
Potassium cyclopentadienide(VIII) was made by reacting cyclopentadiene with metallic potassium in benzene and ether.

By using this mixture of solvents instead of benzene alone, a product is obtained which is more finely divided and not as apt to contain very small pieces of unreacted potassium. If this potassium-cyclopentadiene salt does contain metallic potassium, then the next reaction on this salt would be very vigorous, and usually would end in a fire.

Regeneration of cyclopentadiene(IX), in a yield of 43%, was afforded by addition of cold conc. hydrochloric acid:

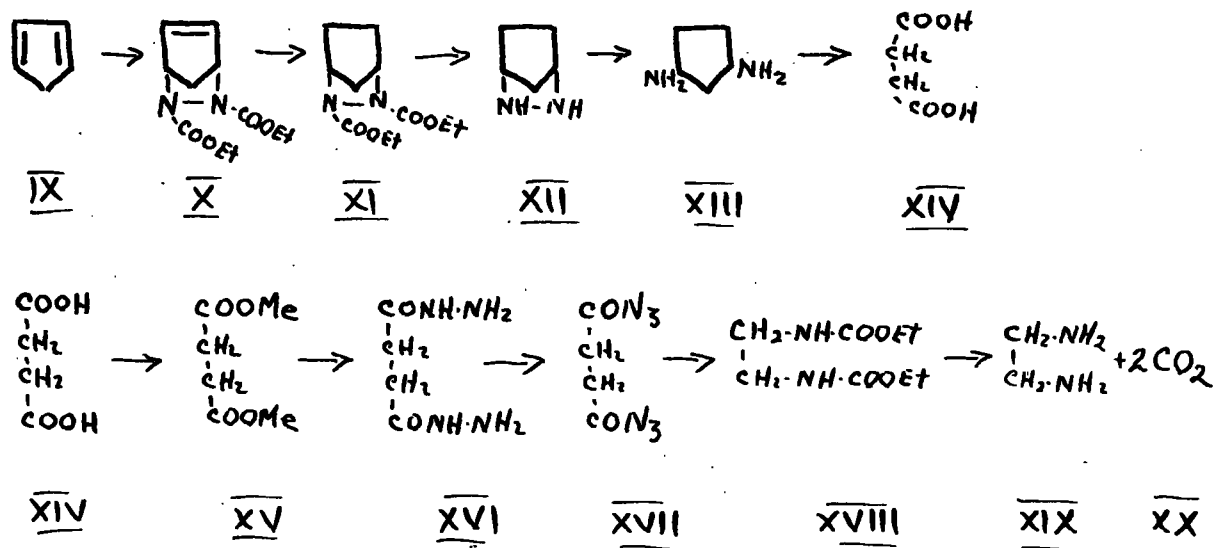


In future work, probably higher yields of cyclopentadiene could be obtained by dissolving the potassium salt in tetrahydrofuran, and then adding the theoretical amount of hydrogen chloride gas. Thiele (54) mentioned that cyclopentadiene is regenerated from potassium salt by the addition of water. Repetition of Thiele's work resulted in a resin formation together with a poor yield of cyclopentadiene. In this reaction



the reacting mixture becomes basic as the reaction proceeds. Thus, probably, the cyclopentadiene formed is rapidly polymerized, as acids and bases catalyze such polymerization.

By adapting former degradations of cis-cyclopentane-1,2-diamine(45) and succinic acid(7), the scheme for the location of the carbon-C14 in the cyclopentadiene samples is as follows:



The di-ethyl ester of 2,3-diazabicyclo(2.2.1)-5-heptene-2,3-dicarboxylic acid(X) was obtained by a Diels-Alder reaction between cyclopentadiene and ethyl azodicarboxylate.

Hydrogenation of the Diels-Alder adduct gave the diethyl ester of 2,3-diazabicyclo(2.2.1)heptane-2,3-dicarboxylic acid(XI), which, on hydrolysis with methanolic potassium hydroxide, gave 2,3-diazabicyclo(2.2.1) heptane (XII), isolated as the cuprous chloride complex. Reduction of XII with tin and hydrochloric acid gave cis-cyclopentane-1,3-diamine(XIII), which was oxidized with neutral potassium permanganate to succinic acid(XIV).

Using the Curtius degradation method(3,4), the succinic acid(XIV) was degraded along the sequence of the dimethyl ester(XV) -- dihydrazide(XVI) -- diazide(XVII) -- diurethan(XVIII), and finally to ethylenediamine(XIX) and carbon dioxide(XX). The over-all yield of ethylenediamine from cyclopentadiene was 0.4%

The location of the carbon-14 in the cyclopentadiene would, hypothetically, be determined in the following manner: The difference between the maleic anhydride adduct of cyclopentadiene(IX) and the succinic acid(XIV) would represent the activity of the methylene group in IX. The carbon dioxide produced in the oxidation of XIII cannot be used for the measurement of the activity of the methylene group in the cyclopentadiene(IX) because potassium permanganate oxidation of cis-cyclopentane-1,3-diamine(XIII) would be expected to cleave other parts of the ring. As the 1,4- and 2,3-positions are equivalent in cyclopentadiene, then the difference in radioactivity of XIV and XIX would represent the activities of the 1- and 4-positions of IX. The activity of XX, isolated as barium carbonate, could be used as a check for the activity of the 1,4-positions. Finally, measurement of the activity of XIX would give the activity of the 2,3-positions. A check for the activity of the methylene group, would be obtained by adding the activities of XIX and XX, and subtracting this value from the value obtained for IX.

The complete synthetic and degradation route listed above was done using "non-labelled" compounds. Most of the reactions were done at least twice. Using carbon-14, the above work was repeated to the (cis-trans)cyclopentane-1,2-diol(VI). A number of attempts were made in trying to synthesize cyclopentadiene-C<sup>14</sup>; however they all failed, and lack of time prevented any further research.

In future research, more experimental details on the dehydration of (cis-trans)cyclopentane-1,2-diol have to be obtained first, before the Cl<sup>14</sup>-phase of the work can be completed to shed some light on the structure of the cyclopentadienyl anion.

### EXPERIMENTAL (#)

#### A. REAGENTS AND SOLVENTS

Chloroform For infrared measurements, reagent grade chloroform was shaken with conc. sulfuric acid, washed with 3% sodium bicarbonate solution and then with water. The resulting chloroform was dried first with calcium chloride, then with calcium sulfate, and finally distilled. The fraction collected boiled at 61° (24).

Ethanol For reactions involving metallic sodium, this reagent was made "absolute" by the Lund and Bjerrum method (22).

Ether For reactions involving metallic sodium or potassium, commercial "absolute" ether was dried over sodium wire and then distilled from phosphorous pentoxide, b.p. 35°.

Ethyl Oxalate Reagent grade as supplied by Eastman Kodak, was shaken with 3% sodium bicarbonate, washed with water, dried with calcium sulfate and vacuum distilled at 42-44° at 0.6 mm.

(#) All melting points reported in the present work, were obtained by heating a copper block containing the sample and thermometer, and are uncorrected.

Methanol When "absolute" methanol was needed, commercial reagent grade methanol was dried and purified by the Lund and Bjerrum method (23).

Platinum Oxide Catalyst for hydrogenations, was used as supplied by Brickman and Company.

Alumina Catalyst for dehydrations, in pellets of approximately 3 mm. in diameter, as supplied by The Harshaw Chemical Company.

Sodium Ethoxide Prepared by adding freshly cut sodium to an approximately ten-fold excess of "absolute" ethanol in a nitrogen "dry-box". A reflux condenser was then attached to the reaction vessel and under a slow stream of dry nitrogen, the reaction was allowed to proceed at room temperature. After the reaction was complete (approx. 24 hrs.) the excess ethanol was removed at the water pump. To remove the alcohol completely, the sodium ethoxide was dried at 100° at 0.1 mm. for approximately four hours. Careful work will result in a product which is easy to powder, and white in color.

p-Toluenesulfonyl Chloride C. P. grade, as supplied by Eastman Kodak, was purified by shaking a benzene solution with 5% sodium hydroxide, washing with water and vacuum distilling (25). The product which crystallized in the receiver, had a m.p. of 68.5°. Lit., 69° (25).

Ethyl hydrazodicarboxylate Prepared from 85% hydrazine hydrate and ethyl chloroformate(45) in 83% yield with a m.p. of 127.5-130°. Lit. 131° (45)



Ethyl Azodicarboxylate Prepared by oxidizing ethyl hydrazodicarboxylate with chlorine gas(45 in 57.2% yield. The product, a beautiful orange-red liquid, boiled at 104° at 11.0 mm. Lit. 111° at 15 mm.(45).

Nitrosomethylurea Prepared by adding a 50% sodium nitrite solution to a hot, prefiltered solution of methylamine hydrochloride and potassium cyanate, followed by the addition of cold 15% sulfuric acid to this solution at -5 to 0° (58). The slightly cream colored crystalline product was filtered off, thoroughly washed with water and dried over phosphorous pentoxide at 0.5 mm. pressure. The product stored at approximately -15°, and protected from light, was still stable and usable six months later.

#### B. SYNTHETIC AND DEGRADATIVE PROCEDURES

##### Tetraethyl Propane--1,1,3,3-tetracarboxylate (I) (11)

To a mixture of 320 gm. of freshly redistilled diethyl malonate and 84 ml. of 35% formaldehyde, cooled to 2° in an ice-bath, was added 6.0 gm. of potassium chloride and then 5.0 gm. of freshly distilled diethylamine. The components were well shaken and then allowed to come to room temperature and thus kept for 16 hours with occasional shaking. The reaction mixture was then heated on a steam bath for six hours, cooled to room temperature, the water separated off and the remaining liquid vacuum distilled. The fraction collected boiled at 143-146° at 0.5 mm. and weighed 266.4 gm. (82.7%).

Glutaric Acid (II) (11)

Into a three-necked flask, fitted with a reflux condenser, stirrer and thermometer, was placed 386.4 gm. of tetraethyl propane-1,1,3,3-tetracarboxylate and 780 ml. of 50% hydrochloric acid. With stirring, the reaction mixture was slowly refluxed until the mixture became homogenous (approx. six hours). The reaction mixture was then distilled under reduced pressure until the water and hydrochloric acid were removed. As on cooling the material in the distillation flask did not solidify, it was further refluxed for two hours with 200 ml. of 50% hydrochloric acid, and then the water and hydrochloric acid removed under reduced pressure. On cooling, 147.0 gm. (104.5%) of crude glutaric acid was obtained. A small portion recrystallized twice from benzene, had a melting point of 95-96°, Lit. 97° (30). A mixed m.p. with authentic, once recrystallized glutaric acid showed no depression.

Ethyl Glutarate (III) (42)

Into a one-liter distillation flask were placed 146.5 (1.11 moles) of crude glutaric acid, 400 ml. of absolute ethanol, 200 ml. of toluene and 0.83 ml. of conc. sulfuric acid. The flask was connected to an ordinary distilling apparatus and heated until the azeotropic mixture of ethanol, toluene and water began to distil at 75°. Distillation was continued until the b.p. of the distillate reached 78°. The distillate was dried with 170 gm. of anhydrous potassium carbonate, filtered and returned to the distillation flask which was again heated until the b.p. of the distillate reached 80°. At this point

vacuum distillation was commenced. The product collected boiled at 112-119°, at 10-11 mm., and weighed 124.0 gm. (59.6%).

In other runs, when the glutaric acid used was recrystallized from benzene, a yield of 88.6% of ethyl glutarate was obtained, boiling at 136-137° at 32 mm.,  $n_D^{20}$  1.4234. Lit.,  $n_D^{20}$  1.4241; bp. 103-104° at 7 mm. (30).

#### 3-5-Dicarboethoxycyclopentadione-1,2 (IV) (17)

To 88.0 gm. (1.29 moles) of ethanol-free, white sodium ethoxide, covered with 500 ml. of anhydrous ether, contained in a one-litre round-bottomed flask fitted with a reflux condenser, 95.8 gm. (0.656 moles) of freshly redistilled ethyl oxalate was added. On mixing this turned into a pale yellowish-orange color. Now 123.4 gm. (0.656 moles) of ethyl glutarate was added dropwise over a period of 30 minutes, the reaction mixture deepening in color during this addition. The mixture was refluxed for one hour, the ether distilled off, and the residue heated to 125-130° for four hours, when it changed to a yellowish-brown, dry cake. This residue was ground into a fine powder and slowly added to a well stirred ice-cold solution of 10% sulfuric acid, whereupon the ester precipitated out as a cream-colored solid. The precipitate was washed with ice-cold water, filtered, sucked dry on the Buchner funnel and recrystallized from approximately 500 ml. of 95% ethanol. The dried crystalline product weight was 110 gm. (69.2%) and had a m.p. of 115.5-116.5°. A small portion of the ester, recrystallized once more, had a m.p. of 116-117°. The literature reports a m.p. of "near 118°, and a yield of 50%. (17)

Cyclopentadione-1,2 (V) (31)

In a one-litre round-bottomed flask equipped with a reflux condenser were placed 108.6 gm. (0.499 moles) of 3,5-dicarboethoxycyclopentadione-1,2, 400 ml. of 17% sulfuric acid and 20 ml. of ethanol. The mixture was refluxed for 110 mins., with a bath temperature of 117°. The resulting solution turned reddish-brown in color. After cooling (under nitrogen), the solution was continuously extracted with ether for eleven hours. Maintained under an atmosphere of nitrogen the ether was removed on a water bath and the product vacuum distilled. Cyclopentadione, which crystallized in the receiving flask, boiled at 70-80° at 1.7-1.9 mm., and weighed 24.2 gm. (55.0%). It melted at 54-55°. Lit. 56° (31).

Air very rapidly decomposes this diketone. However, when sealed off under nitrogen and kept at approximately 0° it is stable for at least six months. On contact with skin, prominent black spots form after some time, and remain for a long period.

Cyclopentane-1,2-diol (VI)

Into a glass-liner was placed a solution of 12.5 gm. (0.128 moles) of cyclopentanedione-1,2 in 50 ml. of absolute ethanol and 0.104 gm. of platinum oxide. The liner was placed in a bomb whose total void was 278 cc. The air was thoroughly flushed out of the bomb with hydrogen. The bomb was then charged to 500 p.s.i. with hydrogen, and shaking commenced at room temperature. In one-half an hour the pressure dropped 280 p.s.i., whereupon the bomb was recharged to 400 p.s.i.

with hydrogen and shaking recommenced. After 42 hours a total drop of 450 p.s.i. occurred. Complete hydrogenation required a drop of 400 p.s.i. The catalyst was filtered off, and the ethanol removed under reduced pressure at the water pump. A clear, colorless, viscous liquid was obtained. On cooling to approximately  $-10^{\circ}$  some crystallization occurred, but on warming to  $20^{\circ}$  complete solution resulted.

The di-p-nitrobenzoate, prepared in the usual manner, was recrystallized from ethanol, m.p.  $90-104^{\circ}$ . Recrystallized once more, m.p.  $93-125^{\circ}$ . Lit., cis-  $117^{\circ}$ ; trans -  $145^{\circ}$  (44)

For infrared analysis some of this hydrogenated product was vacuum distilled twice, and made into a 3.0% solution in pure chloroform. (Fig. 1, p. 37)

#### Cyclopentadiene (VII)

The dehydrating column consisted of a Pyrex tube, 30 cm. long and 22 mm. i.d., wound externally in a spiral with approximately 900 cm. of No. 27 Chromel-"A" wire. A thermocouple well was constructed so that it would rest in the centre of the catalyst mass. To one end of the tube, an inlet was provided so that the substance to be dehydrated and nitrogen gas could be introduced simultaneously. To the "exit-end" of the tube, a narrower piece of glass tubing was affixed, which in turn could be connected to two consecutive "Dry-ice"-acetone cooled traps.

This tube was filled with pellets of commercial 8-mesh alumina. With a slow stream of nitrogen flushing through, it was heated at  $400^{\circ}$  for approximately 48 hours to dry and

activate the catalyst. With the temperature at  $400 \pm 3^{\circ}$ , the exit end connected to the two "Dry-ice"-acetone traps, and a slow stream of nitrogen flushing through the tube, 2.47 gm. of trans-cyclopentane-1,2-diol was slowly introduced into the column over a period of 10-15 minutes. The product, which possessed the very characteristic odor of cyclopentadiene, consisted of 0.4 ml. (21%) of a slightly greenish oil floating on approximately one ml. of water.

The maleic anhydride adduct of this product, twice recrystallized from ether had a m.p. of  $161.5-162.5^{\circ}$ . Lit.  $165^{\circ}$  (32).

#### Potassium Cyclopentadienide (VIII)

Cyclopentadiene was generated by slowly refluxing dicyclopentadiene and collecting the distillate at  $44-46^{\circ}$  (43). This material was stored at "Dry-ice" temperature to keep polymerization at a minimum. Just before use the cyclopentadiene was redistilled - b.p.  $41-42^{\circ}$ .

The potassium used in this reaction was handled in the following manner: Inside a box from which all air was displaced with dry nitrogen gas, the potassium was placed into a deep mortar containing pure anhydrous benzene. The outer oxide-coating was cut off, and the freshly cut metal transferred into a tared beaker containing anhydrous benzene. The required potassium (10.7 gm.) was then introduced into a 500 ml. round-bottomed flask containing approximately 100 ml. of pure, anhydrous benzene. The flask was then stoppered. The potassium scraps remaining in the mortar were immediately decomposed by

the cautious addition of dry tert-butyl alcohol. Small specks of potassium remaining on the knife and tweezers were also decomposed with tert-butyl alcohol.

The flask containing 11.0 gms. (0.282 moles) of potassium was unstoppered, and heated until the metal liquified. Once again the flask was stoppered, wrapped in a towel and sharply shaken three times. An efficient reflux-condenser was then attached to the flask in place of the stopper, and with dry nitrogen slowly sweeping into the flask, the contents were allowed to come to room temperature. Then, without introducing air, a solution of 23.0 gm. (0.348 moles) of cyclopentadiene in 100 ml. of pure, anhydrous ether was slowly added to this fine granular potassium in benzene. After the initial reaction had subsided, the mixture was refluxed for four hours. The ether and benzene were removed under reduced pressure and the slightly pinkish salt finally dried at 0.1 mm. at 60° for three hours.

This dry salt, kept in a well-stoppered flask, was stable for at least three months.

#### Cyclopentadiene (IX) from Potassium Cyclopentadienide

Into a 100 ml. round-bottomed flask was placed 4.37 gm. of potassium cyclopentadienide, and then cooled to -80°. To this cold salt, approximately 30 ml. of cold (-80°) concentrated hydrochloric acid was added, the contents in the reaction flask being well stirred. Twenty ml. of ice-cold water was next introduced, and the mixture distilled at a bath temperature of 60°. The receiver collecting the product was cooled in "Dry-ice" acetone mixture. Approx. 1.2 gm of cyclopentadiene was obtained. (43.3%).

A slow addition of 20 ml. of redistilled butanol at just above its freezing point to 24 gm. of potassium cyclopentadienide, followed by a distillation, using a reflux condenser with a jacket temperature of 50° as a column yielded 3.9 gm. (26%) of cyclopentadiene.

Diethyl ester of 2,3-dihydrazobicyclo (2.2.1.)-5-heptane-2,3-dicarboxylic acid (X) (18)

N,N-Dicarbethoxy-endomethylenetetra hydropyridazine

In a 250-ml. round-bottomed flask equipped with an efficient reflux condenser were placed 3.9 gm. of the cyclopentadiene obtained in the last reaction and 11.0 gm. of cyclopentadiene obtained from dicyclopentadiene. Through the reflux condenser 33.27 gm. of ethyl azodicarboxylate in 80 ml. of pure anhydrous ether was slowly added. The reaction mixture warmed up on this addition. After refluxing for approximately 12 hours, the resulting mixture was colorless, indicating the disappearance of ethyl azodicarboxylate. The ether was removed under reduced pressure, and the remaining very viscous, slightly yellowish liquid was vacuum distilled, yielding 43.9 gm. (96%) of product boiling at 109-112° at 0.2-0.25 mm.: Dibromo deriv., m.p. 66.0-66.5° Lit. b.p. 120° at 0.5 mm.; dibromo derv., m.p. 67° (18)

(Di-ethyl ester of 2,3-Diazabicyclo(2.2.1) heptane-2,3-dicarboxylic acid) (XIO (18))

Into a glass-liner were placed 11.55 gm. (0.0481 moles) of diethyl ester of 2,3-dihydrazobicyclo(2.2.1) 5-heptane-2,3-dicarboxylic acid in 38 ml. of absolute methanol and 0.087 gm.



of platinum oxide. The liner was attached to the hydrogenator with a total void of 4260 cc., and the air completely flushed out with hydrogen. The liner was then charged with hydrogen to 239 p.s.i., and shaking commenced. The required theoretical drop of 4.1 p.s.i. occurred in two hours, whereupon hydrogenation was stopped, the liner removed from the hydrogenator and the catalyst removed by filtration. The product in this methanol solution was used directly in the next reaction.

In a preliminary run, 9.29 gm. of diethyl ester of 2,3-dihydrazo(2.2.1) 5-heptene-2,3-dicarboxylic acid was hydrogenated at 22.00 p.s.i. After one hour 97% of the theoretical amount of hydrogen was absorbed; in two hours hydrogenation was complete. Further hydrogenation for an hour resulted in no further drop in pressure. The product was isolated by filtering off the catalyst, removing the methanol at the water-aspirator, and vacuum distilling the residue. The fraction boiling at 115-117° at 0.9-1.0 mm. was collected and weighed 7.80 gm. (84.3%)

2,3-Diazabicyclo(2.2.1) heptane (Cuprous Chloride Complex)  
(XII) (18)

To the methanolic solution of the diethyl ester of 2,3-diazabicyclo(2.2.1)heptane-2,3-dicarboxylic acid obtained in the last reaction, 16.0 gm. of potassium hydroxide was added. The resulting slightly yellowish solution was gently refluxed on a water-bath for two hours. The potassium carbonate, which formed in the reaction, was filtered off, and

washed twice with 10 ml. of absolute methanol. The potassium carbonate, after drying, weighed 13.24 gm. (99.8%). The combined methanolic filtrate and washings was carefully evaporated off under reduced pressure and the residue was steam distilled. Steam distillation was continued until no red color was produced when cupric chloride was added to a few drops of the distillate. To the steam distillate, 8.2 gm. (0.0481 moles) of cupric chloride dihydrate was slowly added with stirring. The red cuprous chloride complex immediately started to precipitate as long glistening prisms. The next day this red precipitate was filtered off, washed with 30 ml. of water, and dried at 0.1 mm. for two hours over phosphorous pentoxide. This dried product weighed 3.42 gm. (35%). In a week, a second crop was collected. The total weight of product was 4.37 gm. (44.6%) (From diethyl ester of 2,3-dihydrazobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid)

Anal. Calcd. for  $C_5H_8N_2 \cdot CuCl \cdot \frac{1}{2}H_2O$  : Cl, 17.37

" "  $C_5H_8N \cdot CuCl$  : Cl, 18.17

Found: Cl, 18.01, 18.10

Cis-cyclopentane-1,3-diamine (Stannous Chloride Complex) (XIII)(18)

A mixture of 2.707 gm. of the cuprous chloride complex of 2,3-diazabicyclo(2.2.1) heptane, 24.5 gm. of mossy tin and 40 ml. of concentrated hydrochloric acid was heated in a boiling water bath for 6.5 hours. Then to the still hot reaction mixture, 10 ml. of concentrated hydrochloric acid was added.

After cooling to 60°, the resulting mixture was filtered through a sintered-glass funnel. After standing at 5° overnight, the long silky needles were filtered off. Drying over phosphorous pentoxide and sodium hydroxide pellets at 1.0 mm. for six hours in a vacuum desiccator gave 5.563 gm. (74.3%) of a product melting at 155-163°, Lit. 145-146° (46); 172° (18).

Anal. Calcd. for  $C_5H_8(NH_2)_2 \cdot (SnCl_2)_2 \cdot 2HCl \cdot H_2O$  : H, 4.91%

" "  $C_5H_8(NH_2)_2(SnCl_2)_2 \cdot 2HCl$  : N, 5.07%

Found: N (Duma<sup>s</sup>) 4.90, 4.97%

#### Succinic Acid (XIV) (46)

To 5.06 gm. of the stannous chloride complex of cis-cyclopentane-1,3-diamine dihydrochloride, a solution of 12.24 gm. of potassium permanganate in 122.5 ml. of water was added. The mixture was refluxed in a boiling water bath for 15 minutes and immediately cooled. The manganese dioxide was filtered off and washed with water. The combined filtrates, if colored, were decolorized with sulfur dioxide and continuously extracted with pure ether for 60 hours. The ether from this extract was evaporated, leaving a mixture of white and slightly yellowish crystals. Recrystallization from water (charcoal) yielded 0.109 gm. (9.7%) of product with a m.p. of 176-178°. A small portion, recrystallized twice more, had a m.p. of 179-180°. The reported m.p. of succinic acid is 188° but the above once-recrystallized product did not depress the mixed m.p. with authentic succinic acid.

M.p. of once recrystallized commercial succinic acid : 184-185.5°  
mixed m.p. : 184.5-186°

Di-p-biomphenacyl ester, m.p. 208.5 - 210°

Lit. m.p. 211° (36)

Dimethyl Succinate (XV)(7) (Characterized as the Hydrazide)

To a solution of 15 mgm. of succinic acid in approximately 4.5 ml. of methanol at 0°, a slight excess of diazomethane in cold ether was slowly added with swirling. After approximately 15 minutes the resulting solution was allowed to come to room temperature and the ether, diazomethane, and methanol removed in a stream of nitrogen.

To the ester obtained in the same test-tube, used in the above preparation 0.14 ml. of 85% hydrazine hydrate was added together with 5 drops of methanol. The contents of the tube were cooled in a "Dry-ice"acetone mixture, the tube evacuated, sealed and then heated at 120° for one hour. After cooling, the tube was opened and the crystalline product scraped out and pressed on filter paper to dry. Recrystallization from ethanol gave white crystals which melted at 164-165°. Lit. 167° (14). The above crystals, when mixed with succinyl hydrazide obtained from authentic diethyl succinate, gave a m.p. of 163.5-164.5°.

Succinyl Hydrazide (XVI) (9,14)

Into a 20 ml. Carius tube containing 1.00 gm. (0.00569 moles) of ethyl succinate at 0°, 0.59 ml. (0.0103 moles) of hydrazine hydrate at 0° was added. The contents of the tube

were frozen out in a "Dry-ice"-acetone mixture, the tube evacuated, sealed, and then heated at 120° for one hour. The crystalline product recrystallized from ethanol weighed 0.77 gm. (91.6%), had a m.p. of 164.5-165.5°. Lit. 167°(14).

Ethylene Diurethan (XVII) (13)

To 0.592 gm. of succinyl hydrazide in a 100 ml. beaker, 6.0 ml. of 1N hydrochloric acid and 4 ml. of water were added. After the hydrazide dissolved, 10 ml. of ether was added and the mixture cooled to -5° in an ice-salt bath. To this cold mixture, 0.689 gm. of sodium nitrite was slowly added with stirring. The temperature of the reaction mixture was not allowed to rise above 2°. After the addition was completed, the mixture was well stirred and the ether layer separated. The aqueous layer was extracted once with 10 ml. of fresh ether and the combined ether extracts were shaken once with sodium bicarbonate solution, filtered, and then washed once with 15 ml. of water. The ether layer was separated, dried with calcium chloride for five minutes and finally with anhydrous calcium sulfate. To this dried ether solution of succinyl azide placed in an Erlenmeyer flask, 20 ml. of absolute ethanol was added, and the solution boiled gently on a hot plate. When the total volume was reduced to approximately 1 ml. the Erlenmeyer was transferred to a steam bath where evaporation was proceeded to dryness. This white crystalline product weighed 0.145 gm. (17.5%) and had a m.p. of 106.5-108°. Lit. 116° (13)

Hydrolysis of Ethylene diurethan (XVIII) (7)

In a 30 ml. two-necked flask, 130 mg. of ethylene-diurethane in 6.0 ml. of 48% hydrobromic acid was refluxed for two hours with a slow stream of CO<sub>2</sub>-free nitrogen sweeping the system. This nitrogen swept the carbon dioxide generated in the reaction out through the condenser into a gas dispersion tube immersed in 1N-carbonate free sodium hydroxide solution. Addition of 100 ml. of 1N ammonium chloride solution and 0.28 gm. of barium chloride in 20 ml. of water to the sodium hydroxide precipitated the BaCO<sub>3</sub>. This carbonate, after being filtered through a glass-sintered crucible (M-porosity), washed with boiling water and absolute alcohol and then dried for one hour at 120° weighed 239 mgm. (94.8%).

The contents of the reaction flask were evaporated just to dryness at room temperature under reduced pressure. Excess methanolic KOH was added, and the solution again distilled to dryness, the distillate collected in a receiver cooled in a "Dry-ice"-acetone mixture. Hydrogen chloride was bubbled into the distillate, and the resulting precipitate was filtered off. Recrystallized from water-methanol, the ethylene diamine dihydrochloride, after drying over P<sub>2</sub>O<sub>5</sub> and KOH pellets, weighed 70.9 mgm. (85%).

Picrate, recrystallized from absolute ethanol, melted with dec. at 229.5-232°. Lit. 230 - 235° (33)

Cyclopentanone (XX) (57)

Two hundred gm. of powdered adipic acid and 10.0 gm. of powdered  $\text{Ba}(\text{OH})_2$  were thoroughly mixed and then heated at  $300^\circ$  in a salt-bath. The crude cyclopentanone and water distilled over at  $101-102^\circ$ . The distillate was saturated with anhydrous  $\text{K}_2\text{CO}_3$ . The cyclopentanone was separated, dried with anhydrous  $\text{CaCl}_2$ , and distilled through a short column to yield 886 gm. (77.1%) of a cyclopentanone boiling at  $128-129^\circ$  at atmospheric pressure.

Cyclopentanol (XXI) (47)

Cyclopentanone (88 gm., 105 moles) was slowly added, over a period of 105 minutes, to a well stirred suspension of 12.3 gm. (0.324 moles) of lithium aluminum hydride in approx. 300 ml. of pure, anhydrous ether. The reaction mixture was then refluxed for one and a half hours. Cautiously, wet ether was then introduced, followed by cold 10%  $\text{H}_2\text{SO}_4$ , until most of the inorganic solids dissolved and two distinct phases formed. This mixture was then continuously extracted with ether for 20 hours, and the resulting ether extract distilled. The fraction boiling at  $124-128^\circ$  was collected. This distillate dried with  $\text{CaSO}_4$  and redistilled yielded 38.8 gm. (43.5%) of cyclopentanol boiling at  $138-139.5^\circ$ .

Cyclopentene (XXII) (16)

In a 250 ml. two-necked flask, equipped with a separatory funnel and a 20 cm. long, four-necked Wurtz column filled with pieces of glass tubing (5 mm. long and 6 mm. in diameter), was placed 15.0 gm. of 85% phosphoric acid. The column was attached to a condenser, and the receiving flask was heated to 173°, using a salt-bath of potassium nitrite and potassium nitrate. From the dropping funnel, over a period of two hours, 43.0 gm. of cyclopentanol was slowly added. After this addition, the bath temperature was raised to 200° and maintained at 200° for 40 minutes. The temperature of the distillate did not rise above 85° during the whole operation. The distillate was dried with anhydrous calcium chloride, then with anhydrous calcium sulfate. The dried distillate was distilled through a 25 cm. long - 1 cm. i.d. column, packed with 4 mm. glass helices, yielding 32.0 gm. (95.9%) of product boiling at 42-44°. Lit. 46°.

Trans-cyclopentane-1,2-diol (XXIII) (44)

In a 3-necked, 1-litre flask, equipped with a condenser, dropping funnel and stirrer, was placed 31.5 gm. (0.464 moles) of cyclopentene. Controlling the temperature of the reaction mixture so that only slight refluxing was obtained, a mixture of 207 gm. of 30% hydrogen peroxide (0.547 moles) and 558 gm. of 90% formic acid (10.9 moles) was slowly added with stirring through the dropping funnel.



After this addition was complete, the reaction mixture was kept at 40° for four hours. The next day, the formic acid and water were removed under reduced pressure (water aspirator). The remaining oil was dissolved in approximately 100 ml. of 12% sodium hydroxide, and then refluxed for 40 minutes. To the contents of the reaction flask, dilute sulfuric acid was added until the mixture was just slightly basic (pH.8). The water was distilled off under reduced pressure and the remaining oil was vacuum distilled. The product, which had a b.p. of 110-113° at 2-3 mm., weighed 26.4 gm. (55.9%).

Di-p-nitrobenzoate, crystallized from ethanol, m.p. 141.5-142.5°. Lit. 143° (44).

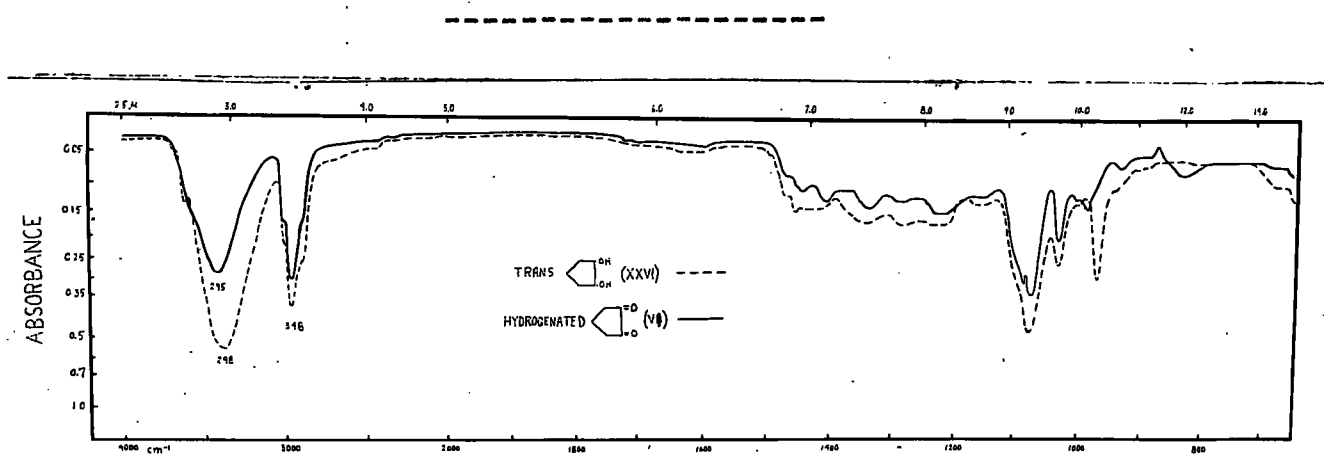


Fig. 1.--Infrared spectrum of (cis-trans) cyclopentane-1,2-diol, (VII), and trans-cyclopentane-1,2-diol (XXVI), as 3% solutions in chloroform. The analysis was done by E. H. Pol, of the British Columbia Research Council.

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