The Reactions of gem-Dihalocyclopropanes with Organometallic Reagents

by

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ABSTRACT

Part I: The reaction of 6,6-dibromobicyclo[3.1.0]hexane with methyllithium at low temperature afforded a high yield of a 3:1 mixture of cis-syn-cis- and cis-anti-cis-pentacyclo[18.4.0.^{2,7} 0.^{8,13} 0^{14,19}] tetracosa-2,12,14,24-tetraene. The chemistry of these systems leading to the assignment of their structures is presented.

The reaction of the dibromocyclopropane with methyllithium in refluxing ether and other solvents led to a high yield of trans-tricyclo [6.4.0.0^{2,7}] dodec-2,12-diene which was reduced to trans-tricyclo[6.4.0.0^{2,7}]dodec-1-ene. The elucidation of the structure of these compounds is presented.

Simple olefins did not trap an intermediate from the reaction of the dibromocyclopropane with methyllithium; however, styrene was found to be an efficient trapping agent, forming a 2.2:1.0 mixture of exo- and endo-7-phenylbicyclo[4.2.0]oct-1-ene. These olefins were hydrogenated to exo- and endo-7-phenylbicyclo[4.2.0]octane and these hydrocarbons were equilibrated to mixtures of the two compounds in which the exo-hydrocarbon predominated. The double bonds in these olefins were cleaved oxidatively to form 2-(3-carboxypropyl)-3-phenylcyclobutanone and this keto-acid was further oxidized to a mixture of 3-phenyl-4-(3-carboxypropyl)-butyrolactone and 2-(3-carboxypropyl)-3-phenylbutyrolactone in which the former predominated. Other chemistry of all of the above compounds is described.

The mechanism involved in the formation of the hydrocarbons described above is believed to involve 1,2-cyclohexadiene as a highly reactive intermediate. This intermediate is believed to react with itself to form an activated dimer which can ring close near room temperature to form the cyclobutane but itself dimerizes at -80° to form the tetraenes. Detailed mechanistic interpretations are discussed.

The reaction of 6,6-dichlorobicyclo[3.1.0]hexane with organometallics did not parallel the reaction of the dibromocyclopropanes, giving rise to a very complex reaction mixture.

The alkylation of 2,3-dibromocyclohexene with n-butyllithium afforded 2-bromo-3-n-butylcyclohexene. The identification of this monobromide and its solvolysis and reduction products are described.

Part II: The products of the addition of dibromo- and dichlorocarbenes to bicyclo[2.2.1]heptene and dibromocarbene to bicyclo[2.2.1]heptadiene are presented along with their structural elucidation and derivatives. A mechanistic consideration is given for the addition of dihalocarbenes to the above olefins and the formation of the products of such additions.

Thesis Supervisor: William R. Moore
Title: Assistant Professor of Chemistry

FOR

WILLIAM II AND E. ALEX

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The author wishes to express his sincere gratitude to Professor William R. Moore, for his expert and imaginative guidance during the course of this thesis, and for many hours devoted to the careful explanation of topics of chemical interest.

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Sincere appreciation is offered to Jean King, Vera Kramar and Nancy Alvord for the measurement of spectroscopic data; to Dr. S.M. Nagy and associates for elemental analyses and to Mr. Norman Nicholson for aid in the construction of equipment.

Thanks also to my parents, Mr. and Mrs. E.V. Moser, Sr. for their patience and example.

I especially wish to thank Terry for her understanding during the long hours which I spent away from the family during the course of this work. Furthermore, a large measure of gratitude is extended to her for the typing of all manuscripts pertaining to this thesis; and special thanks are offered for the careful typing of the final manuscript, under conditions which were less than ideal. Her faith and forbearance during this period, I will forever remember.

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Introduction

A convenient preparation of gem-dihalocyclopropanes was discovered by Doering and Hoffman[1] by the treatment of a haloform with an alkoxide in the presence of an olefin. Since this time the chemistry of these systems has been widely studied and reviewed.[2,3,4]

The studies which are pertinent to the work described herein are the reactions of gem-dihalocyclopropanes with organometallic reagents. Moore and Ward[5] found that 1,2-undecadiene, 2,3-heptadiene and 1,2-cyclodecadiene could be prepared in high yield by treatment of the appropriate gem-dibromocyclopropane with an organometallic reagent.[6] It was previously reported[7] that certain acyclic allenes could be prepared by treating gem-dihalocyclopropanes with magnesium in ether. In the above cases, no evidence could be cited for the existence of a carbene intermediate. However, the reaction of 7,7-dibromobicyclo[4.1.0]heptane (1) with an organometallic reagent [5,8] was found to proceed through a carbene intermediate. Although no allene (1,2-cycloheptadiene) could be detected in this reaction, hydrocarbons such as 2 a-c which could result from a carbene, self-insertion reaction, were isolated.

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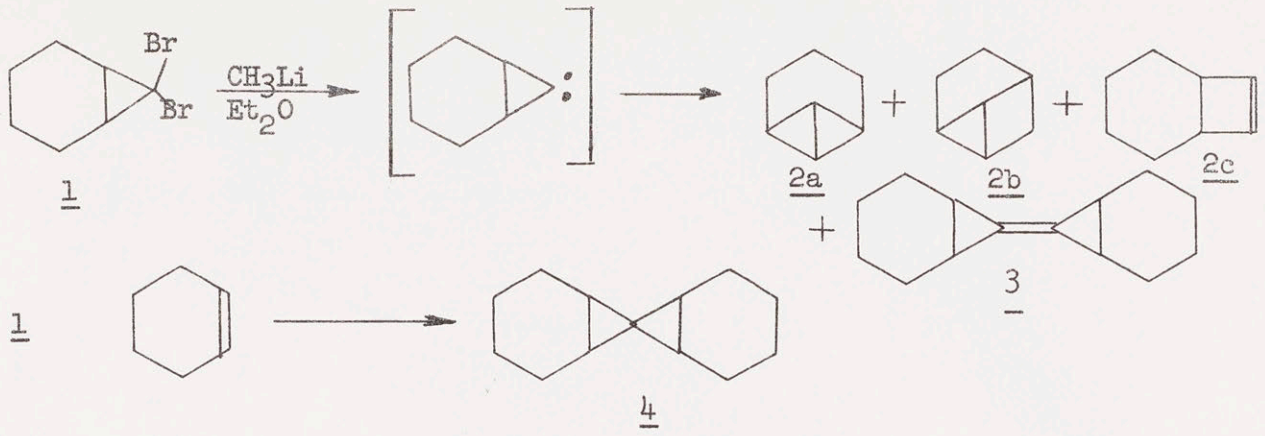
(1) W.von E.Doering and A.K.Hoffmann, J.Am.Chem.Soc., 76, 6162, (1954).
(2) W.E.Parham and E.E.Schweizer, Org.Reactions, 13, 55 (1963).
(3) P.Miginiac,Bull.Soc.Chem. France., 2000 (1962).
(4) W.Kirmse, Angew.Chem., 73, 161 (1961).
(5) W.R.Moore and H.R.Ward, J.Org.Chem., 25, 2073 (1960).
(6) L.Skattebøl, Tet. Let., 167 (1961).
(7) W.von E.Doering and P.M.La Flamme, Tetrahedron, 2, 75 (1958).
(8) W.R.Moore, H.R.Ward, and R.F.Merritt, J.Am.Soc., 83, 2019 (1961).



Additional evidence for the carbenoid character of the reaction intermediate was demonstrated by the trapping of spiropentane 4 when the reaction was carried out in the presence of cyclohexene.

Although Skell and Garner first reported [9] the preparation of 6,6-dibromobicyclo[3.1.0]hexane 5, the compound reported was probably 2,3-dibromocyclohexene 6 rather than the gem-dihalocyclopropane 5 based on a comparison of the refractive indices of compounds 5 and 6 and that of the reported compound. The present work showed, as did the report by Winstein and Sonnenberg,[10] that 6,6-dibromobicyclo[3.1.0]hexane 5 was cleanly rearranged by a facile thermal process to 2,3-dibromocyclohexene 6. The dichloro analog was found to rearrange more slowly in a similar manner.[11] These rearrangements must be mechanistically related to the silver ion catalyzed solvolysis of dihalobicyclo[3.1.0]hexanes reported[12] by Skell and Sandler.

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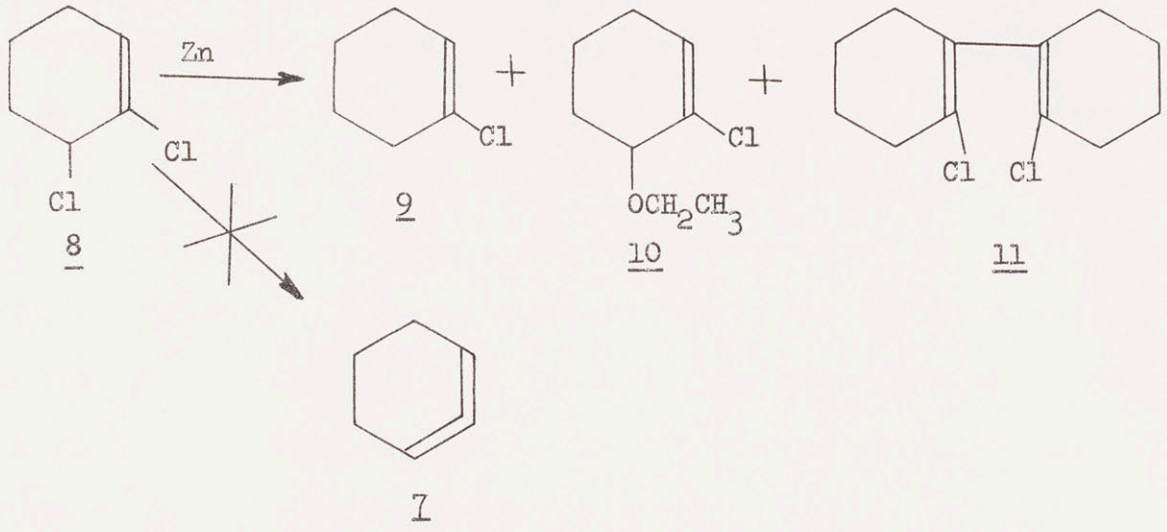
(9) P.S.Skell and A.Y.Garner, J.Am.Chem.Soc., 78, 5430 (1956).

(10) J.Sonnenberg and S.Winstein, J.Org.Chem., 27, 748 (1962).

(11) E.Bergman, J.Org.Chem. 28, 2210 (1963).

(12) P.S.Skell and S.R.Sandler, J.Am.Chem.Soc., 80, 2024 (1958).

N.A. Domnin[13] attempted to synthesize 1,2-cyclohexadiene 7 by treating 2,3-dichlorocyclohexene 8 with zinc in refluxing ethanol. The products isolated from this reaction are depicted below:



By carrying out the reaction in dioxane, formation of compound 10 was eliminated. The treatment of the dichloride 8 or the dichloride 11 with sodium in ether reported a 39% yield of a material which was thought to be a tetramer of C_6H_8 as well as an unspecified amount of undistillable material which was said to be an octamer of C_6H_8.

Ball and Landon attempted to prepare 1,2-cyclohexadiene 7 by the action of sodium amide in liquid ammonia[14] on 1-chlorocyclohexene. The reported product was an undistillable polymer.

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(13) N.A.Domnin, J.Gen.Chem. (U.S.S.R.), 15, 461 (1945).

(14) W.J.Ball and S.R. Landon, J.Chem.Soc., 2298 (1962).

Discussion

When methyllithium in ether was added to a solution of 6,6-dibromobicyclo[3.1.0]hexane (5) in ether at -80°, the product analysis on several gas chromatographic columns showed that no C_6H_8 hydrocarbon could be detected. The course of the reaction did not parallel that found for the reaction of 7,7-dibromobicyclo[4.1.0]heptane (1) mentioned previously. Programmed temperature gas chromatographic analysis established that the product consisted of traces of "dimeric" material, $(C_6H_8)_2$, a small amount of "trimeric" material $(C_6H_8)_3$, and mainly "tetrameric" material, $(C_6H_8)_4$. Similar results were obtained on adding the dibromide 5 to the methyllithium and on using n-butyllithium rather than methyllithium. When the dibromide 5 was added to methyllithium in refluxing ether, the dimeric material $(C_6H_8)_2$ was the principal product.

Whereas simple olefins were found to "trap" an intermediate in the reaction of 7,7-dibromobicyclo[4.1.0]heptane (1) with methyllithium,[5,8] it was found that cyclohexene, furan, and isobutylene did not "trap" any intermediate. The products indicated above were formed in essentially the same amounts as in the absence of these olefins. However, styrene was found to be an efficient "trapping agent" leading to the formation of two products, $C_{14}H_{16}$, corresponding to 1:1 adducts of styrene and C_6H_8.

Since the products obtained from the reaction of the dibromide 5 with methyllithium were clearly different from those found from 7,7-dibromobicyclo[4.1.0]heptane (1) with methyllithium, the major part of this study became the establishment of the structures of the principal products. In the following sections the structure proofs for these compounds are presented.

The addition of methyllithium in ether to a dilute solution of dibromide in ether at -80° afforded a product mixture which was shown to consist of 2% of material whose retention time was slightly greater than that of dimeric material, 13% of "trimeric" material, and 61% of "tetrameric" material. The balance of the material was accounted for as a non-volatile "polymeric" material.

The materials believed to be "trimeric" by virtue of their gas chromatographic retention times were not investigated, principally because this material consisted of at least six compounds.

Although the "tetrameric" material appeared as a single peak on two gas chromatograph columns, a combination of crystallization and elution chromatography allowed the resolution of the mixture into two pure crystalline compounds in an isolated ratio of 3:1.

It was found that increasing the concentration of the dibromide resulted in a somewhat lower yield of volatile products accompanied by a corresponding increase in the amount of "polymer" formation (material which was not eluted from the gas chromatographic columns employed.)

In preparative experiments, employing these conditions, the combined yield of "tetrameric" material as determined by gas chromatograph fell in the range of 40-50%. Since the same product composition as above was found when the reaction mixture was hydrolyzed at -80° after 5 minutes, the reaction was shown to be rapid. Also, addition of the dibromide to the organometallic (inverse addition) and gas chromatographic analysis showed no change in the product composition. n-Butyllithium in ether at -80° showed essentially the normal product distribution.

It was found that by direct crystallization of the crude reaction mixture from methylene chloride, the major tetramer could be isolated in 33% yield as a white crystalline solid A, m.p. 133 - 134°. Addition of acetone to the mother liquor precipitated a non-volatile white solid leaving an oil which upon elution from a chromatographic column and crystallization from methylene chloride afforded ansecond white crystalline solid, B, m.p. 84.4 - 86.1°, in 11% yield.

Elemental analysis and molecular weight determination by mass spectrometry, freezing point depression in benzene, and vapor pressure lowering in benzene (employing an osmometer) established that the higher melting solid A (the major product) has a molecular formula of $C_{24}H_{32}$.

Elemental analysis of the low melting solid B (minor product) and mass spectrometry showed that the compound was consistent with the molecular formula $C_{24}H_{32}$. The mass spectra of the isomers A and B were very similar, and their gas chromatographic retention times were identical.

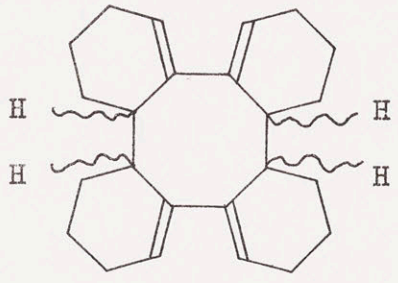
The major isomer A showed a shoulder in the U.V. spectrum (see appendix) at 215 mμ (ϵ 13,100) and a maximum at 187 mμ (ϵ 25,800). The n.m.r. spectrum showed signals due to four olefinic protons at 5.41δ as a triplet with fine splitting; 12 allyic protons, partially overlapping with the upfield signals, centered at 2.03δ with a shoulder at 2.19δ; and a broad band from 1.15 - 1.83δ arising from sixteen protons. Its infrared spectrum showed bands at 3000, 1630 and 800 cm^{-1}.

The minor isomer B showed a shoulder in the U.V. spectrum (see appendix) at 234 mμ (ϵ 7,800) and a maximum at 187 mμ (ϵ 22,700). The n.m.r. spectrum of this isomer showed signals arising from four olefinic protons at 5.38δ as a broad, complex band; and the upfield signals consisting

of 28 protons fell between 0.70-3.2δ as a very broad, complex band. This isomer also showed bands in the infrared spectrum at 3000, 1630, and 800 cm^{-1}.

Quantitative microhydrogenation of the major isomer A over platinum in acetic acid established the presence of 4.0 double bonds per molecule, a number verified by quantitative bromination by the method of Buckwalter and Wagner.[15]

Based on the spectroscopic data and the similarity of the major A and minor B isomer, the analytical and chemical data presented thus far, as well as mechanistic considerations (presented in a latter section) it seemed probable that the tetramers were two of the stereoisomers of structure 12.



12

This structure includes two conjugated diene systems which provide the correct number of double bonds, vinyl protons and allylic protons. Although one might anticipate that this structure 12 would show more intense absorption at longer wave lengths in the U.V. than was observed, due to the two

(15) H.M.Buckwalter and E.C.Wagner, Org.Anal., 3, 237 (1956).

1,3-diene systems, examination of molecular models shows that the conjugated double bonds are substantially skewed. Recently Wynberg, De Groot and Davies[16] have shown that 2,3-di-t-butylbutadiene, a compound which must have skewed double bonds, does not show U.V. absorption typical of conjugated dienes; they report λ max 185 mμ (logϵ 3.8) with a shoulder at 209 mμ (logϵ 3.4) for the diene in the gas phase.

Numerous attempts to dehydrogenate the solid tetramer A to the aromatic system, tetraphenylene, utilizing a large variety of quinone reagents and noble metals were unsuccessful. Although several of the reactions produced a material which had the same gas chromatograph retention time as tetraphenylene, the product mixtures were generally quite complex.

The major tetramer A was reduced rapidly by adding a tetrahydrofuran solution of the material to a solution of lithium in a mixture of liquid ammonia, tetrahydrofuran, and t-butyl alcohol. Previous attempts showed that the major isomer could not be reduced by adding the material as a solid to sodium in liquid ammonia in a variety of solvents or in refluxing n-amyl alcohol, presumably due to the insolubility of the solid under these conditions. The major product from the lithium reduction was a white crystalline solid C, m.p. 154-155°, obtained in 38% yield by crystallization of the product mixture from methylene chloride, leaving an oil D which gas chromatography showed to consist of three compounds in yields of 7.6, 39, and 7.6%. Elemental analysis of the crystalline

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(16) H.Wynberg, A.De Groot and D.W.Davies, Tet. Letters 17, 1083 (1963).

product C was consistent with a molecular formula of $C_{24}H_{36}$. The solid C showed no olefinic protons in the n.m.r. spectrum, but a very broad band was observed between 1.05-3.2δ. The U.V. spectrum showed a maximum at 204 mμ (ε 19,200). This compound absorbed bromine rapidly. Attempted catalytic hydrogenation of the solid in acetic acid at 58° utilizing a platinum catalyst failed as shown by quantitative recovery of starting material. This failure was presumably due to the insolubility of the compound in acetic acid. Reduction over platinum in 1:1 acetic acid-cyclooctane at 50° afforded a mixture of at least five compounds.

The crystalline product C from the lithium reduction could not be oxidized with a mixture of potassium permanganate-sodium periodate in dioxane-water according to a modified procedure of Lemieux and Rudloff.[17] However, it was ozonized to give a 33% yield of a diketone which was shown by comparison of infrared spectra and melting points to be identical to the crystalline isomer of 2,2′-dioxodicyclohexenyl (13a) prepared by the method of Moore.[18] This author found that heating a mixture of cyclohexanone and di-t-butylperoxide afforded a crystalline and a non-crystalline isomer of 2,2′-dioxodicyclohexenyl (13) . Kharasch, McBay and Urry[19] also prepared this same mixture of diketones by the action of diacetyl peroxide on cyclohexanone. Although these authors did not make an assignment of the stereochemistry to these diketones, the stereochemistry of several other products from the treatment of other ketones with acetyl peroxide was proved. In all of the cases where the stereochemistry was investigated,

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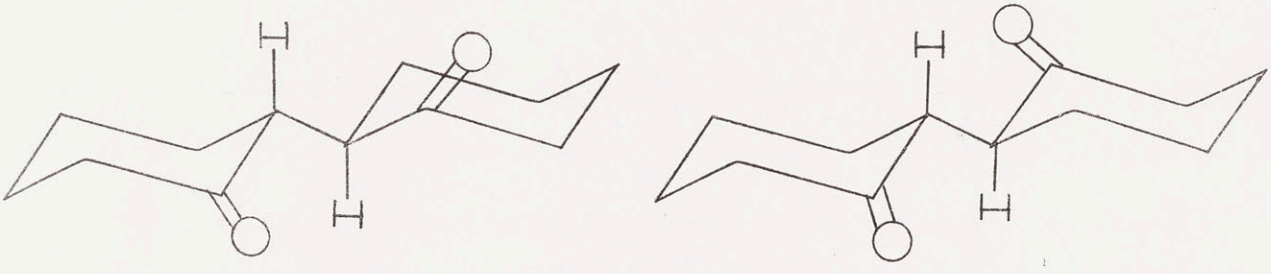
(17) R.U.Lemieux and E.Rudloff, Can.J.Chem., 33, 1701 (1955).

(18) C.G.Moore, J.Chem. Soc., 236 (1951).

(19) M.S.Kharasch, H.C.McBay and W.H.Urry, J.Am.Chem.Soc., 70, 1269 (1948).

the higher melting isomers and the more stable isomers were shown to be the meso diketones. In the above cases, the crystalline isomer of 2,2'-dioxodicyclohexenyl (13a) was shown to be identical to the diketone obtained by Plant.[20] This author obtained only the crystalline 2,2'-dioxodicyclohexenyl (13a) from the saponification and decarboxylation of the diketo ester obtained upon alkylation of 2-carbethoxycyclohexanone with 2-bromocyclohexanone. Since Plant's diketone was obtained from boiling 10% aqueous sodium hydroxide, it seems certain that it was the more stable isomer. This order of relative stabilities was verified in the present study. Treatment of the solid and liquid diketones with aqueous base resulted in no change in the solid isomer but the liquid isomer was converted to the solid diketone (based on infrared and n.m.r. data). Examination of molecular models indicates that the preferred conformation for the meso and dl diketones should be as shown below.



dl
13a

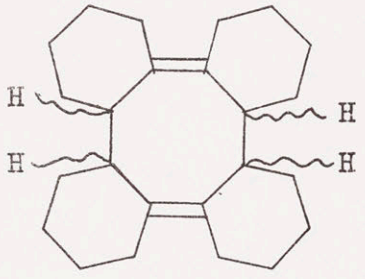
meso
13b

Electronic considerations suggest that the meso form, which has the two highly negative oxygen atoms opposed, should have a lower energy than the

(20) S.G.P.Plant, J.Chem. Soc., 1595 (1930).

dl form . In a polar solvent such as water, the carbonyl groups will be highly solvated, greatly increasing their effective bulk. This effect, which would introduce steric repulsion in the dl form should further shift the equilibrium toward the meso form.

The isolation of 2,2′-dioxodicyclohexenyl from the ozonization of the crystalline diene C requires that the latter be one of the stereoisomers of 14.



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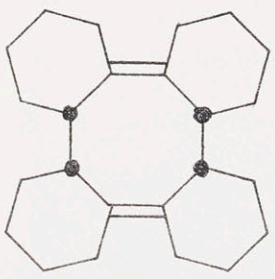
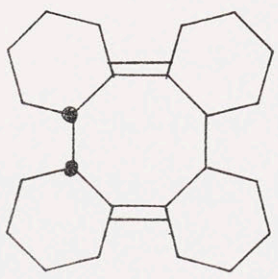
Since a single diketone was obtained, both pairs of adjacent tertiary protons in the solid C must be either cis or trans. On the assumption that the crystalline 2,2′-dioxodicyclohexenyl (13a) is the meso form, both pairs of tertiary hydrogens must be cis. Furthermore, examination of molecular models indicates that of the two possible cis fused isomers 15 and 16 only the former is capable of existence.



15

C



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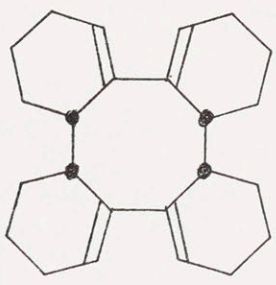


17

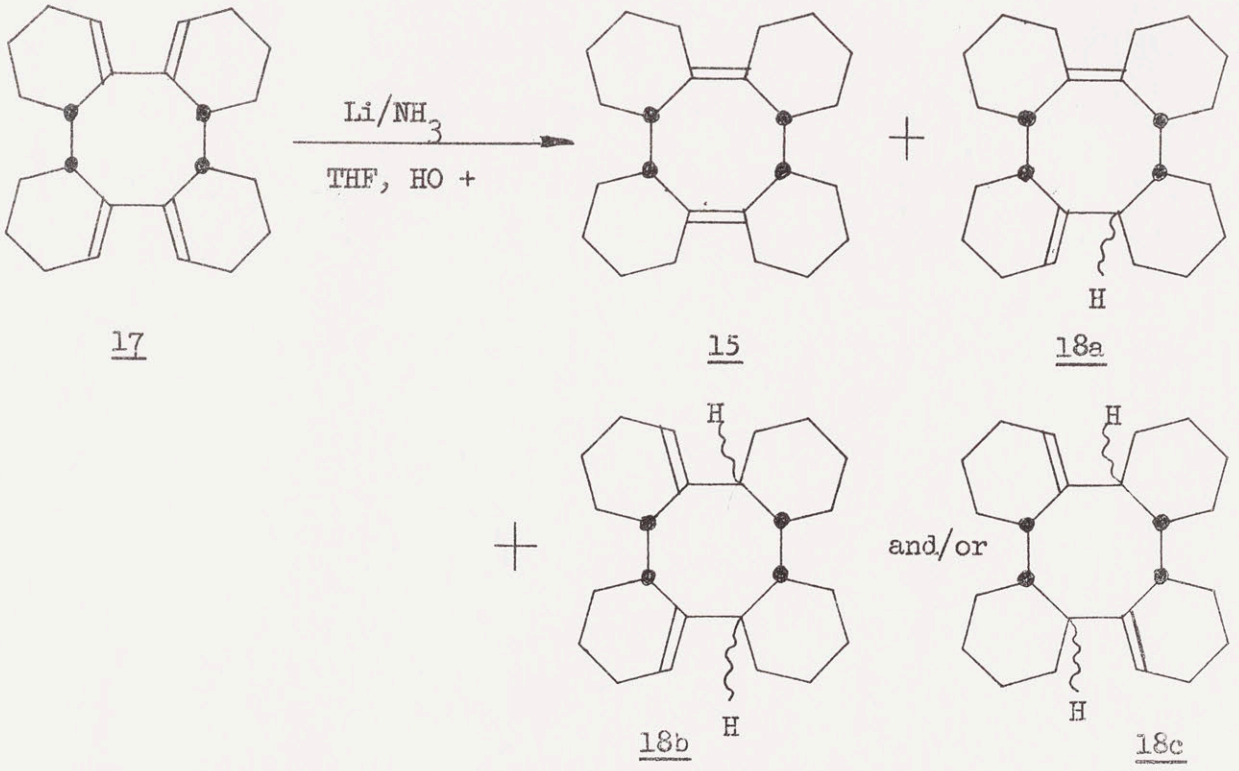
A

Since the reduction of the major tetramer A would not change the stereochemistry of the tertiary hydrogens, and since the ozonization of the reduction product was carried out under nonequilibrating conditions, the structure of the major tetramer A and the crystalline reduced isomer C are assigned as 17 and 15 respectively.

Given that the structure of the major tetramer is 17, one might raise the question as to why any product except a tetrasubstituted diene should arise on alkali metal reduction inasmuch as the latter is the expected product of a 1,4-reduction of a conjugated diene. Nevertheless, elemental analysis of the three component mixture of the oil D obtained after the crystalline product was removed form the lithium reduction of the major tetramer 17, was consistent with a mixture of $C_{24}H_{36}$ isomers. The compounds in the mixture were shown not to be secondary products arising from the solid 15 by observing a quantitative recovery of 15 upon treatment of 15 under the same reductive conditions. The fact that all of the products were formed via 1,2-reductions of major tetramer was found by investigating the n.m.r. spectrum of the mixture. From a comparison of the signals due to olefinic protons to that due to upfield protons, it was found that the spectrum is consistent with the formulation that the major component of the mixture (the 39% compound) contained one tetrasubstituted double bond and one trisubstituted double bond; and that the other two compounds (7.6% yield each) contained two trisubstituted double bonds. The U.V. spectrum (see appendix) of the mixture showed a maximum at 193 mμ (ϵ 15,700).

Based on the above data, the three components in the oil D are assigned structures 18a, 18b and/or 18c. It is not known whether the

two isomers obtained in 7.6% yield are 18b and 18c instead of being two epimers of 18b or two epimers of 18c. The fact that 54% of the product of the reduction of the major tetramer 17 resulted from 1,2-reduction can be accounted for by assuming that the badly skewed diene systems of 17 would substantially retard 1,4-reduction.



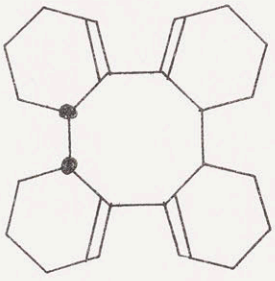
17 15 18a 18b 18c

Evidence confirming that none of the products from the lithium reduction of A or B arose from either a transanular ring closure of a 1,5-cyclo-octadiene system or from a reduction of an isolated double bond came from the observation that 1,5-cyclooctadiene was reduced very slowly under the reaction conditions above.

Reduction of the minor tetramer B with lithium as in the above reductions, afforded a 97% yield of a glass E with an elemental analysis which was consistent with the molecular formula $C_{24}H_{36}$. The gas chromato-

graphic analysis of the product mixture showed at least eight compounds. The n.m.r. spectrum of the glass E showed 2.06 ± 0.1 olefinic protons between 4.94 - 5.72δ and 34 protons between 0.50 - 3.30δ. These data indicate that the resultant dienes from the above reaction were formed by exclusively 1,2-reduction of the minor tetramer B. A maximum at 193 mμ (∈13,300) was observed in the U.V. spectrum (see appendix) and the infrared spectrum showed bands at 1628 and 820 cm^{-1}.

Based on the chemical and spectroscopic data, as well as the products from the lithium reduction, it seemed probable that the structure of the minor tetramer B could be represented by one of the structures 19, 20, 21 or 22.



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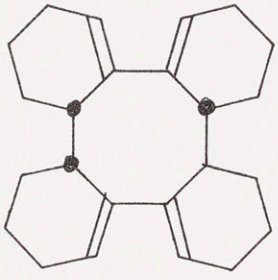

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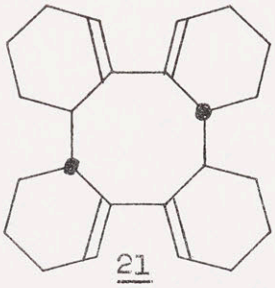

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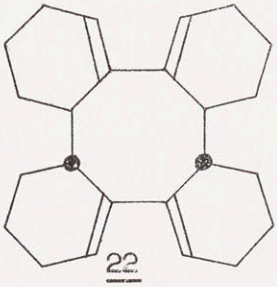


22

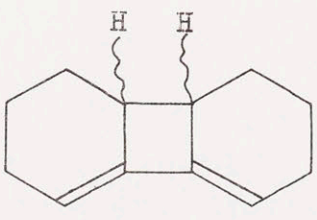
An examination of the molecular models of each of the above compounds indicates that all of them can easily be put together and would seem to be relatively stable molecules. However, if one attempts to construct the models of the compounds which would be obtained by a single 1,4-reduction on one of the conjugated diene systems of each of the above com-

pounds 19, 20, 21 and 22, it can be seen that the molecule resulting from 19 cannot be put together, even with severe distortion of the models. The models of the compounds resulting from 20, 21 and 22 can be put together easily. The molecular models for the compounds resulting from two 1,4-reductions of structures 19, 20, 21 and 22 likewise show that the molecules resulting from 20, 21 and 22 can easily be constructed, whereas the molecule resulting from 19 can not be constructed. Since it was found experimentally that the minor tetramer was reduced with lithium exclusively in a 1,2 fashion, structures 20, 21 and 22 do not seem to be consistent with this since some of the 1,4-reduction would be expected. However, structure 19 is in complete accord with the observed 1,2-reduction; therefore, the assignment of structure 19 is made to the minor tetramer B.

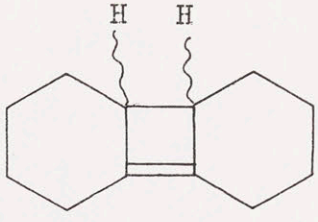
The temperature dependence in the reaction of 6,6-dibromobicyclo[3.1.0]hexane (5) was demonstrated by conducting the reaction in refluxing ether. The addition of a solution of the dibromide 5 to a solution of methyllithium in refluxing ether afforded a 55% yield of a dimer of C_6H_8 F, a 9.8% yield of "trimeric" material and a 5.2% yield of "tetrameric" material. In a preparative experiment the "dimeric" material F could be purified by a simple distillation or by sublimation at 25° at 0.05 mm. pressure. The hydrocarbon was shown to be $C_{12}H_{16}$ by elemental analysis and mass spectrometry (see appendix). The dimer F showed a U.V. maximum at 238 mμ (ϵ 14,200), and its infrared spectrum showed bands at 3010, 783 and 700 cm^{-1}. The n.m.r. spectrum of the dimer F showed signals due to two olefinic protons at 5.29δ and a very complex and broad pattern between 0.70 - 2.65δ arising from 14 protons. Quantitative microhydrogenation showed that the molecule contained two double bonds. The conjugated diene

F was shown to absorb one mole of oxygen very rapidly. Attempted Diels-Alder condensations with maleic anhydride led to polymeric material. The dimer F was rapidly reduced by sodium in liquid ammonia to a compound in 83% yield which was shown to be $C_{12}H_{18}$ by its mass spectrum (see appendix) and elemental analysis. The n.m.r. spectrum of this liquid G showed only upfield absorption between 0.5δ - 2.5δ, and its U.V. spectrum (see appendix) showed a miximum at 210 mμ (ϵ 31,000). The infrared spectrum of this compound G showed a weak band at 1695 cm^{-1} and a strong band at 815 cm^{-1}. When this compound was heated at 200° for 30 minutes in a sealed tube, it was converted quantitatively to 1,1′-dicyclohexenyl (23). This product was identified by comparison with a sample of 1,1′-dicyclohexenyl which was prepared by an independent route.

Based on the molecular formula of the dimer F; its establishment as being a conjugated diene, the ready conversion of the dimer F to a compound G which contained no olefinic protons and the clean conversion of this compound to 1,1′-dicyclohexenyl (23); structures 24 and 25 can be assigned to the dimer F and its reduction product G without indicating the stereochemistry of the bridgehead protons.



24
(F)



25
(G)

Cyclobutene 25, with unassigned stereochemistry, was reported by Crowley[21] to have been formed from the photolysis of 1,1'-dicyclohexenyl (23) utilizing a vicor-covered irradiation probe. When this conversion was attempted, in the present work, utilizing a quartz covered probe, gas chromatographic analysis showed that the product mixture consisted of two compounds with retention times which did not match that of the cyclobutene G obtained from the reduction of the dimer F . In the reaction mixture only a small peak had the same retention time as the cyclobutene G. As the irradiation was continued, one of the two major peaks was converted to the other. This result was verified by Dauben.[22] A comparison of the infrared and n.m.r. spectra (see appendix) of the cyclobutene G obtained from dimer F with the spectra of the initially formed cyclobutene H from the photolysis [23] of 1,1'-dicyclohexenyl showed that these two compounds were not the same. Since both of the cyclobutenes G and H were converted to 1,1'-dicyclohexenyl (23), it seems highly probable that they are cis and trans isomers of cyclobutene 26. A comparison of the n.m.r. spectra of Dauben's compound H and the cyclobutene G obtained from the dimer F showed that there were two protons (1.8 measured) in the former compound centered about 15 c.p.s. downfield from the lowest band in the cyclobutene G obtained in this study. Molecular models of both the cis- and trans- cyclobutenes 26, show that the bridgehead protons in the trans- compound 26a are in a favorable position to be shielded by

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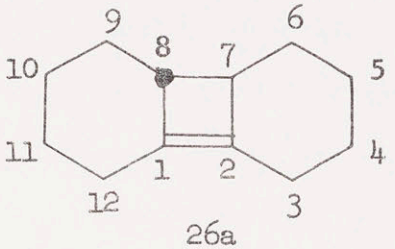
(21) K.J.Crowley, Proc.Chem. Soc., 334 (1962).

(22) Private communication from Prof. W.G.Dauben.

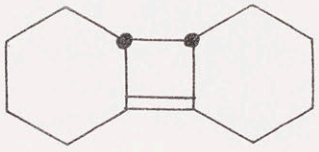
(23) These spectra were generously supplied by Prof. W.G.Dauben.

the (cis) C_6-C_7 and C_8-C_9 bonds; whereas, in the cis-compound 26b the bridgehead protons should be deshielded by the (trans) C_6-C_7 and C_8-C_9 bonds.



26a

(G)

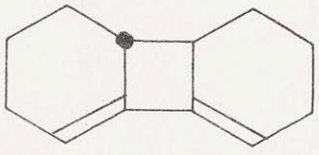


26b

(H)

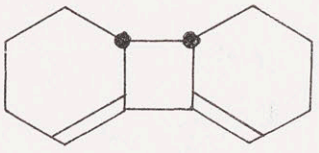
Such shielding and deshielding arises from the magnetic anisotropy[24] of the C-C bond and had been adequately demonstrated in the studies[25] of several cyclic systems. This arguement points to the trans-cyclobutene 26a for the compound G obtained in the present study.

Investigation of the molecular models of the cis- and trans- dienes 27a and 27b shows that the trans-compound 27a can be constructed readily;



27a

(F)



27b

however, even severe distortion of the molecular models does not allow the formation of the cis-compound 27b. It seems likely, then, that there is a large difference in stability of the two dienes 27, a difference which should also be a relevant factor in the formation of dimer F.

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(24) A.A.Bothner-By and C.Naar-Colin, Ann.N.Y.Acad.Sci.70, 833 (1958).

(25) W.B.Moniz and J.A.Dixon, J.Am.Chem.Soc., 83, 1671 (1961).

There is good reason to believe as is brought out in a later mechanistic discussion, that dimerization should result in the formation of the less strained diene. On this basis, the dimer F is assigned the trans stereochemistry of 27a. In turn, if one accepts this assignment chemical support is derived for the assignment of the trans stereochemistry to the cyclobutene G obtained from the sodium reduction because it seems certain that this reduction would not have altered the stereochemistry of the bridgehead protons. If this assignment is correct, this must mean that Dauben's cyclobutene H must have the cis stereochemistry 26b.

Attempted ozonization of the cyclobutene 26a afforded a low yield of a compound which had the same gas chromatographic retention time as 2,2-dioxodicyclohexenyl (13).

The highest yield of dimer 27a (68%) from dibromide 5 was obtained in refluxing cyclohexene; the dimer was formed in 17% yield when the reaction was carried out in ether at -18°. n-Butyllithium afforded only a 20% yield of dimer 27a when it was allowed to react with the dibromide 5 in refluxing ether. It was shown that the low yield of dimer 27a could not be attributed to the action of n-butyllithium on the dimer 27a.

An intermediate in the reaction of 6,6-dibromobicyclo[3.1.0]hexane (5) with organometallics could be trapped by adding methyllithium in ether to a mixture of the dibromide 5 and pure styrene at -15°. The product formed in 76% yield; was found to be a 2.2:1.0 mixture of two compounds J and K, respectively. The yield of dimer 27a was 4.6% and the balance of the product was "tetrameric" material, left as a distillation residue. Other studies showed that the product composition in this case was the same when the methyllithium was made from either methyl iodide

or methyl bromide. When the reaction was carried out in mixtures of styrene and ether, the yields of the two compounds J and K were somewhat lower.

The major styrene trapping product J could be obtained in a pure form by spinning band distillation; whereas, it was necessary to collect the pure minor trapping product K by gas chromatography.

The major trapping product J was shown to be $C_{14}H_{16}$ by elemental analysis and mass spectrometry. Its infrared spectrum showed olefinic and aromatic hydrogen absorption in the 3μ region and bands at 1603 (aromatic C=C) and 700 cm^{-1} (monosubstituted benzene). The spectrum of this olefin J was substantially different in the fingerprint region from that of the minor product K. The n.m.r. spectrum (see appendix) of J showed five aromatic protons as a sharp line at 7.31δ, one broad olefinic proton at 5.41δ, four protons in a relatively sharp band at 2.99δ, and six protons in a broad band between 0.55 - 2.3δ.

The minor trapping product K was shown to be $C_{14}H_{16}$ by elemental analysis and mass spectrometry. Its infrared spectrum showed olefinic and aromatic absorption in the 3μ region, and aromatic bands at 1603 (aromatic C=C) and 700 cm^{-1} (monosubstituted benzene). The n.m.r. spectrum (see appendix) of product K showed five aromatic protons at 7.32δ in a sharp line; one olefinic proton at 5.46δ as a broad band; a triplet of doublets centered at 3.70δ arising from one proton which partially overlapped a complex three-proton pattern in the 2.5-3.9δ region; and six protons in a broad band between 0.35 - 2.50δ.

Quantitative microhydrogenation of the major product J showed that the molecule contained one double bond. The hydrogenation product L was

shown to be $C_{14}H_{18}$ by elemental analysis and mass spectrometry. The infrared spectrum showed the normal aromatic bands for a monosubstituted benzene. The n.m.r. spectrum of L showed the benzylic proton at 3.55δ as four bands superimposed on a broad base and the remaining protons as a very broad set of bands between 0.70 - 3.00δ. Gas chromatographic analysis showed that the product was a single compound.

Quantitative microhydrogenation of the minor trapping product K showed that the compound contained one double bond. Elemental analysis and mass spectrometry (see appendix) showed that the hydrogenation product M was $C_{14}H_{18}$. Its infrared spectrum showed typical absorption for a monosubstituted aromatic ring, and this spectrum was substantially different from that of the dihydro product L obtained from the reduction of the major trapping product J. The n.m.r. spectrum (see appendix) showed signals due to a single benzylic proton in a four line pattern superimposed on a broad base centered at 3.55δ. Gas chromatographic analysis of the hydrogenated minor styrene trapping product M showed that it contained none of the reduction product L obtained from the major trapping product J. Compounds L and M could be separated only with a Craig polyester succinate column.

The carbocyclic skeleton of the reduction products L and M was established by an independent synthesis of hydrocarbon M starting with 1,3-cyclooctadiene (28). The irradiation of 1,3-cyclooctadiene (28) by the procedure of Dauben and Cargill[26,27] afforded a 24% yield of bicyclo[4.2.0]

(26) W.G.Dauben and R.L.Cargill, J.Org. Chem. , 27, 1910 (1962).

(27) S.F.Chappell and R.F.Clark, Chem. and Ind., 1198 (1962).

oct-7-ene (29) after purification. This material was treated with diborane and oxidized with chromic acid[28] resulting in a 60% yield of bicyclo[4.2.0] octan-7-one (30). This cyclobutanone 30 was treated with phenyllithium, and 7-phenylbicyclo[4.1.0]octan-7-ol (31) was isolated in 87% yield. The n.m.r., I.R. and elemental analysis were consistent with structure 31. Hydrogenolysis of this benzylic alcohol 31 over palladium in acetic acid at 60° afforded an 84% yield of 7-phenylbicyclo[4.2.0]octane 32. This hydrocarbon was shown to be $C_{14}H_{18}$ by elemental analysis and mass spectrometry. The infrared spectrum of this synthetic material was identical to the spectrum of the reduction product M of the minor trapping product K, and their gas chromatograph retention times on a wide variety of columns were identical.

As a further check on the structure of hydrocarbon M, an authentic sample of bicyclo[4.1.0]octan-7-ol was oxidized to the cyclobutanone with chromic acid in an ether-water system. The ketone 30 was treated with the same succession of reagents that were employed above, and in this way, a hydrocarbon was obtained which had an infrared spectrum identical to that of the 7-phenylbicyclo[4.2.0]octane (32) obtained as described above.

Utilizing the reagent of Cram, Kingsbury and Rickborn,[29] hydrocarbon M was easily converted to its more stable epimer L., by heating it in diethyl sulfoxide at 58° in the presence of potassium methylsulfinyl

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(28) H.C. Brown and C.P.Garg, J.Am.Chem.Soc., 83, 2951 (1961).

(29) D.J.Cram, C.A.Kingsbury and B.Rickborn, J.Am.Chem.Soc., 3688 (1961).

carbanion. The product mixture was found to be an 86:14 epimer mixture of L to M after a reaction time of 19 hours. Utilizing the same reagent at 58° for 10 days, the more stable epimer L was converted to a 90:10 mixture of epimers L to M. The latter ratio represents a more realistic equilibrium concentration due to the longer reaction time. The infrared spectra of the materials from the latter equilibration and the former equilibration were identical except for very small differences in intensity in the 14 μ region, due to slightly different concentrations of the minor epimer M in the mixtures. Epimerization of hydrocarbon L to M was also observed when a 2.2:1.0 mixture of hydrogenated trapping products L and M was treated with sodium amide in liquid ammonia for 12 hours. The infrared spectrum of the product mixture from this reaction was nearly identical to the spectrum of the product obtained from the ten-day equilibration of L reported above.

In the original work by Dauben and Cargill[26] it was shown that the photo product 29 possessed a cis-ring fusion by oxidation of the cyclobutene to cis-cyclohexane dicarboxylate. It appears almost certain, in the present work, that the configuration at the bridgehead position would not change during the course of the subsequent transformations performed on this compound.

If this is true, then the synthetic 7-phenylbicyclo[4.2.0]octane 32 must have a cis-ring fusion and therefore both of the hydrocarbons obtained from reduction of the styrene trapping products must also have the cis stereochemistry at the bridgehead. In order to define the configuration at the bridgehead positions in L and M independently, a 2.2:1.0 mixture of olefins J and K was treated with diborane and then oxidized with

chromic acid. The resultant ketone 33 , was stirred with 10% methanolic potassium hydroxide to affect (possible) epimerization at C-1 insuring that the more stable cis-ring fusion was established. Then the keto function was reduced utilizing the modified Wolff-Kishner method.[30] The product of this reaction was shown to be identical to the mixture of L and M obtained from the catalytic reduction of a 2.2:1.0 mixture of olefins J and K.

Based on the comparison of both the products L and M from the reduction of the major and minor styrene trapping products J and K with authentically prepared material, the structures of the reduced products L and M can be assigned as 34 and 32 respectively. The fact that 32 could be epimerized to 34 means that the synthetic sample was endo-7-phenylbicyclo[4.2.0]octane (32), and that it was formed from the benzylic alcohol 31 by either a dehydration followed by addition of hydrogen from the least hindered side of the molecule, or by a concerted backside displacement of the protonated hydroxyl by hydrogen. The alcohol 31 would be expected to have the exo configuration of the phenyl group since phenyllithium should have added from the least hindered side of the ketone 30. The chemistry of the compounds described above is summarized in Chart I.

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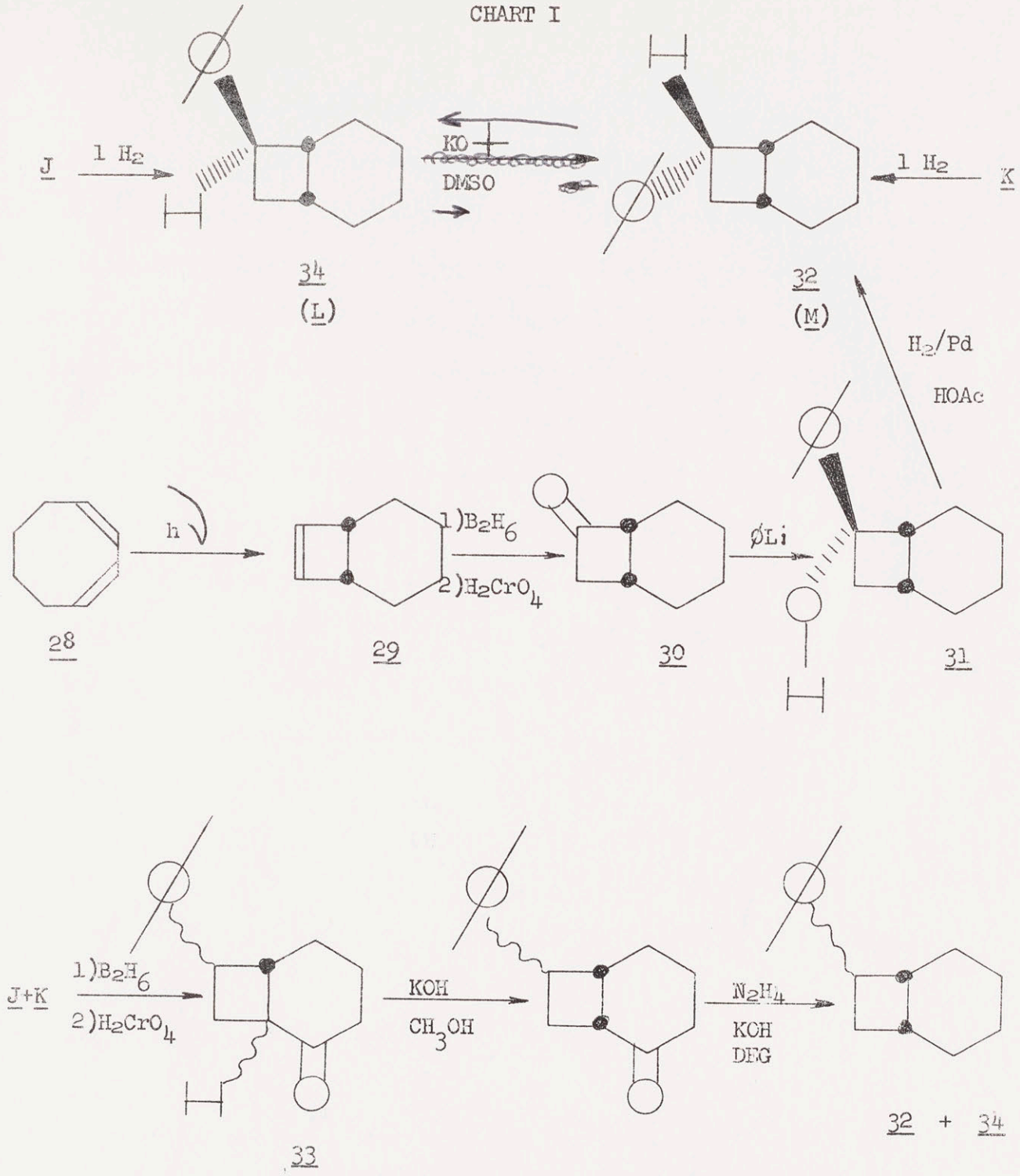
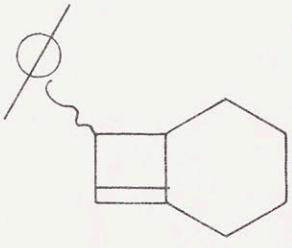
(30) Huang-Minlon, J.Am.Chem.Soc., 68, 2487(1946).

CHART I

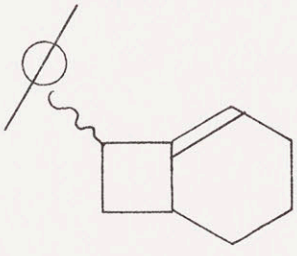

J
1 H2
KO
DMSO
1 H2
K
34
(L)
32
(M)
H2/Pd
HOAc
h
1)B2H6
2)H2CrO4
ØLi
28
29
30
31
J+K
1)B2H6
2)H2CrO4
KOH
CH3OH
N2H4
KOH
DEG
33
32 + 34

The evidence presented above establishes, beyond question, the carbocyclic skeleton of the reduced major and minor trapping products 34 and 32. It follows that the trapping products J and K must have the same carbocyclic arrangement. However, the position of the double bond in each of the trapping products must now be established. Although a chemical proof will be developed subsequently for this assignment, the position of the double bond in the two products J and K can be established logically by spectroscopic and analytical data. These data are present in the immediately following section.

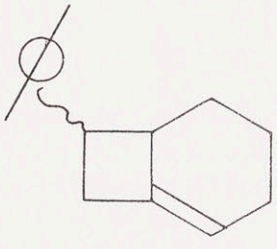
Inasmuch as both of the styrene trapping products must have a single olefinic proton (n.m.r.) (see appendix) and neither can have the phenyl group attached to the carbon-carbon double bond U.V., only structures 35, 36 and 37 need be considered.



35



36

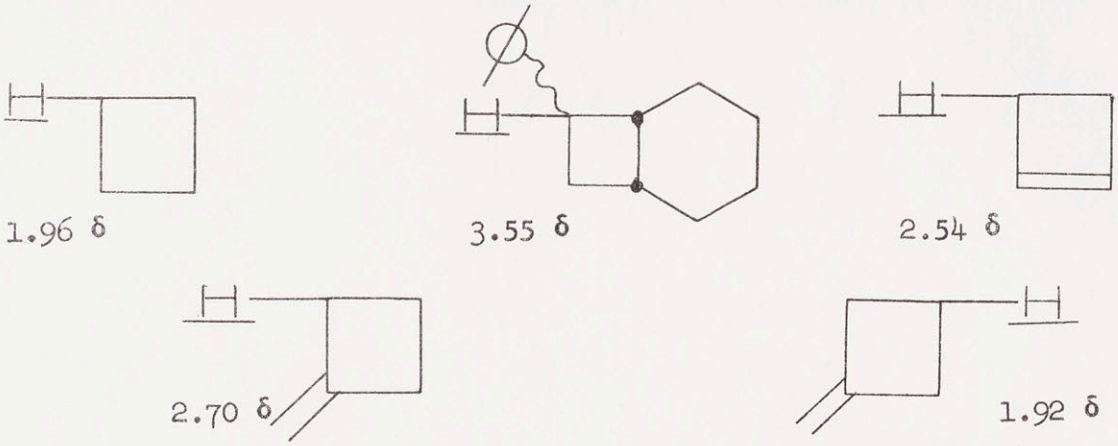


37

Structure 35 can be eliminated on the basis that the calculated n.m.r. peak position for the benzylic proton (based on cyclobutane[31] the 3-proton of cyclobutene;[31] and the benzylic proton of compound 32) is 4.13δ, a value

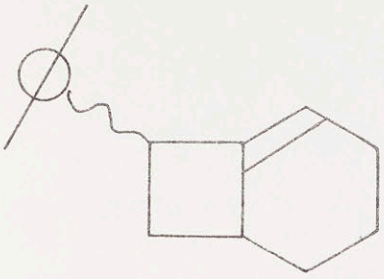
(31) K.B.Wiberg and B.J.Nist, J.Am.Chem. Soc., 83, 1226 (1961).

which is substantially lower than the observed benzylic proton in products J and K. The lowest cyclobutane proton in the observed spectra appeared at 3.70δ. Also, the observed spectra showed four cyclobutane protons as opposed to the two which structure 35 would demand. The choice between the two remaining structures 36 and 37 can be made utilizing the n.m.r.

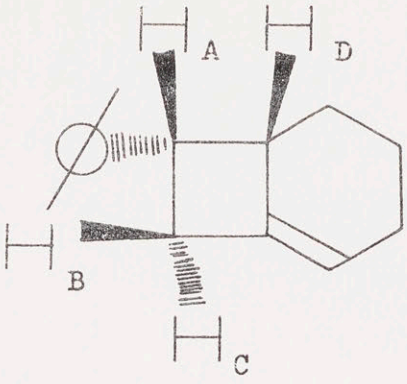


chemical shifts for the alpha- and beta-hydrogens of methylene cyclobutane;[32] cyclobutane;[31] and the benzylic hydrogen of 7-phenylbicyclo[4.2.0]octane (32). The calculated peak position for the benzylic proton in structure 36 is 4.29δ. The calculated peak position for the corresponding proton in the gross structure 37 proposed for both of the trapping products is 3.51δ, and the lowest observed proton in the minor trapping product K was 3.70δ. The fact that the benzylic proton was at higher field (2.99δ) in the spectrum of the major trapping product J as compared to the calculated value (3.51) will be discussed later. In addition to the inconsistency with the above calculated position of the benzylic proton, structure 36 is not consistent with the splitting observed of the benzylic proton in the minor trapping product K. (Nothing can be said about the benzylic proton of the major product J since it was obscured by the three other cyclobutane protons.)

(32) N.M.R. Spectra Catalog., Varian Associates, Palo Alto Calif., Spectrum No. 109.



36



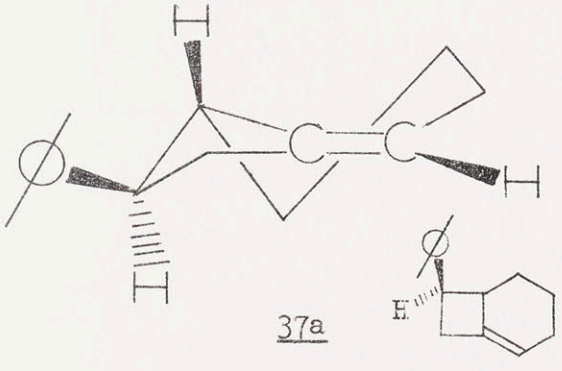
37b

The spectrum observed for the minor trapping product K showed the benzylic proton centered at 3.70δ as a triplet of doublets with coupling constants of $J_1 \approx J_2 \approx 9$ and $J_3 \approx 3$ cps. Molecular models of the proposed structure 37b show that the molecule is rigid and cannot vary the dihedral angle between the benzylic proton and its neighboring protons by more than a few degrees. The measured dihedral angles (Dreiding Models) between H_A-H_C, H_A-H_D and H_A-H_B were 110°, 18°, and 24° respectively. The calculated coupling constants[33] for vicinyl protons with the above dihedral angles are 3.1, 7.1, and 6.8 cps. respectively. Therefore, the observed triplet of doublets would be entirely consistent with the formulation 37b. Irrespective of the stereochemistry of the benzylic proton in the alternate structure 36 a coupling constant of 3 cps. is considered too large to be due to coupling of H_A with the olefinic proton. Models of 36 also show that the benzylic proton, in either the exo- or endo- configuration, is not in a favorable

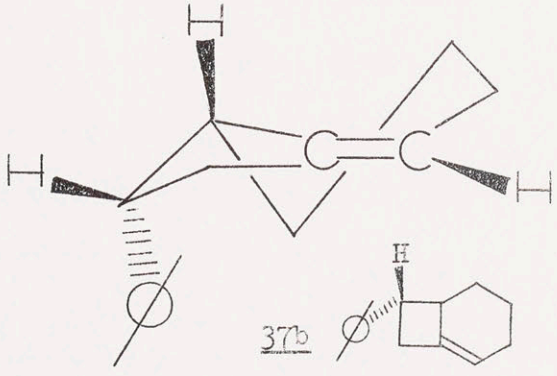
(33) Conroy, Advances in Org. Chem., Methods and Results, Vol. II, 1960 p. 311.

position to line up with the H_D hydrogen for the type of backside coupling that Wiberg, Lowry and Nist[34] observed in the bicyclo[2.1.1]hexane system. Since the observed pattern cannot be accounted for by structure 36 but is entirely consistent with structure 37b, structure 37b is assigned to the minor trapping product K.

To show that the structures of the trapping products J and K were consistent with one another with respect to both the position of the double bond, and the stereochemistry assigned, it was observed that the n.m.r. spectrum of the reduced major trapping product 34 showed its benzylic proton at 2.55δ whereas in the olefin J this proton appeared at ~2.99δ . This downfield shift of the benzylic proton in the reduced product 34 clearly indicates that it was being shielded in the parent olefin J. The benzylic proton in minor trapping product K appeared at 3.70, and it appeared at 3.55δ in its reduced product 32. This small change in chemical shift indicates that this proton is not in a stereochemical position to feel any large electronic effect from the double bond. The drawings shown below approximate the stereochemistry shown in the models of these exo-37a and endo-37b epimers. Examination of the models shows



37a



37b

(34) K.B.Wiberg, B.R.Lowry and B.J.Nist, J.Am.Chem.Soc., 84, 1594(1962).

that the benzylic proton in structure 37a is in a favorable position for shielding by the double bond, whereas the same proton, in the epimeric compound 37b is not. The benzylic protons in both reduction products gave rise to broad complex signals centered at ca. 3.55δ. The patterns are roughly that of strongly perturbed quartets[35] indicating fairly strong coupling of the order of 6-8 cps., with three protons.

Examination of models demonstrates that these saturated compounds 32 and 34 are much more flexible than the parent olefins. As a consequence it appears that cis and trans vicinal coupling of the protons on the cyclobutane ring may be roughly equal.

The combined spectroscopic arguments, then, lead to the assignment of structure 37a to the major and structure 37b to the minor styrene trapping products J and K. At this point it should also be indicated that the structures 37a and 37b would be the expected product according to the mechanistic interpretation which is presented later.

The mass spectra of these hydrocarbons 37a and 37b (see appendix) are virtually identical showing only minor differences in peak intensities, a finding consistent with the epimeric assignment. It is worth noting that the molecular ion produced from 37b, the more crowded epimer, is somewhat less intense than that of 37a. (In this comparison the percent of the molecular ion of the entire fragmentations was used instead of the percent of the molecular ion of the largest peak.) Biemann[36] has noted that although epimers usually show very similar fragmentation patterns, at least

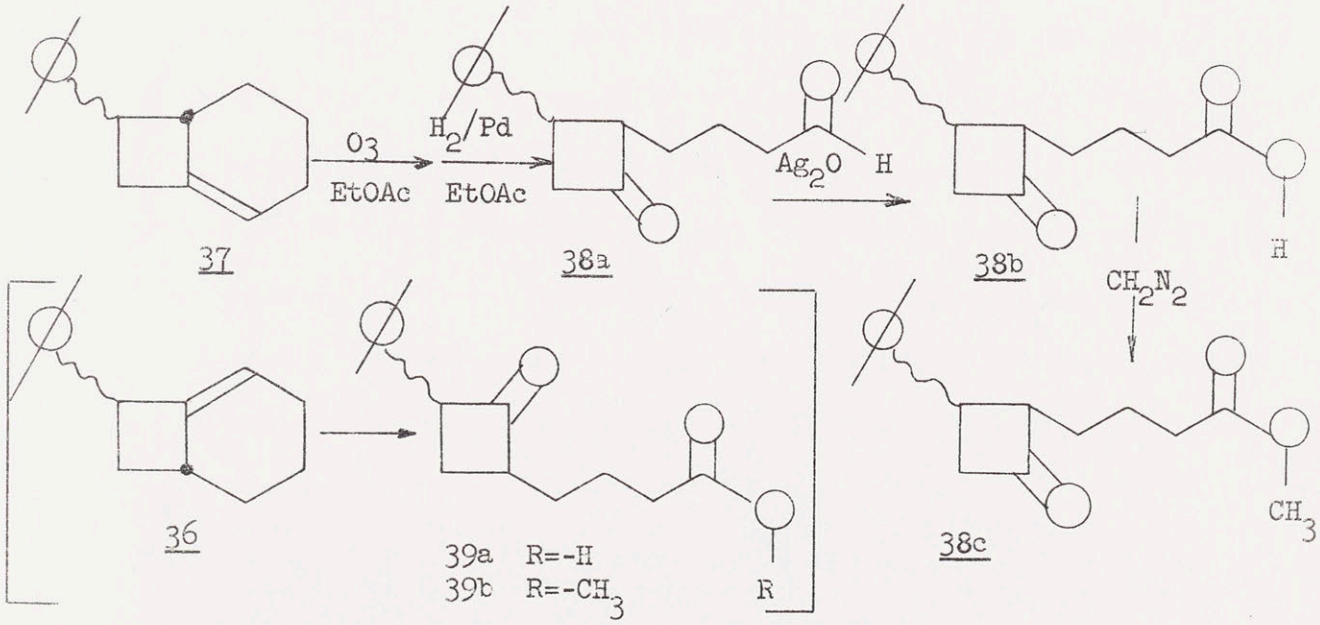
(35) Any such pattern must be complicated by both"virtual" coupling and also small coupling to the ortho protons of the phenyl group.

(36) K.Biemann, Mass Spectrometry, McGraw Hill, Inc., 1962, p.145.

in certain cases the more crowded epimer gives the less intense molecular ion.

A chemical proof confirming the assignment of structures 37a and 37b to the styrene trapping products has been obtained by ozonolysis of these olefins. If these structures are correct, this oxidation should afford epimeric cyclobutanone with only one substituent alpha to the carbonyl group.

Several studies were made in order to determine the optimum conditions for effecting the conversion of the styrene trapping products 37a and 37b to their corresponding cyclobutanones 38 (See the experimental section.) The best results were obtained when the olefins were ozonized in ethyl acetate at -80°, worked up immediately by a catalytic hydrogenation over 10% palladium on carbon followed by oxidation of the aldehyde with silver oxide. In this way from a 2.2:1.0 mixture of 37a and 37b a 71% yield of the keto-acid 38b could be obtained which was contaminated by only trace amounts of other compounds.



Treatment of the keto-acid 38b with potassium carbonate in deuterium oxide for 14 hours followed by n.m.r. analysis of the acidic residue showed that 2.4 to 2.6 hydrogen atoms per molecule had been replaced by deuterium.[37]

The deuterated acid was then converted to its keto-ester by treatment with ethereal diazomethane. N.m.r. analysis of this keto-ester prior to purification by gas chromatography showed the same extent of exchange found in the keto-acid. However, in several experiments it was found that the keto-ester collected by gas chromatography contained substantially less deuterium than was found in the original material; the values found ranged from 0.5 to 2.5 deuterium atoms per molecule. Apparently the conditions required for gas chromatography resulted in appreciable D → H exchange on the columns employed.

The presence of a cyclobutanone moiety in keto-acid 38b and the related methyl ester 38c was clearly established by the presence of a strong band at ca. 1780 cm^{-1} in the infrared spectra of both. This finding by itself definitely excludes the possibility that either of the styrene trapping products could have structure 35, because the latter would yield a cyclohexanone on oxidation. Structures 36 and 37 would both yield cyclobutanones. But the cyclobutanone derived from 36 would have only two hydrogen atoms alpha to the keto group, and thus capable of undergoing H → D exchange, whereas that from 37 would have three. Although the extent of exchange realized was a little less than three deuterium atoms permolecule, it was sufficient to demonstrate that

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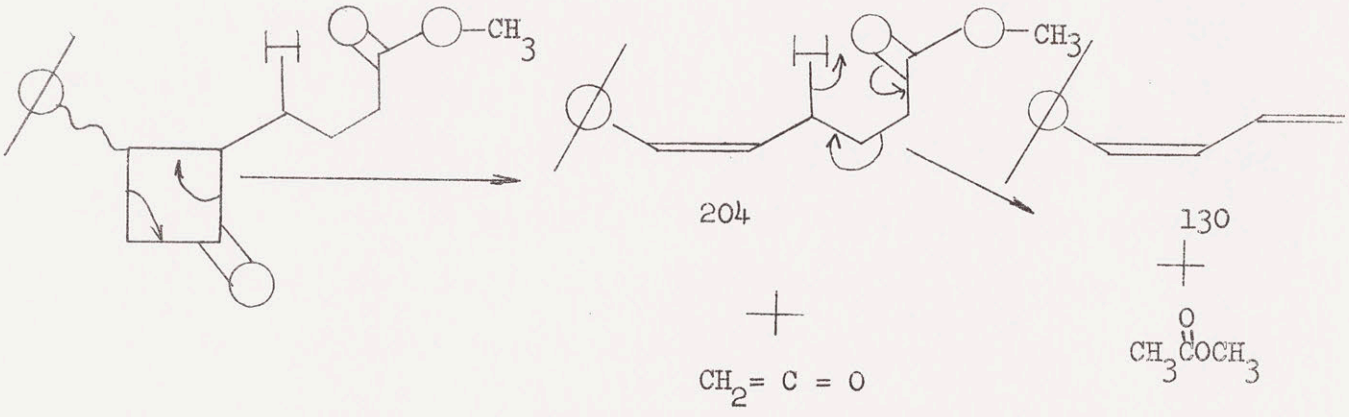
(37) There is ample precedent for the implied contention that the methylene group alpha to the carboxyl group would not undergo deuterium exchange under the conditions employed. Furthermore, the n.m.r. spectra establish this point in the present case.

the keto-acid must have more than two hydrogen atoms capable of undergoing exchange. Inasmuch as structure 37 alone can fit this requirement, one can conclude, validly, that the styrene trapping products must be the epimers of 37.

The mass spectrum (see appendix) of keto-ester 38c strongly supports the assigned structure. Although no molecular ion is present, intensive peaks at m/e 204 and 130 are found. A plausible fragmentation is depicted below.

(38)



The keto-ester 39b which would be derived from structure 36 could not give this fragmentation pattern.

Another route to the chemical proof of the position of the double bond in the styrene trapping products 37a and 37b was found by ozonization of these olefins followed by a direct (Baeyer-Villiger) oxidation of the intermediate cyclobutanone to the corresponding lactones.

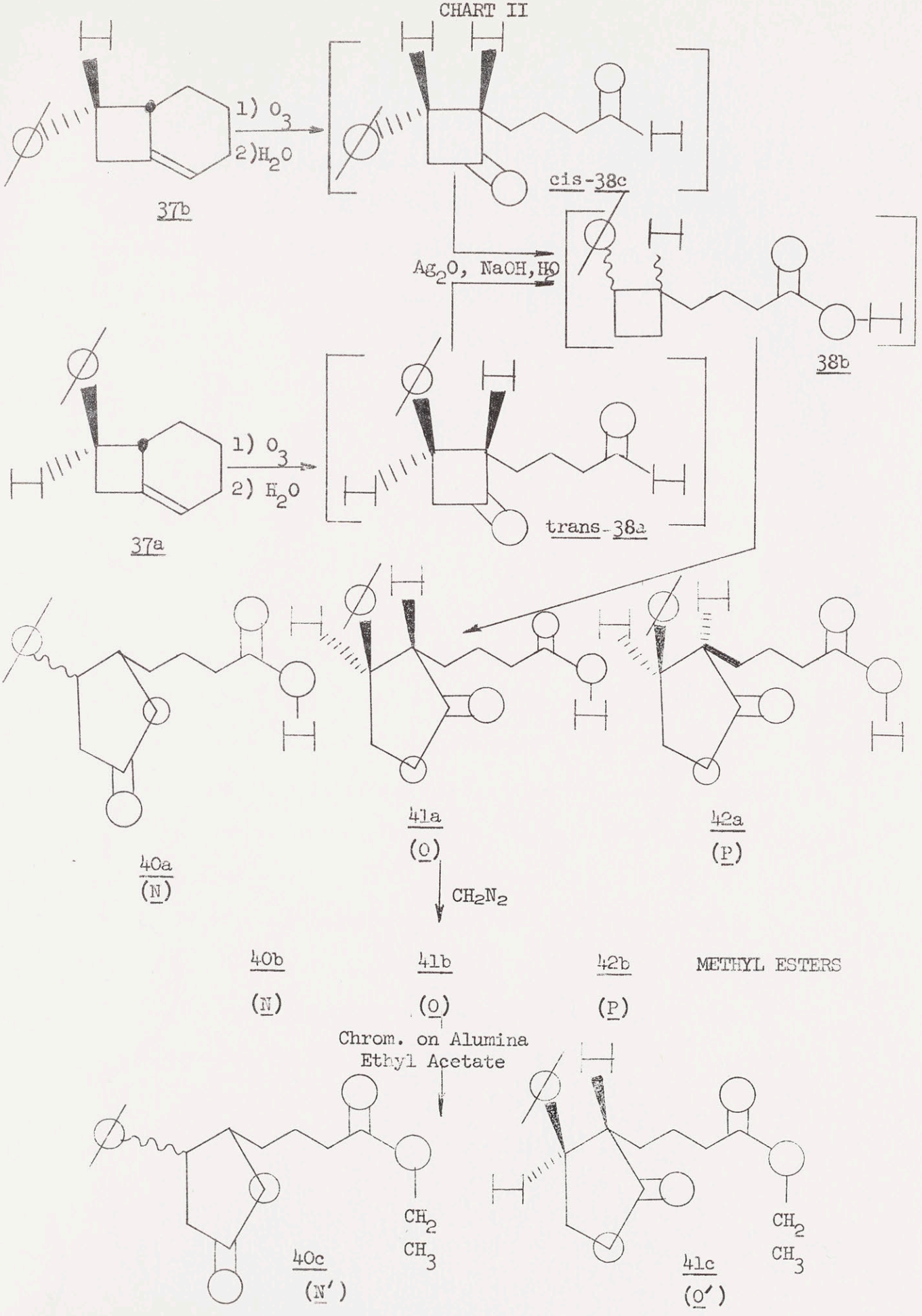
A mixture of the olefins 37a and 37b was ozonized in methanol at -80°, and the reaction mixture was treated directly with silver oxide in

(38) K. Biemann, op. cit., p.126.

aqueous sodium hydroxide at 25°. The products from this series of reactions were methylated with diazomethane. This sequence afforded, principally, two lactones N and O and a trace of a third P. The ratio of the major lactone N in the mixture to the sum of the minor lactone O and trace compound P was 3.8:1.0 in a combined yield of 76%. Treatment of the minor trapping product 37b with the same reagents afforded a lactone mixture in which the ratio of the major lactone N to the sum of the other two lactones was 3.4:1.0. However, in this case P was no longer a trace component; the P:O ratio was ca. 2. These transformations are depicted in Chart II according to the assignment of structures 37a and 37b as the major and minor styrene trapping products respectively.

That these compounds were lactones was shown by elemental analysis and determination of the saponification equivalent of the lactone mixture from the oxidation of the major trapping product 37a. All of the mixtures of N, O and P exhibited intense bands in the infrared at 1785 and 1740 cm^{-1} establishing that these compounds were γ-lactone-esters. From a mixture of the N, O, and P lactones, N and O could be obtained preparatively by a combination of elution and gas chromatography. However, during the course of the elution chromatography, which employed alumina, the methyl esters were transesterified to the corresponding ethyl esters N′ and O′ presumably by the ethyl acetate used as an eluent. These ethyl esters N′ and O′ were readily transesterified in methanol back to the methyl esters N and O. Since only one minor lactone, O′, was eluted from the column it seems probable that O and P were epimers and that O represented the less stable cis- configuration which, on the alumina column, underwent both epimerization and transesterification to yield O′. On this basis, O is considered

CHART II


1) O_3
2) H_2O
37b
cis-38c
Ag_2O, NaOH, H_2O
38b
1) O_3
2) H_2O
37a
trans-38a
40a
(N)
41a
(O)
42a
(P)
CH_2N_2
40b
(N)
41b
(O)
42b
(P)
METHYL ESTERS
Chrom. on Alumina
Ethyl Acetate
CH_2
CH_3
40c
(N')
CH_2
CH_3
41c
(O')

to be the trans epimer.

It is probable that the major lactone N, in all of the product mixtures, also consisted of a mixture of epimers, although if so, their retention times must have been nearly identical. Some indication of a slight separation of epimers was noted in the shape of the gas chromatographic peak of N obtained from the oxidation of the minor styrene trapping product 37b. This peak was broad and skewed on the trailing edge when compared with the peak obtained from the major lactone N derived from the major styrene trapping product 37a. Epimers 37a and 37b represent epimerically pure compounds which, in principle, would give epimerically different cyclobutanones, 38. The major trapping product 37a would initially give the more stable trans-epimers of these ketones 38 which would not be expected to undergo significant epimerization; thus predominantly trans-lactones 40a and 41a would be formed. However, the less stable cis epimers of these ketones 38 derived from the product 37b, in all cases must have undergone some epimerization prior to lactonization, thus leading to the formation of an epimeric mixture of lactone 40a, and 41a and 42a.

The elution chromatography resulted in partial separation of the epimers of N'. Several fractions were obtained which gas chromatography indicated were epimerically pure, while later fractions showed (from peak broadening in the gas chromatographic analysis) that increasing amounts of the minor epimer were present. On this basis, it is believed that the samples of N and N' isolated represented the trans-lactones 40b and 40c.

The n.m.r. spectra (see appendix) of trans lactones N and O support the structural assignments. The spectrum of trans-N showed signals due to five aromatic protons at 7.35δ; one proton at 4.42δ for the proton on the carbon bearing oxygen, a broad band with the appearance of a severely perturbed doublet with J=8 cps; three methoxyl protons at 3.60δ; three lactone ring protons located bwtween 2.5 - 3.6δ as a complex ABC pattern (discussed later); two protons next to the carbomethyoxyl group as a broad signal between 2.00 - 2.5δ; and the four remaining side chain protons which appeared as a broad signal between 1.36 - 2.0δ. The n.m.r. spectrum (see appendix) of O showed signals arising from five aromatic protons at 7.31δ; two protons, on carbon bearing oxygen between 3.78 -4.83δ as ca. six lines; two other protons on the lactone ring located in a complex set of lines between 2.42 - 3.41δ; the methoxyl group as three protons at 3.54δ; two protons on the carbon adjacent to the carbonmethoxyl group centered at 2.17δ and the four other protons on the side chain as a complex band centered at 1.62δ. The infrared spectrum of both trans-N and O showed strong bands at 1785, 1740 and 700 cm^{-1}.

The expected course of the base -catalyzed Baeyer-villiger oxidation of the intermediate cyclocutanone 38 obtained from structure 37 should lead to the formation of lactone N as the major product and minor amounts of lactone O (i.e.-CHR migration in preference to $-CH_2-$). Analogies[39,40,41] for this order of group migration are depicted in the following examples:

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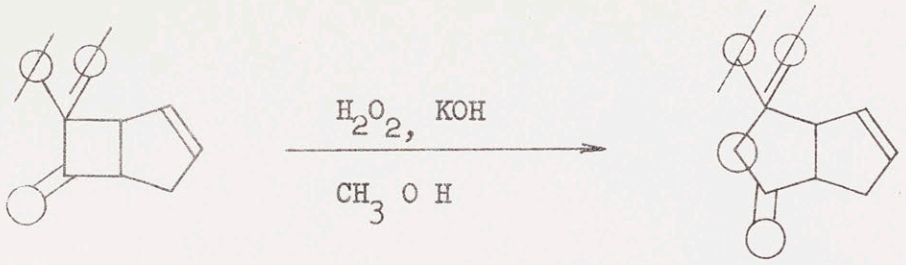
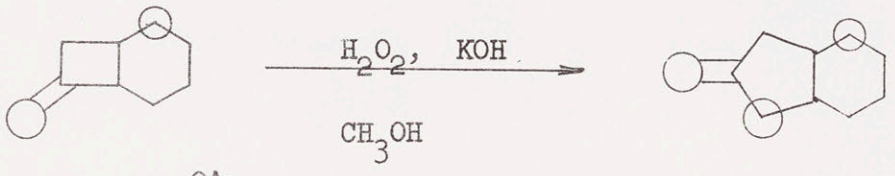
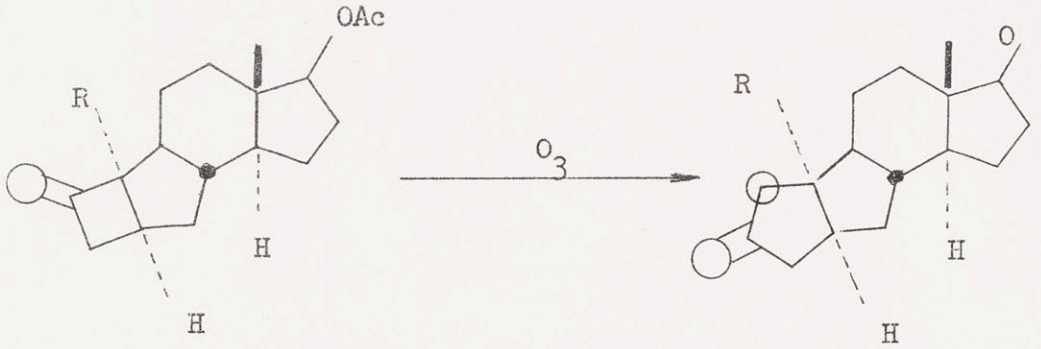
(39) J.R.Lewis, G.R. Ramage, J.L.Simonsen, and W.G.Wainwright, J.Chem.Soc., 1837 (1937).
(40) C.D.Hurd, and R.D.Kimbrough, J.Am.Chem.Soc., 82, 1373(1960).
(41) J.J.Bonet, H.Wehrli and K.Schaffner,Helv.Chim.Acta., 46, 1776(1963).



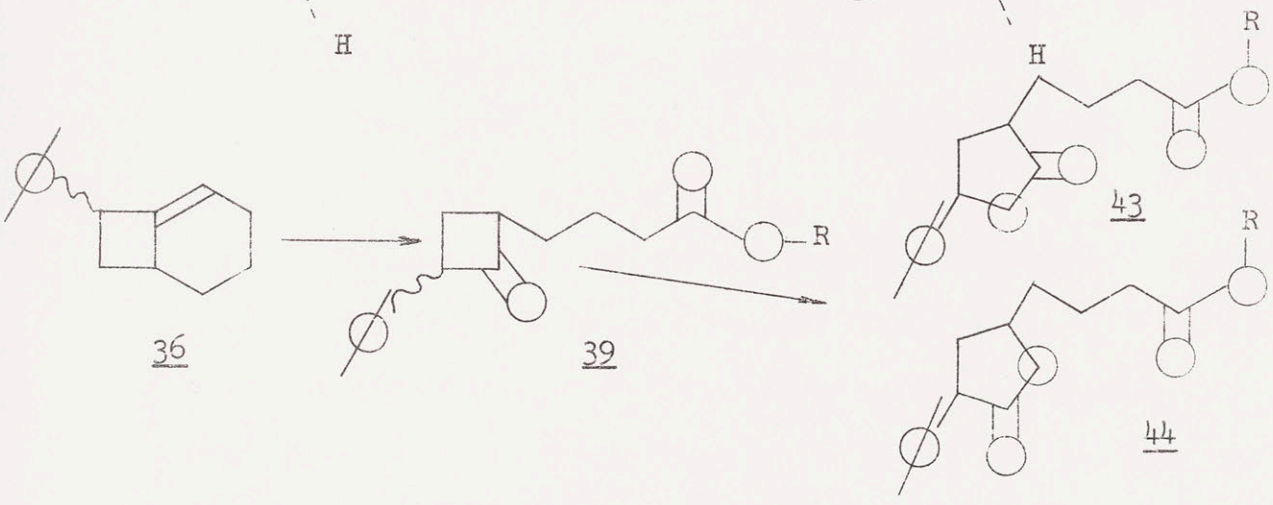
(39)



(40)



(41)



Ozonization of the compound represented by the alternate structure 36 would lead to cyclobutanone 39, and further oxidation of this ketone by a Baeyer-Villiger reaction would lead to the formation of a major lactone 43 and a minor lactone 44. This expected order of lactone formation is verified by the analogies[39,40,41] cited previously.

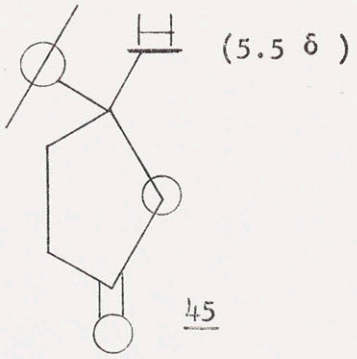
The chemical shift in the n.m.r. for the proton in the lactone 43, which is located on a carbon atom bearing both phenyl and oxygen would be

expected to give signals near 5.5δ, based on the observation that this type of proton in 4-phenylbutyrolactone (see appendix) (45) appeared at 5.48δ. The fact that lactone 43 was absent in the lactone mixture obtained from oxidation of the styrene trapping products 37, was shown by observing that the lowest field n.m.r. signal in the observed mixture of lactones (other than aromatic protons) appeared at 4.42δ.

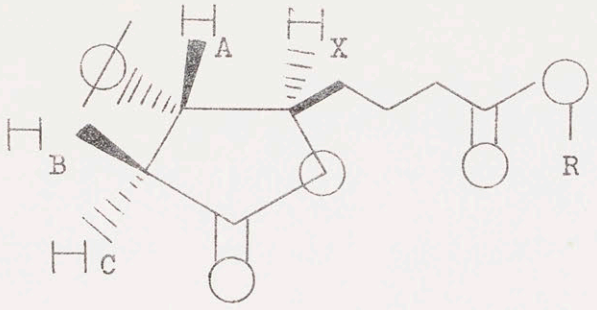
Since the major lactone 43 was not in the observed lactone mixture, the minor lactone 44 could not have been present either, nor could structure 36 have been the correct formulation for the styrene trapping products.

The n.m.r. spectrum of the observed minor lactone is consistent only with its formulation as 41 since the spectrum showed two protons on carbon bearing oxygen. The alternate structures 43 and 44 demand one such proton, as does the major lactone 40.

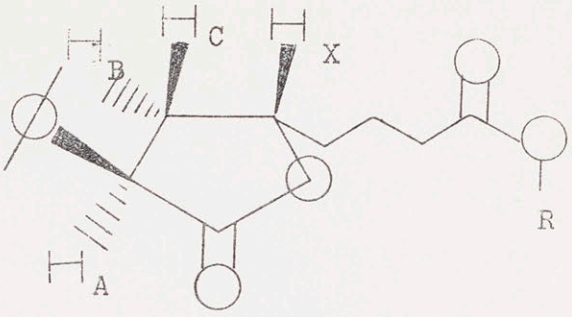
That the formulation of the major lactone was consistent with structure 40 and not the structure of the alternate minor lactone 43 (depicted below) was shown by investigation of the region of the n.m.r. spectrum (see appendix) between 2.5 - 3.6δ. This region in the observed spectrum was interpreted as an ABC pattern where the low field A proton was further split, J≈8cps., by an X proton whose chemical shift from A was relatively large and at lower field.



45



trans-40



44

A comparison of this region with calculated ABC spectra[42] showed that $J_{AX} \simeq J_{AC} \simeq J_{AB} \simeq$ 8cps; $J_{BC} \simeq -2J_{AB}$; $J_{BX} = J_{CX} = 0$; A≃3.3δ; B≃2.8δ and C≃2.7δ

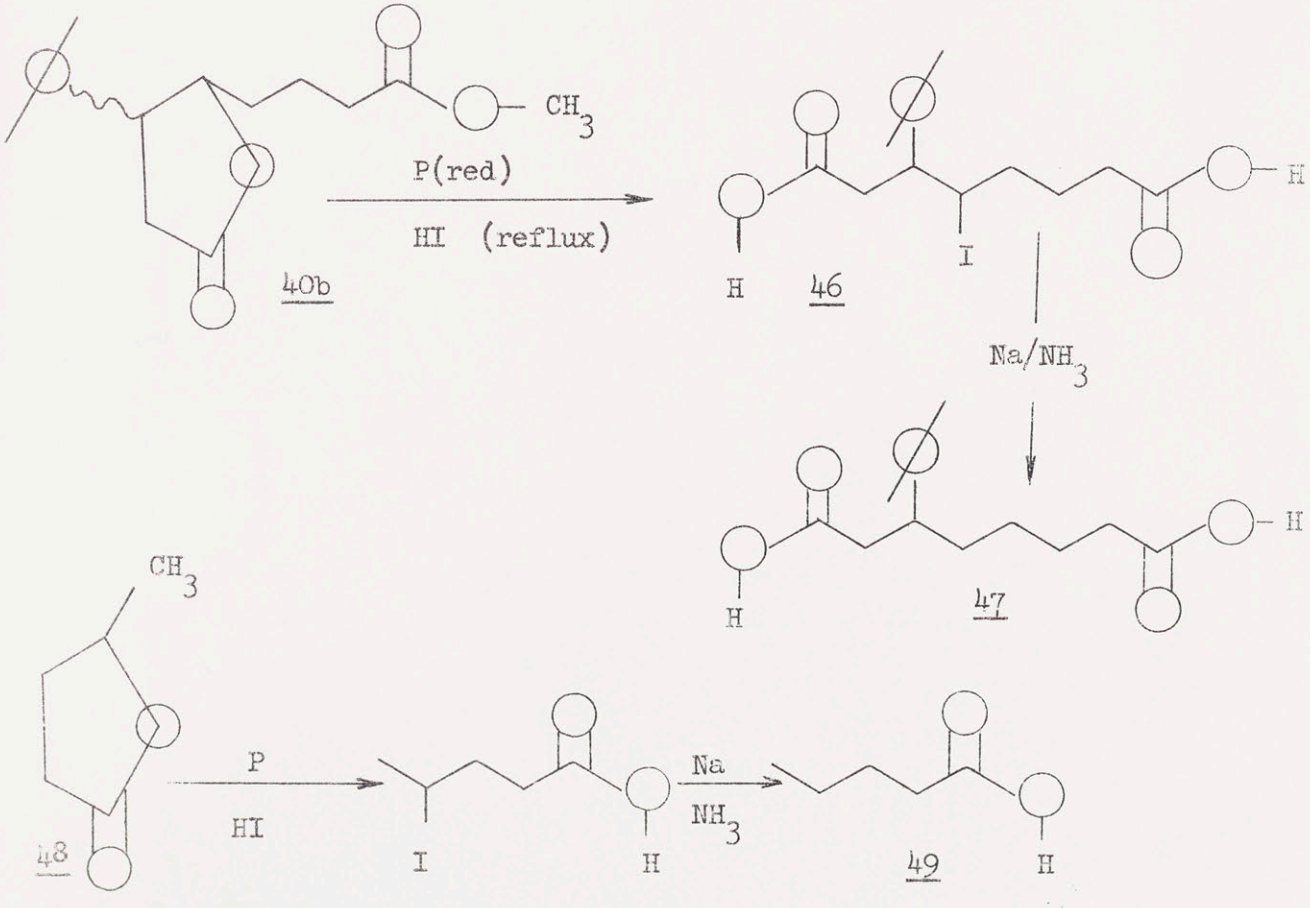
Structure 40 is consistent with these data since it should give rise to an ABC pattern in which the low field A portion (benzylic proton) would be further split by an X proton (the proton on carbon bearing oxygen). Moreover, line separation of the perturbed doublet at 4.42δ (the X proton) was ≃8 cps. which was the same splitting observed in the A portion of the ABC pattern. Although an ABC pattern would be expected for H_A, H_B, and H_C of structure 44 this structure cannot be correct since it would demand that the BC portion of the pattern be split by X, rather than the A portion being split by X.

An interesting observation was that 43% of the keto-ester 38c was converted to a 13:1 mixture of lactones 40b and 41b when it was stirred with a slight excess of 30% hydrogen peroxide in methanol for 20 min. Base catalysis of this lactonization was demonstrated by the fact that a 68%

(42) The observed X ABC pattern was very similar to the calculated ABC spectra in the following reference except that in the calculated spectra no consideration was given to the further splitting of the A portion by an X proton.
K.B.Wiberg, and B.J.Nist, The Interpretation of N.M.R.Spectra, 1962, spectra 3B-98 (p.102) and 3C-98 (p.164).

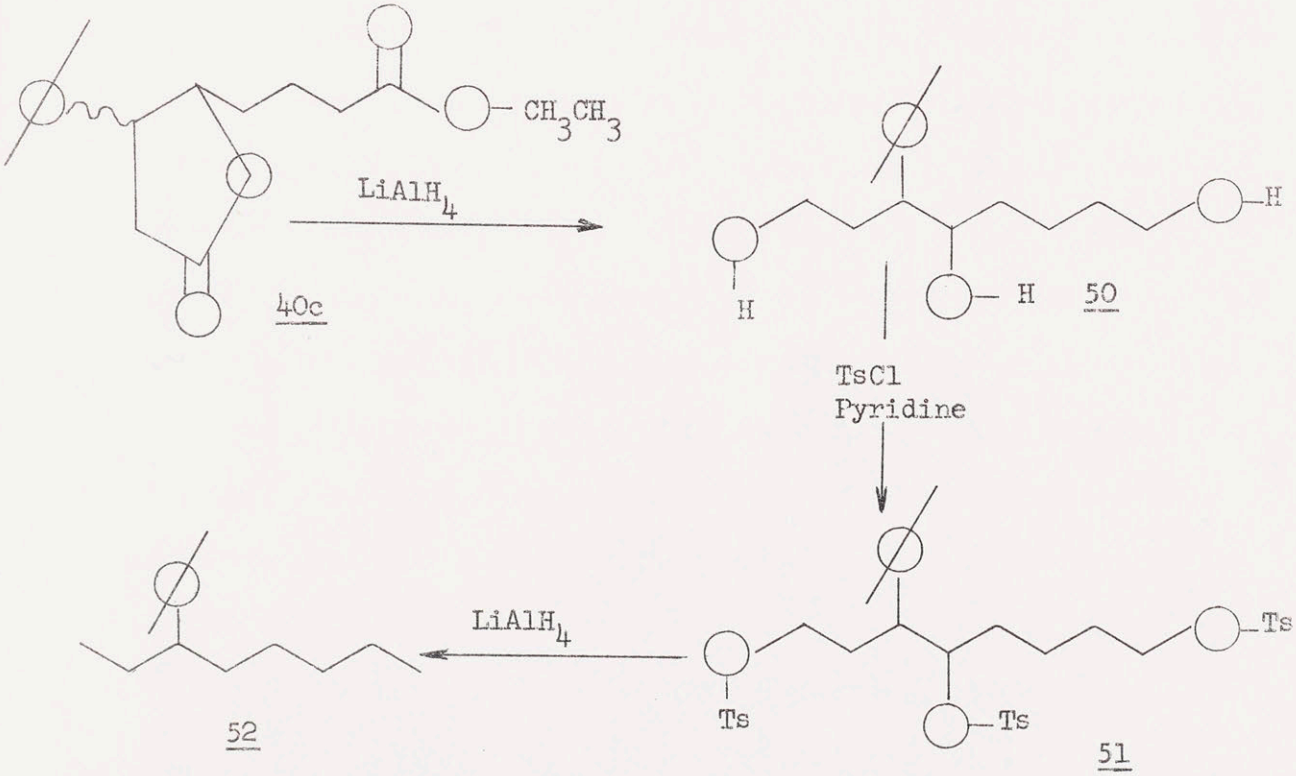
conversion to the same lactone mixture (13:1) was observed when the keto-ester 38c was stirred under the same conditions for only two minutes with an added trace of base. The change in lactone ratio from that expected (~4:1) in the previously discussed lactone formation from olefins 37a and 37b, may be due to the fact that the lactonizations were carried out under widely different conditions. In the previous work the conditions utilized a more basic, aqueous solution and the oxidation presumably occured mainly on the keto-acid.

It was thought that yet another approach to the identification of the lactones would be the treatment of the lactone mixture 40b and 41b with red phosphorus in refluxing hydriodic acid, and treatment of the resultant iodide 46 with sodium in liquid ammonia.



This would afford a diacid 47 which could be compared with authentically prepared material. 4-Valerolactone (48) was treated with the above sequence of reagents mainly to determine whether the iodization would readily occur. This sequence afforded a high yield of valeric acid 49. However, when the same sequence was utilized on the lactone mixture 40b and 41b fragmentation occured during the sequence. After methylation of the product from the sodium in ammonia reaction with diozomethane, the gas chromatographic analysis showed that the product mixture was extremely complex; and that no compound was found whose retention time was greater than diethyladipate.

Following the scheme shown below through intermediate 50 and 51 it was thought that the lactones 40c and 41c could be converted to hydrocarbons (52) which could be compared with authentic material.

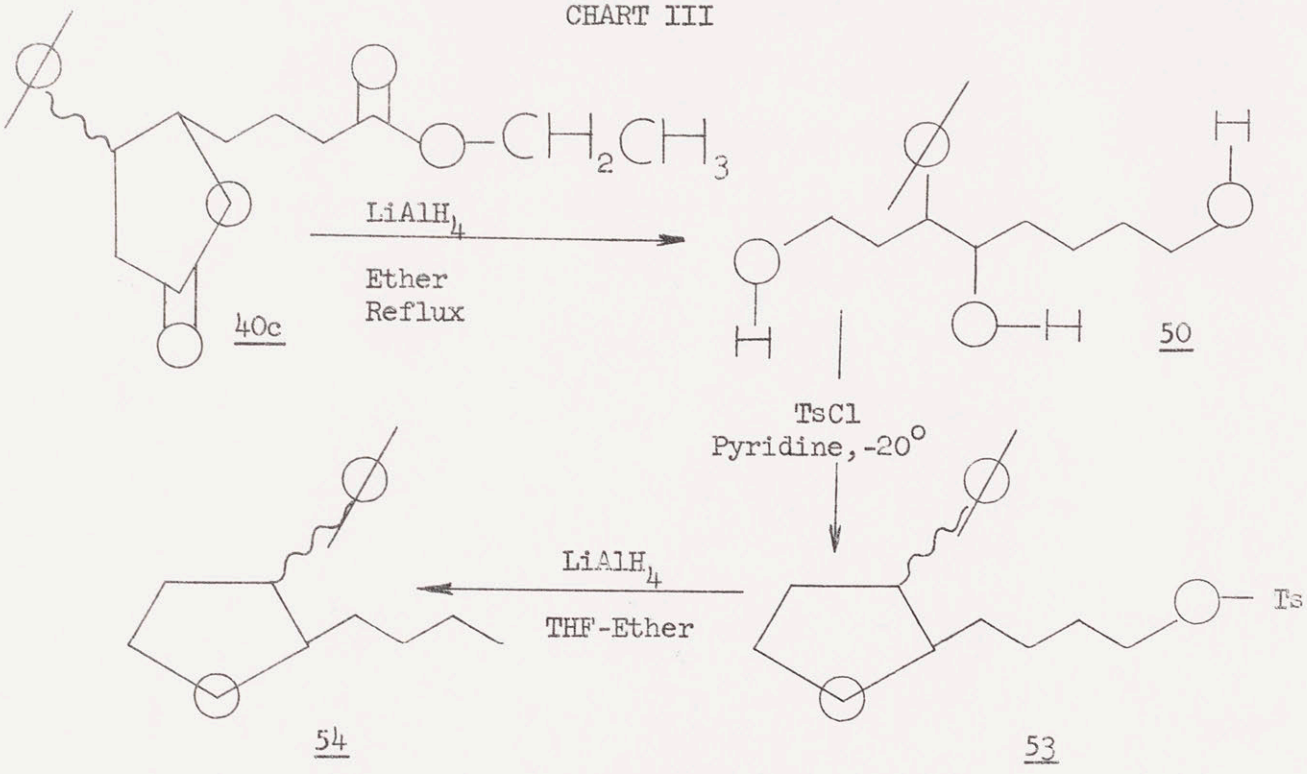


The reduction of the major lactone 40c with lithium aluminum hydride in refluxing ether afforded a triol 50 in 90% yield which showed a total of five protons on carbons bearing oxygen. The triol 50 was treated under conditions which have been shown to be optimum for the formation of a 1,4-ditosylate without tetrahydrofuran formation.[43] A large excess of p-toluenesulfonyl chloride in pyridine at -20° was added to the triol 50 in pyridine at -20°. However, the product from the reaction was the ring closed monotosylate 53 in 58% yield. The compound was shown to be a monotosylate by an examination of its infrared and n.m.r. spectra for bands due to the tosylate moiety. When the tosylate group was removed by hydrogenolysis with lithium aluminum hydride in refluxing ether tetrahydrofuran, a cyclic ether 54 was formed in 83% yield. The infrared spectrum of this compound showed aromatic bands in the 3μ region and at 1600 and 700 cm^{-1} as well as a strong broad band at 1065 cm^{-1} (-C-O stretching frequency). Its n.m.r. spectrum showed 5 aromatic protons at 7.23 δ as a sharp line; 3 protons on carbons bearing oxygen between 3.32-4.26δ, two of which were found in four sharp lines of equal intensity centered at 3.93δ; a very complex set of lines from 1.69 - 3.32δ, resulting from the other three protons on the tetrahydrofuran ring. The n-butyl group was located in a complex pattern of nine protons at 0.43-1.69δ. The cyclic ether 54 gave a mass spectrometric (see appendix) molecular ion at 204 and an intense fragment at 118 in addition to medium bands at 147 and 29. A possible fragmentation pattern is depicted in Chart III.

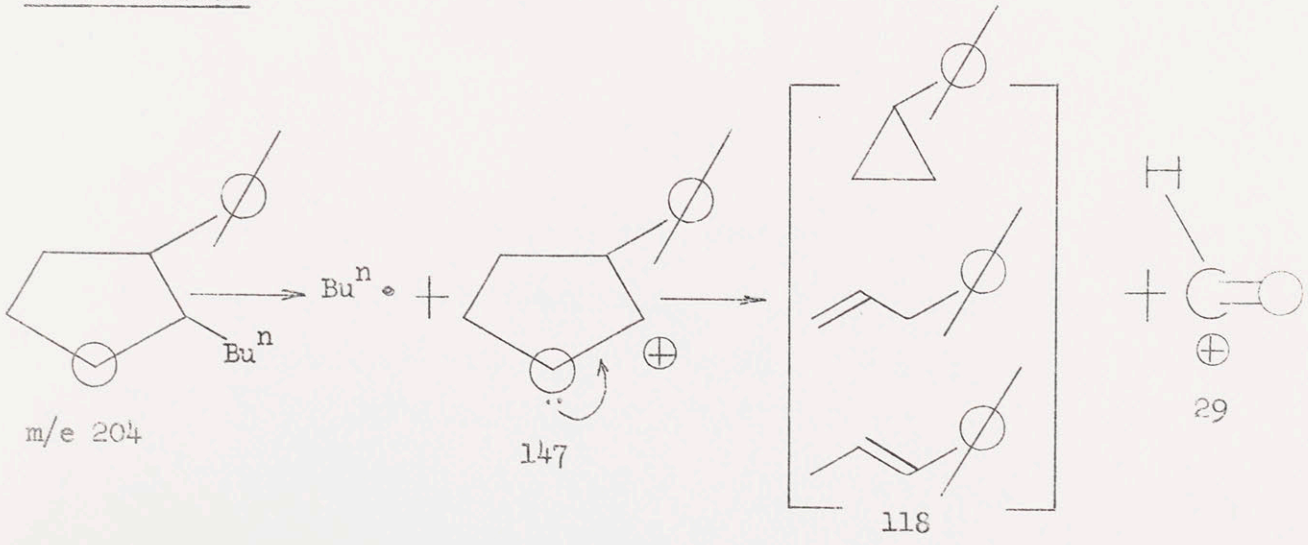
(43) A.Mehta, Ph.D. Thesis, Mass. Inst. Technology, June 1963.

The interesting observation that the tertiary proton on carbon bearing oxygen appeared in the n.m.r. spectrum at a higher field than the methylene protons attached to carbon bearing oxygen is explained by a slight shielding by the adjacent aromatic ring. This effect as well as the total n.m.r. spectrum is consistent with structure 54 for the cyclic ether.

CHART III

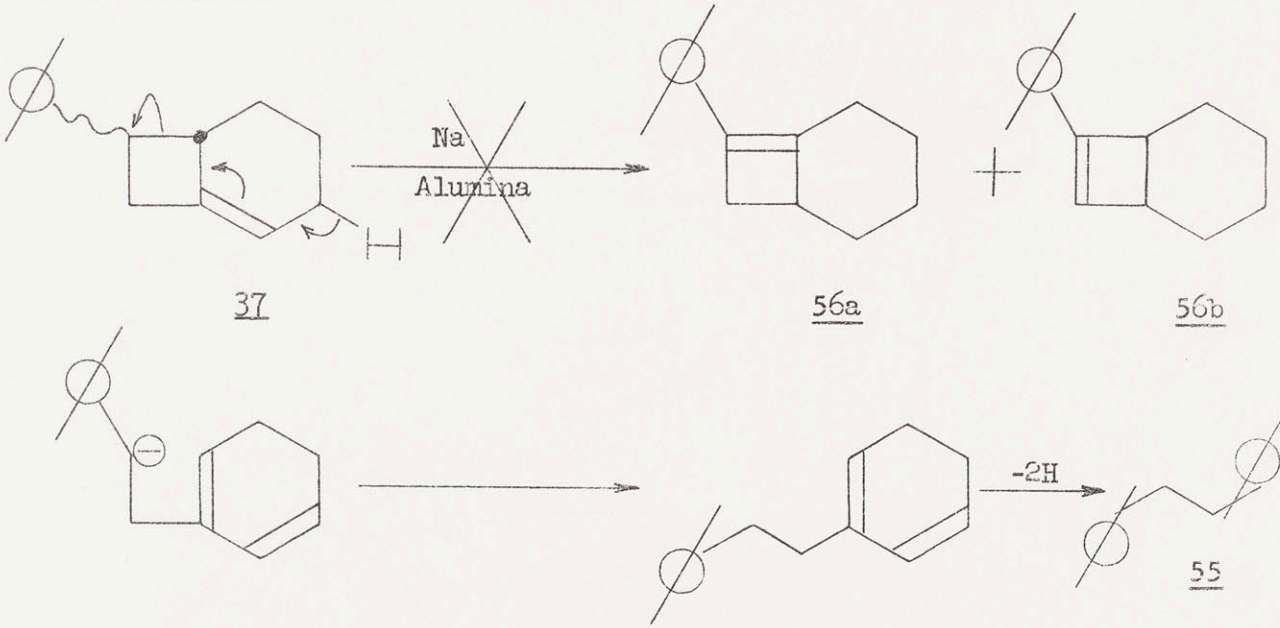


MASS SPECTRUM



In order to effect a rearrangement of the double bond of the trapping product mixture 37 into conjugation with the aromatic ring, the mixture 37 was passed over high surface sodium[44] on alumina at 200°. A mixture of hydrocarbons was obtained in 45% yield which was shown to contain four components. The bulk of the material was a compound found in 35% yield, which was shown to be bibenzyl (55). When the olefin mixture 37 was treated with high surface sodium [44] in refluxing diglyme, the gas chromatographic analysis of the product showed the presence of five compounds. Collection of the major peak by gas chromatograph and measuring its U.V. spectrum showed that it was neither of the conjugated olefins 56, [$\lambda_{max.}^{ethanol}$ 263 mμ (ε 924)].

A possible mechanism for the former transformation to bibenzyl 55 is shown below.



37 56a 56b

55

Direct methods of obtaining compounds whose carbocyclic skeletons were the same as those of the trapping products 37a and 37b were attempted by photolytic reactions. These studies showed that no 1:1 adduct could be

(44) E.Gil-Av and J.Herling, Tet.Letters, 27 (1961).

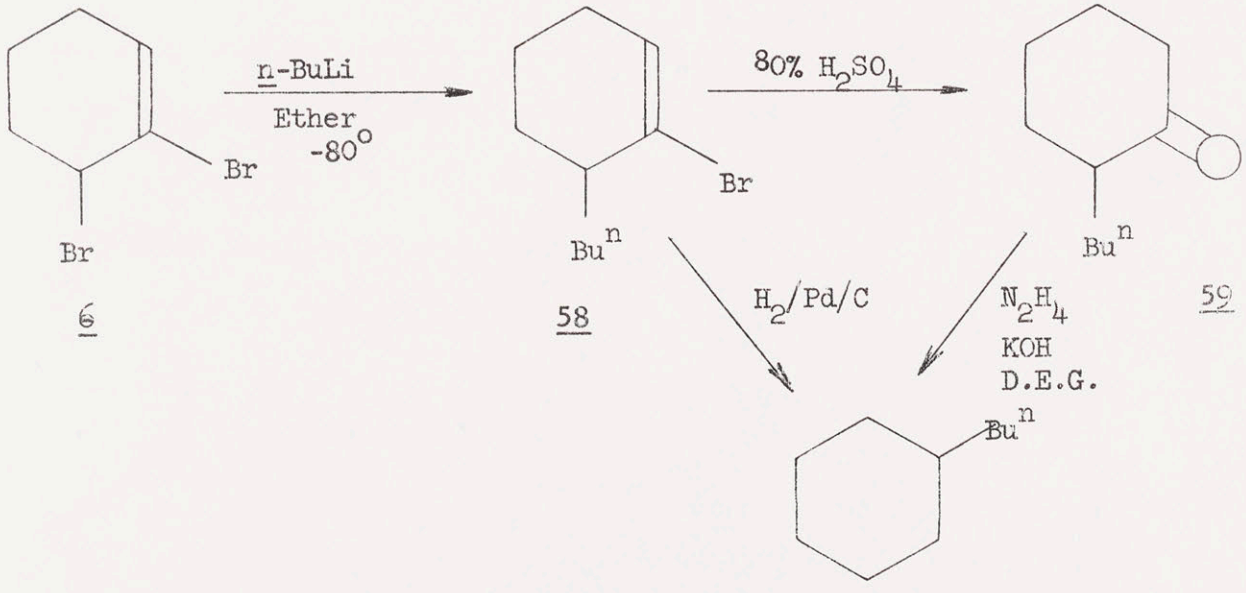
obtained with styrene and cyclohexene or styrene and phenylacetylene.

The Reactions of 6,6-Dichlorobicyclo[3.1.0]hexane (57) with Organometallics

The reaction of 6,6-dichlorobicyclo[3.1.0]hexane (57) with organometallic reagents follows an entirely different course from the reactions of its dibromo analog. The dichloride 57 did not react with methyllithium in ether at -80° or in refluxing ether after 10 hrs. It was also inert to n-butyllithium in pentane or ether at -80°. However, at room temperature or in refluxing ether a rapid reaction occurred between n-butyllithium and the dichloride. The latter reaction afforded no dimer 27a but did form a product whose gas chromatographic retention time was the same as tetramer. The gas chromatographic analysis of this product showed a minimum of 14 strong to moderately strong peaks (see experimental) evenly distributed from a retention time slightly greater than that of dimer to the retention time of tetramers. The product composition was not altered when the reaction was carried out in a solution saturated with lithium bromide.

The reaction of Butyllithium with 2,3-Dibromocyclohexene (6)

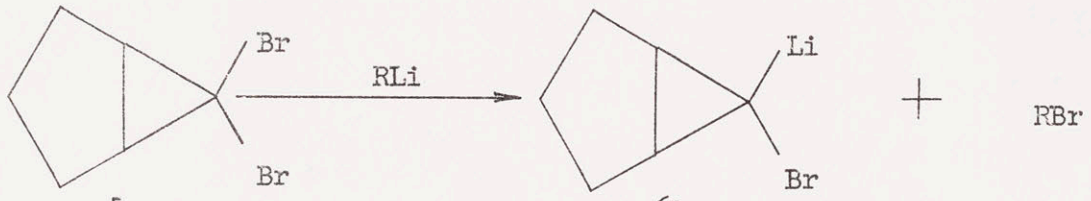
A mixture of 2,3-dibromocyclohexene (6) and dibromide 5 was treated with n-butyllithium at -80° in ether. The product obtained from the olefin 6 was the alkylated vinyl bromide 58. (see experimental). This compound was shown to have a molecular formula consistent with $C_{10}H_{17}Br$ by elemental analysis and its infrared spectrum showed a medium intensity band at 1630 cm^{-1}. The vinyl bromide 58 was solvolyzed to the ketone 59 with 80% sulfuric acid, and this ketone was found to be identical to an authentically prepared sample of 2-n-butylcyclohexanone (59). Catalytic reduction of the vinyl bromide 58 afforded a compound that was identical to an authentically prepared sample of n-butylcyclohexane (60) . The ketone 59 was also converted to the same hydrocarbon via a Wolff-Kishner reaction.



60

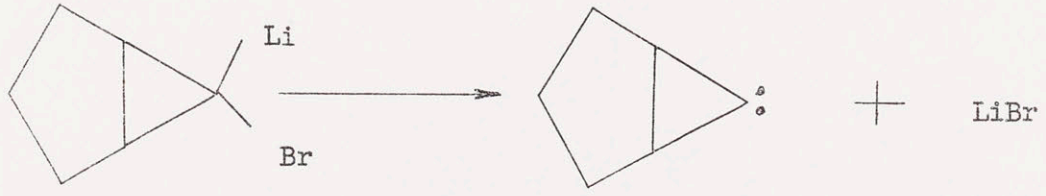
Mechanistic considerations

In the preceding section, emphasis has been placed on establishing the nature of the product formed from the reaction of 6,6-dibromobicyclo [3.1.0]hexane (5) with methyl and butyllithium. From the preliminary studies of 6,6-dichlorobicyclo[3.1.0]hexane (57) it is clear that the course of the reaction with butyllithium is, at least in the main, quite different from the pattern of the reaction of dibromide 5 . Hence in the following discussion possible mechanisms of reaction will be considered only for the latter.



5 61

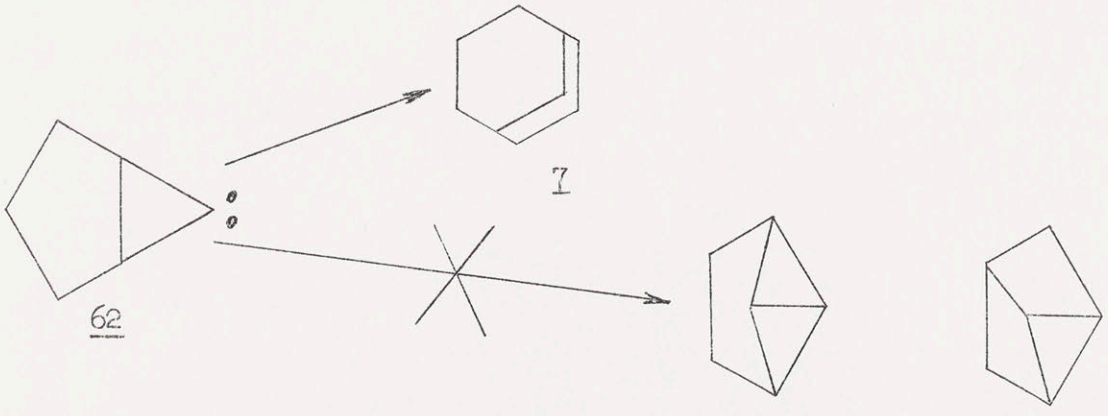
To date, the reactions of gem-dihalocyclopropanes with organolithium reagents have veen believed to involve an initial halogen-metal exchange. In the present case, species 61 would thus be expected to be the first-formed intermediate. It has been assumed that such species then undergo α-elimination to generate a carbene such as 62.



61 62

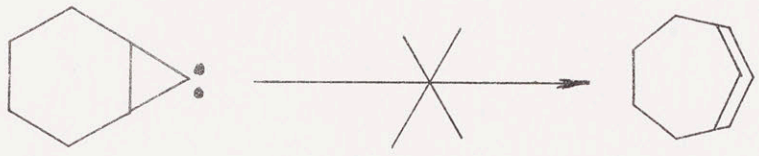
In cases where this carbene 62 can isomerize to a stable allene,[5,6,45] this course of reaction is found, although the isolation of allenes does not allow one to say with any certainty whether or not a carbene precursor or even an organometallic intermediate had actually been formed, i.e., the whole sequence might be concerted. Yet the isolation of certain compounds[5,8, 46,47,48] which seemingly had to be derived from carbenes related to 63, lends considerable support to the proposed existence of these species as reaction intermediates.

Thus, it is believed that in the present studies, species 62 was probably formed. If so, however, it did not lead to any of the products expected from a cyclopropylidene, no intra or inter molecular insertion products were formed and simple olefins did not "trap" any intermediate. Thus if 62 was formed it seems highly likely that it had a very short life-time before it underwent isomerization to some other reactive species. The simplest type of isomerization that could occur, is ring-expansion to 1,2-cyclohexadiene (7). This allene 7 would certainly not be "normal" by any criteria and one would not expect it to be an isolable compound.



(45) Z.Gaibel, B.S.Thesis, Mass. Inst. of Technology, Cambridge, Mass.,June, 1963.
(46) W.M.Jones, M.H.Grasley, and W.S.Brey, J.Am.Chem.Soc. 85, 2754(1963).
(47) L.Skattebøl,Chem. and Ind., 2146(1962).
(48) F.W.Carson, B.S.Thesis Mass. Inst. of Technology, Cambridge,Mass,June, 1961.

Inasmuch as "1,2-cyclohexadiene" (7) must be a highly strained species, a valid question arises. Why should cyclopropylidene 62 undergo isomerization, in particular, since the higher homolog 63 does not isomerize to 1,2-cycloheptadiene 64?

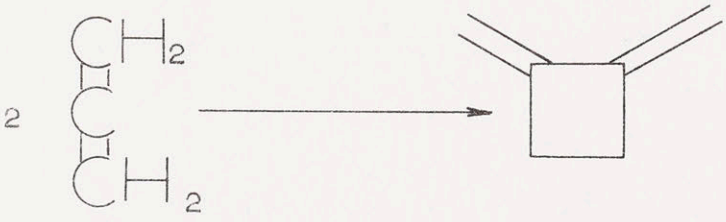


63 64

Two factors may be relevant: 1) By virtue of ring strain, 62 should be substantially more highly strained[10,11,12] than is 63; 2) There may be some structural factor which can lead to stabilization in 7 which is lacking in 64.

In summary, 1,2-cyclohexadiene (7) appears to be a probable intermediate in the reactions under study. The following pages will attempt to indicate how this species could lead to the products observed.

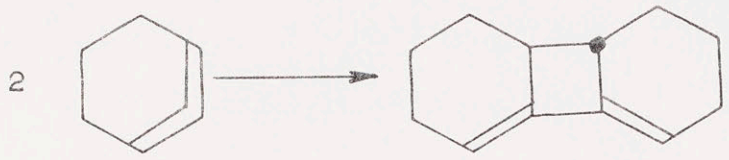
Although allenes are known to dimerize upon heating;[49,50] a highly-strained allene might be expected to do so very readily. Such dimerization invariably leads to conjugated rather than non-conjugated dienes:



(50)

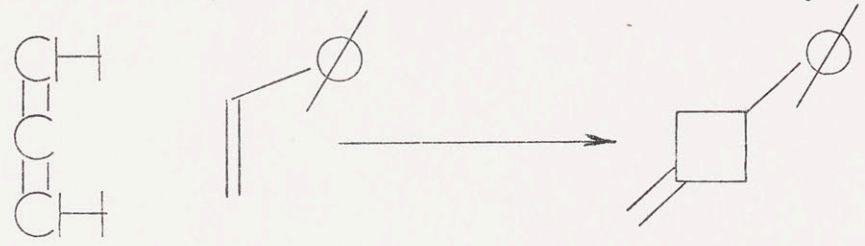
(49) J.D.Roberts, and C.MShartz., Org. Reactions 12, 1 (1962).
(50) A.T.Blomquist and J.A.Verdal, J.Am.Chem.Soc., 78; 109 (1956).

Thus the formation of dimer 27a, is at least, not without precedent:



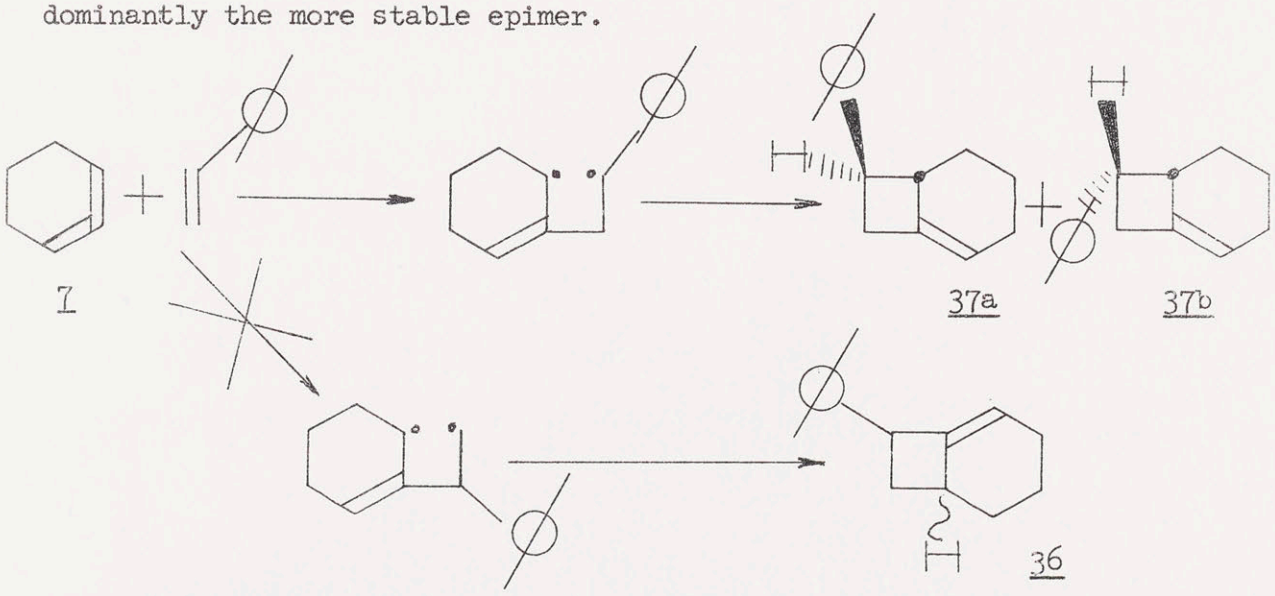
7 27a

Ball and Landor,[14] who have claimed to have prepared 1,2-cycloheptadiene, (64) have reported just this sort of reaction. Furthermore, allenes are known to be capable of adding to activated olefins[49,51] and the direction of addition is always in the sense indicated for the styrene-allene adduct:



(51)

Hence a fast reaction of 7 with styrene also seems plausible: and may involve the intermediate diradical indicated which closes to give predominantly the more stable epimer.



7 37a 37b 36

(51) H.N.Cripps, J.K.Williams, and W.H.Sharkey, J.Am.Chem. Soc., 81, 2723, (1959).

Thus the general features indicated for the reactions of the proposed intermediate, 1,2-cyclohexadiene (7) , seem to be in accord with the general pattern of reaction of "ordinary" allenes.

But a striking change in this pattern was found. In refluxing ether, dimer 27a was the major product, whereas at -80°, tetramers 17 and 19 were the sole products. That dimer 27a was not a precursor of the tetramers, i.e., that it did not itself dimerize, is certain.

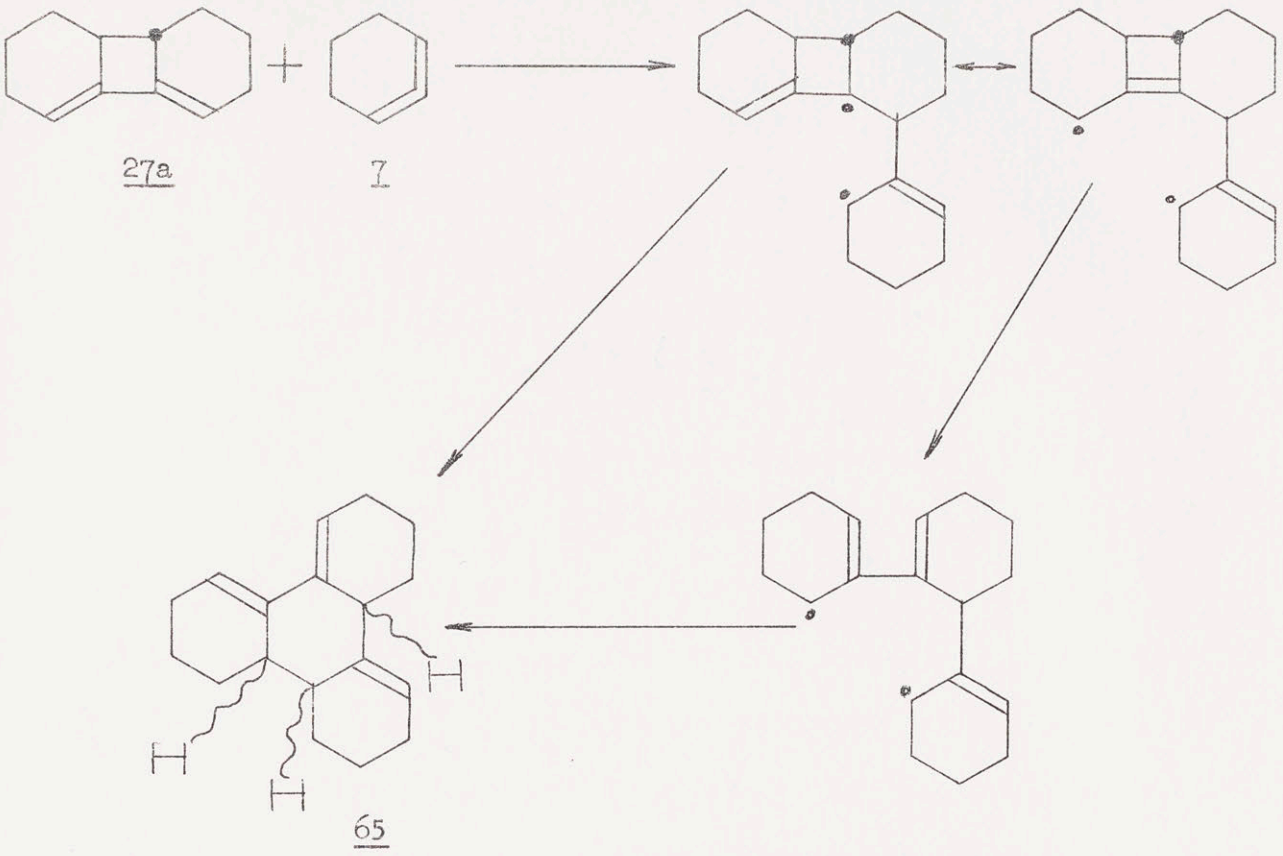
One possible explanation for the above facts might be conceived on the basis of a "stepwise" addition of monomer units, viz the 1,2-cyclohexadiene (7) following the scheme shown below, in which C_6 represents a C_6H_8 unit, etc.:

1) $C_6 + C_6 \longrightarrow C_{12}$

2) $C_{12} + C_6 \longrightarrow C_{18}$

3) $C_{18} + C_6 \longrightarrow C_{24}$

Here one would have to propose that a "chain" of C_6 units ultimately builds up to the tetramers. It seems improbable that any mechanism involving some type of diradical-like species, growing on the ends of the "chain", could ultimately lead to cyclization to C_{24} units and in particular do so stereospecifically, forming only two of the possible six isomers. A more plausible path might involve the reaction of dimer 27a, (C_{12} in the scheme above) with 7 to form a trimer 65 which is capable of reacting further with C_6 to yield the tetramers. The reaction of C_6 with the dimer is not unreasonable and might be expected to follow the course shown below:



27a 7 65

Thus formation of C_{18} units (6 isomers are possible) is possible, and indeed, such a pathway might at least in part account for the formation of a complex mixture of "trimeric" compounds, a small amount of which was observed. But there appears to be no rational way that such trimers 65 can react with 1,2-cyclohexadiene (7) to yield two tetramers 17 and 19. Other, less plausible, trimeric structures could be proposed, but again none of these is capable of serving as precursors to the tetramers. Thus it appears highly unlikely that any sequential addition of C_6 units can account for tetramer formation.

A more reasonable process is shown in the scheme below. In this,

two C_6 units add to form a highly reactive C_{12}^* unit which subsequently dimerizes.

$$C_6 + C_6 \longrightarrow C_{12}^*$$

$$C_{12}^* + C_{12}^* \longrightarrow C_{24}$$

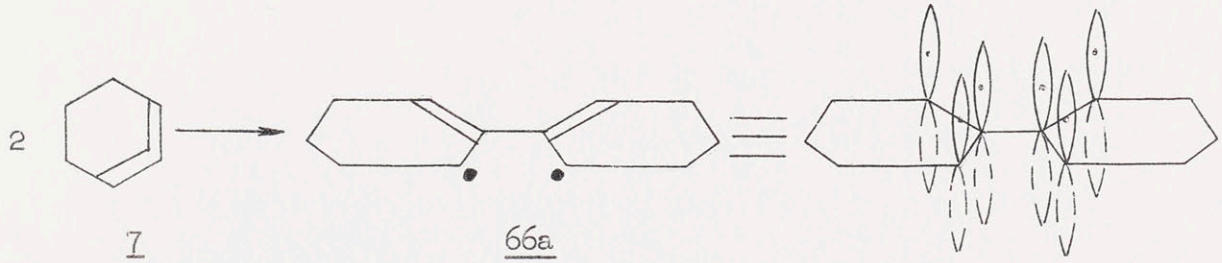
$$C_{12}^* \longrightarrow C_{12}$$

Side reaction:

$$C_{12}^* + C_6 \longrightarrow C_{18}$$

If the species C_{12}^* possesses the appropriate structural features, it might be able to dimerize in a stereospecific fashion to give only two tetramers, just as the C_6 unit is capable of dimerizing to yield a single stable dimer (C_{12} in the scheme above). In the C_6 dimerization the "unstable" dimer, C_{12}^*, must also be a precursor of the stable dimer C_{12}. To explain the temperature dependence i.e., dimer formation at 35° and tetramer formation at -80°, C_{12}^* must possess some stability and it must be sufficient to permit it to exist long enough at low temperatures to dimerize. At low temperatures the rate of conversion of C_{12}^* to C_{12} must be slow compared to the rate of dimerization of C_{12}^* to C_{24}. But at higher temperatures, conversion of C_{12}^* to C_{12} must compete effectively with its dimerization.

Although the features proposed for both this scheme, as well as the "unstable" dimer are rather unusual, it seems possible that both might be fulfilled if C_{12}^* has structure 66b.

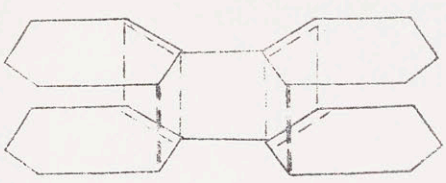


7 66a 66b

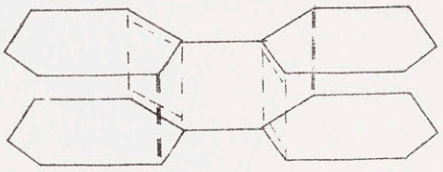
From the drawing it can be seen that all six of the p-orbitals implied by structure 66b may be overlapping, but this does not mean that the system is necessarily planar. Based on the slight non-planarity of biphenyl, it would seem that this species might be ca. the same degree out of plane. Thus this species might be sufficiently stable to have a finite existence. The manner in which the two C_6 units have been joined is the same as has been proposed for the initial stage of allene dimerization.[49] i.e., the two central carbon atoms are joined which forms a species with the greatest amount of resonance stabilization. Allenes dimerization might, if steric requirements permit, produce intermediate species with the geometry shown for 66b, but since such dimerizations to date have been effected only at relatively high temperatures,[49] the stability of such intermediates would be vanishing. The combination of some resonance stabilization of 66b together with the reflection of the ring strain introduced on conversion to the stable species 27a might provide a sufficient barrier to such conversion to account for the proposed finite existence of 66b. The activation energy required to bring this species into a planar configuration in the formation of 27a could explain the observed temperature effect where no dimer was formed at -80° but was formed at higher temperatures.

Furthermore, species 66b can explain the stereospecificity observed in tetramer formation. If two of these intermediates dimerize by a process in which the π-π'- systems overlap to a maximum extent 67a, as shown in Chart IV, only the two tetramers 17 and 19 which were isolated can be formed. In the drawing of 67a, it is likewise observed that the two rings of each dimer moiety are not completely planar but that significant orbital

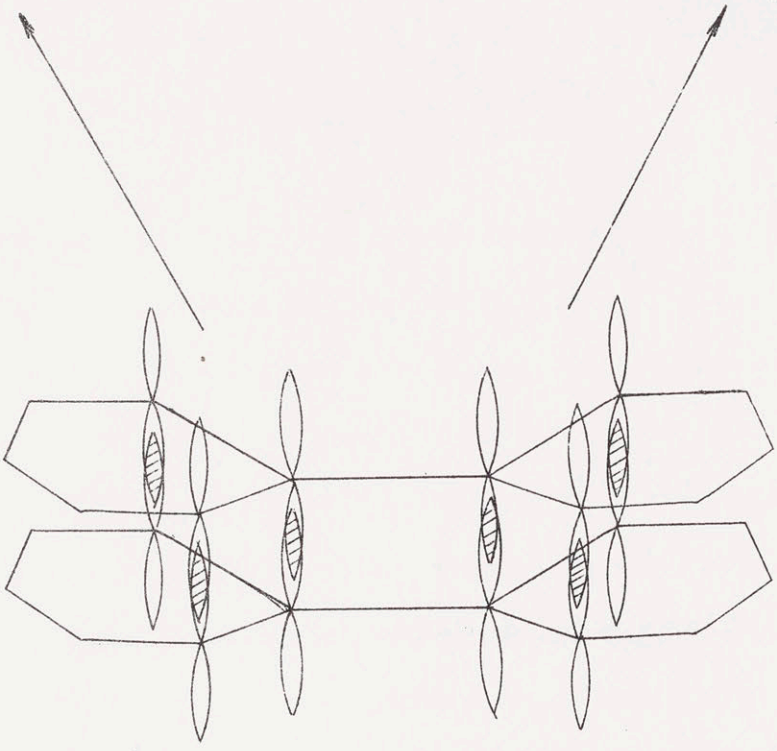
CHART IV



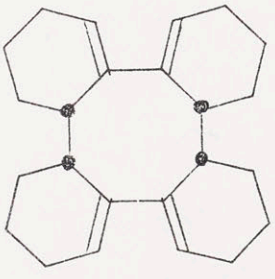
67b



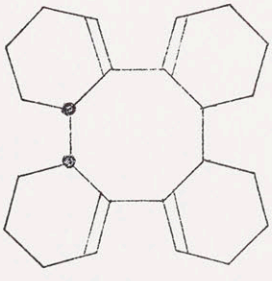
67c



67a



17



19

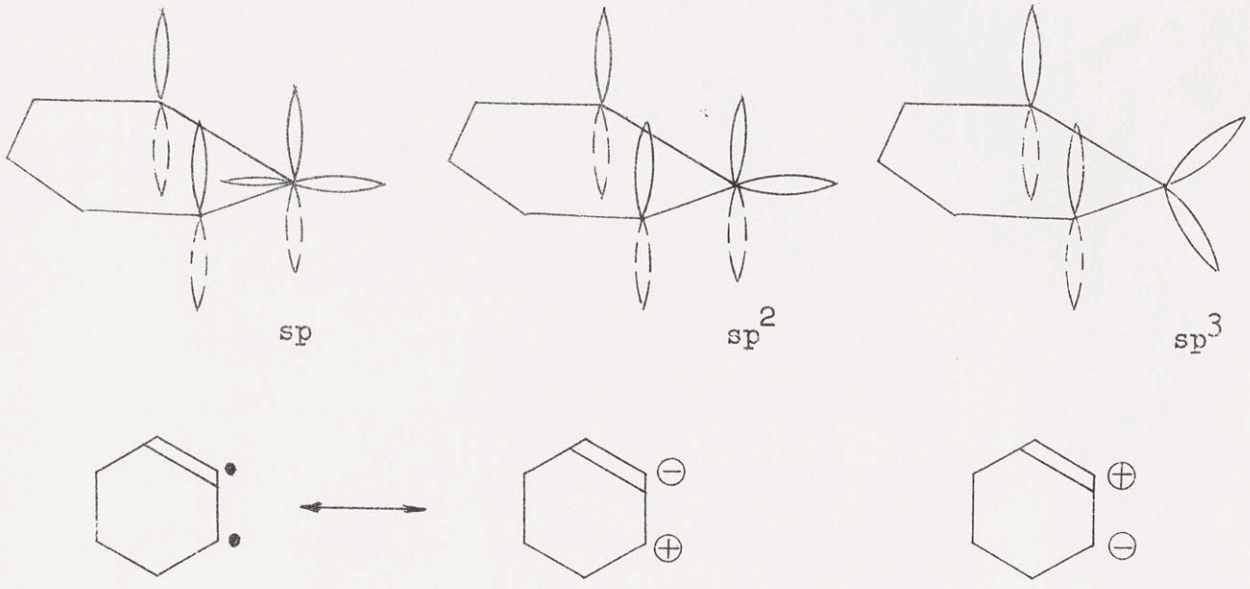
overlap occurs both within the dimer and between the two halves. Furthermore, it is highly likely that significant bond formation occurs between either 1 - 1′, 3 - 3′, 5 - 5′ or 6 - 6′ (equivalent positions) as the two species initially came together; and the remaining π - π′ overlap directs the steric course of the remaining bond formation resembling a selectivity mechanism which may exist in the course of the Diels-Alder reaction.

It may be possible that 66b is a triplet state species and this could account for the observed temperature dependence of the reaction. If the interconversion between the singlet and triplet states in solution is rapid and the triplet state species is of slightly lower energy, it may be possible that the triplet state species would predominate at -80°, preventing ring closure to 27a. As the temperature of the reaction is increased, the concentration of the singlet state species would increase and ring closure to 27a would be possible. Tetramers 17 and 19 could be formed at either low or high temperature since two triplet state species of 66b can ring close to these tetramers.

Finally, one should consider what the electronic structure of 1,2-cyclohexadiene (7) might be. Certainly, the three "allenic" carbon atoms cannot be colinear. The most reasonable geometric arrangement seems to be one in which the ring is planar or nearly so and more or less a regular hexagon. In a "normal" allene, the central carbon atom of the allenic bond is sp hybridized and the terminal carbon atoms are sp^2 hybridized. But in 1,2-cyclohexadiene, (7) although sp^2 hybridization must be retained for the terminal carbon atoms of the allenic bond, the central atom might

be sp, sp^2 or sp^3 hybridized as shown in Chart V.

CHART V



It seems likely, that a change in hybridization from sp to sp^2 or sp^3, or something intermediate between sp^2 - sp^3 might lead to overlap sufficient to provide substantial stabilization beyond that expected for a bent allene. In resonance terms, one might consider that, 1,2-cyclohexadiene should be represented as shown in the lower part of the chart. Crudely, the implication is that this species might benefit from something akin to allyl stabilization. It is interesting to note that on this basis, 1,2-cyclopentadiene and 1,2-cyclobutadiene might also possess some stabilization.

Experimental

General. - Infrared spectra were determined in chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), carbon disulfide (CS_2), as pure liquids (PL) or potassium bromide (KBr) pellets. The instruments utilized in the analyses were Perkin-Elmer Models 21, 137, 237, and 337 spectophotometers. All infrared bands are expressed in wave numbers and their intensities are expressed as band absorbance. The n.m.r. spectra were determined in carbon tetrachloride unless otherwise stated, deuterochloroform (DCl_3), or as pure liquid (PL) utilizing tetramethylsilane as an internal standard. The concentration of the solutions used was about 25% and the instrument employed was a Varian A-60 variable temperature probe, spectrometer. Elemental analyses were performed by Dr. S.M.Nagy and associates at this institute. Mass spectra were determined with a consolidated Electrodynamics Model 21-130 mass spectrometer with an ionizing potential of 70 volts. Molecular ions and pertinent fragments are recorded in this section with the appropriate compound, and line drawings of all mass spectra are recorded in another part of this manuscript. Ultraviolet spectra were recorded with a Cary Model 14 spectrophotometer. Gas chromatographic (G.C.) columns generally employed were 0.5 × 200 cm., 1.5 × 200 cm., 0.2 × 150 cm. and 0.2 × 300 cm. with thermal conductivity detectors in the case of the first two sizes and with a flame ionization detector (Wilkins A-600) in the case of the latter two sizes. The support was either acidic, basic, or neutral chromasorb P or W (Johns-Mansfield) and the liquid phases employed were: Carbowax 20M, (C-20M), Silicone oil 550 (S-550), Silicone oil 710 (S-710), tetraethyl-

eneglycol-Carbowax (TEG-C), SE-30 silicone rubber (SE-30), ethyleneglycol adipate (EGA), Versamid 900 (V-900), silicone nitrile XF-1150 (XF-1150), silicone nitrile XE-60 (XE-60) and Craig's polyester succinate (CPS). Internal standards were employed utilizing response factors where appropriate, and the areas were determined by planimetering. Melting points are corrected and boiling points are not. All reactions employing organometallic reagents, active metals, alkoxides, hydrides, photolysis, pyrolysis, and diborane were conducted under a nitrogen atmosphere. Methyllithium was prepared utilizing methylbromide unless otherwise stated. T.L.C. is used as an abbreviation for thin layer chromatography.

Cyclopentene.[52] - Cyclopentene was prepared according to a modified procedure of Carson and Ipateff. Phosphoric acid (85% aq., 610 g., 6.2 moles) was added to a flask and the temperature was brought to 135°. Cyclopentanol (500 g., 5.82 moles) was added dropwise to the acid with stirring and cyclopentene was removed from the reaction flask, as it was formed, by distillation through a Vigreux column. After the distillate was water washed and dried, the weight of cyclopentene collected was 328 g., 4.83 moles, 83% yield. Infrared and gas chromatographic analysis showed that the product was pure cyclopentene.

Potassium t-butoxide[1] (general procedure). - Potassium (1.2 moles) was added cautiously in 2 g. pieces to 1.5 l. of t-butyl alcohol (previously distilled from sodium hydride.) When the addition was completed, the solution was stirred and allowed to reflux until all of the potassium had dissolved. Then the excess alcohol was removed by distillation and

(52) B.B.Carson and V.N.Ipateff, Org. Syntheses, Coll. Vol. II, 153 (1943).

the powdery white solid residue was heated at 50° for 10 hrs. under a pressure of 0.1 mm.

6,6-Dibromobicyclo [3.1.0] hexane (5). - A solution of bromoform (278 g., 1.1 mole, freshly-distilled) in 100 ml. of pentane was added dropwise to a slurry of 68 g., 1 mole of cyclopentene, 1.2 moles of potassium t-butoxide and 300 ml. of pentane. The temperature of the reaction flask was maintained at -15° and the flask was equipped with a Dry Ice condenser. When the addition was completed, the cooling bath was removed and with continued stirring, the mixture was allowed to warm to room temperature. Water and pentane were added and the product was extracted with pentane and worked-up in the usual way. The pentane was then removed at room temperature under 30 mm. pressure, and the product was distilled (short path, 1 mm., bath at 50°). Fractional distillation afforded (204 g., 85% yield) of a colorless liquid, b.p. 77° (6mm.), $n^{25}D$ 1.5568. Infrared (PL): 3020 (0.22), 2920 (1.4), 2850 (0.86), 1070 (1.1), 745 (>1.5) and 645 cm^{-1} (0.31). The n.m.r. spectrum (PL) showed a broad band with fine splitting at 2.26δ overlapping with a larger, broad band centered at 1.90δ. This compound was stored at -15° under nitrogen to prevent isomerization.

Reaction of 6,6-dibromobicyclo [3.1.0] hexane (5) with methyllithium in ether at -80°. - Dibromide 5 (1.72 g., 7.21 mmoles) was added to 300ml. of anhydrous ether and the mixture was cooled to -80° for 30 minutes. Then 10 mmoles of methyllithium in 5 ml. of ether were added dropwise; after the completion of the addition, the mixture was allowed to stir for 40 minutes at -80° and for 30 minutes after reaching room temperature. Water was added to destroy the excess methyllithium and then the product was extracted with ether. G.C. analysis (5%, SE-30,

prog., tetraphenylene as internal standard) showed that compounds 17 and 19 which were eluted as a single peak, were formed in 61% yield, while material with a retention time slightly greater than that of dimer 27a was formed in 2% yield. Dimer 27a was not found in the reaction mixture.

When the reaction was carried out at -80° as above utilizing 4.3 mmoles of dibromide 5 and 8 mmoles of methyllithium in 25 ml. of ether with a total reaction time of ca. 5 minutes and the reaction mixture was decomposed at -80° by addition of 15 ml. of methanol, G.C. analysis indicated a 45% yield of tetramers and a 4.7% yield of trimeric material.

Addition of a solution of 23.5 mmoles of dibromide 5 to 80 mmoles of methyllithium in 80 ml. of ether at -80° followed by the usual work-up and G.C. analysis (silicone grease, 285°) showed the same product ratios as were obtained when the methyllithium was added to the dibromide.

Reaction of 6,6-dibromobicyclo [3.1.0] hexane (5) with n-butyllithium at -80°. - Dibromide 5 (1.86 g., 7.73 mmoles) was added to 50 ml. of anhydrous ether and the mixture was cooled for 20 min. to -80°. Then 15.5 moles of n-butyllithium (Foote Co.) in 8 ml. of n-hexane was added dropwise, and the mixture was allowed to stir at -80° for 30 min. followed by another 30 min. after warming to room temperature. Water was added and the product was extracted with ether. G.C. analysis (prog. 5% SE-30, tetraphenylene as internal standard) showed a 47% yield of tetramers, 8% of "trimers", and 4% of material with a retention time slightly greater than that of dimer 27a, none of which was present. No change in products was observed employing pentane as a solvent or upon using n-butyllithium prepared from butyl bromide and lithium and ether as a solvent.

Reaction of 6,6-dibromobicyclo [3.1.0] hexane (5) with methyllithium in ether at -80° (preparative scale). - Dibromide 5 (58.8 g., 0.245 mole) was added to 2 l. of anhydrous ether and the temperature of the solution was lowered to -80°. Methyllithium (0.30 mole) was added dropwise to the stirred solution. Upon completion of the addition, the reaction mixture was allowed to come to room temperature. Water was added and the product was worked-up in the usual manner. The ethereal solution was dried and the solvents were removed at room temperature under 30 mm. pressure. The white oily residue was dissolved in methylene chloride while being kept under a constant stream of nitrogen. This solution was allowed to stand at -10° for two days; subsequent filtration afforded 6.73 g. of a white solid which melted between 131.2° - 134.1°. Recrystallization of this product from methylene chloride afforded 6.49 g. of the major tetramer 17 which melted between 132.5° - 133.9° (33.2% yield). The infrared spectrum of this product and the white solid from the first crystallization were identical. The infrared spectrum (CS_2) of the white solid showed bands at : 3000 (0.28), 2920 (1.50), 2815 (0.58), 1630 (0.22), and 800 cm^{-1} (0.45). N.m.r. ($CDCl_3$): 5.41δ (4H, triplet, -C=C-H); 1.83 - 2.6δ (12H) two broad overlapping clusters, center of major band at 2.03δ (-CH=C-CH_2) and center of minor at 2.19δ (-CH=C-CH-); 1.15 - 1.83δ (16H, $-CH_2-CH_2-$) moderately broad with fine splitting. Ultraviolet (heptane): shoulder at 215 mμ (ε 13,100) and λ max 187 mμ (ε 25,800). Its mass spectrum showed a peak at m/e 320 (molecular ion).

Determination of the molecular weight of 17 cryoscopically in benzene saturated with water gave a value of 325 (320 calcd.). 9-Anthraldehyde (calcd. 206; found 204) and dianthramethane (calcd. 368; found 363) served as controls. The molecular weight was also verified utilizing a

Mechrolab vapor pressure Osmometer, model 30A and was found to be 324.

Anal. Calcd. for $C_{24}H_{32}$: C, 89.94; H, 10.06. Found: C, 89.95; H, 10.06.

Acetone was added dropwise to the mother liquor from the above crystallization until no further precipitation of solids was observed. Filtration of this solution afforded 2.86 g. (15% yield) of a white polymer which turned brown with decomposition in a melting point tube over a very broad temperature range. This product could not be eluted at 260° from a G.C. column (2% E.G.A.) which allows the elution of tetramers at 175°, nor was it eluted from an SE-30 column at 340°.

The solvents from the above mother liquor were removed at room temperature under 30 mm. pressure leaving 9.38 g., of a residual oil. This residue was chromatographed on Woelm activity 1 alumina using petroleum ether as an eluent. The course of the chromatogram was followed by G.C.. The first 24 fractions afforded 2.24 g. (11% yield) of a colorless liquid which solidified upon standing at room temperature to a white solid, m.p. 82° - 86°. This material was shown to be homogeneous by G.C. analysis (2% E.G.A. at 175° and 2% SE-30 at 200°) and its retention time was identical to that of tetramer 17. Two recrystallizations from concentrated methylene chloride solutions afforded 1.09 g. of a white solid 19 m.p. 84.4° - 86.1°. Infrared (CS_2): 3000 (0.21), 2920 (1.25), 2815 (0.51), 1630 (0.13), and 800 cm^{-1} (0.47). N.m.r.: 5.38δ (4H, -C=CH-) broad and complex; 0.70 - 3.2δ (28H) very broad and complex. Ultraviolet (heptane): shoulder 234 mμ (ϵ 7,840); λ end 187 mμ (ϵ 22,700). The mass spectrum showed a peak at m/e 320 (molecular ion).

Anal. Calcd for $C_{24}H_{32}$: C, 89.94; H, 10.06. Found: C, 90.01; H, 9.98.

Further elution of the chromatographic column afforded a complex mixture of "trimeric" material along with progressively smaller amounts of tetramer as the course of the chromatogram continued. Prolonged elution afforded no more material.

It was necessary to keep the G.C. preheater temperature below 230° in order to prevent rearrangement of the tetramers being analyzed. Utilizing a preheater temperature of 300° the major tetramer 17 was rearranged mainly to a compound with slightly shorter retention time on an SE-30 column; the same analysis on the minor tetramer 19 afforded mainly a compound with a greater retention time.

Hydrogenation of major tetramer 17. - A mixture of 0.092 g. of platinum oxide in 5 ml. of glacial acetic acid was stirred under one atmosphere of hydrogen for 3.5 hours. Then 4.7 mg. of the major tetramer 17 was injected into the hydrogen flask in 100 µl of methylcyclohexane. After 13 hrs., 1.64 ml. (4.00 molar equivalents) of hydrogen was consumed and no further uptake was observed. In a similar experiment employing methylcyclohexane as a solvent only 1.88 molar equivalents of hydrogen was absorbed over a period of 16 hours.

Determination of the bromine number[15] of the major tetramer 17. - Using samples of 28.0 mg. (0.0875 mmole) and 30.3 mg. (0.0946 mmole) of the major tetramer 17, the bromine number was determined by allowing each sample to stand in the presence of 3.00 ml. of 0.20 N bromine in carbon tetrachloride solution in the dark for ten and twenty minutes respectively. At the end of these periods, 20.00 ml. of a 20% aq. potassium iodide solution was allowed to react with each sample for 10 min. in the dark. Then each sample was titrated to a starch endpoint using 0.01243 N solution of sodium thiosulfate. By plotting the number of moles

of bromine absorbed per 80 molecular weight units against the reaction time and extrapolating to zero time a value of 1.104 moles of bromine per 80 molecular weight unit was determined.

Lithium in liquid ammonia reduction of major tetramer 17. - Major tetramer 17 (3.21 g., 10.0 mmoles) was dissolved in 15 ml. of tetrahydrofuran and added to a mixture of 0.8 g. (0.1 g. at.) of lithium, 100 ml. of anhydrous ammonia, 25 ml. of tetrahydrofuran and 15 ml. of dry t-butyl alcohol. After the blue colored solution had stirred for 15 min., ammonium chloride was added until the blue color faded. Then ether was added and the Dry Ice condenser was replaced with a Vigreux column. After the ammonia had been removed by distillation, water was added and the product was extracted with ether. The organic layer was worked-up in the usual way and the solvents were removed at room temperature at 30 mm. pressure leaving a white semi-solid residue. The latter was dissolved in 25 ml. of methylene chloride and allowed to stand at -10° for two days. Filtration of this material afforded a solid which melted at 151.5° - 155.0°. A recrystallization of this material from methylene chloride afforded 1.23 g. of a white solid 15 which melted between 153.5° - 155.0° (38% yield). This compound 15 showed the following bands in its infrared spectrum (CS_2): 3000 (0.10), 2920 (0.63), 2850 (0.41); 855 cm^{-1} (1.0). N.m.r.: 1.05 -3.2δ, very broad with major band centered at 1.53δ. Ultraviolet (heptane): λ max 204 mμ (ϵ 19,200). This compound decolorized a bromine solution and was shown to be homogeneous by G.C. (2% E.G.A. at 175° and 2% SE-30 at 200°).

Anal.Calcd. for $C_{24}H_{32}$: C, 88.82; H, 11.18. Found: C, 88.71;H, 11.30.

The residue 18 from the mother liquor could not be crystallized from

a wide variety of solvents. The colorless oil was purified by a short path distillation which afforded 1.75 g. of a glass (53% yield). G.C. analysis of this product 18 (2% E.G.A., 178°) showed three compounds in the following relative amounts (retention time in minutes) 16.2 min., 14%; 19.9 min., 72% and 23.2 min., 14% . Each compound in the mixture was shown to absorb bromine rapidly. Infrared (CS_2): 2920 (0.96) and 2850 cm^{-1} (0.42). The 7 to 12μ region was very complex. Ultraviolet (heptane): λ max. 193 mμ (ε 15,700). The n.m.r. spectrum (CCl_4) showed two clusters of vinyl protons between 5.25 - 5.84δ (-$\dot{C}$=C<u>H</u>-) and very broad and complex absorption between 0.60 - 3.00δ.

The ratio of olefin to non-olefinic protons was 1.00/28.2. For a total of 36 protons per molecule this means that the three compounds have an average of 1.23 olefinic protons per molecule. Assuming that the major component has one tetra- and one trisubstituted double bond and both of the minor components have two trisubstituted double bonds, based on the G.C. analysis the mixture should have an average of 1.28 olefinic protons per molecule.

<u>Anal</u>. Calcd. for $C_{24}H_{36}$: C, 88.82; H, 11.18. Found: C, 88.83; H, 11.21.

Another run in which the reaction mixture was analyzed after 0.5, 5.0, and 10.0 hr. showed that the product composition at each of these times was the same as that given above. Treatment of the crystalline isomer 15 under the same conditions as above for 3 hr. afforded a quantitative recovery of 15 . Because the tetramer has only very little solubility in polar solvents, the exact conditions of the dissolving metal reduction were critical.

It was found that in order to achieve complete reduction of the tetramer 17, it was necessary to add a tetrahydrofuran solution of the tetramer to a mixture of a large excess of lithium in the ammonia-tetrahydrofuran-t-butyl alcohol system. Under these conditions, reduction must have been very fast, occuring before the tetramer could precipitate. When lithium was added to a mixture of the tetramer in the mixed solvent system, only partial reduction occurred (giving the same ratios of the former reduction products noted above); a substantial amount (up to 50%) of the starting material was recovered. Prior to this finding, attempts to reduce the tetramer with sodium in ammonia utilizing ether or tetrahydrofuran as co-solvents, as well as an attempted reduction with sodium in amyl alcohol all failed, presumably because the tetramer was not in solution after the sodium was added.

Catalytic hydrogenation of the crystalline reduction product 15 over platinum in acetic acid at 54° afforded a complete recovery of starting material after two days. When the crystalline material was reduced with platinum in 1:1 cyclooctane-acetic acid at 50°, slow hydrogen uptake was observed over a period of one week. G.C. analysis (2% SE-30, 200°) showed the presence of a minimum of five compounds.

Ozonization of diene 15. - The crystalline solid 15 (21.2 mg., 0.0663 mmole) was ozonized in 15 ml. of methylene chloride over 3 min. at -80°. To the cold solution an aqueous solution of sodium bisulfite was added until a negative starch-iodide spot plate test was obtained. Ether and triphenylmethane (as internal standard) were added; the organic layer was washed with water, dried and analyzed by G.C. (2% E.G.A., isothermal at 150° for 20 min. and then programmed.) This analysis showed a

single compound in 33% yield which had a G.C. retention time on two columns (2% E.G.A., and 2% SE-30) identical to that of 2,2′-dioxodicyclohexenyl (13a). A subsequent preparative reaction carried out in the above manner utilizing 251 mg. (0.776 mmole) of the crystalline reduced product 15, afforded after Hickman still distillation 88 mg. (0.45 mmole, 29% yield) of a slightly yellow solid with an infrared spectrum which was the same as that of 2,2′-dioxodicyclohexenyl (13a) except for one minor intensity band. Three recrystallizations of this material from petroleum ether afforded 65 mg. of a white solid, with a m.p. of 70.5 - 72.0°, no depression upon admixture with 2,2′-dioxodicyclohexenyl (13a). The infrared spectra of the latter and of the white solid, 13a were identical.

Another ozonization utilizing the same conditions and work-up as in the above case except that the solvent was a mixture of 1:1 methylene chloride-methanol, afforded a 22% yield of 13a via G.C. analysis (2% E.G.A.).

2,2′-Dioxodicyclohexenyl (24 mg.) was ozonized in methanol for 2 min. at -80° and worked-up as before with sodium bisulfite. G.C. analysis (2% E.G.A., triphenylmethane as internal standard) showed a quantitative recovery of the starting material. Attempted oxidation of the diene 15 in 1:9 dioxane-water with potassium permanganate, and sodium metaperiodate in a slightly basic solution afforded the starting material as the only product. The failure of this reaction was likely due to the insolubility of the dienes.

Preparation of 2,2′-dioxodicyclohexenyl[18] (13). - Cyclohexanone (96 g.) and 24.4 g. of ditertiarybutylperoxide were heated at gentle reflux for 24 hr. with stirring. Distillation removed a 93 g. forerun of low boiling materials and gave 9.4 g. of a higher boiling fraction, b.p. 93 - 115° (0.2 mm.) from this mixture, after cooling overnight at -15°, 3.61 g. of a white solid was collected by decanting the liquid 13b and washing the

solid with a small volume of petroleum ether. Two recrystallizations of the white solid from petroleum ether afforded 2.11 g. of a solid 13a m.p. 70.5° - 72.1° (lit.[18, 19] 70-71°). G.C. analysis of the solid 13a and liquid 13b (XE-60, SE-30 and E.G.A.) showed no separation of the meso and dl-diketones.

In the study of several pairs of meso and dl-1,4-diketones by Kharasch, McBay and Urry,[19] the higher melting and the thermodynamically more stable compound was shown to be the meso isomer. However in this same study, the stereochemistry of the solid 13a and liquid 13b isomers of diketone 13 was not assigned. In the present study, a base catalyzed deuterium exchange on both the solid 13a and the liquid 13b isomer in deuterium oxide-dioxane afforded products whose n.m.r. and infrared spectra were very similar. The n.m.r. spectra of the deuterated material also showed a loss of the signal due to the protons alpha to the keto groups. The liquid isomer 13b was shown to be the thermodynamically less stable compound by its isomerization to the solid isomer upon treatment with base in water-dioxane, as shown by I.R. and n.m.r. spectra.

Lithium in liquid ammonia reduction of minor tetramer 19 . - The minor tetramer 19 (173 mg., 0.541 mmole) in tetrahydrofuran was added to a solution of 50 ml. of liquid anhydrous ammonia, 25 ml. of tetrahydrofuran, 10 ml. of t-butyl alcohol and 0.1 g. (0.01g. at.) of lithium wire. After the blue solution had stirred for 60 min., the product was worked-up in the usual way and analyzed by G.C. (2% E.G.A., 184°). This analysis showed a minimum of eight compounds. Distillation of the product (flask to flask, short path, 0.05 mm., bath at 150°) afforded 0.171 g. (0.526 mmole, 97% yield) of a glass. Infrared (CS_2): 3000 (sh, 2920 (>1.50), 2850 (1.50),

1628, 799 and 820 cm^{-1}. N.m.r. spectrum; 4.94 - 5.72δ (2H, complex, -C=CH-); 0.50 - 3.30δ (34H) broad and complex. Ultraviolet (heptane): λ max 193 mμ (ϵ 13,300).

Anal. Calcd. for $C_{24}H_{36}$: C, 88.82: H, 11.18 Found: c,89.15; H, 10.85.

The observation that this mixture showed two olefinic protons per molecule (found value 2.06 $\pm$ 0.1 requires that the products be compounds with two trisubstituted double bonds per molecule.

Attempted dehydrogenation of major tetramer 17 to tetraphenylene. - All reaction mixtures were analyzed with a silicone grease G.C. column at 290° $\pm$ 10°. Metal catalysts were removed by filtering the hot solutions, and the removal of the quinone and hydroquinone reagents was accomplished by filtering the reaction mixtures at room temperature. The results of these experiments are found in Table I. In this table the symbol t_R refers to the retention time of the peak from the point of injection, and the symbol T_p refers to the compound tetraphenylene,[53] and T_t refers to tetramer 17.

Table I

Weight of Tetramer 17	Oxidizing Agent	Refluxing Solvent	Time Hr.	Gas Chromatographic Analysis
1) .308 mmole	Chloranil 5.16 mmoles	Xylene	36	Broad peaks near t_R of T_p and T_t.
2) .072 mmole	2,3-dichloro -5,6-dicyano-benzoquinone	Benzene	30	Same as run no.1.
3) .28 mmole	Same as no.2 (2.75 mmoles)	Benzene	90	1 sharp peak with same t_R as T_p, cluster of peaks with t_R near T_t and 1.4 times T_t.

(53) The author wishes to thank Prof. A.C.Cope for the sample of tetraphenylene utilized in this work.

Table I (continued)

Weight of Tetramer 17	Oxidizing Agent	Refluxing Solvent	Time Hr.	Gas Chromatographic Analysis
4) .21 mmole	Same as no.2 (2.17 mmoles)	Toluene	144	Broad peak of t_R slightly less than T_p very broad peak of t_R equal to T_t.
5) .36 mmole	Same as no.2 (2.26 mmoles)	Naphthalene	120	1 broad peak with t_R equal to .75 times t_R of T_p.
6) .088 mmole	30% palladium on carbon (.254 g.)	p-cymene	20	Same as no.4.
7) .33 mmole	Same as no.6 (.13 g.)	Naphthalene	120	5 peaks close together with t_R equal to .89-1.48 times t_R of T_p.
8) .18 mmole	Same as no.6 (.45 g.)	p-cymene	90	1 main peak with t_R equal to t_R of T_p plus 4 peaks of t_R both greater and less than that of T_p.
9) .49 mmole	Same as no.6 (.65 g.)	p-cymene	178	1 main peak t_R equal to t_R of T_p plus six peaks of t_R both greater and less than that of T_p.
10) .23 mmole	5% Rhodium on Alumina(.23g.)	Benzene	24	1 extremely broad peak ; t_R near that of T_p.
11) 3.80 mmole	Same as no.10 (.60 g.)	Benzene in bomb, 300°	24	Same as no.10.
12) .54 mmole	30% palladium on charcoal (1.0 g.)	Benzene in bomb, 280°	48	1 major peak with a shoulder; t_R equal to t_R of T_p and 2 others; t_R near that of T_t

Hydrogenation of tetraphenylene . - Platinum oxide (.15 g.) and 15 ml. of propionic acid were heated to 81° and the catalyst was reduced under an atmosphere of hydrogen. Tetraphenylene (51.0 mg., 0.168 mmole) was added to the mixture as a solid. The hydrogen uptake ceased after the absorption of 57% of the theoretical amount.

Tetraphenylene (124 mg., 0.41 mmole), 50 ml. of ethanol and 1.5 g. of Raney-nickel were heated for 48 hr. at 100° under 1500 psi. of hydrogen. After work-up, the G.C. analysis (silicone grease, 284°) showed one peak of retention time equal to tetraphenylene and a broad cluster of peaks near the retention time of tetramer 17.

Tetraphenylene (152 mg., 0.498 mmole), 0.75 g. of platinum oxide and 20 ml. of glacial acetic acid were heated at 160° for 58 hr. under 1500 psi. of hydrogen. G.C. analysis (silicone grease, 284°) of the product showed a major peak with the same retention time as tetraphenylene, a second minor peak as a shoulder, and a third peak with an area of about one-third that of the largest peak, with a retention time 1.1 times that of tetramer 17.

Tetraphenylene (352 mg., 1.15 mmoles), 1.0 g. of Raney nickel and 25 ml. of absolute ethanol were reduced at 160° for 48 hr. under 1400 psi of hydrogen. G.C.analysis (silicone grease, 298°) showed a minor peak at 0.78 times the retention time of tetraphenylene; a major peak (with a shoulder) at 1.13 times the retention time of the tetramer 17, and a third minor peak at a retention time 1.49 times that of tetramer 17.

Reduction of 1,5-cyclooctadiene with lithium metal. - 1,5-Cyclooctadiene (3.390 g., 0.0314 mmole) was added to a flask containing 600 ml.

of anhydrous ammonia 200 ml. of tetrahydrofuran and 200 ml. of dry t-butyl alcohol. Then 7.5 g. (1.1 g. at.) of lithium was added and the solution was allowed to stir for 64 hr. During this reaction time, an additional 5 g. of lithium was added. Work-up of the products in the usual way followed by G.C. analysis (C-20M at 95° and TEG-C at 85°) showed that the products were cyclooctane, cis-cyclooctene and 1,5-cyclooctadiene in a ratio of 0.11:0.76:1.0 respectively. The first two compounds were identified by comparison of their infrared spectra with those of authentic material as well as a comparison of their retention times. The last compound was identified by retention time only since it was retained much longer than the other two compounds.

In another run the course of the reaction was followed by G.C. analysis similar to the above case. This study showed that less than 1% of the diene was reduced over a period of 30 min. After a reaction time of 3.1 hr., 8.6% of the diene had been converted to a mixture of cis-cyclooctene and cyclooctane. Continued G.C. analysis showed that the reduction of the diene proceeded smoothly at a slow rate.

Reaction of 6,6-dibromobicyclo[3.1.0]hexane 5 with methyllithium in refluxing ether. - Dibromide 5 (0.958 g., 3.99 mmoles) was added dropwise to a solution containing 7 mmoles of methyllithium in 25 ml. of anhydrous ether. When the addition of the dibromide was completed, the mixture was allowed to reflux for 10 min. and then it was hydrolyzed and extracted with ether. Naphthalene was added and the product composition was determined by G.C. utilizing a 2% SE-30 programmed column. Dimer 27a was shown to be formed in 55% yield and "trimeric" and "tetrameric" materials were found in 5.2% and 9.8% of the total product compo-

sition respectively.

In a subsequent preparative run the dimer 27a could be easily isolated via a simple distillation or by sublimation at 25°/0.01 mm. Distillation at 55°/0.5 mm. afforded a colorless material which soon solidified, m.p. 54.8 - 56.1°. Infrared (CS_2): 3010 (0.35), 2900 (>1.5), 1450 (0.51), 783 (1.11), and 700 cm^{-1} (0.53). N.m.r. (CCl_4): 5.29δ (2H, moderately broad): 0.70-2.65δ (14H, very complex). Ultraviolet spectrum (ethanol): λ max 238 mμ (ε 14,200). Its mass spectrum showed a peak at m/e 160 (molecular ion).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C,89.21; H,10.18.

The diene could be stored at -15° under nitrogen with little decomposition but it rapidly consumed oxygen when exposed to the atmosphere. For this reason, difficulty was encountered in obtaining reproducable elemental analysis. Allowing the solid compound to sit in an atmosphere of oxygen at 25° for one week afforded a sample which represented the addition of one mole of oxygen.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C,74.72;H, 8.36.

When the reaction was carried out at -17 - -19° employing 5.6 mmoles of dibromide 5 and 9.0 mmoles of methyllithium in ether followed by the usual work-up, G.C. analysis (naphthalene as an internal standard, SE silicone grease at 173°) showed a 17% yield of dimer 27a.

When refluxing n-heptane was employed as a solvent, a deep yellow reaction mixture resulted. Analysis indicated a 12% yield of dimer 27a and trace amounts of "trimeric" and "tetrameric" material.

Reaction of 6,6-dibromobicyclo[3.1.0]hexane 5 with n-butyllithium in ether. (reflux). - Dibromide 5 (1.574 g., 6.55 mmoles) was added drop-

wise in 15 ml. of ether to 10 mmoles of n-butyllithium (Foote Co.) in 100 ml. of refluxing anhydrous ether and 6 ml. of hexane. Then the mixture was allowed to reflux for 10 min. followed by hydrolysis and work-up in the usual way. Naphthalene was added as an internal standard and the product mixture was analyzed by G.C. (5% SE-30, slow prog.). The yield of dimer was 20.1%; material eluted 1 min. after dimer was 5.2%; "trimeric" material was 16.3% and tetramer was formed in 42% yield.

The treatment of 10 mg. of diene 27a in 5 ml. of ether with 1 mmole of n-butyllithium at room temperature afforded starting material as the sole product. Under the G.C. conditions used to analyze the product (5% SE-30, prog.), tetramers 17 and 19 would have been eluted.

Hydrogenation of dimer 27a. - Diene 27a (4.3 mg., 0.028 mmole) was stirred with a suspension of 30% palladium on carbon in ethanol at 25° under one atmosphere of hydrogen. After 20 min., the absorption of hydrogen ceased at an uptake of 1.26 ml. (96% of the calculated amount for two double bonds.)

Sodium in liquid ammonia reduction of dimer 27a. - Sodium (0.2 g. 0.09 g. at.) was added to a solution of 35.7 mg. (0.223 mmole) of diene 27a in 40 ml. of anhydrous liquid ammonia. The blue solution was stirred under reflux for 5 hr., then ammonium chloride and pentane were added and the ammonia was allowed to distill from the reaction mixture. Naphthalene was added as an internal G.C. standard and the product was analyzed with a C-20M column at 196°. (These conditions probably isomerized 26a to 23 in the inlet system.) This analysis showed the formation in 83% yield of a single compound with a retention time of 0.93 (0.85 for the starting material), relative to naphthalene.

In another reaction 61.1 mg. (0.381 mmole) of the diene 27a was reduced using the same conditions as above except that the reaction time was decreased to 30 sec. G.C. analysis showed a 70% yield of the reduction product 26a and an 8% recovery of starting material.

A preparative run was carried out utilizing 0.697 g. (4.36 mmoles) of the dimer 27a, 100 ml. of anhydrous ammonia, and addition of sodium until the blue color persisted. After the mixture had stirred for 30 min., the product was worked-up in the usual way. Short path distillation (0.5 mm., bath temp 60°) afforded 0.521 g. (74% yield) of the cyclobutene 26a, $n^{25}D$ 1.5124. The product was found to have no contaminants when analyzed by G.C. (C-20M at 200°, and 2% E.G.A. at 114°, preheater not above120°). Utilizing the latter column and the conditions specified, the cyclobutene could be analyzed with no rearrangement to 1,1′-dicyclohexenyl (23). Infrared (PL): 2900 (> 1.5), 2620 (0.23), 1695 (0.08), 1172 (0.90), and 817 cm^{-1} (0.87). Its n.m.r. spectrum showed complex absorption between 0.58 - 2.5δ. Ultraviolet (iso-octane): λ max 210 mμ (ε 31,000). Its mass spectrum showed a peak at m/e 162 (molecular ion).

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.89; H, 11.12.

Thermal isomerization of cyclobutene 26a to 1,1′-dicyclohexenyl (23). - Cyclobutene 26a (3.0 mg., 0.018 mmole) was drawn into a capillary tube and flushed with nitrogen. The sealed capillary tube was heated in an oil bath at 200° for 20 min. Then the entire sample was dissolved in 30 ml. of carbon tetrachloride and its infrared spectrum was measured. The spectrum so obtained was identical with the infrared spectrum (CCl_4) of 1,1′-dicyclohexenyl (23). The retention times of this material on C-20M (at 200°)

and 2% E.G.A. (at 115°). G.C. columns were identical to those of dicyclohexenyl (23).

Attempted Diels-Alder reactions of dimer 27a . - Diene 27a (0.114 g., 0.71 mmole) and 84 mg. (0.86 mmole) of maleic anhydride were heated in refluxing benzene under nitrogen for 9 hr. At the end of this time, a very viscous oil had separated which was soluble only in chloroform. T.L.C. (1:1 benzene-chloroform and pure chloroform on silica gel) showed no products other than a trace of a material which was eluted near 27a and a substance which appeared at the baseline and streaked upwards.

In a second experiment, a mixture of 40 mg. (0.25 mmole) of diene 27a, 22 mg. (0.23 mmole) of maleic anhydride and 3 mg. of 2,5-ditertiarybutylhydroquinone was sealed under nitrogen in 5 ml. of benzene and was heated at 100° for 20 hrs. T.L.C. analysis (chloroform, silica gel) showed one spot due to the hydroquinone and one spot due to a material which streaked from the baseline. Unchanged diene could not be detected in the product mixture.

Ozonization of cyclobutene 26a. - Cyclobutene 26a (35.5 mg., 0.209 mmole) was ozonized in 10 ml. of ethyl acetate at -80°, then 2 ml. of water and 0.1 g. of 10% palladium on carbon were added and this mixture was allowed to stir until the solution gave a negative starch-iodide test. G.C. analysis of the product (2% E.G.A., prog. with triphenylmethane as an internal standard) showed the presence of one compound (5.6% yield) with a retention time identical to that of 2,2'-dioxodicyclohexenyl (13).

In another experiment cyclobutene 26a (36.3 mg., 0.224 mmole) was ozonized in 15 ml. of methanol at -80° and immediately after the ozone

consumption ceased, an aqueous sodium bisulfite solution was added dropwise until a negative starch-iodide test was obtained. G.C. analysis (as above) showed an 8.7% yield of a second compound with a retention time time identical to that of 2,2'-dioxodicyclohexenyl (13) and a 5.1% yield of a second compound with a retention time 0.59 times that of 13.

Photolysis of 1,1'-dicyclohexenyl[21] (23). - 1,1'-Dicyclohexenyl (23) (1.99 g.) was added to 400 ml. of anhydrous ether and photolyzed utilizing a 550 W. Hanovia lamp with a quartz probe. The progress of the reaction was followed by analysis of the product mixture on a 2% E.G.A. gas chromatographic column at 112° with preheater temperature of 120° (higher preheater temperatures resulted in ring opening to dicyclohexenyl (23). Analysis after one hour showed that 30% of the starting material had been converted to a minimum of four compounds with retention times relative to that of the starting material of 0.22 (%), 0.30 (%), 0.39 (%), and 0.50 (%). As the photolysis was continued, the intensity of the major peak decreased relative to that of the medium intensity peak. The retention time of the cyclobutene 26a was the same as that of the 0.22 peak.

In another prolonged photolysis utilizing a low intensity lamp, a mixture of the two major peaks was collected by G.C. (C-20M) at 200°. The collected material contained ca. 4% dicyclohexenyl and approximately equal amounts of the two major compounds. The n.m.r. spectrum of this mixture showed bands at : 5.47δ, broad and complex; 0.75 - 3.0 δ, broad. The ratio of olefinic to upfield absorption was 1:11.5. Infrared (PL): 3020 (0.41), 2930 (>1.5), 1698 (0.20), 1645 (0.09), and 725 cm^{-1}(0.73). A comparison of this spectrum with the spectrum of the cyclobutene 26b

obtained by Dauben[22] showed that all of the bands in the latter compound could be found in the mixture. The mass spectrum of the mixture showed a peak at m/e 162 (molecular ion).

Anal. Calcd. for : $C_{12}H_{18}$: C,88.82; H,11.18. Found: C, 88.50; H, 11.52.

1,1'-Dihydroxydicyclohexenyl[54](68) . - Cyclohexanone 300 g. (3.06 moles) 0.21 g. of mercuric chloride and 51 g. of granular aluminum metal were added to a flask containing 300 ml. of dry benzene under nitrogen. This mixture was stirred under reflux for 1 hr. and then 200 ml. of water and 300 ml. of benzene were added. This mixture was allowed to reflux for 1 hr. followed by filtration of the entire mixture. The salts were washed several times, and then the benzene solution was dried and concentrated. Allowing this solution to stand at 0° for 6 hr. afforded 82.1 g. (33% yield) of a white solid which melted at 127 - 130° (lit.[54] 128.5 - 129.5°). The infrared spectrum (CCl_4) of this diol 68 showed bands at 3600 (0.16), 3400 (0.15), 2940 (1.00), and 965 cm^{-1} (0.80).

Preparation of 1,1'-dicyclohexenyl[55] from diol 68. - Diol 68 (91 g., 0.46 mole) was added to 475 ml. of reagent pyridine; and to this mixture, 90 ml. of phosphorus oxychloride was added. This mixture was cautiously heated on the steam bath until a very exothermic reaction began and the speed of the reaction was then moderated by use of an ice bath. When the vigorous reaction subsided, the mixture was heated on a steam bath for 8 hr. under nitrogen. Ice cold water was added and the reaction mixture was shaken vigorously to dissolve water soluble products. The olefin was then extracted with pentane and the bulk of the pyridine was removed from the product mixture by distillation at 15 mm. pressure.

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(54) E.E.Gruber, and R.Adams, J.Am.Chem.Soc., 57, 2555 (1935).

(55) D.S. Greidinger and P.Ginsbury, J.Org. Chem. 22, 1406 (1957).

Distillation of the residue (67°/0.56 mm.) afforded 62.9 g. (85%) yield of a low melting white solid which was shown to have a minor impurity by G.C. analysis (C-20M, 200°). Low temperature crystallization (-80°) from pentane afforded a white solid which melted between 26.0 - 27.3°, (lit.[56] m.p. 28°): $n^{26}D$ (on melt) 1.5343 (lit. $n^{20}D$ 1.5322). Infrared spectrum (CCl_4): 3030 (0.33), 2950 (1.50), 1610 (0.09), and 920 cm^{-1} (0.67). N.m.r. spectrum 5.74δ (2H, moderately broad with fine splitting -C=CH-) Ultraviolet spectrum (ethanol): λ max 232, 238 mμ (ε 17,000); sh. at 247 mμ.

Reaction of 6,6-dibromobicyclo[3.1.0]hexane (5) with methyllithium in styrene . - Dibromide 5 (65.6 g. , 0.273 mole) was added to 500 ml. of styrene and stirred rapidly at -15° while methyllithium (0.33 mole) was added dropwise . When the addition was completed the mixture was allowed to stir at -15° for 15 min. and at room temperature for 30 min. Water was added and product was worked up in the usual way. Distillation afforded 36.11 g. (0.196 mole, 74% yield) of a mixture of olefins 37a and 37b b.p.78°. (.04 mm.), $n^{28}D$ 1.5561 and a residue of 3.9 g. G.C. analysis (5% E.G.A., 150°) showed in the forerun a 4.6% yield of dimer 27a and in the forerun a ratio of olefin 37a to minor olefin 37b equal to 2.17:1. A subsequent run afforded a 76% yield of the olefin mixture. The U.V. spectrum (ethanol) of the olefin mixture showed only aromatic bands at 250 mμ (333). Infrared (PL): 3070 (0.12), 3050 (0.19), 3020 (0.29), 2920 (0.97), 1603 (0.18), 1498 (0.40) and 700 cm^{-1}(0.97).

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.08; H, 8.68.

Distillation through a 3 ft. spinning band column gave a pure sample

(56) E.Barnett and C.A. Lawrence, J.Chem. Soc., 1104 (1935).

of the major isomer 37a and a fraction enriched in the minor isomer 37b from which the pure minor isomer was obtained by gas chromatography (20% E.G.A., 140°.)

The infrared spectrum (PL) of the major isomer 37a showed bands at 3070 (0.28, 3050 (0.48), 3020 (0.95), 2920 (>1.5), 1603 (0.64), 1498 (1.50), 770 (1.0), 750 (>1.5), and 700 cm^{-1} (>1.5). N.m.r. 7.31δ (5H, $C_6\underline{H}_5$-sharp line); 5.41δ (1H, broad, -C=C-H); 2.99δ (4H, relatively sharp, C_6H_5-CH-CH_2 -CO-CH) broad base; 0.55 - 2.3δ (6H,complex -CH_2-CH_2-). The mass spectrum showed a peak at m/e 184 (molecular ion).

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found C, 91.34; H, 8.76.

The infrared spectrum (PL) of the minor isomer 37b showed bands at: 3070 (0.25), 3050 (0.39), 3020 (0.91), 2920 (>1.5), 1603 (0.35), 1498 (1.05), 765 (0.95) and 700 cm^{-1}(> 1.50). N.m.r.: 7.32δ (5H, sharp, $C_6\underline{H}_5$-), 5.46δ (1H,broad, -C=C-H); 2.50 - 3.9 δ (4H, complex, C_6H_5-CH-CH_2-CO-CH-) including a triplet of doublets centered at 3.70δ (C_6H_5-CH-); 0.35 - 2.50δ (6H, -CH_2-CH_2) comples). It mass spectrum showed a peak at m/e 184 (molecular ion).

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.27; H, 8.79.

When this reaction was carried out using equal volumes of styrene and ether at -40° and methyllithium made from methyl iodide and lithium, the ratio of the major olefin 37a to the minor olefin 37b was 2.2/1.0 (unchanged.)

Hydrogenation of the major styrene trapping product 37a. - Olefin 37a (98.1 mg., 0.534 mmole) was added to a prereduced mixture of 30% palladium on charcoal and absolute ethanol and reduced over 40 min. under an atmosphere of hydrogen at room temperature. The uptake of hydrogen ceased

after 14.48 ml. of hydrogen had been consumed (calculated amount equals 13.00 ml.). The product was worked-up in the usual way and distilled from flask to flask. The distillate weighed 94.2 mg. (95% yield). and its infrared spectrum (PL) showed the following bands: 3070 (0.31), 3050 (0.48), 3020 (0.84), 2920 (> 1.5), 1603 (0.55), 1498 (0.93), 765 (1.24), and 700 cm^{-1} (> 1.5). N.m.r. spectrum: 7.37δ (5H, sharp, C_6H_5-); 3.55δ (1H, minimum of four bands with a broad base absorption, C_6H_5-$\underline{C}$-$\underline{H}$-); 0.70 - 3.00δ (12H, complex). The product 34 was shown by G.C. to be a single compound and to contain none of the isomer 32 from reduction of olefin 37b.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; h, 9.74. Found: C, 90.33; H, 9.69.

Hydrogenation of minor trapping product 37b. - Olefin 37b (16.4 mg., 0.0892 mmole) was hydrogenated in absolute ethanol with 30% palladium on charcoal, at room temperature, over 9 minutes under one atmosphere of hydrogen. The hydrogen uptake ceased after 2.21 ml. of hydrogen (calculated was 2.16 ml; 98% of theoretical amount) was consumed. A flask to flask distillation of the product afforded a colorless liquid with a pure liquid infrared spectrum which was identical to the pure liquid spectrum of the hydrocarbon resulting from the hydrogenolysis of 7-phenyl-7-bicyclo[4.2.0] octanol reported in a subsequent section. The G.C retention times of these two compounds were also identical (CPS, 120°; 5% E.G.A., 150°, and 5% XE-60).

Epimerization[29] of hydrocarbon 32 . - Hydrocarbon 32 (46 mg., 0.25 mmole) was added to a solution of potassium t-butoxide (made by adding 40 mg. of potassium to 2 ml. of dry t-butyl alcohol, followed by evaporation of the alcohol ultimately at 0.01 mm. for 8 hr.) in 2 ml. of dry dimethyl

sulfoxide at room temperature under a nitrogen atmosphere. After 4.5 hours, G.C. analysis (CPS, 120°) showed only a very slight change in the starting material. Therefore, the reaction mixture was heated at 58° for 19 hours. G.C. analysis (same conditions as above) showed the gradual disappearance of the starting material and the appearance of a compound with a retention time of 1.05 times that of the starting material. The ratio of the new product to starting material after 19 hours was 86:14. Work-up of the product in the usual way afforded 31 mg. (0.165 mmole) of a hydrocarbon mixture of starting material and epimer. The infrared spectrum (PL) of this mixture showed all bands found in the spectrum of compound 34 and weak bands resulting from the starting material.

Epimerization[29] of hydrocarbon 34. - Hydrocarbon 34 (19 mg., 0.10 mmole) was treated with the same concentration as above of potassium t-butoxide in dimethylsulfoxide at 58° for 10 days. Work-up of the product in the usual way afforded a hydrocarbon mixture which was a 90:10 ratio of starting material 34 to the less stable isomer 32. The infrared spectra (PL) of this mixture and of the above epimerization mixture when the less stable isomer 32 was utilized as starting material were identical except for slightly less intense bands resulting from the less stable isomer 32.

Epimerization of mixture 32 and 34 with potassium amide in liquid ammonia.- The hydrocarbon mixture, 2.2:1.0 of 34 to 32 (0.075 g., 0.41 mmole) was added to a 0.1 molar solution of potassium amide in liquid ammonia and the reaction mixture was allowed to stir under nitrogen for 12 hr. The product was worked-up in the usual way, and extracted with pentane. The infrared spectrum (PL) showed that some epimerization of hydrocarbon 32

to 34 had occured by observing the decrease in the intensity of the band at 760 cm^{-1}. While the pure minor epimer 32 has a strong band at 760 cm^{-1}, the pure major epimer has none. The spectrum was very nearly the same as that of the 90:10 mixture obtained from epimerization in dimethylsulfoxide.

Investigation of the stereochemistry of the ring juncture in hydrocarbon 37. - The styrene trapping product 2.2:1.0 mixture 37 (0.075 g., 0.41 mmole) was added to a dry flask at 0° under nitrogen, and stirred while a 50% excess of diborane[57] in tetrahydrofuran was added dropwise. After the reaction mixture was allowed to stir for 12 hr. at room temperature, the excess diborane was hydrolyzed with water, and then a 25% excess of chromic acid in water and 10 ml. of ether were added. The reaction was allowed to continue for 48 hr. with stirring at room temperature. The infrared spectrum of the product after work-up showed a strong band at 1710 cm^{-1}. The product mixture was allowed to stir with a methanolic 10% potassium hydroxide solution under nitrogen for 40 hr. Then 25 ml. of diethylene glycol was added, the methanol was removed by distillation followed by addition of 4 ml. of an aqueous 68% hydrazine solution.[30] After this mixture was allowed to reflux for 5 hr., the excess water was removed by distillation, and the mixture was then allowed to reflux under nitrogen for another 43 hr. G.C. analysis (C-20M) of the pentane extract of the acid-washed product showed a compound with a retention time identical to that of the mixture of 32 and 34.

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(57) The diborane was prepared from sodium borohydride and from trifluoride etherate and collected by distillation into tetrahydrofuran. H.C.Brown, and P.A. Tierney, J.Am.Chem.Soc., 80, 1552 (1958).

Ozonization of olefins 37a and 37b to yield lactones. - A 2.2:1.0 mixture of isomers 37a and 37b (0.518 g., 2.82 mmoles) was ozonized in methanol at -80°. Water (2 ml.) was added and after warming to room temperature the mixture was added dropwise to a suspension of silver oxide in 10 ml. of aqueous sodium hydroxide, at 25° (0.99 g., 5.9 mmoles of silver nitrate and 12.5 mmoles of sodium hydroxide). The resultant mixture was stirred for 15 min. and then solids were removed by filtration and washed with hot water. A small amount of material was removed from the aqueous filtrate by ether extraction. Acidification of the aqueous layer followed by ether extraction gave 0.505 g., (2.22 mmoles, 79%) of acidic material which was treated with ethereal diazomethane. Analysis of the resulting product by G.C. (2% E.G.A., 25°) showed trace amounts of rapidly-eluted materials in addition to two peaks due to lactones 40b and 41b in a ratio of 3.8:1.0 (rel. ret. times 1.13:1.00). Also a trace amount of a compound was detected whose relative retention time was 0.89. The n.m.r. spectrum of this mixture was consistent with a mixture of 40b and 41b. No bands could be detected other than those arising from 40b and 41b. The infrared spectrum of this mixture showed strong bands at 1785 and 1740 cm^{-1} and was very similar to the pure major lactone 40b.

In a larger scale experiment utilizing 4.28 g., of the 2.2:1.0 mixture of epimers 37 after short-path distillation 4.52 g. (75%) of the 3.8:1.0 mixture of methyl ester lactones 40b and 41b was obtained. This material was chromatographed on 200 g. of Woelm activity 1 alumina and the progress of the chromatogram was followed by G.C. (2% E.G.A., 250°). Elution with petroleum ether-ethyl acetate removed the traces of materials which were rapidly eluted on G.C. Elution with pure ethyl acetate, which resulted

in transesterification of methyl esters to ethyl esters, gave in the initial fractions, A, 0.211 g. of material shown to be a 65:35 mixture of lactones 41c and 40c. The combined middle fractions, B, totalling 1.81 g., consisted of increasing ratios of 40c to 41c; the next combined fractions, C, consisted of 1.66 g. of pure 40c. Prolonged elution produced 0.42 g. of a dark oil which was a mixture of trans-40c and cis-40c as judged by significant G.C. peak broadening.

A pure sample of lactone 41c was obtained from fraction A by G.C. (10% E.G.A., 230°). The n.m.r. spectra of this compound showed signals at 7.36δ (5H, singlet, $C_6\underline{H}_5$-); 3.78 - 4.74 δ (4H, complex, quartet of $-O\underline{CH}_2CH_3$ and lactone $-O\underline{CH}_2$-); 2.47 - 3.78 δ (2H, complex, $C_6H_5\underline{CH}\text{-}\underline{CH}\text{-}C{=}O$); 2.16δ (2H, broad band, $-\underline{CH}_2CO_2Et$); 1.67δ (4H, broad band, $-\underline{CH}_2\underline{CH}_2$); and 1.18δ (3H, triplet, $-OCH_2\underline{CH}_3$). Its infrared spectrum showed strong bands at 1785 and 1740 cm^{-1}. This material was transesterified over a two-day period in 20 ml. of refluxing methanol containing two drops of concd. hydrochloric acid and distilled (short path, 0.1 mm., bath at 150°). N.m.r.: 7.31δ (5H, singlet $C_6\underline{H}_5$-); 3.78 - 4.83δ (2H, complex ~six lines, lactone $-O\underline{CH}_2$); 3.54δ (3H, singlet, $-O\underline{CH}_3$); 2.42 - 3.41δ (2H, complex, $C_6H_5\underline{CH}\text{-}\underline{CH}\text{-}C{=}O$); 2.17δ (2H, broad band, $-\underline{CH}_2CO_2CH_3$); and 1.62δ (4H, broad band, $-\underline{CH}_2\underline{CH}_2$). Infrared ($CCl_4$): 3070 (0.09), 3050 (0.11), 3020 (0.19), 2940 (0.37), 1785 (1.3), 1740 (0.93), and 700 cm^{-1} (0.63.)

The major lactone ethyl ester 40c, obtained from fraction C, was distilled (short path, 0.1 mm., bath at 150°); $n^{19}D$ 1.5156. Infrared (CCl_4): 3070 (0.04), 3050 (0.06), 3020 (0.11), 2920 (0.22), 1785 (1.4), 1740 (1.1) and 700 cm^{-1} (0.45). N.m.r.: 7.30δ (5H, singlet, $C_6\underline{H}_5$); 3.81 - 4.67 (3H, complex, quartet of $-O\underline{CH}_2CH_3$ and lactone $-O\underline{CH}$-); 2.5 - 3.66δ (3H, sharp

complex pattern, $C_6H_5\underline{C}\underline{H}\text{-}CH_2\text{-}\underline{C}\text{=}O$); 2.09δ (2H, broad, $-\underline{CH_2}CO_2Et$); 1.58δ (4H, broad, $-\underline{CH_2}\underline{CH_2}-$); 1.08δ (3H, triplet, $-OCH_2\underline{CH_3}$).

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found:C, 69.89; H, 7.49.

Transesterification of this ethyl ester lactone 40c in methanol gave the methyl ester lactone 40b which was purified by distillation (short path, 0.1 mm. bath at 150°); $n^{19}D$ 1.5222. Infrared (CCl_4): 3070 (0.02), 3050 (0.05), 3020 (0.09), 2920 (0.19), 1785 (0.90), 1740 (0.81), and 700 cm^{-1} (0.39). N.m.r.: 7.35δ (5H, singlet, $C_6\underline{H_5}$); 4.42δ (1H, doublet with a broad base, lactone $-\underline{C}\underline{H}\text{-}O-$); 3.60δ (3H, singlet,$-O\underline{CH_3}$); 2.50 - 3.50δ (3H, complex seven line patter, $C_6H_5\underline{C}\underline{H}\text{-}\underline{CH_2}\text{-}\underline{C}\text{=}O$); 2.29δ (2H, broad, $-\underline{CH_2}CO_2CH_3$); 1.72δ (4H, broad, $-\underline{CH_2}\underline{CH_2}-$).

Transesterification with methanol of a portion of fraction C gave a 3:1 mixture of the methyl esters of the major and minor lactones 40b and 41b. Their infrared and n.m.r. spectra were consistent with a mixture of the above lactones. A distilled sample of this mixture was analyzed.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.57; H, 6.85.

Ozonization of 6.44 mmoles of the pure major trapping product 37a at -80° in the manner described above, followed by oxidation of this product with silver oxide (from 2.62 g. of silver nitrate and 1.25 g. of sodium hydroxide) afforded 76 mg. of a neutral fraction. This fraction was shown to be very complex by G.C. (2% E.G.A., prog.). The acidic portion, 1.28 g. (76% yield) showed infrared bands (CCl_4) at 1780 and 1710 cm^{-1}. Treatment of this material with an ethereal solution of diazomethane afforded a colorless liquid, $n^{25}D$ 1.5180, which was distilled (short path, 0.1 mm., bath at 125°) without residue. G.C. analysis of

the product showed the formation of two compounds in a composition of 3.56:1.00, with retention times of 1.13:1.00, respectively. The neutralization equivalent of this mixture was found to be 135 (131 calculated). The oil showed infrared bands at 1785, 1740 and 700 cm^{-1}.

The pure minor trapping product 37b (0.0735 mmole) was ozonized in 10 ml. of methanol at 80°. Oxidation of the product with silver oxide (from 0.16 mmole of silver nitrate and 0.39 mmole of sodium hydroxide) at 25° for 30 min. followed by methylation with diazomethane afforded 13.4 mg. of a three component mixture, 42b, 41b and 40b. The relative retention times were: 0.89; 1.00; 1.14; and the retention times of the 1.00 and 1.14 compounds were the same as the lactones obtained above. The ratio of the area of the 1.14 compound 40b to the sum of the areas of the 0.89 and 1.00 compounds was 3.4:1.0, and the ratio of the 0.89 to 1.00 peaks was ca. 2:1. The infrared spectrum (CCl_4) of the G.C. collected (10% E.G.A., 230°) mixture of the three peaks showed bands at 3070 (0.14), 3050 (0.19), 3020 (0.30), 2950 (0.62), 1785 (1.10), 1740 (1.20), 1140 (0.73)broad; and 700 cm^{-1} (0.45).

In the actual isolation of lactones 40b and 41b described earlier, the compound in the above mixture whose relative retention time was 0.89 was present in the mixture of lactones added to the alumina chromatographic column. G.C. analysis of all of the material eluted from the alumina column showed that the 0.89 peak 42b was not present. Therefore, it seems likely that it was equilibrated to one of the other lactones 40b or 41b. Since lactone 40b cannot undergo equilibration whereas lactones 41b and 42b can, it follows that the 0.89 peak was the thermodynamically less stable cis-lactone, 42b; and it was

converted on the alumina column to the trans-lactone 41b.

Ozonization of the styrene trapping product mixture 37a and 37b to obtain the corresponding cyclobutanone 38 . - A 2.2:1.0 mixture of the trapping product mixture of 37a and 37b (2.19 g., 11.9 mmoles) was ozonized in 20 ml. of ethyl acetate at -80°. Then the volume of solvent was reduced to 10 ml., and the mixture was injected onto a prereduced mixture of 5% palladium on carbon in 10 ml. of ethyl acetate under one atm. of hydrogen. Hydrogen uptake ceased after 23.5 hr. during which time 166 ml. of hydrogen was consumed (68% of theory) (a parallel ozonization and reduction gave a 90% uptake.)

After the catalyst was removed by filtration, the residue, after solvent removal, was an oil 38a, which showed infrared bands at 1785, 1710, and 700 cm^{-1}. N.m.r.: 9.67δ (1H, -CO$\underline{H}$); 7.28δ (5H, sharp singlet, $C_6\underline{H}_5$); 2.59 - 3.75δ (4H, C_6H_5-C$\underline{H}$-C$\underline{H}_2$-CO-C$\underline{H}$-) sharp band centered at 3.20δ superimposed on broad absorption; 2.32δ (2H, broad, -C$\underline{H}_2$-C-H-) and 1.70δ (4H, broad, -C$\underline{H}_2$-C$\underline{H}_2$-).

The entire residual oil 38a was dissolved in 10 ml. of ethyl acetate and was added dropwise to a mixture of silver oxide (made from 2.06 g. of silver oxide and 2.06 g. of sodium hydroxide) in 100 ml. of ethanol and 100 ml. of ethanol and 100 ml. of water. After this mixture was allowed to stir for 8hr. at room temperature, the solids were removed by filtration and washed with hot water. The basic solution was washed with ether giving 0.283 g. of neutral material which showed bands in the infrared spectrum (CCl_4) at 3400 and 1780 cm^{-1} (no other carbonyl band). The aqueous layer was acidified and extracted several times with ether. Removal of the solvents under reduced pressure gave

1.95 g. (71%) of the keto-acid 38b which showed bands in the infrared ($CHCl_3$) at 1710 and 1780 cm^{-1} with a very broad band in the 3μ region, This material, which could not be distilled without decomposition, was analyzed by TLC (silica gel, $CHCl_3$ sat. with formic acid) which showed one intense spot and one minor spot at a lower R_f value. From the TLC and n.m.r. data reported later under the deuteration experiments, as well as the G.C. results obtained for the methylation product reported below, this material appeared to be fairly pure (probably > 90%).

The keto-acid 38b was treated with an excess of diazomethane in ether and the product was distilled (short path, 0.08 mm., bath at 125°) without residue. G.C. analysis (2% E.G.A., 270°) of this material showed one major and three minor compounds with relative retention times of 0.7 (1%), 1.0 (93%), 1.4 (1%) and 3.7 (5%). The major product, keto-ester 38c, was collected by G.C. (10% E.G.A., 220°) and short-path distilled; $n^{25}D$ 1.5237. Infrared (CCl_4): 3070 (0.7), 3050 (0.11), 3020 (0.23), 2940 (0.43), 1785 (1.3), 1740 ((1.2), 1140 (0.55), 1175 (0.53) and 700 cm^{-1} (0.64). N.m.r. : 7.29δ (5H, singlet, $C_6\underline{H}_5$) 3.60δ (3H, singlet, $-O\underline{CH}_3$); 3.21δ (2H, singlet with broad base, $C_6H_5\underline{CH}\text{-}\underline{CH}\text{-}\underline{C}=O$); 1.92 - 3.05δ(4H, complex, $-\underline{CH}_2\underline{C}=O$ and $-\underline{CH}_2\text{-}CO_2CH_3$) and 1.2 - 1.96 δ (4H, broad, $-\underline{CH}_2\underline{CH}_2-$). The mass spectrum of this keto ester 38c showed no molecular ion, but showed fragments at m/e 204, 130, 117, 115 and 104.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found:C, 73.21; H,7.23.

Attempted saponification of this keto ester 38c with 25% potassium hydroxide in 60:40 water ethanol at reflux for 2 hr. resulted in a loss of the 1785 cm^{-1} infrared band.

Baeyer-Villiger oxidation of keto-ester 38c . -

a.) Base catalyzed. Keto-ester 38c (5 mg.) was added to 2 ml. of methanol, 5 µl. of 30% hydrogen peroxide, and 5 mg. of sodium hydroxide. This mixture was stirred at 25° for 2 min., then 30% palladium on carbon and a drop of concd. hydrochloric acid were added . After this mixture had been stirred for 1 hr., the G.C. analysis (2% E.G.A., 250°) showed a 68% conversion of the keto-ester 38c to the lactone-ester 40b and 41b. The ratio of the major 40b to the minor 41b lactone-ester was 13:1.

A second preparative, base catalyzed reaction was carried out on 140 mg., and the lactone-esters were collected by G.C. (10% E.G.A., 240°). The collected sample showed an n.m.r. spectrum (CCl_4) which was very similar to the spectrum of the pure, major lactone-ester 40b. Infrared (CCl_4): 3070 (0.06), 3050 (0.10), 3020 (0.15), 2940 (0.28), 1785 (1.00), 1740 (0.86), 1150 (0.60), and 700 cm^{-1}(0.41).

b.) Uncatalyzed.- Keto-ester 38c (5 mg.) was treated as above, except that no base was added and the reaction time was 20 min. Work-up as in the above case and G.C. analysis showed that the conversion of keto-ester 38c to lactone-ester 40b and 41b was 43%. The major to minor lactone-ester ratio was nearly the same as above.

Attempted hydrogen-deuterium exchange on keto-ester 38c . - Keto-ester 38c (126 mg., 0.510 mmole) was stirred under nitrogen at room temp. for 35 min. in a solution prepared by dissolving 50 mg. of sodium in 2 ml. of deuteriomethanol. The solvent was removed by evaporation under reduced pressure. Then 2 ml of deuteriomethanol was added and the mixture was stirred for 30 min. This process was repeated; then 10 ml of deuterium oxide was added and the product was extracted with methylene chloride

and worked-up in the usual way. The weight of the neutral residue was 9.3 mg. and its infrared spectrum (CCl_4) showed bands at 1785 (0.22), 1740 (0.96), and 700 cm^{-1} (0.68). Acidification of the aqueous layer, extraction with methylene chloride and work-up as usual afforded 74 mg. of a material which showed bands in the infrared ($CHCl_3$) at 1710 (0.97) and 700 cm^{-1} (0.48). No band near 1785 cm^{-1} could be found and a very broad band in the 3μ region was found.

Deuteration of keto-acid 38b . - A mixture of 85 mg. of keto acid 38b, 0.3 g., of potassium carbonate and 20 ml. of deuterium oxide was stirred for 4 hr. under nitrogen at room temperature. Then the mixture was acidified to a pH of 4 and extracted with ether. An n.m.r. spectrum of this product showed that the deuteration had not gone to completion. The entire product was again added to 0.3 g. of potassium carbonate in 25 ml. of deuterium oxide and the mixture was allowed to stir at room temperature under nitrogen for 14 hr. The mixture was acidified with a buffer solution of acetic acid sodium acetate and the product was extracted with ether. Removal of the solvents under reduced pressure left a residual oil, the deuterated keto-acid. Infrared: 1785 (1.13), 1710 (1.4), 1603 (0.09), 1498 (0.17), 700 cm^{-1}(0.53), and a very broad band in the 3μ region. N.m.r. ($CDCl_3$) : 9.68δ (1H, singlet, COO$\underline{H}$), 6.93δ (5H, singlet, $C_6\underline{H}_5$), 3.04δ (~1H, singlet $C_6H_5C\underline{H}$-), 2.18δ (~2H, broad band, -$C\underline{H}_2CO_2H$), 1.52δ (~4H, broad band, -$C\underline{H}_2C\underline{H}_2$-). The non-deuterated keto-acid 38b gave the following spectrum: n.m.r. ($CDCl_3$): 9.53δ (1H, singlet, COOH), 6.90δ (5H, singlet, $C_6\underline{H}_5$), 3.03δ (2H, singlet with broad base, $C_6H_5C\underline{H}$-$C\underline{H}$-C=O); 1.9 - 2.83 δ (4H complex: apparent triplet centerat 2.58δ, -$C\underline{H}_2$C=O and a broad band at 2.13δ, -$C\underline{H}_2CO_2H$); 1.58δ

(4H, broad base, $-CH_2CH_2-$). The ratio, determined by integration of aromatic to higher field protons for the non-deuterated keto-acid 38b was 5.0:10.2 (calcd. 5.0:10.0). The corresponding ratio observed for the deuterated keto-acid was 5.0:7.6. The observed difference thus corresponds to 2.6 deuterium atoms per molecule of the deuterated keto-acid. Both the non-deuterated and deuterated keto-acids were converted to methyl esters with diazomethane. N.m.r. spectra were measured for both esters without collection by G.C. The non-deuterated keto-ester 38c showed an observed ratio of aromatic to higher field protons of 5.0:12.9 (calcd. 5.0:13.0), the corresponding ratio observed for the deuterated keto-ester was 5.0:10.5. This difference corresponds to 2.4 deuterium atoms per molecule of deuterated keto-ester. Samples of both non-deuterated and deuterated keto-esters were then collected by G.C. (10% E.G.A., 220°). The corresponding integral ratios were found to be 5.0:13.4 for the non-deuterated keto-ester and 5.0:12.6 for the deuterated keto-ester. From these data, it seems likely that the deuterated keto-ester underwent some deuterium-hydrogen (D→H) exchange on the G.C. column.

Ozonization of a 2.2:1.0 mixture of olefins 37a and 37b leading to complex mixtures. -

a.) Hydrogen peroxide-acetic acid work-up. The olefin mixture (212 mg., 1.15 mmoles) was ozonized in methanol at -80°; hydrogen peroxide (30%, 0.1 ml.) and acetic acid (0.1 ml.) were added, and the mixture was stirred for 2 hr. The methyl ester was made by adding a drop of mineral acid and heating for 8 hr. The G.C. analysis of the product showed the presence of five major and five minor products. A previous run, in which

the methyl ester was made via diazomethane, showed a very complex product mixture by thin layer chromatography.

b.) Chromium trioxide in acetic acid work-up. - The olefin mixture (0.181 g.) was ozonized in ethyl acetate at -80°; the ozonide was oxidized by addition to a mixture of chromium trioxide in acetic acid, and the product was esterified by heating with methanol containing a drop of mineral acid. T.L.C. analysis showed a very complex reaction product. When the methyl ester was made with diazomethane, the composition of the product did not change.

c.) Triethyl amine reductive work-up. - The olefin mixture (5.16 g., 28.1 mmoles) was ozonized in methylene chloride at -80°; 10 ml. of triethyl amine was added and the mixture was allowed to stir at room temperature for 15 min. The product was oxidized with silver oxide (61 mmoles) in a solution containing 62 mmoles of sodium hydroxide. T.L.C. analysis of the acidic material showed the presence of six compounds, and the infrared analysis showed a ratio of 1785 cm^{-1} to 1710 cm^{-1} absorption of 40:88.

d.) 5% Palladium on calcium carbonate reductive work-up. The olefin mixture (3.66 g., 19.8 mmoles) was ozonized in methanol at -80° and the product was reduced with 5% palladium on calcium carbonate under an atmosphere of hydrogen. The product from the reduction was oxidized with silver oxide in the usual way. The acidic product was treated with diazomethane. G.C. analysis showed the presence of eight compounds. The two major compounds in the mixture were in a ratio of 1:2 and their respective retention time ratio was 4.7:1.

e.) 10% Palladium work-up. - The olefin mixture (144 mg., 0.782

mmole) was ozonized in ethyl acetate at -80°. The product was stirred with a suspension of 0.2 g. of 10% palladium on carbon in acetone-water (3:1) until a negative starch-iodide test was obtained. The product from this treatment was oxidized with silver oxide in the usual way, and the acidic product obtained was converted to its methyl ester with diazomethane. G.C. analysis showed the presence of two major compounds in equal amounts along with several minor components. The retention times of the two major products matched those of the keto-ester 38c and 40b lactone-ester.

f.) Sodium bisulfite reductive work-up. - The olefin mixture (209 mg., 1.13 mmole) was ozonized in methanol at -80°; aqueous sodium bisulfite was added dropwise until a negative starch-iodide test was obtained, and the product was oxidized with silver oxide in the usual way. The acidic product was treated with an excess of diazomethane, and the G. C. analysis of the product showed an extremely complicated product mixture.

Attempted oxidation of olefin mixture 37a and 37b with sodium meta-periodate-osmium tetroxide[58]. - A 2.1:1 mixture of olefins 37a to 37b (2.19 g., 11.9 mmoles) was added to 60 ml. of water, 60 ml. of ether and 0.2 g. of osmium tetroxide. Then 5.8 g. (27 mmoles) of solid sodium meta-periodate was added over a period of 1.5 hr. This mixture was allowed to stir between 22 - 25° for 12 hrs. The residue obtained after ether extraction and removal of solvents was stirred for 9 hr. with silver oxide in a basic ethanol-water solution. work-up in the usual way afforded 0.721 g. of a neutral fraction which consisted mainly of starting material. The acidic fraction was treated with meth-

(58) R.Pappo, D.S.Allen, R.V.Lemieux and W.S.Johnson, J.Org.Chem.,21, 478(1956).

anol and a drop of mineral acid and heated overnight. This reaction produced 0.424 g. of a black oil which showed a weak band in the infrared at 1785 cm^{-1}.

Treatment of the styrene trapping products with high-surface sodium.[44] - High-surface sodium on alumina was prepared by shaking a mixture of molten sodium (1 part) with anhydrous alumina (5 parts, Alcoa grade F, non-base washed, dried under 0.1 mm. pressure at 200°) under nitrogen. A 60 x 1.2 cm. pyrolysis tube packed with high-surface sodium was maintained at 200° and a slow stream of nitrogen was passed through the column. A 2.2:1 mixture of olefins 37a to 37b (5.11 g., 27.8 mmoles) was passed rapidly through the pyrolysis tube. G.C. analysis (20% C-20M, 209°) of the white solid product which collected at the end of the pyrolysis chamber showed the presence of four components with the following relative retention times and % yields: 0.61 (4.6%); 0.71 (4.2%); 1.0 (2.1%), and 1.2 (35%). The material with retention time 1.0 was identified as starting material and the major component was shown to be 1,2-diphenylethane by comparison of G.C. retention times, infrared spectra and melting points.

In another experiment, a mixture of high surface sodium 1.0 g. on alumina, (5.0 g.), 20 ml. of anhydrous diglyme and 0.300 g. (1.63 mmoles) of the 2.2:1.0 mixture of olefin 37a to 37b was stirred at reflux for 24 hr. The reaction mixture was hydrolyzed with methanol and the product was extracted with pentane. G.C. analysis (20% C-20M, 210°) of the product mixture showed the presence of five products with the following relative retention times and percent composition: 0.62, 4.2%; 0.68, 48.2%; 0.76, 17.7%; 1.0, 16.7%; , and 2.0, 13.1%. The compound

with relative retention time 1.0 was found to be identical with starting material. The ultraviolet spectrum (ethanol) of the material with relative retention time 0.68 showed complex bands with a principal maximum at 263 mμ (924.)

Preparation of 4-phenylbutyrolactone (45) - β-Benzoylpropionic acid (10.0 g., 0.0565 mole) was added to 200 ml. of methanol which had been adjusted to pH of 8 with sodium hydroxide. The 2.6 g. (0.57 mole) of sodium borohydride in 25 ml. of methanol was added to the solution at 0°. When the addition was completed, the reaction mixture was stirred at room temperature for 15 min. followed by a one-hour period at reflux. The solution was acidified, extracted with ether, and the product was worked-up as usual. The residue after solvent removal was distilled from boric acid with a bath temperature of 140°. Redistillation of the product at 135°/2mm. afforded 8.04 g. (0.0496 mole, 88% yield)of a colorless liquid which solidified upon standing, m.p. 45°. (lit.[59] m.p. 46°). Infrared (CCl_4): 3070 (0.25), 3050 (0.44), 3020 (0.54), 2950 (0.40), 1790 (>1.5), and 700 cm^{-1} (1.50). N.m.r.: 7.48δ (5H, singlet, $C_6\underline{H}_5$); 5.48δ (1H, triplet with fine splitting, $C_6H_5\underline{C}H$-O); 1.66 - 2.72δ (4H, very complex pattern of sharp lines, -$C\underline{H}_2C\underline{H}_2$-).

Preparation of 7-bicyclo[4.2.0]octene[26] (29) . - 1,3-Cyclooctadiene (28) (70.0 g., 0.662 mole) was added to 2.9 l. of anhydrous ether and irradiated with a 550 W., Hanovia, mercury-arc lamp for 152 hr. Distillation of the product afforded 17.1 g. (24% yield) of a colorless liquid, b.p.129-135°,

(59) R.R.Russel and C.A. Vander Werf, J.Am.Chem.Soc.,69, 11(1947).

which was shown to be 95% pure by G.C. (12% TEG - 12% Carbowax, 91°). Purification by preparative G.C. (S550, 104°) afforded 11.6 g. (0.107 mole, 17.2% yield) of a colorless liquid with an infrared spectrum identical to the spectrum of the material obtained by Dauben and Cargill. Infrared: (PL) ; 3100 (0.14), 3025 (0.97), 2920 (> 1.5), 790 (1.07), 775 (0.98), 725 (0.87), and 720 cm^{-1} (0.77). N.m.r.: 6.17δ (2H, singlet, -CH=CH-); 2.88δ (2H, broad with fine splitting, =C-CH-CH-CH=); 1.0 - 2.2δ (8H, broad with center at 1.58δ, $-CH_2CH_2CH_2CH_2-$).

In the above photolysis as well as in an acetophenone sensitized reaction, an unidentified peak appeared in the G.C. (TEG-C, 90°) shortly after the photolyses were begun. The retention time of this compound was 1.2 times that of 1,3-cyclooctadiene (28) , and its concentration remained ca. one-third that of 28 during the course of the photolysis. The conversion of 28 to cyclobutene 29 was also found to be very slow in pentane.

7-Bicyclo[4.2.0]octanone (30) . - 7-Bicyclo[4.2.0]octene (29) (7.33 g., 67.8 mmoles) was added to a dry flask under nitrogen and 49 mmoles of diborane in 85 ml. of tetrahydrofuran[28] was added to the pure liquid at 0°.

After this solution was allowed to stir for 10 hr. at room temperature, water was cautiously added to destroy the excess diborane. The bulk of the tetrahydrofuran was evaporated (15mm.), then 95 mmoles of a chromic acid solution (made from 16.5 g., of sodium dichromate, 12 ml. of concd. sulfuric acid, and 60 ml. of water) and 50 ml. of ether were added. This mixture was stirred at 25° for 8 hours. Ether and water were added and the product was extracted with ether. Distillation afforded 5.03 g.,

(40.6 mmoles, 60% yield) b.p. 65° (6.5 mm.) $n^{25}D$ 1.4742, of a compound with an infrared spectrum identical to the spectrum[60] of 7-bicyclo [4.2.0]octanone 30. Infrared (CCl_4): 2930 (0.60), 2850 (0.28), 1780 cm^{-1} (>1.5). N.m.r.: 2.83 - 3.68δ (2H, pair of doublets superimposed on broad, complex absorption); 0.6 - 2.83 (10H broad and complex.)

7-Phenyl-7-bicyclo[4.2.0]octanol (31) . - The cyclobutanone 30 (2.72 g., 21.9 mmoles) was added to 25 ml. of anhydrous ether and cooled to -80°. Then 28 mmoles of phenyllithium in ether was added dropwise, and the mixture was allowed to stir for 40 min. at room temperature. After hydrolysis and extraction with ether, the residue after solvent removal was 3.86 g., (19.1 mmole, 87% yield). G.C. analysis (15% V-900 at 220°, 2% E.G.A. at 180°) showed that this product had trace impurities near the retention time of a C_{14} hydrocarbon. The alcohol was purified via a short path distillation (110/0.02 mm.) which afforded the pure alcohol 31 as demonstrated by G.C. (2% E.G.A. at 180°.) Infrared (PL): 3400 (0.86), broad; 3070 (0.26), 3050 (0.45), 3020 (0.35), 2920 (>1.5), 2850 (1.50), 1603 (0.19), 1498 (0.69), 765 (>1.5), and 700 cm^{-1} (> 1.5). N.m.r.: 7.50δ (5H, sharp complex bands $C_6\underline{H}_5$-); 0.50 - 3.05δ (13H, complex with temperature dependent band as a sharp peak at 2.20δ at 30°, -O<u>H</u>). Refractive index: $n^{25}D$ 1.5513.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.08; H, 9.21.

Hydrogenolysis of 7-phenyl-7-bicyclo[4.2.0]octanol (31). - A synthetically prepared sample of 7-phenyl-7-bicyclo[4.2.0]octanol (31) (161 mg., 0.796 mmole, synthesis indicated in another section) was injected onto a prereduced mixture of 30% palladium on charcoal in acetic

(60) A.C.Cope and R.W. Gleason, J.Am.Chem.Soc.,84, 1928 (1962).

acid at 58° and reduced under an atmosphere of hydrogen. Over a period of 25 min., 20.25 ml. of hydrogen was taken up at an even rate (calculated was 19.48 ml.). Very slow uptake was observed over the next 26 minutes; thus, the hydrogenation was stopped. Distillation of the product from flask to flask afforded 124 mg. (0.664 mmole, 84% yield) of a colorless liquid, $n^{25}D$ 1.5332 which was shown to be pure by G.C. (C.P.S., 120° 5% E.G.A., 150°, and 5% EX-60). The G.C. analysis on C.P.S. showed that none of the hydrocarbon 34 resulting from catalytic reduction of olefin 37a could be detected. The infrared spectrum (PL), of this liquid was identical to hydrocarbon 32 as indicated before and showed bands at : 3070 (0.29), 3050 (0.42), 3020 (0.73), 2920 (>1.5), 1603 (0.35), 1498 (1.4), 760 (>1.5), and 700 cm^{-1} (>1.5). N.m.r. spectrum (CCl_4): 7.29δ (5H, moderately narrow base but complex, $C_6\underline{H}_5$-); 3.55δ (1H, broad and complex, C_6H_5-C<u>H</u>-); 0.50 - 2.95δ (12H , complex).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.30; H, 9.69

Preparation of the minor reduced trapping product 32 from 7-bicyclo[4.2.0]octanol. - 7-Bicyclo[4.2.0]octanol[61] (1.07 g., 8.50 mmoles) in 15 ml. of ether was added to a 75% excess of a solution of chromic acid in water. After the mixture had stirred for 4 hr., more ether and water were added; and the aqueous layer was washed several times with ether. The product was worked-up in the usual way, and the resultant ketone (0.938 g., 7.58 mmoles, 89% yield) showed a strong infrared band at 1780 cm^{-1}. The infrared spectrum of this ketone was identical to that of 7-bi-

(61) This alcohol was made from a hydride reduction of exo-bicyclo[4.2.0] oct-7-ene epoxide. (See reference 60)

cyclo[4.2.0]octanone obtained by Gleason. This product in ether was added dropwise to an ethereal solution containing 16 mmoles of phenyllithium. The mixture was allowed to stir at room temperature for 45 min., then an aqueous solution of ammonical ammonium chloride was added dropwise. After the product was extracted with ether and the solvents were removed, the crude product (0.945 g., 4.33 mmoles, 57% yield) showed strong hydroxy absorption in the 3μ region and an aromatic band at 70 cm^{-1} in its infrared spectrum. This benzylic alcohol was hydrogenolyzed with 30% palladium on carbon in acetic acid at 24° under an atmosphere of hydrogen. The hydrogen uptake ceased after 79% of the calculated amount had been absorbed. This product was worked-up in the usual way, and then it was short-path distilled. Its infrared spectrum was identical to the spectrum of the trapping product 32 obtained by the two ways described previously. Its mass spectrum showed a molecular ion at 186 and a very large fragment at 104.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.28; H, 9.69

Catalytic reduction of the alcohol utilizing 30% palladium on carbon in ethanol at room temperature proceeded at a very slow rate.

The conditions for the above hydrogenolysis were determined by using dimethylphenylcarbinol as a model. These studies showed that with this compound utilizing 10% palladium on carbon in ethanol at 26° under an atmosphere of hydrogen after a period of 17 hr., absorption of hydrogen ceased with an uptake of 1.0 mole. Utilizing 30% palladium on carbon in acetic acid at 28° under one atmosphere of hydrogen, one mole of hydrogen was absorbed within one hour (hydrogenolysis) followed by a very slow uptake due to the reduction of the aromatic ring.

Reaction of 6,6-dibromobicyclo[3.1.0]hexane (5) with methyllithium in the presence of olefins (furan, cyclohexene, isobutylene.) - Dibromide 5 (8.36 g., 34.8 mmoles) and 75 ml. furan (freshly distilled from sodium) were cooled to -80°. Methyllithium (42 mmoles) was added dropwise with stirring, and the reaction mixture was worked up as usual. Analysis by G.C. (20% S-710 and 20% C-20M, 200°) showed that the products were the same as those obtained in ether at -80°; no new products were formed.

Similarly, reaction of 34 mmoles of dibromide and 48 mmoles of methyllithium in a mixture of 75 ml. of isobutylene and 75 ml. of ether at -80° followed by the usual work-up and G.C. analysis (sil. grease, 180° and 300°) showed that the product composition was the same as in the absence of isobutylene; no new products were formed. The same result was obtained using a 1:1 (mol.) mixture of cyclohexene and ether at -80°.

Addition of 7.6 mmoles of dibromide 5 in 10 ml. of ether to 10 mmoles of methyllithium in 50 ml. of isobutylene at -17° to -19° followed by the usual work-up and a G.C. analysis (sil. grease 190° and 280°) gave a 21% yield of dimer 27a; no new products were obtained.

Dropwise addition of 9.2 mmoles of dibromide 5 to 16 mmoles of methyllithium in 20 ml. of refluxing cyclohexene followed by the usual work-up and G.C. analysis (naphthalene as internal standard, 5% SE-30 prog; S-550, 200°), showed that dimer 27a was formed in 68% yield. No cyclohexene trapping product was observed.

Attempted preparation of the 7-phenylbicyclo[4.2.0]octane system by photolysis. -

a.) Styrene (15.1 g., 0.145 mole) and 150 g., of cyclohexane were added to 500 ml. of ether and irradiated for 7 days. G.C. analysis showed

that no product resulting from a dimerization of cyclohexene and styrene could be detected.

b.) Styrene (15.5 g., 0.148 mole) was added to 500 ml. of cyclohexene and irradiated for 40 hr. G.C. analysis showed that no product resulting from a 1:1 adduct of styrene and cyclohexene could be detected.

c.) Phenylacetylene (5.45 g.), 175 ml. of cyclohexene and 190 ml. of n-hexane were irradiated with a 550 W. Hanovia lamp in a for 71 hr. G.C. analysis showed that no dimer of phenylacetylene and cyclohexene was formed.

Rearrangement of 6,6-dibromobicyclo[3.1.0]hexane (5). - 6,6-dibromobicyclo[3.1.0]hexane (5) (10g.) was added to a distillation flask and heated for 1 hr. at 200°. Distillation of the product afforded a colorless liquid 6 which was collected at 61° (0.6 mm.), $n^{25}D$ 1.5761. Infrared (PL): 3020 (0.08), 2940 (1.20), 2850 (0.54), 2815 (0.49), 1625 (0.46), 740 (>1.5), 640 (>1.5), and 532 cm^{-1} (0.40). N.m.r.: 4.69δ (1H, multiplet -CBr=CH-); 3.10δ (1H, multiplet, -C-H(Br) -CH=); 2.11 - 2.60δ (2H, complex allylic); 1.5 - 2.11δ (4H, broad, $-CH_2-CH_2-$). Slow distillation of 5 above 80° or standing at room temperature also led to extensive isomerization of 5 to 6.

Anal. Calcd. for $C_6H_8Br_2$: C, 30.03; h, 3.36; Br, 66.61. Found: C, 30.24; H, 3.29; Br, 66.34.

Sodium in liquid ammonia reduction of 6,6-dibromobicyclo[3.1.0] hexane (5). - 6,6-dibromobicyclo[3.1.0]hexane (5) (o.344 g., 1.44 mmoles), 25 ml. of pentane and 50 ml. of pentane and 50 ml. of liquid ammonia were allowed to stir together while small pieces of sodium were added until a permanent blue color was obtained. Then ammonium chloride was added and

the product was worked-up in the usual way. G.C. analysis (TEG-carbowax, 68°) showed that the product consisted of bicyclo[3.1.0]hexane and cyclohexene in a ratio of 93:7.

6,6-Dichlorobicyclo[3.1.0]hexane (51). - Chloroform (50 g., 0.42 mole) in 100 ml. of pentane was added dropwise to a stirred slurry of 25 g., 0.38 mole of cyclopentene, 0.79 mole of potassium t-butoxide and 200 ml. of pentane at -10°. When the addition was completed the reaction mixture was allowed to come to room temperature then water and more pentane were added. The product was worked-up in the usual way under 30 mm. pressure. Distillation of the product afforded 30.58 g., 54% of 57, b.p. 40° (5 mm.), $n^{18}D$ 1.4974. Infrared (PL): 3020 (.24), 2920 (1.5), 2850 (0.90), 1075 (0.96), 810 (>1.5), 790 (1.3), and 650 cm^{-1} (0.17). Its n.m.r. spectrum (PL) showed complex absorption between 1.35 - 2.68 δ and centered at 2.09δ.

Reaction of 6,6-dichlorobicyclo[3.1.0]hexane (57) with n-butyllithium in ether (-80 to 25°). - Dichloride 57 (1.24g., 8.24 mmoles) was added to 50 ml. of anhydrous ether and cooled to -80°. n-Butyllithium (17 mmoles in 8 ml. of hexane, Foote Co.) was added dropwise with stirring. No salt formation was observed over a period of 20 minutes; therefore, the Dry Ice-acetone bath was replaced with a water bath. Within two minutes salts had precipitated from the solution. After the mixture was allowed to stir for 30 min., water was added and the product was worked up in the usual way. Programmed temperature G.C. analysis (starting at 94°, 2% SE-30) showed a minimum of 14 peaks as follows (temperature of peak elution; %composition based on areas only); 1.7% (110°); 15% (150°); 3.8% (179°); 4.6% (184°); 8.6% (196°); (cluster; 39%, 208°; cluster; 8.3%, 225°; clus-

ter of two peaks; 19%, 245°.) No compound in the mixture had the same retention time as dimer 27a however; the major component in the cluster eluted at 245° had the same retention time as tetramers 17 and 19.

Dropwise addition of 8.6 mmoles of dichloride 57 to 11 mmoles of n-butyllithium in 100 ml. of ether followed by work-up and analysis as above showed no change in the product composition. No significant change resulted when the ether was saturated with lithium bromide.

Dichloride 57 was recovered unchanged from attempted reactions with methyllithium in ether at -80° and at reflux and from n-butyllithium in pentane at -80°.

Reaction of 2,3-dibromocyclohexene (6) and butyllithium .- In the preliminary phases of this work, when it was discovered that 5 underwent facile isomerization to 6, several mixtures of 5 and 6 were treated with butyllithium in ether at -80°, (the reaction of pure 5 with butyllithium is reported in an earlier section.) The allylic bromide 6 was found to undergo alkylation to give a 2-bromo-3-butylcyclohexene 58. Yields varied from 30 to 60%, based on the total amounts of bromides 5 and 6 taken; but based on the estimated amounts of 6 actually present in the mixtures, the yields appeared to be in the range of 80 to 90%. These reactions were worked-up in the usual way. Distillation afforded samples of pure 58, b.p. 78° (2mm.), $n^{25}D$ 1.4979. Infrared: 3070 (0.15), 2930 (1.00), 1630 (0.23).

Anal. Calcd. for $C_{10}H_{17}Br$: C, 55.11; H, 7.87; Br, 36.67. Found: C, 55.25; H, 7.65; Br, 36.82.

A mixture of 0.352 g. (1.67 mmol.) of vinyl bromide 58 and 3 ml. of 80% sulfuric acid was stirred under nitrogen for four hours at room tem-

perature. After hydrolysis and pentane extraction, G.C. analysis indicated the formation of a single product which was shown to be 2-n-butylcyclohexanone by comparison of infrared spectra and G.C. retention times (S-710, 113°; C-20M, 120°)

The starting material was recovered from attempted hydrolyses using 50 and 60% sulfuric acid at room temperature (5 hours). The use of 80% sulfuric acid at 60° (one hour) gave mainly tars.

n-Butylcyclohexane (60). - Butyrophenone (0.78 g., 0.066 mole) was reduced under an atmosphere of hydrogen utilizing the folowing reagents in succession; 30% palladium on carbon, ethanol, 26°; 30% palladium on carbon, acetic acid, 26°; platinum, acetic acid, 60°. These three conditions led to the absorption of ca. one, one, and three molar equivalents of hydrogen respectively. Distillation of the product after work-up afforded 8.25 g. (95% yield) of a colorless liquid which showed an infrared spectrum[62] identical to that of n-butylcyclohexane (60)

n-Butylcyclohexane from vinyl bromide 58. - Vinyl bromide 58 (114 mg., 5.25 mmoles) was stirred with 30% palladium on carbon and 3 ml. of absolute ethanol under one atmosphere of hydrogen at 26°. After 16 hr. 24.40 ml. of hydrogen was consumed (96% of theoretical). Distillation of the product afforded a material which showed an infrared spectrum which was identical to that of n-butylcyclohexane (60) obtained earlier. G.C. analysis (S-710 at 128°, C-20M at 122°) showed that the two compounds had identical retention times.

2-n-Butylcyclohexanone (59). - The pyrrolidine enamine of cyclohexanone (9.31 g., 0.062 mole) and 75 ml. of anhydrous toluene were heated

(62) Sadtler Standard Spectra No. 11838 of n-butylcyclohexane

while 6.43 g. (0.042 mole) of n-butyl bromide was added dropwise. After the mixture was allowed to reflux for 9 hr., water was added and the product was extracted with ether. G.C. analysis (C-20M, S-710) showed a 1:1 mixture of cyclohexanone and a second compound. Distillation afforded 2.55 g. (39% yield) of a colorless compound 59, b.p. 92° (13mm.) (lit., b.p. 90 - 92° (13 mm.)) Its infrared spectrum (CCl_4) showed bands at 2930 (95) and 1710 cm^{-1} (83). This spectrum was identical to the spectrum of the ketone obtained from the above solvolysis of vinyl bromide 58.

In other studies this ketone 59 could not be obtained by treatment of the morpholine enamine of cyclohexanone with n-butyl bromide in refluxing toluene for 14 hr.

n-Butylcyclohexane (60) from 2-n-Butylcyclohexanone (59). - 2-n-Butylcyclohexanone (59) (74 mg., 4.8 mmole) from the enamine preparation was stirred with 0.052 g. of potassium hydroxide, 0.057 g. of 95% hydrazine , and 1.3 g. of diethylene glycol at reflux for 6 hr. After hydrolysis and pentane extraction, the distilled product showed an infrared spectrum and G.C. retention time (S-710, C-20M) which were identical with that of n-butylcyclohexane (60).

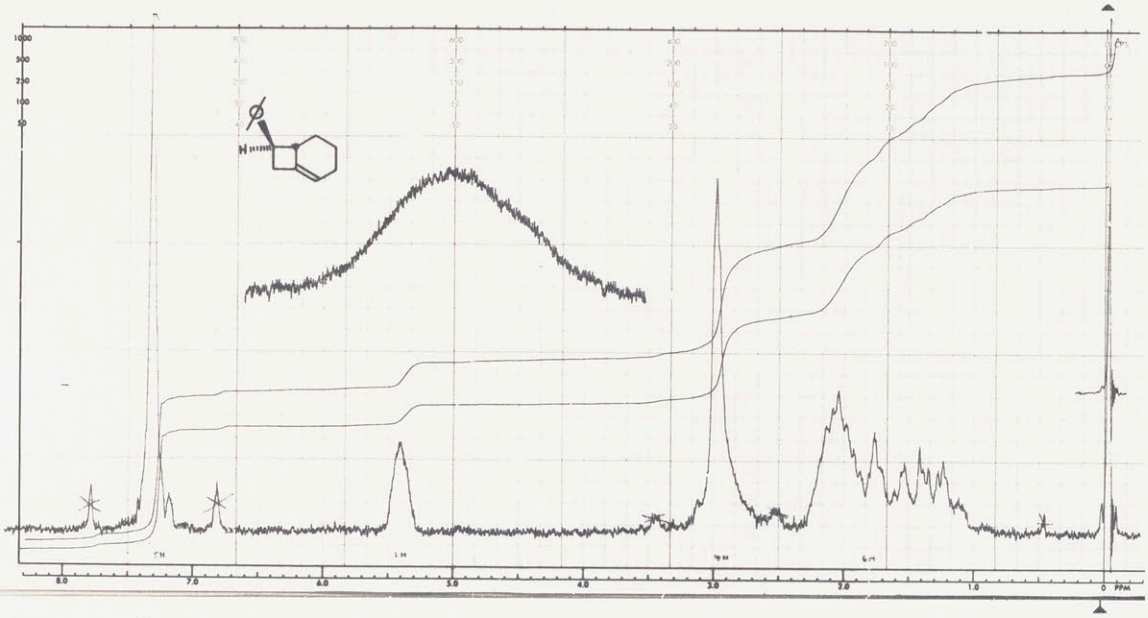
APPENDIX

N.M.R. Spectra, Ultraviolet Spectra, Mass Spectra and Consistent Names of Compounds

All n.m.r. samples were determined on ca. 25% carbon solutions. Ultraviolet curves were determined utilizing heptane solutions and flushing the instrument with nitrogen. The mass spectral line drawings are recorded as percent peak intensities of the largest peak.

N.M.R.Curves

A



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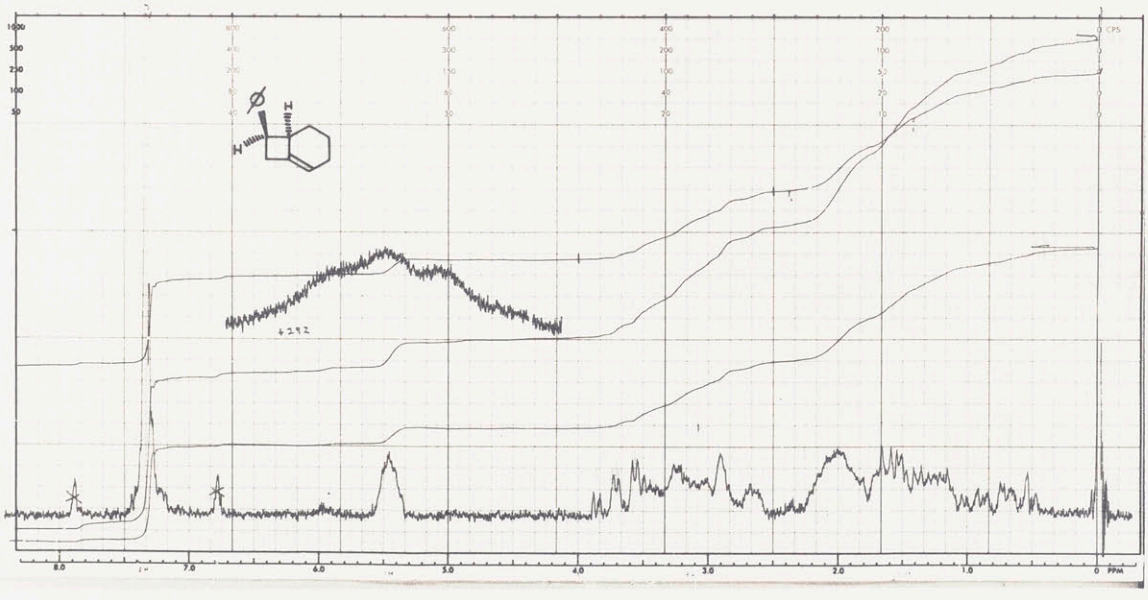

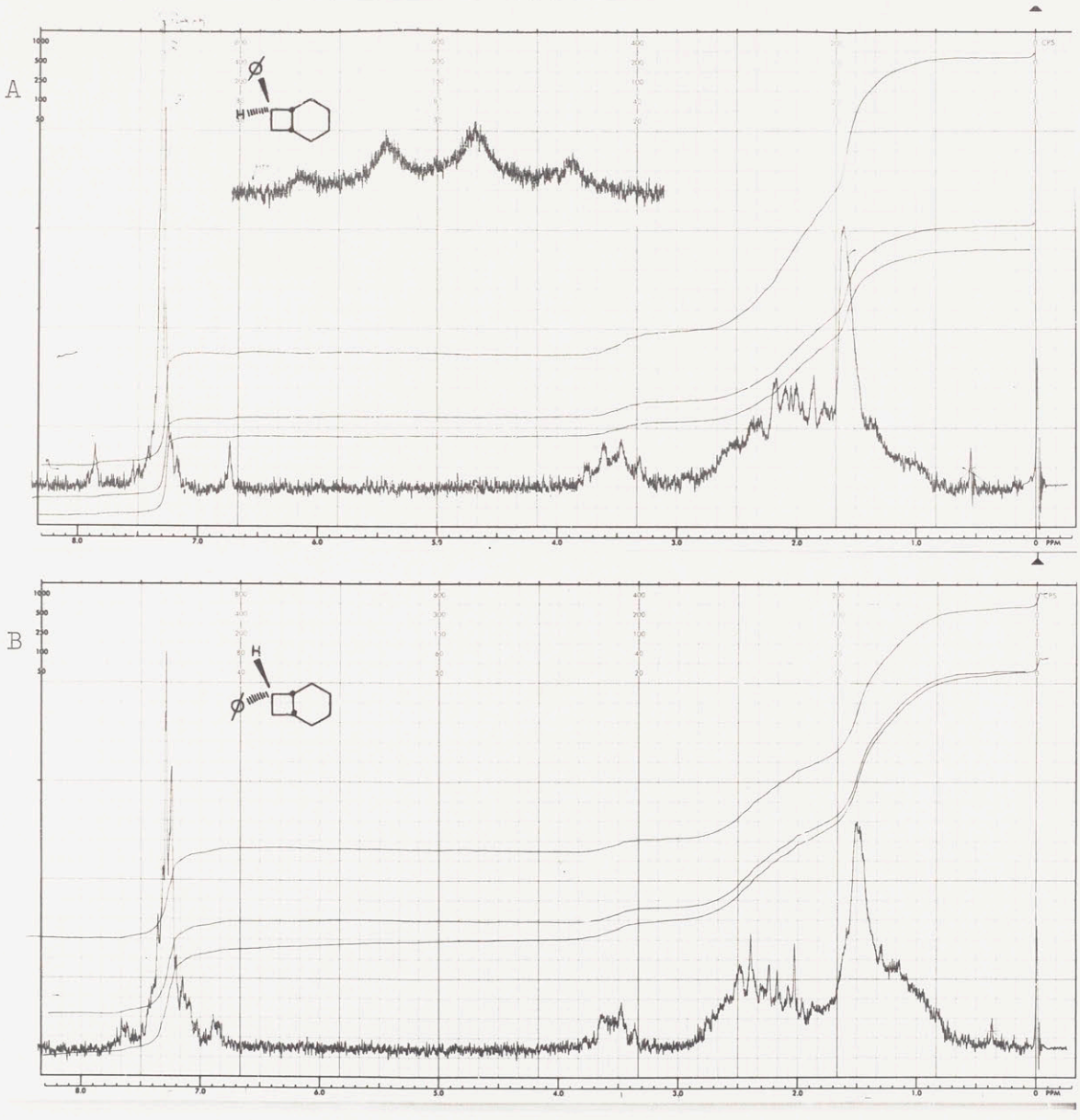
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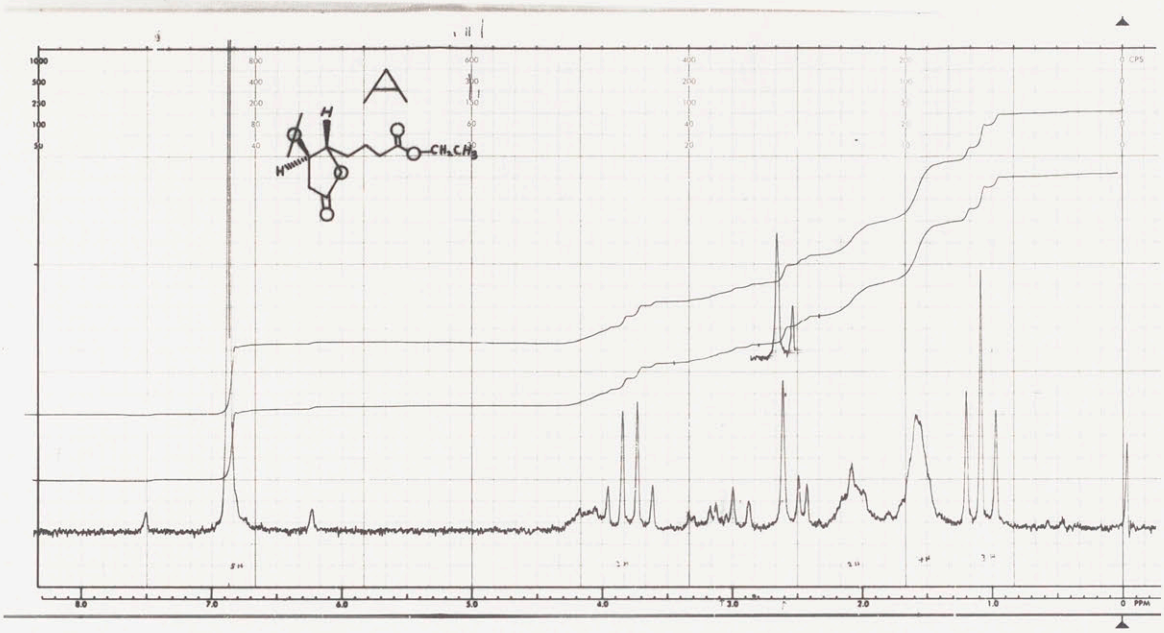
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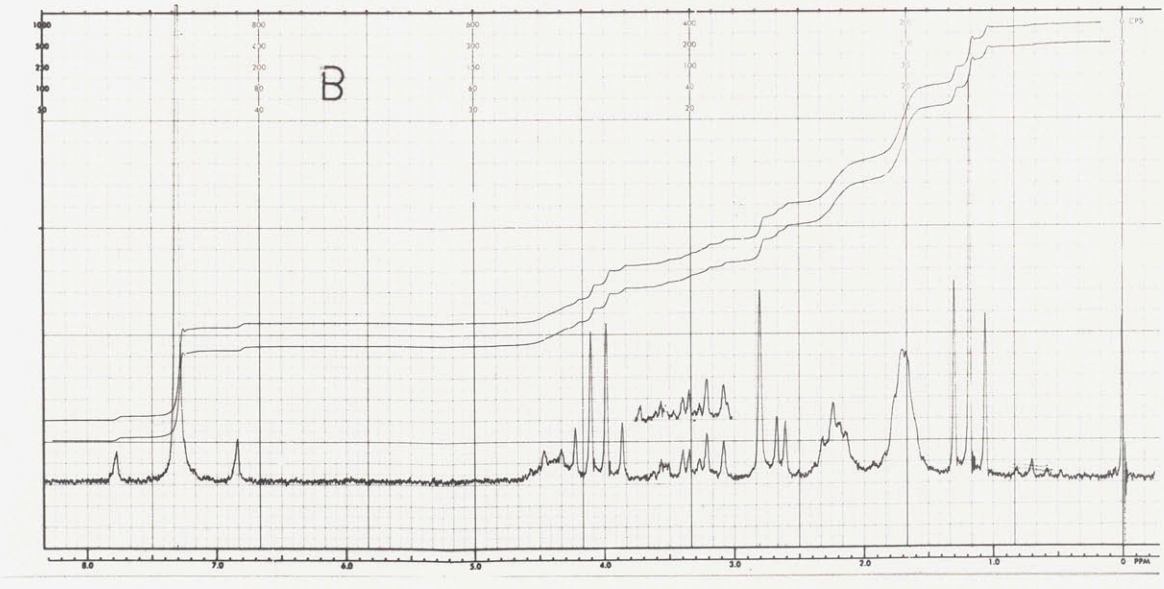
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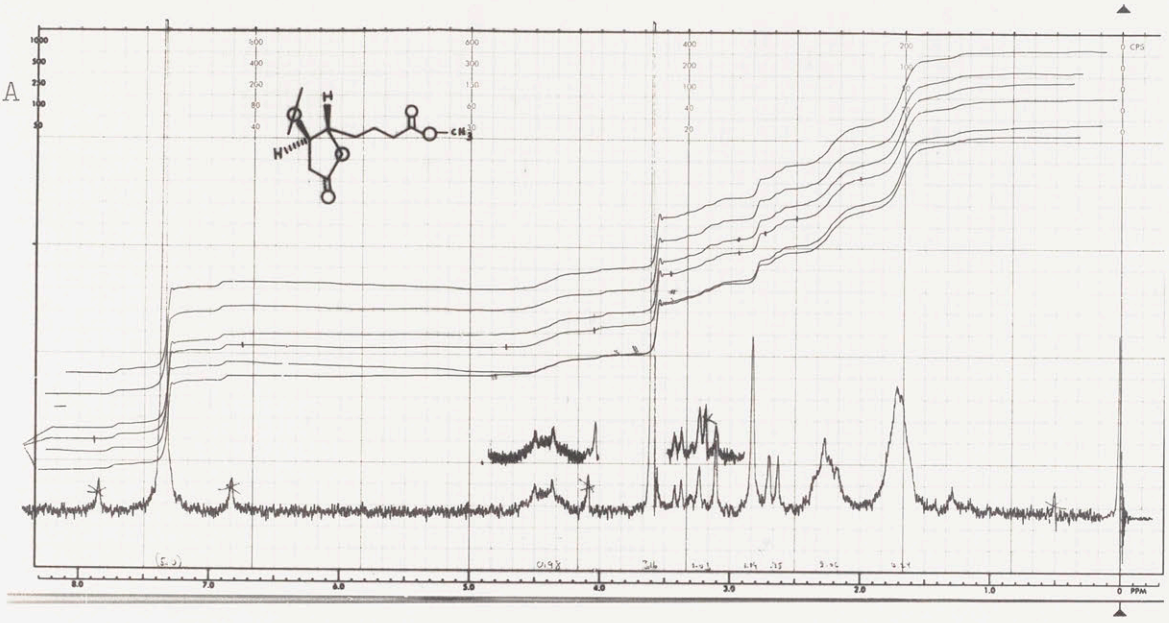
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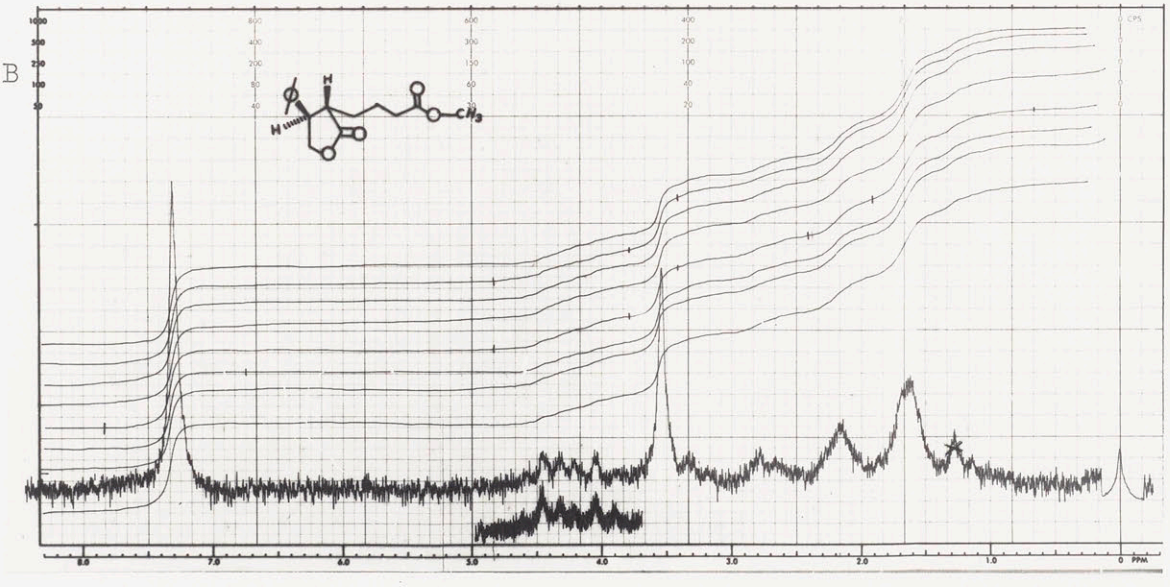
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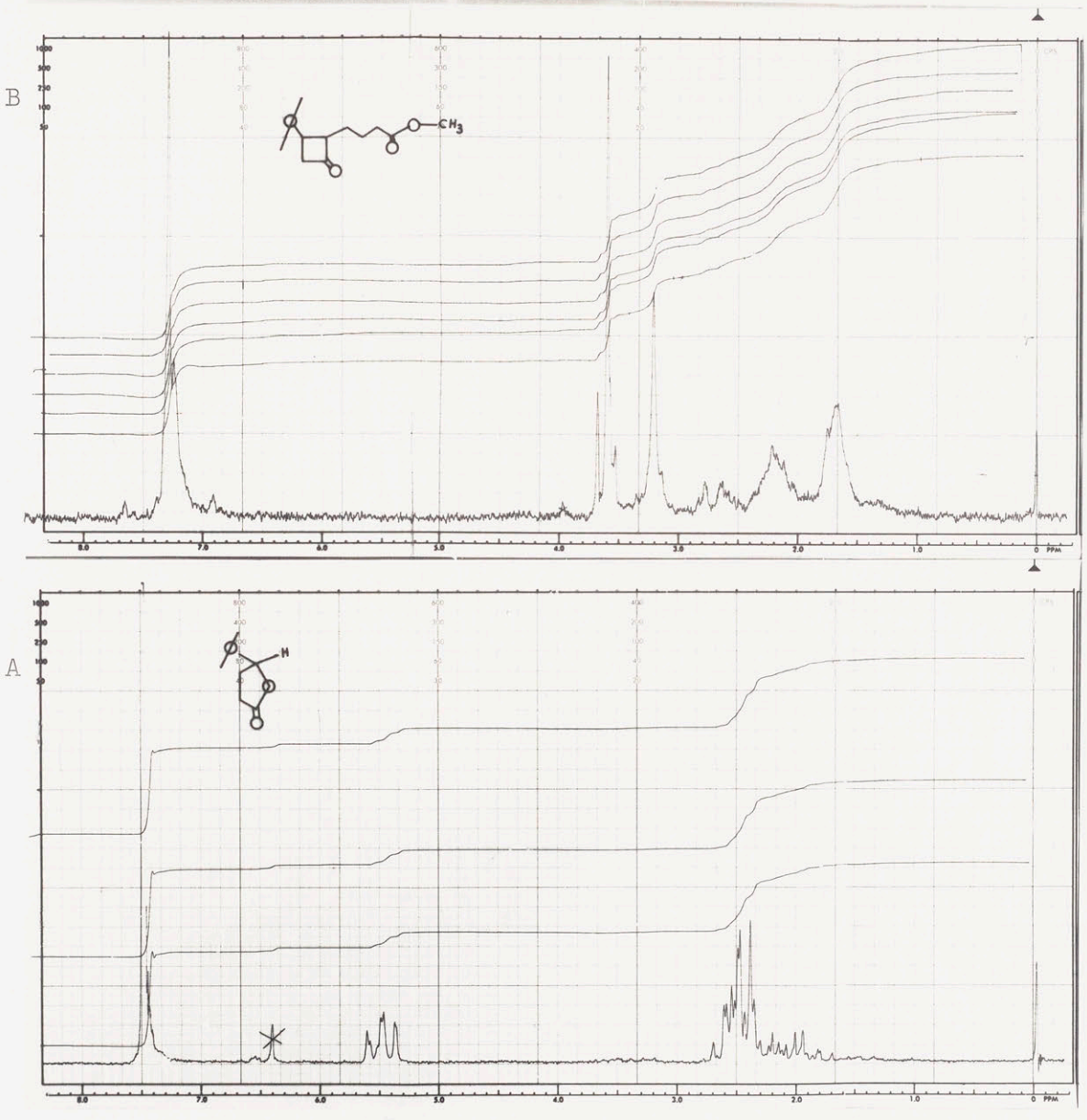
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A
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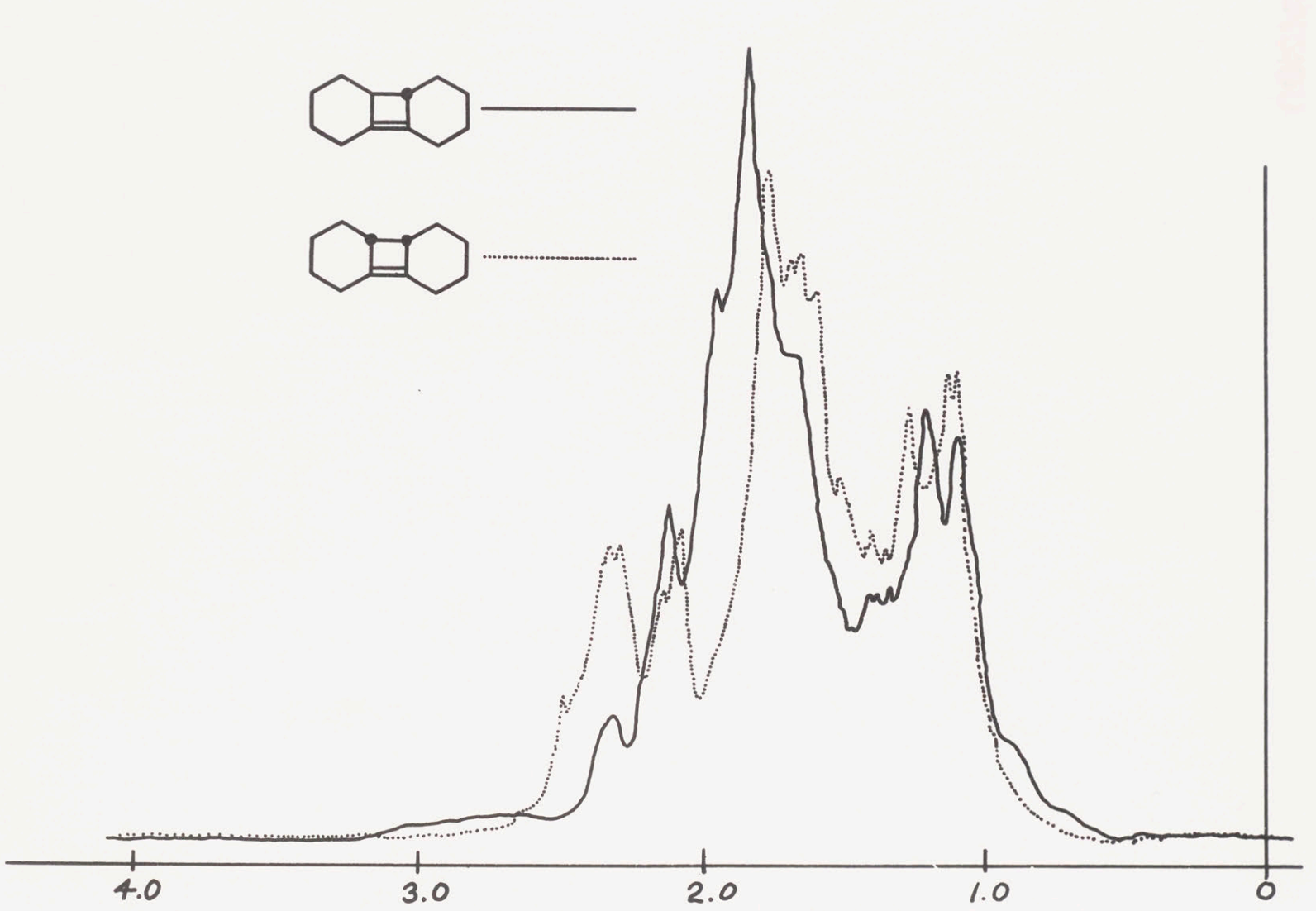

4.0
3.0
2.0
1.0
0

Ultraviolet Curves

Conjugated diene, major tetramer 17 — — — — — — — — — —

Conjugated diene, minor tetramer 19 . . . . . .

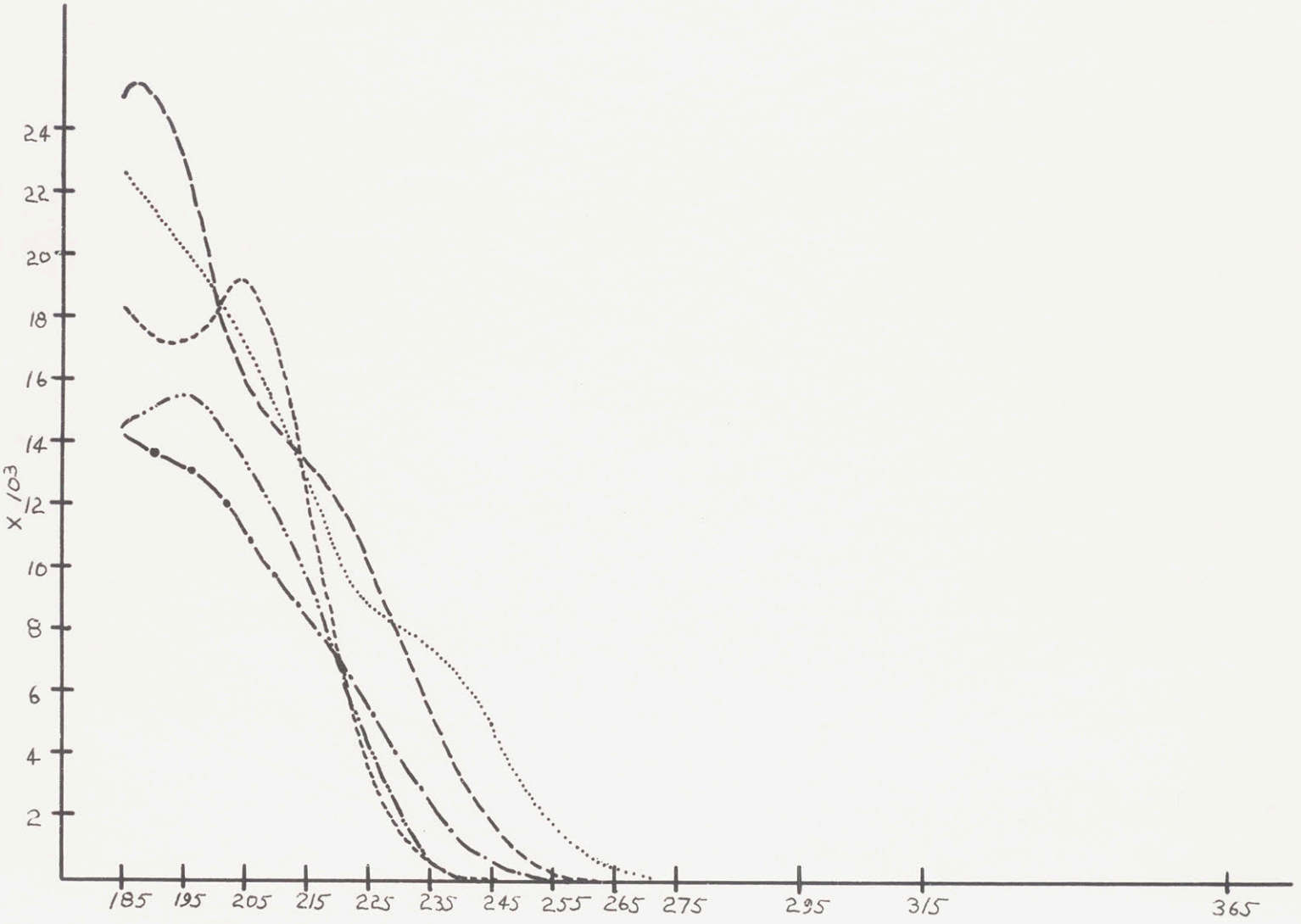
Tetrasubstituted diene 15 - - - - - - - - - - - - - - - -

Mixture of tri- and tetrasubstituted dienes 18 — · — · — · — · —

Mixture of trisubstituted diene, glass E (p.23) — · — · — · — · —

a.) The curve on page 127 is a plot of wavelength vs. molar extinction

b.) The curve on page 128 is a plot of wavelength vs. molar extinction/ no. of double bonds


X 10³
24
22
20
18
16
14
12
10
8
6
4
2
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195
205
215
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235
245
255
265
275
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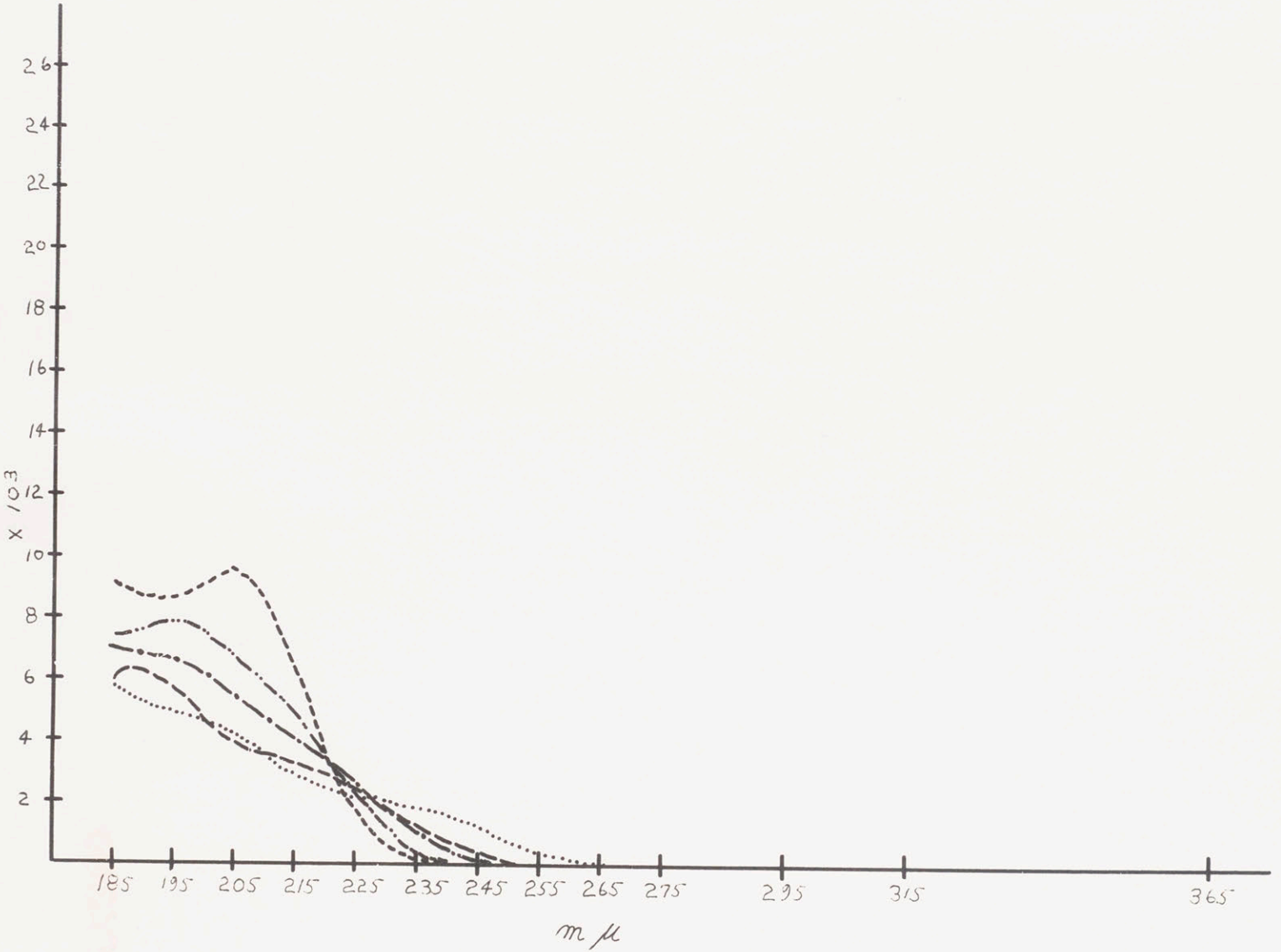
315
365


26
24
22
20
18
16
14
12
10
8
6
4
2
X 10 3
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195
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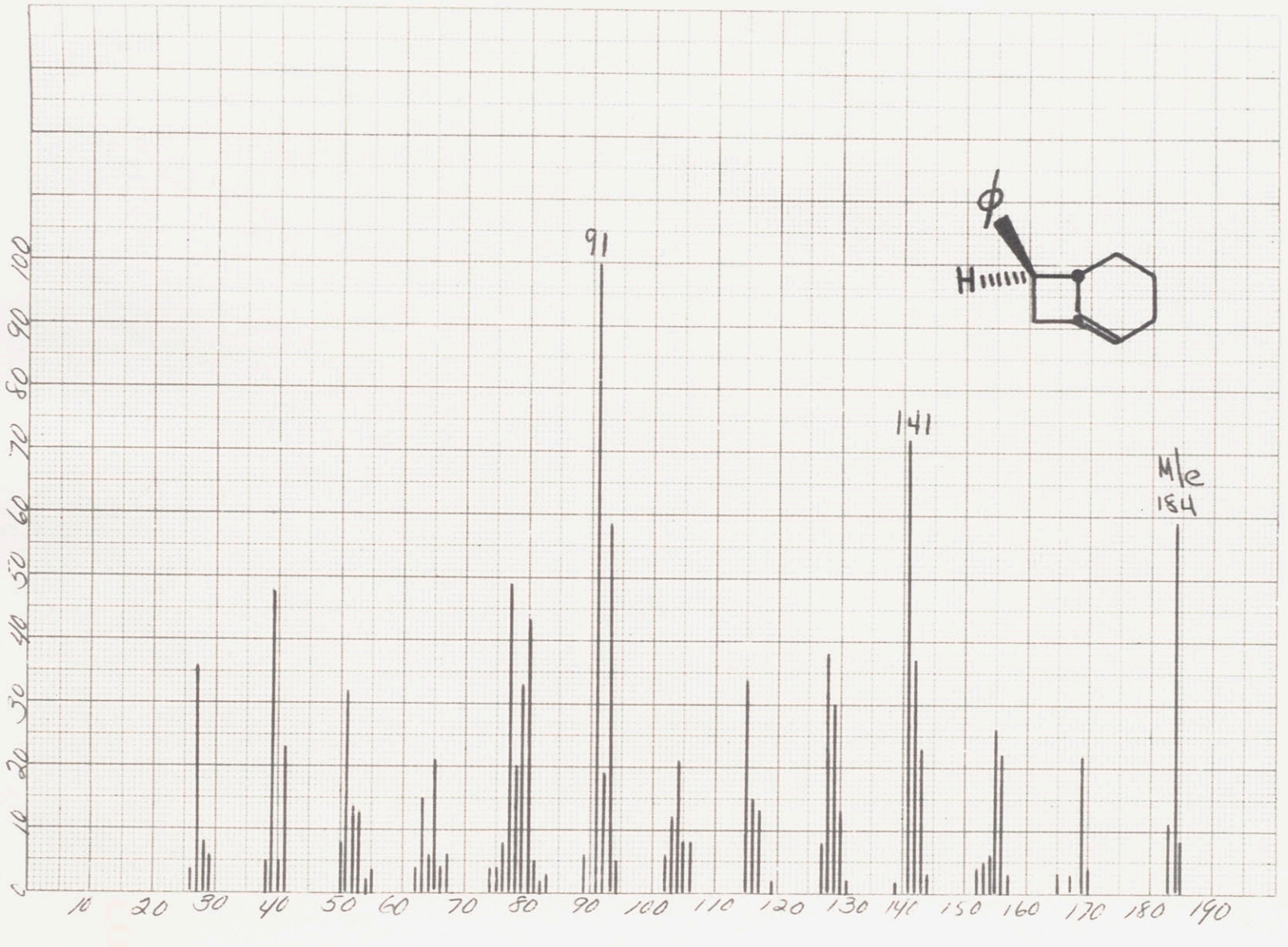
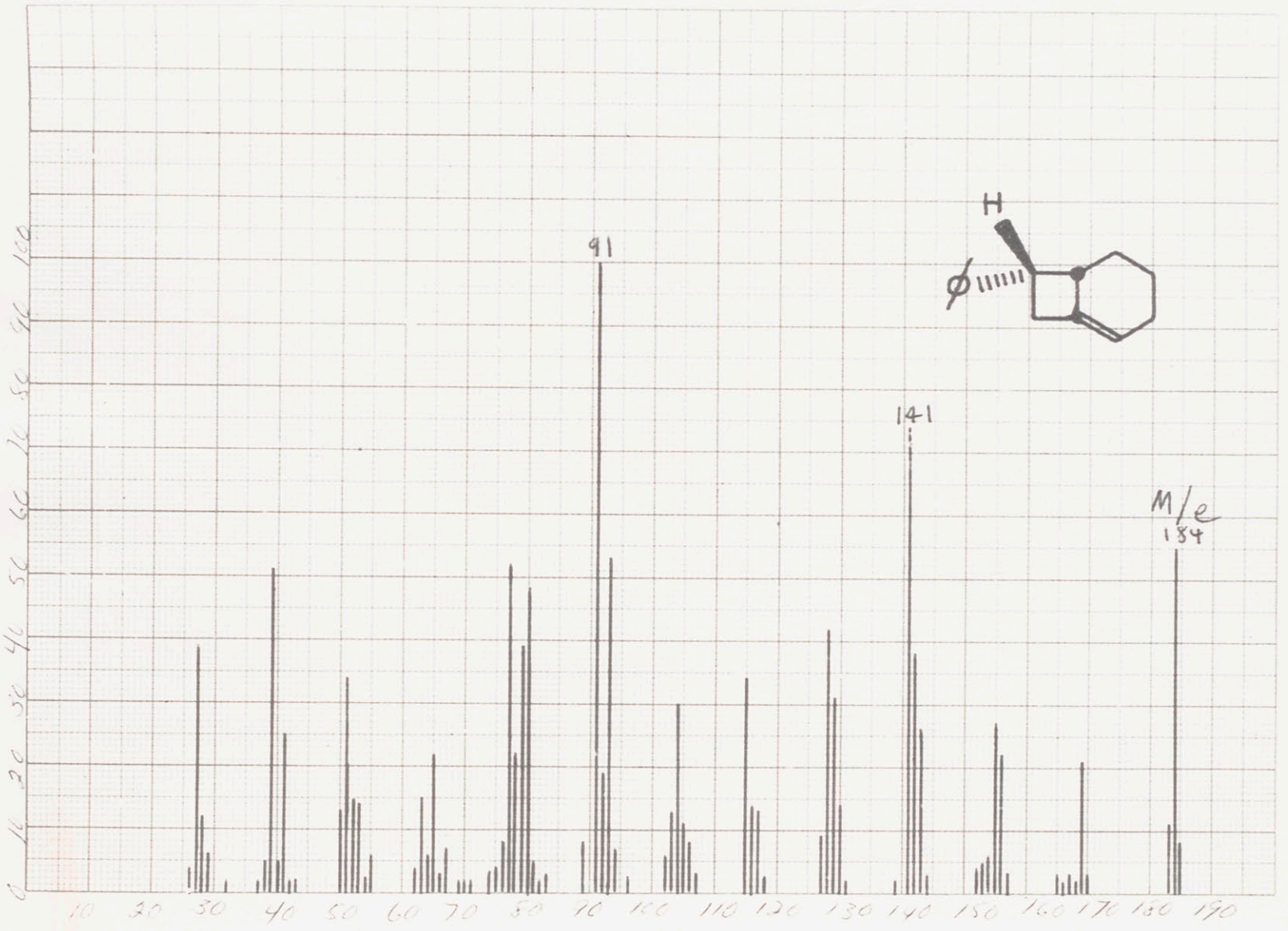
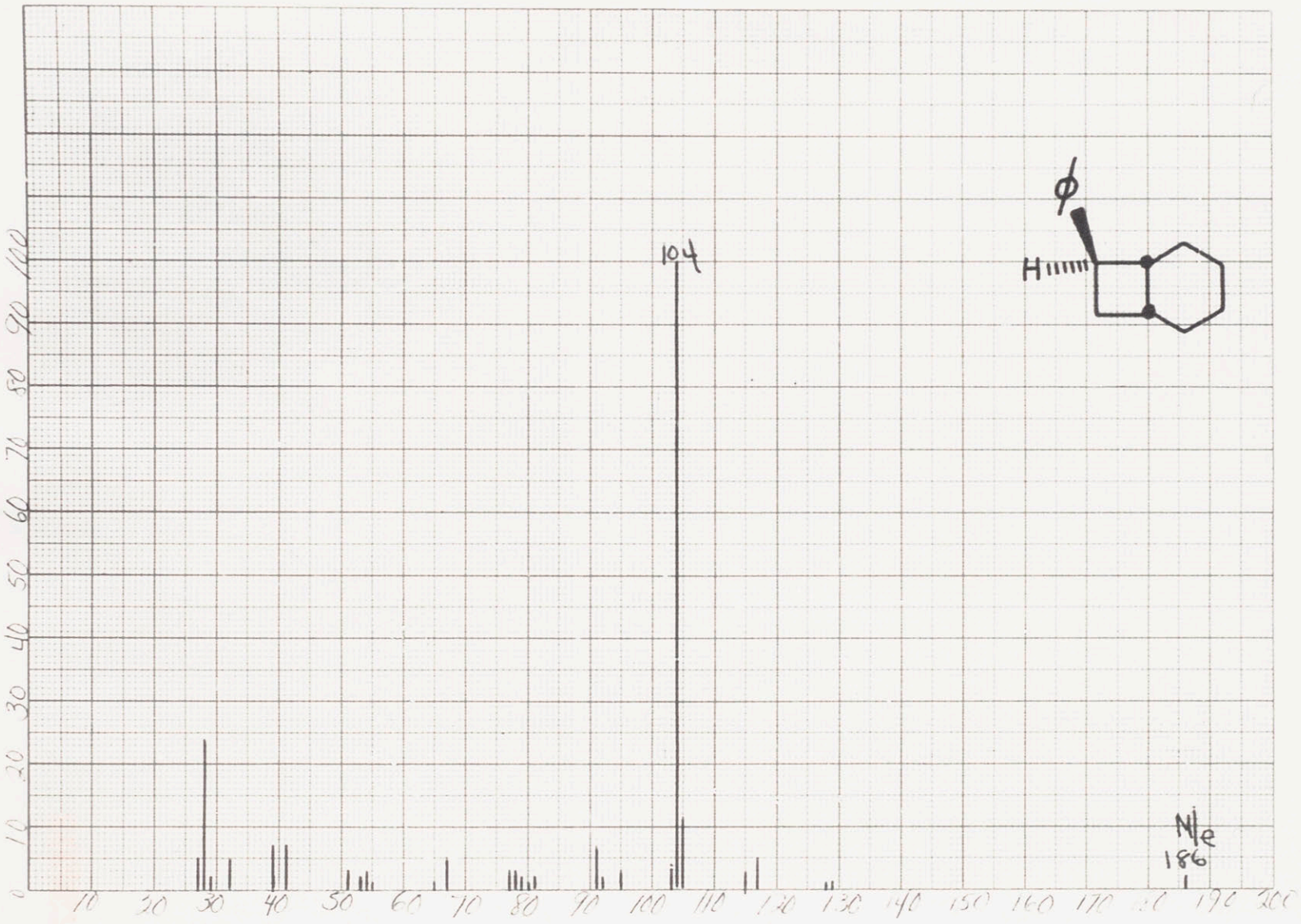
225
235
245
255
265
275
295
315
365
mμ

Mass Spectra


91
141
M/e
184
ϕ
H
10 20 30 40 50 60 70 80 90 100 110 120 130 141 150 160 170 180 190


H
91
141
M/e
184
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190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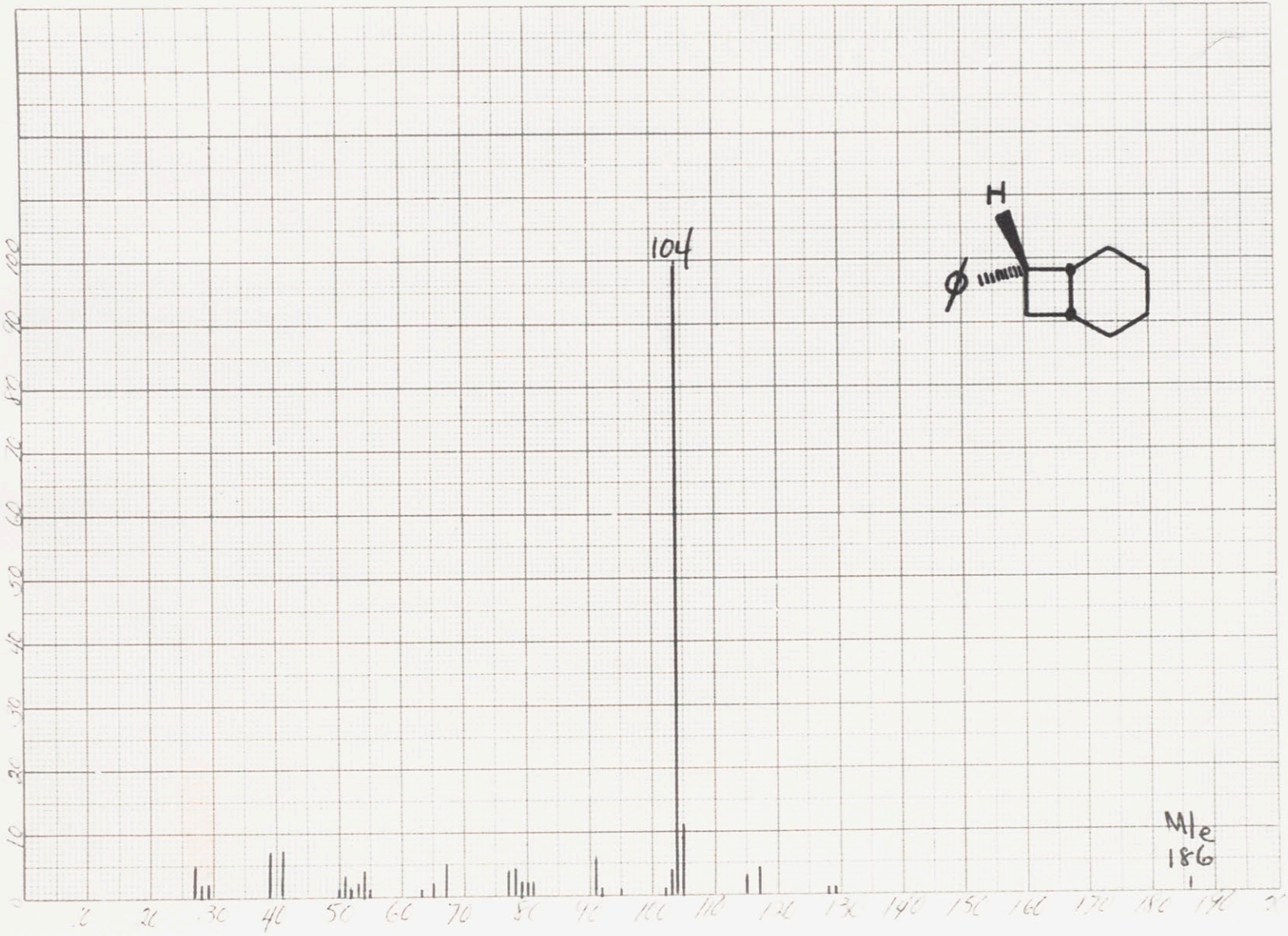
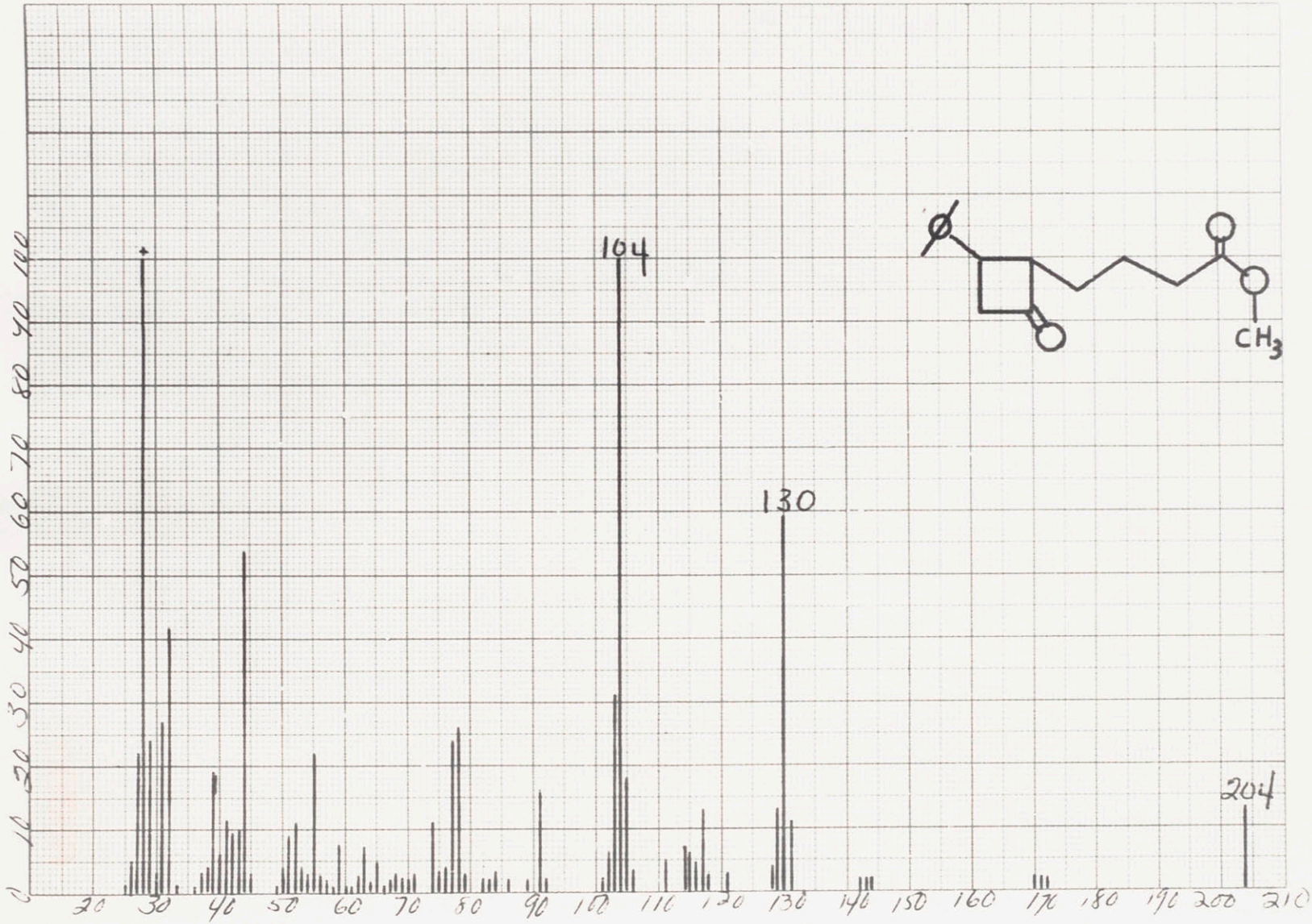
ϕ
H
M/e
186


104
H
ϕ
M/e
186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130
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CH3
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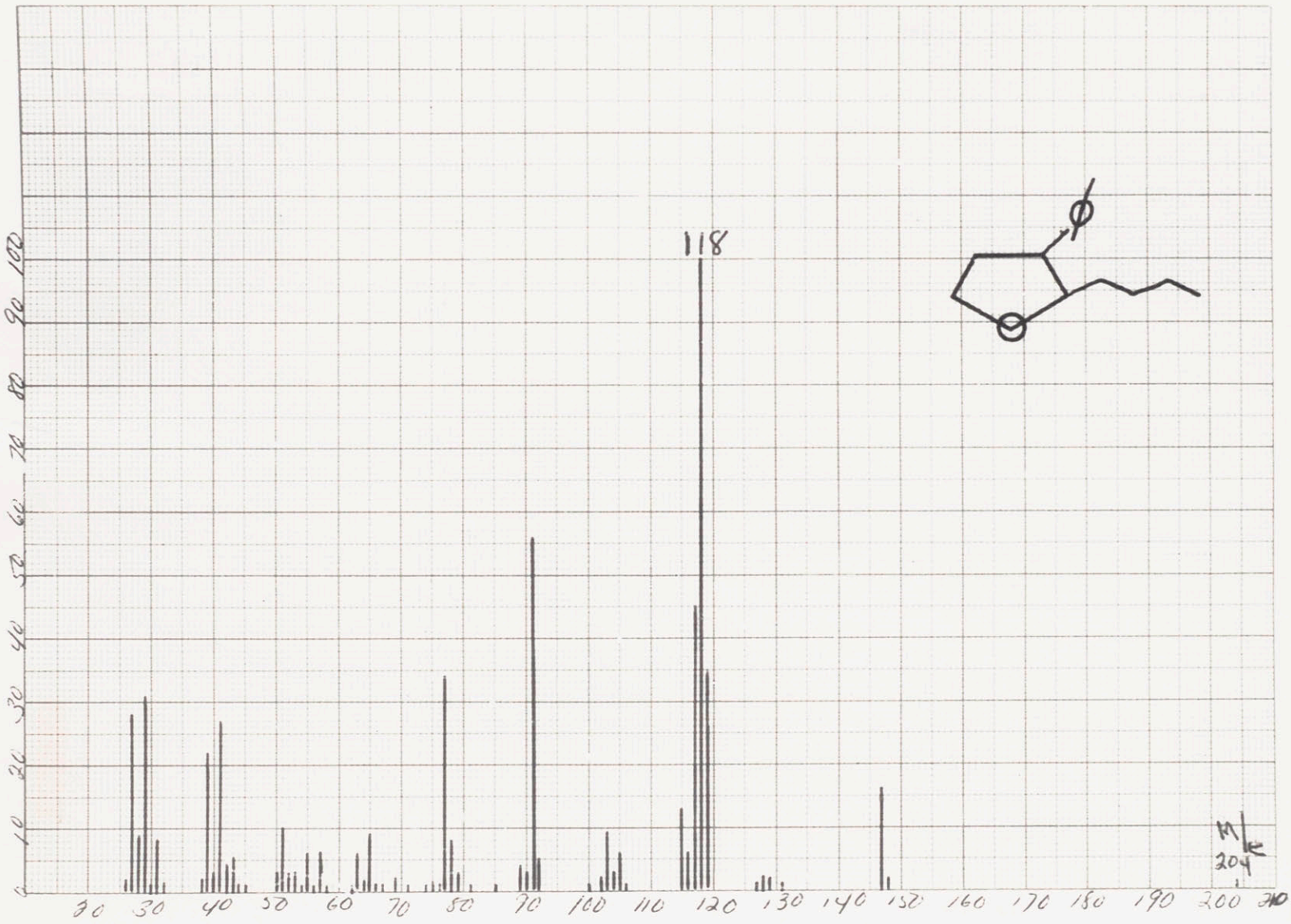
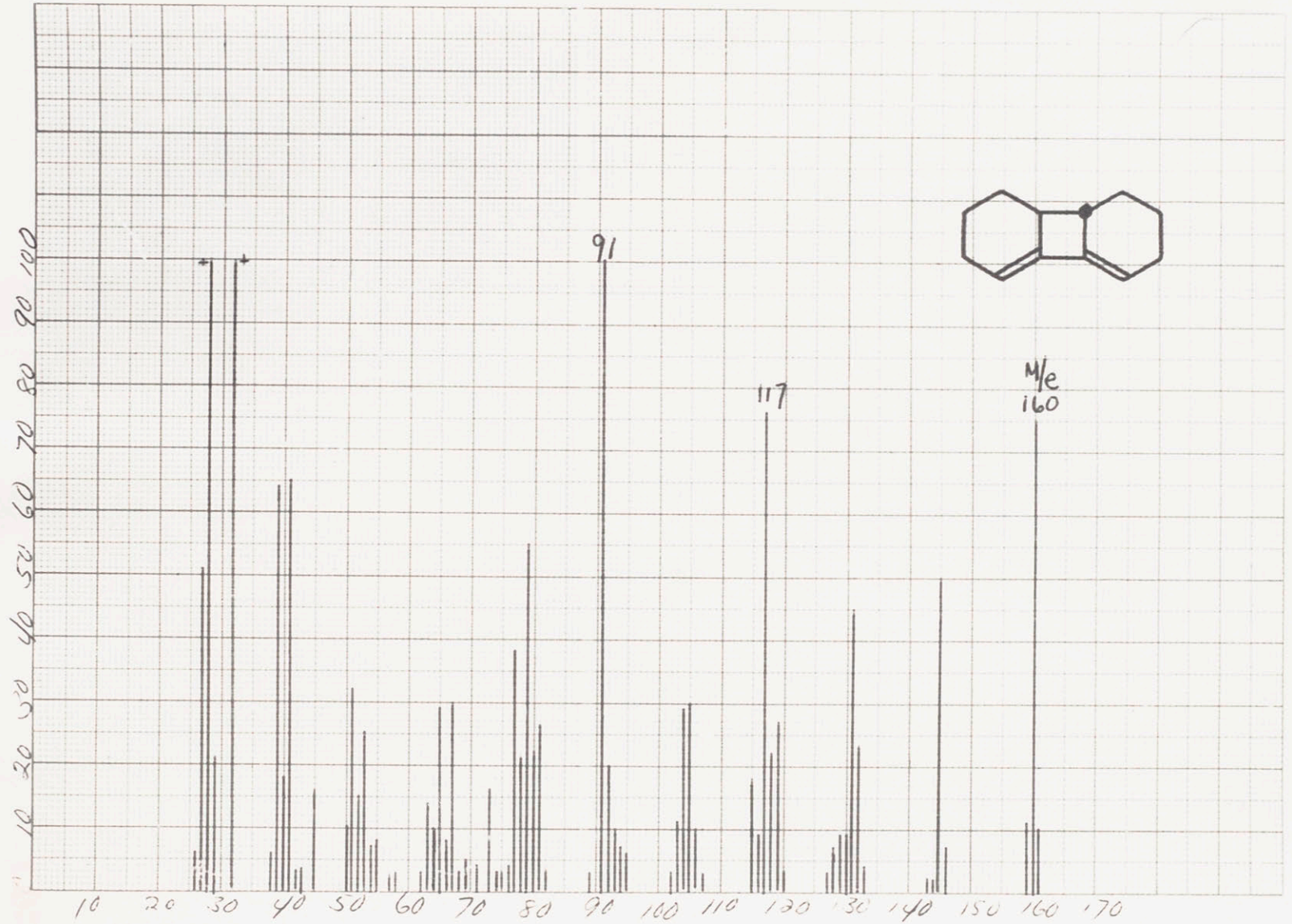
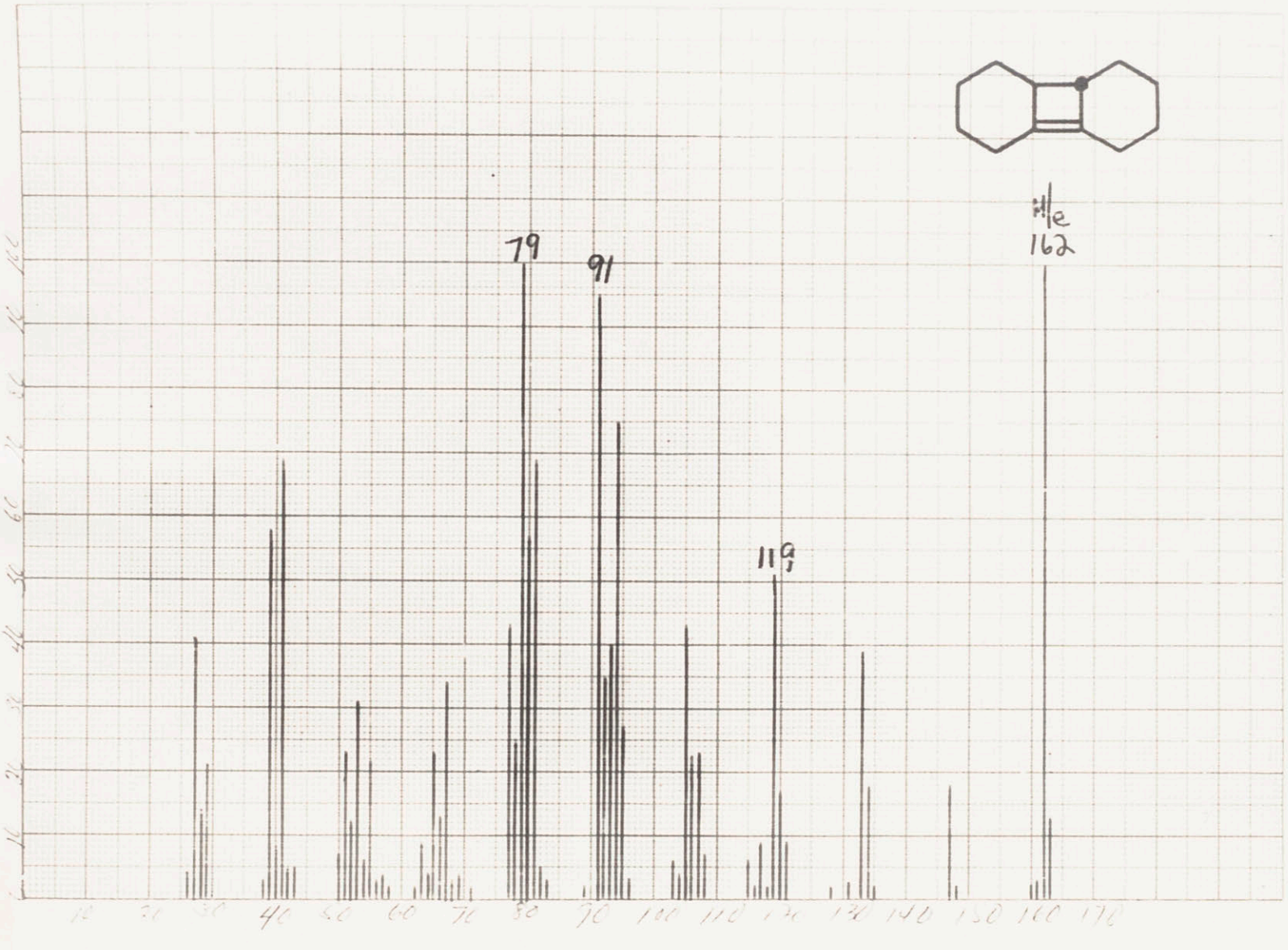
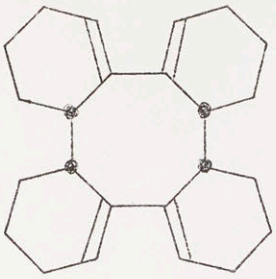
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210


118
M/E
204

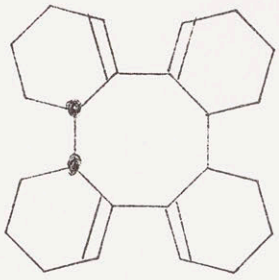

91
117
M/e
160
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170


79
91
119
m/e
162

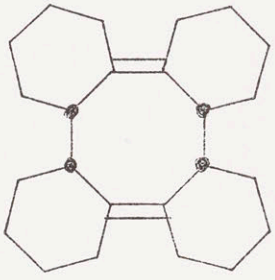
CONSISTENT NAMES



cis-syn-cis-pentacyclo[$18.4.0.0^{2,7}0^{8,13}0^{14,19}$]tetracosa-2,12,14,24-tetraene



cis-anti-cis-pentacyclo[$18.4.0.0^{2,7}0^{8,13}0^{14,19}$]tetracosa-2,12,14,24-tetraene



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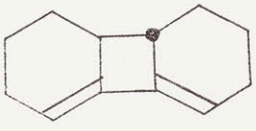
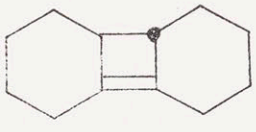
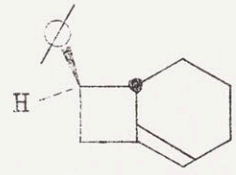


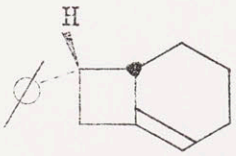
trans-tricyclo[$6.4.0.0^{2,7}$]dodec-2,12-diene



trans-tricyclo[$6.4.0.0^{2,7}$]dodec-1-ene



exo-7-phenylbicyclo[4.2.0]oct-1-ene



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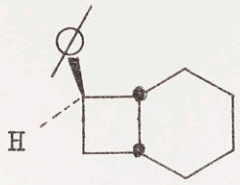

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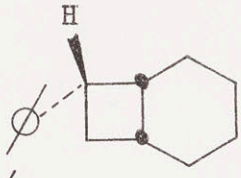

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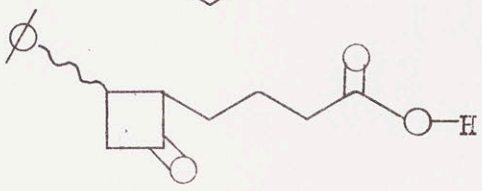

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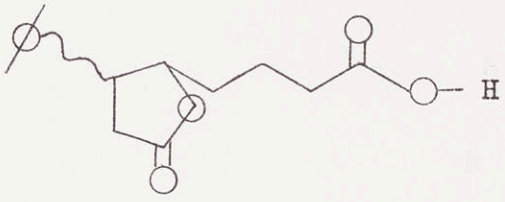
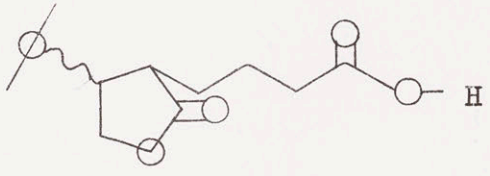


4-(3-carboxypropyl)-3-phenylbutyrolactone



2-(3-carboxypropyl)-3-phenylbutyrolactone

PART II

Reactions of the Dibromocarbene Adducts of Bicyclo[2.2.1]heptene and Bicyclo[2.2.1]heptadiene

[Reprinted from the Journal of Organic Chemistry, **28**, 2200 (1963).]

Reactions of the Dibromocarbene Adducts of Bicyclo[2.2.1]heptene and Bicyclo[2.2.1]heptadiene

William R. Moore, William R. Moser, and Joseph E. LaPrade

[Reprinted from the Journal of Organic Chemistry, **28**, 2200 (1963).]

Reactions of the Dibromocarbene Adducts of Bicyclo[2.2.1]heptene and Bicyclo[2.2.1]heptadiene

WILLIAM R. MOORE, WILLIAM R. MOSER,[1] AND JOSEPH E. LAPRADE

Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Massachusetts

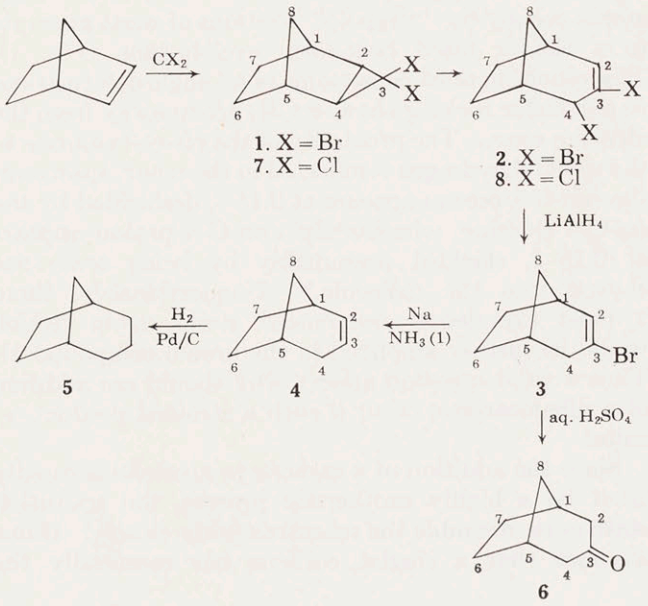
Received March 5, 1963

The addition of dichlorocarbene to bicyclo[2.2.1]heptene gives the expected *exo* dichlorocyclopropane adduct which readily rearranges to *exo*-3,4-dichlorobicyclo[3.2.1]octene-2. The dibromocyclopropane formed upon addition of dibromocarbene to bicyclo[2.2.1]heptene must rearrange directly, since the product isolated was shown to be *exo*-3,4-dibromobicyclo[3.2.1]octene-2. The latter has been converted to several derivatives of bicyclo[3.2.1]octane. Addition of dibromocarbene to bicycloheptadiene gives mainly *exo*-3,4-dibromobicyclo-[3.2.1]octadiene along with smaller amounts of the *endo* epimer and *exo*-3,6-dibromotricyclo[3.2.1.$0^{2,7}$]octene-3. The former two compounds rearrange to the latter on standing. All three compounds are reduced by lithium aluminum hydride to 3-bromobicyclo[3.2.1]octadiene. This vinyl bromide, which can be further reduced to bicyclo[3.2.1]octadiene, upon treatment with aqueous sulfuric acid gave tricyclo[3.2.1.$0^{2,7}$]octanone-3 and 3-bromotricyclo[3.2.1.$0^{2,7}$]octene-3. Mechanistic interpretations of several of these transformations are presented.

The addition of dihalocarbenes to olefins, a reaction discovered by Doering and Hoffmann[2] in 1954, has provided an exceptionally useful synthesis of *gem*-dihalocyclopropanes. When acyclic olefins are employed the dihalides are relatively stable, but certain cyclic olefins have been found to undergo rearrangement to ring expanded products.[3] A particularly pertinent case is the facile rearrangement of 6,6-dibromobicyclo[3.1.0]-hexane to 2,3-dibromocyclohexene.[3c] In the course of studies of the reaction of *gem*-dihalocyclopropanes with alkyllithium reagents,[4,5] we have prepared, or attempted to prepare, a variety of *gem*-dihalocyclopropanes with the intent of extending the self-insertion reactions[5] we have found in certain systems. In one phase of this work, dihalocarbenes were added to bicyclo[2.2.1]heptene and bicyclo[2.2.1]heptadiene and in both systems it was found that the *gem*-dihalocyclopropanes are either not isolable or are particularly prone to undergo rearrangement with ring expansion.[6] In this paper we discuss some of the chemistry of these products of ring expansion.

Bicyclo[2.2.1]heptene Adducts.—The reaction of bromoform with potassium *t*-butoxide in the presence of bicyclo[2.2.1]heptene in pentane at $-15°$ gave a dibromide $C_8H_{10}Br_2$ which infrared and nuclear magnetic resonance (n.m.r.) spectra clearly showed was not the dibromocyclopropane **1** (or the *endo* isomer of **1**) but rather was the dibromoolefin **2**.[7] This assignment was confirmed by the reaction sequence summarized in Chart I. Reduction of dibromide **2** with lithium aluminum hydride gave a vinyl bromide **3** which was further reduced with sodium in ammonia to bicyclo-[3.2.1]octene-2 (**4**). The identity of the latter was confirmed by hydrogenation to bicyclo[3.2.1]octane (**5**), a high-melting solid. The hydrolysis of vinyl bromide **3** with aqueous sulfuric acid has given moderate yields of bicyclo[3.2.1]octanone-3 (**6**). Since bicyclo-[2.2.1]heptene is readily available and it should be possible to telescope the reactions leading to **6**, the route indicated in Chart I appears to be a potentially useful method for synthesizing this ketone.

CHART I



Inasmuch as it was found that, upon addition of dichlorocarbene to bicyclo[2.2.1]heptene, the initially formed *gem*-dichlorocyclopropane **7** could be isolated, although on heating it readily underwent rearrangement to the dichloroolefin **8**, the possibility arose that the corresponding dibromocyclopropane **1** had rearranged to **2** in the course of purification procedures. However, infrared analysis of the dibromocarbene adduct of norbornene isolated without allowing the temperature to

(1) National Institutes of Health Predoctoral Fellow, 1960–1963.

(2) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(3)(a) W. E. Parham and H. E. Reiff, *ibid.*, **77**, 1177 (1955), and later papers by Parham; (b) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958); (c) S. J. Winstein and J. Sonnenberg, *J. Org. Chem.*, **27**, 748 (1962); (d) A. J. Birch and J. M. H. Groves, *Proc. Chem. Soc.*, 282 (1962).

(4) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); **27**, 4179 (1962).

(5) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

(6) (a) In the latter stages of this work we discovered (May, 1962) that R. C. DeSelms was engaged in a study of the dichlorocarbene adducts of these systems. Since this work will be discussed elsewhere, for the most part we will restrict our attention here to the dibromocarbene adducts. (b) After completion of the present studies, E. Bergman, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–12, 1962, p. 79Q, reported that addition of dichlorocarbene to bicyclo[2.2.1]heptene gave **8** (the stereochemistry was not indicated; apparently **7** was not isolated). (c) NOTE ADDED IN PROOF.—C. W. Jefford, *Proc. Chem. Soc.*, 64 (1963), in a brief communication has reported some of the reactions we have outlined in Chart I. L. Ghosez and P. Laroche, *ibid.*, 90 (1963), have reported the isolation of **8**.

(7) Complete spectral data obtained for the compounds encountered in this work are summarized in the experimental section. The n.m.r. assignments can be utilized most readily by referring to the numbered structural formulas appearing in the charts in the text. All n.m.r. chemical shifts, δ, are in parts per million at lower field from internal tetramethylsilane.

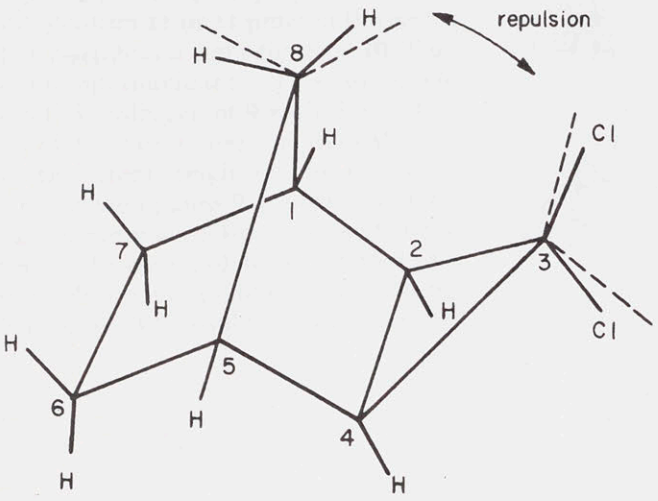


Fig. 1.—*exo*-3,3-Dichlorotricyclo[3.2.1.$0^{2,4}$] octane. Dashed lines represent "normal" bond angles; the deviations from normal bond angles indicate the possible effect of strain.

exceed 25° at any time indicated that this material was essentially pure **2**.

The addition of dihalocarbenes to bicyclo[2.2.1]-heptene could give either *exo* or *endo* adducts. Since this hydrocarbon undergoes *exo* addition (presumably the least hindered approach) with other reagents,[8] the same course of addition appears to be reasonable here. Furthermore, the n.m.r. spectrum of **7** definitely supports the indicated *exo* structure. Molecular models (warped Dreiding models) indicate that in **7** there must be very strong repulsion between the *syn*-C-8 proton (*syn* to the CCl_2 group) and the *cis*-C-3 chlorine; these atoms occupy the "flagpole" positions of what amounts to a rigidly fused boat-form cyclohexane (Fig. 1). This repulsion must cause some bond angle deformation, in particular rocking the C-8 CH_2 group away from the chlorine atom. The proximity of the *cis*-C-3 chlorine to the *syn*-C-8 hydrogen is reflected in the n.m.r. spectrum: the *syn*-C-8 proton appears at 2.15 δ, deshielded by the *cis*-C-3 chlorine, whereas the *anti*-C-8 proton appears at 0.78 δ, shielded presumably by being somewhat shoved into the molecule.[9] Unquestionably, then, **7** must experience pronounced steric strain (which would be further amplified in the bromo compound **1**). Thus a valid question arises: why should *exo* addition of a dihalocarbene occur if such a strained product results?

Since the addition of a carbene to an olefin assuredly must be a highly exothermic process, the transition state must resemble the reactants fairly closely. If one assumes that a singlet carbene has essentially the

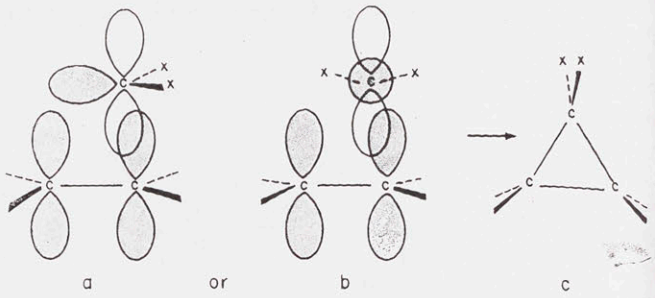


Fig. 2.—Possible transition states for the addition of a carbene to an olefin. Shaded areas represent filled orbitals.

structure proposed by Skell,[10] it seems probable that the bonding in the transition state stems from overlap of the vacant p-orbital of the carbene with the π-orbital of the olefin. Such overlap should be maximized if the carbene, CX_2 of Fig. 2, lies over the olefin in a plane essentially *parallel* to the plane of the double bond and probably closer to one than to the other of the olefinic carbon atoms. It is likely that the groups X of the carbene would be disposed fairly symmetrically over the olefin (Fig. 2a) unless the combined steric requirements of the carbene and the olefin necessitate that an energetically less favorable[11] twisted orientation be assumed (in the limit this becomes Fig. 2b). As the transition state passes on to the cyclopropane, the group CX_2 must rotate into a plane perpendicular to the plane originally defined by the double bond (Fig. 2c). In the case of addition to bicyclo[2.2.1]heptene, this motion would produce the large nonbonded interaction that is noted in Fig. 1, but the resultant repulsion (absent in the transition state) must be more than compensated by the tightening of the bonding.[12]

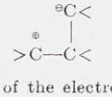
Both **2** and **8** appear to be isomer-free. Since these compounds have identical C-4,C-5 coupling (>CH—CHX—), J = 2.8 c.p.s., it seems fairly certain that both have the same stereochemistry at C-4. Molecular models indicate that the dihedral angle between the C-5 proton and an *exo*-C-4 proton (*endo* halogen) would be *ca.* 44° and that between the C-5 proton and an *endo*-C-4 proton (*exo* halogen) would be *ca.* 78°. A coupling constant of 2.8 c.p.s is compatible with the latter but not with the former, suggesting that in both **2** and **8** the C-4 halogen is *exo*.[13,14]

(8) (a) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954); (b) H. Kwart and W. B. Vosburgh, *ibid.*, **76**, 5400 (1954); (c) S. B. Soloway and H. Kwart, *J. Org. Chem.*, **25**, 327 (1960).

(9) (a) The 2.15- and 0.78-δ signals appear as doublets (J = 11.2 c.p.s., geminal coupling) of, apparently, pentuplets. This fine splitting must arise from vicinal coupling with the C-1 and C-5 protons and long range (1,3) coupling: *anti*-C-8 . . . C-2, C-4, and *syn*-C-8 . . . *endo*-C-6, -C-7, (*cf.* ref. 9b). Any distortion of bond angles in the sense indicated in Fig. 1 should increase both vicinal- and 1,3-coupling of the *syn*-C-8 proton relative to that for the *anti*-C-8 proton. In fact, the fine splitting is greater for the 2.15-δ (*syn*-C-8) than for the 0.78-δ signal. (b) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962). (c) In benzene solution all of the n.m.r. signals of **7** undergo pronounced shifts (0.3–0.4 p.p.m.) to higher field *except* that assigned to the *syn*-C-8 proton (0.07 p.p.m.), a finding we believe to be consistent with the assignment of the 2.15-δ signal to this proton.

(10) (a) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956) and other papers in this series; (b) also, see W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1960), and related papers.

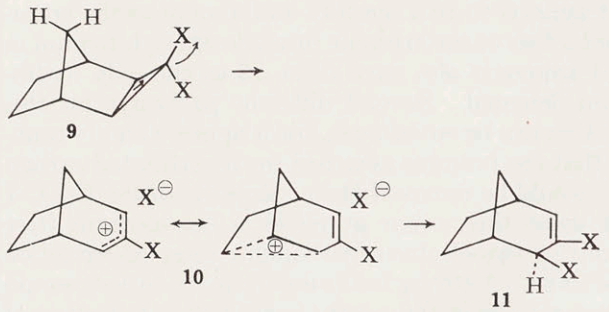
(11) The twisted orientation precludes any overlap (not shown in Fig. 2) of the sp^2-orbital of the carbene with the p-orbital of the second olefinic carbon and would certainly increase the distance between, and thus the potential generated by, any developing charges of the following type.



(12) (a) The demonstration of the electrophilic nature of carbenes (ref. 10) has provided ample evidence for the polar contribution to the transition state of the carbene–olefin reaction, but we interpret the previous representations of the transition state as implying that the geometry is essentially that of the resultant cyclopropane. (b) The recent report by G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962), that arylcarbenes and chlorocarbene react with certain unsymmetrical olefins to produce significantly higher amounts of *cis* than *trans* adducts does not argue for or against the transition state depicted in Fig. 2a. Unless the substituents on the olefin and/or the carbene are fairly bulky, little or no steric repulsion originating from the substituents would be expected if, as we believe, the carbene–olefin bonding has not proceeded far at the transition state.

(13) This argument is substantiated by the coupling constants obtained for the related *exo* and *endo* bromides obtained from bicyclo[2.2.1]heptadiene (discussed later).

The rearrangement of a dihalocyclopropane **9** (eq. 1, X = Cl, Br) to a dihaloolefin **11** must proceed through a transition state that resembles a tight ion pair **10** (that may actually be an intermediate). Due to severe crowding of the *syn*-C-8 hydrogen of **9** with the *cis*-C-3 halogen, migration of the latter may be sterically accelerated. Thus, the great tendency to rearrange shown by the dihalocyclopropanes **9** probably reflects relief of steric strain accompanied by some anchimeric assistance.[15] Whether the cation of **10** is regarded as a "nonclassical" ion, as shown, or as equilibrating "classical" ions, *exo* addition of X^- would be expected.[16,17]

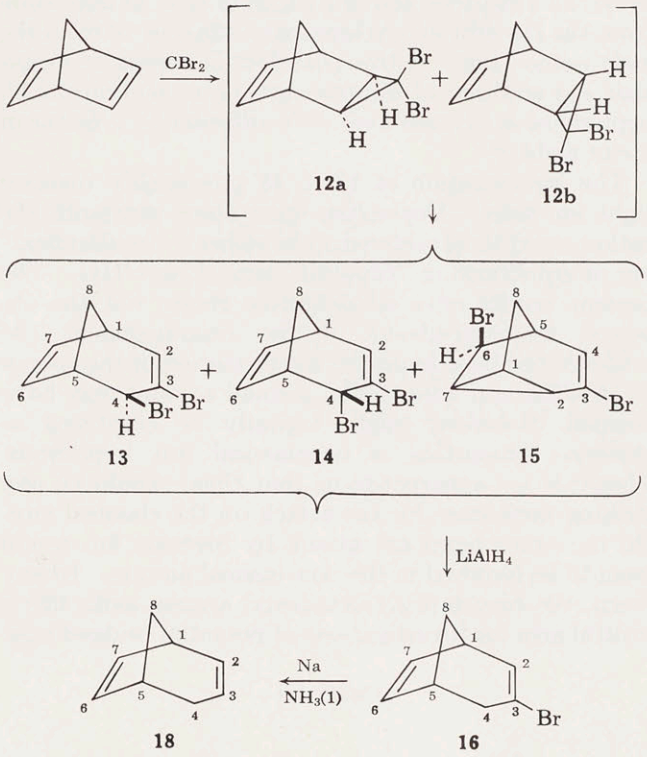


(1)

Bicyclo[2.2.1]heptadiene Adducts.—Addition of dibromocarbene to norbornadiene gave a dibromide fraction with a molecular composition of $C_8H_8Br_2$. Examination of this material by infrared and n.m.r. spectroscopy prior to distillation (the product was not heated above room temperature) indicated that it was not a dibromocyclopropane **12**, but consisted only of rearranged material.

The n.m.r. spectrum of the product clearly established that it consisted of a mixture of predominantly three compounds, **13**, **14**, and **15** in relative amounts 83:11:6. Analysis of the spectrum (aided by that subsequently obtained for **15**) showed that two of these compounds, **13** and **14**, had to be essentially identical and were the epimeric 3,4-dibromobicyclo[3.2.1]octa-2,6-dienes; the most significant spectral difference being due to the signal arising from the proton of the –CHBr– group. In **13**, this proton (C-4) appears as a doublet at 4.44 δ with J = 2.0 c.p.s. while in **14** it appears as a doublet at 4.89 δ with J = 5.0 c.p.s. Molecular models show that in the bicyclo[3.2.1]octadiene system the C-5, *endo*-C-4 dihedral angle must be *ca.* 76° whereas the C-5, *exo*-C-4 angle is *ca.* 45°. On the basis of the dependence of the coupling constant for vicinal protons on the dihedral angle,[14] then, the C-4 bromine must be *exo* in **13** (*endo* proton) and *endo* in **14** (*exo* proton). Furthermore the chemical shifts support this assignment. An *endo* proton at C-4 should experience some long range shielding by the C-6,C-7 double bond, an effect nonexistent for an *exo* proton. In fact, the *endo*-C-4 proton of **13** falls over 0.4 p.p.m. upfield from the corresponding *exo* proton of **14**.

CHART II



Heating or prolonged storage of the mixture of **13**, **14**, and **15** resulted in extensive rearrangement to **15**. Taken together, the n.m.r. and infrared spectra of **15** establish that it is a tricyclic vinyl bromide. The bromine at C-6 potentially could be either *exo*, as shown in Chart II, or *endo*. Subsequently, we have obtained the vinyl bromide **17** (Chart V) corresponding to **15** minus the bromine at C-6. In **17**, C-6 and C-8 are equivalent. However the geminal protons at these positions must experience quite different magnetic environments. The protons *syn* to the C-3,C-4 double bond should be shifted upfield due to long range shielding by the double bond. The spectrum of **17** shows two protons at 0.92 δ as a doublet with J = 11.8 c.p.s. (geminal coupling) which must be the *syn* protons (*syn* to the double bond). The *anti* protons cannot be uniquely distinguished, but must fall in the region of 1.4–1.8 δ. In the spectrum of **15**, the *syn*-C-8 proton appears essentially unchanged as a doublet at 1.04 δ (J = 12 c.p.s.) whereas the *anti*-C-8 proton has been shifted downfield by at least 0.5 p.p.m., appearing at 2.29 δ as an octet with apparent J values of 12, 4.6, and 2 c.p.s.,[18] a deshielding that could only arise with the C-6 bromine *exo* oriented (*anti* to the double bond). Finally, the fact that the proton of the –CHBr– group of **15** appears at 3.65 δ (*i.e.*, at relatively high field, compared to **13** and **14**) is also consistent with a *syn* orientation of the C-6 proton.

We assume that in the reaction of dibromocarbene with bicyclo[2.2.1]heptadiene the dibromocyclopropanes **12a**, **12b** were actually formed but underwent es-

(14) For the dependence of vicinal coupling constants on dihedral angle, see (a) H. Conroy in R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., "Advances in Organic Chemistry: Methods and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 311, and also (b) J. N. Shoolery, "NMR and EPR Spectroscopy," Pergamon Press, Oxford, 1960, p. 115.

(15) In addition to the strain mentioned before, rearrangement relieves the strain inherent in the bicyclo[2.2.1]heptane system and that in the cyclopropane ring.

(16) See H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961), and H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961), who have discussed the evidence for a nonclassical ion related to **10** in the solvolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl tosylate.

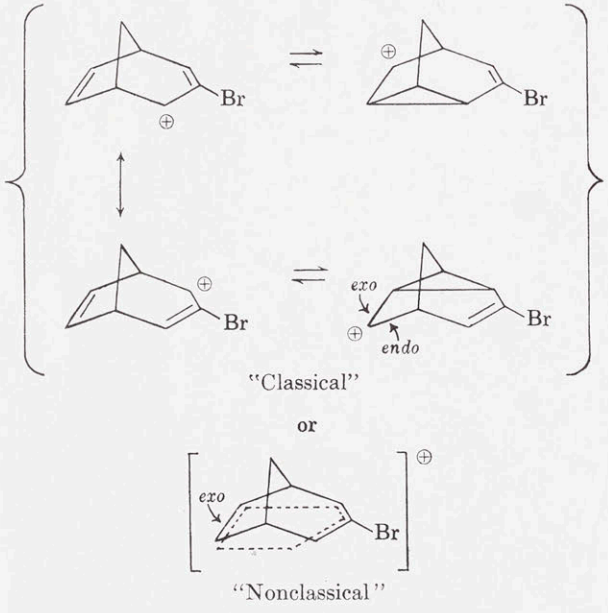
(17) R. C. DeSelms has informed us that he has obtained evidence which indicates that **8** has the *exo*-configuration.

(18) From models it appears that vicinal coupling to the C-1 and C-5 protons should be greater for the *anti*- than for the *syn*-C-6 and -C-8 protons of **15** and **17**, a prediction in agreement with the spectra.

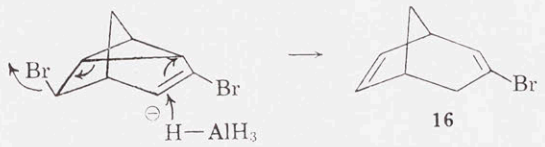
sentially immediate rearrangement to the mixture of **13**, **14**, and **15** initially obtained. This view gains some support from the observation that **13** isomerizes to **15** with little or no isomerization to **14**. The apparent stereospecificity of the similar rearrangement of the bicyclo[2.2.1]heptene adducts suggests that **13** may stem from the *exo* dibromocyclopropane **12a** and **14** from the *endo* isomer **12b**. If this postulate is correct it means that *exo* addition of dibromocarbene to bicyclo[2.2.1]-heptadiene is favored over *endo* addition by a factor of about eight.[19]

The isomerization of **13** to **15** presumably involves tight ion pairs. Depending upon one's viewpoint the cation could be considered to be either a "nonclassical" ion or equilibrating "classical" ions (Chart III). The present results offer no definitive choice but the observed stereospecificity of the rearrangement (no evidence has been found for the formation of the epimer of **15** although, admittedly, a small amount may have escaped detection) might logically be construed as evidence supporting a nonclassical ion hypothesis. Thus it is not apparent to us that there should be any striking preference for *exo* attack on the classical ions. On the other hand *exo* attack by bromide ion would seem to be required in the nonclassical picture. In any event, the bicyclo[3.2.1]octadienyl system looks like a fruitful area for investigations of potential bridged ions.

CHART III



Reduction of any of the mixtures of **13**, **14**, and **15** with lithium aluminum hydride gave good yields of an apparently isomer-free bicyclic vinyl bromide **16** along with varying amounts of recovered dibromides. With increasing reaction times the latter consisted of nearly pure **15**. The formation of **16** from **13** and **14** is to be expected and presumably involves either SN2 or SN2′ displacement of bromide by hydride. The failure of **15** to give the tricyclic bromide **17** might stem from a slow ionization to the ion(s) indicated in Chart III followed by hydride attack at C-2 or C-4, probably the most positive and least hindered centers. Alternatively, a direct hydride attack might occur as depicted in eq. 2.

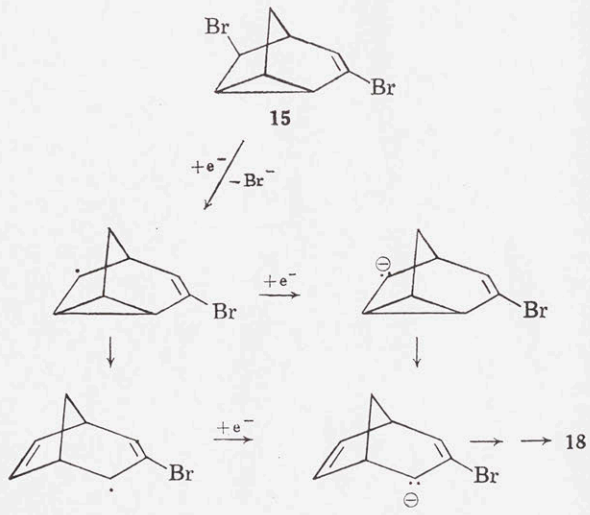


(2)

The structure of **16** was confirmed by reduction with sodium in liquid ammonia to bicyclo[3.2.1]octa-2,6-diene, (**18**), Chart II, which was characterized spectroscopically and by hydrogenation to bicyclo[3.2.1]octane (**5**). Over-all, conversion of bicyclo[2.2.1]heptadiene to **18** appears to be a sensibly useful route to the latter.

Reduction of the tricyclic bromide **15** with sodium in liquid ammonia also gave diene **18** as the only hydrocarbon detected. Several different pathways for this reduction can be envisioned, but it appears highly probable that the bromine attached to the saturated carbon (C-6) would be removed first. Rupture of the C-2,C-7 bond must then occur at either a one-electron (free radical) or two-electron (carbanion) stage of reduction (Chart IV). A strong indication that the former would occur comes from the nearly quantitative reduction of **15** to **16** with tributyltin hydride, a reagent that Kuivila[20] has recently shown appears to reduce halides by a free radical chain mechanism.

CHART IV



Hydrolysis of monobromide **16** with 80% aqueous sulfuric acid gave, in addition to recovered **16**, the isomeric tricyclic bromide **17**, a tricyclic ketone **19**, and small amounts of an unidentified carbonyl compound (about half of the **16** taken was converted to tars). The formation of **17** and **19** can be rationalized as shown in Chart V. Whether bicyclic ketone **20** was not formed or was destroyed under the reaction conditions is not known.[21]

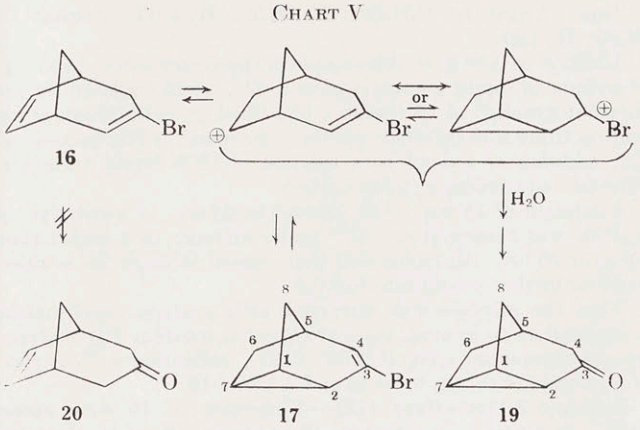
The tricyclic structure assigned to **19** is required by the molecular formula (confirmed by mass spectrometry), the absence of olefinic protons (n.m.r.), the infrared absorption in the 3-μ region reminiscent of that of nortricyclene, and the far-ultraviolet absorption maxi-

(19) (a) Elwood P. Blanchard, Jr., has informed us that application of the Simmons–Smith reaction (ref. 19b) to bicyclo[2.2.1]heptadiene gives both *exo* and *endo* adducts; (b) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(20) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *ibid.*, **84**, 3586 (1962).

(21) In view of the C=O stretching frequency (*ca.* 1745 cm.$^{-1}$) of the unidentified carbonyl compound it seems unlikely that it was **20**.

CHART V



mum in heptane at 192 mμ which is consistent with a "twisted" cyclopropyl ketone chromophore.

Experimental

General.—Infrared spectra were determined in carbon tetrachloride solution or as pure liquids employing Perkin-Elmer Model 21, 137, and 237 spectrophotometers. Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer. Mass spectra were determined with a Consolidated Electrodynamics Model 21-130 mass spectrometer with an inlet temperature of about 130° and an ionizing potential of 70 volts. N.m.r. spectra were recorded on about 25% solutions in carbon tetrachloride with tetramethylsilane as an internal standard employing a Varian A-60 spectrometer. Elemental analyses were performed by Dr. S. M. Nagy and associates at this institute. The gas chromatographs generally employed 0.5 × 200 cm. columns with thermal conductivity detectors (homemade) and 0.2 × 300 cm. columns with a flame ionization detector (Wilkens A-600) employing 80–100-mesh acid and base-washed Chromosorb. The following liquid phases (per cent by weight) were employed: Carbowax 20M, C20M (20%); SE-30 silicone rubber, SE30 (2%); silicone 710, S710 (20%). Internal standards were employed utilizing response factors where appropriate and determining areas by planimetering. Melting points are corrected and boiling points are not. All reactions employing organometallic reagents, active metals, alkoxides, or hydrides were conducted under a nitrogen atmosphere.

exo-**3,4-Dibromobicyclo[3.2.1]octene-2** (**2**).—A solution of 64.4 g. of freshly distilled bromoform in an equal volume of pentane was added dropwise with stirring to a mixture of 31.1 g. of potassium *t*-butoxide[2] and 19.1 g. of bicyclo[2.2.1]heptene in 15 ml. of pentane maintained at −15°. Stirring was continued for 30 min. after the addition was completed. Then, after the mixture had warmed to room temperature, water was added. The hydrocarbon layer was washed with water, dried, and short-path distilled at 80–90° (0.2–0.3 mm.) giving 13.4 g. of **2** (25% based on bicyclo[2.2.1]heptene) which was freed of minor impurities indicated by gas chromatography (S710, 170°) by low temperature recrystallization five times from pentane and redistillation; b.p. 80° (0.2 mm.); n^{25}D 1.5875. Infrared: 3030, 1616 cm.$^{-1}$ with many strong peaks in the fingerprint region. N.m.r.: 1.3–2.4 δ (6H) complex; 2.75 δ (2H) broad band (C-1, C-5); 4.46 δ (1H) doublet, J = 2.8 c.p.s. with ∼1 c.p.s. fine splitting (C-4); 6.31 δ (1H) doublet, J = 7.0 c.p.s. with ∼1 c.p.s. fine splitting (C-2).

Anal. Calcd. for $C_8H_{10}Br_2$: C, 36.1; H, 3.8; Br, 60.1. Found: C, 36.0, H, 3.6; Br 59.9.

The reaction was repeated employing the same work-up, but the volatile materials were removed from the product at low pressure without applied heat (rotary evaporator). The infrared spectrum of the residue was virtually identical to that of pure **2**.

exo-**3,3-Dichlorotricyclo[3.2.1.0^{2,4}]octane** (**7**).—The reaction of 407 g. of chloroform, 1.53 moles of potassium *t*-butoxide, and 100 g. of bicyclo[2.2.1]heptadiene was carried out as described for **2**. Distillation gave a recovery of 63 g. of bicyclo[2.2.1]-heptene and 11.2 g. of **7** (30% based on recovered bicyclo[2.2.1]-heptene) which infrared and n.m.r. analysis showed contained only a trace of **8**; b. p. 41° (0.1 mm.); n^{25}D 1.5223. Infrared: 3030 (doublet), 1305, 1200, 1135, 995, 905 cm.$^{-1}$. N.m.r.: 0.78 δ (1H) doublet, J = 11.2 c.p.s. of (apparently) pentuplets with ∼1 c.p.s. separation (*anti*-C-8); 1.62 δ (2H) sharp band (C-2, C-4) superimposed on 1.0–1.7 δ (4H) complex; 2.15 δ (1H) doublet, J = 11.2 c.p.s. of (apparently) pentuplets with ∼2 c.p.s. separation (*syn*-C-8); 2.63 δ (2H) sharp band (C-1, C-5). The mass spectrum established the molecular formula $C_8H_{10}Cl_2$ based on the isotopic molecular ions, mass numbers 176, 178, 180 in ratios 9:6:1.

Anal. Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69. Found: C, 54.74; H, 5.66.

exo-**3,4-Dichlorobicyclo[3.2.1]octene-2** (**8**).—A sample of **7** was distilled slowly twice, causing rearrangement to **8** which gas chromatography indicated contained only trace impurities; b.p. 79° (1.6 mm.); n^{31}D 1.5310. Infrared: 3040, 1632 cm.$^{-1}$ with many strong bands in the fingerprint region. N.m.r.: 1.15–2.3 δ (6H) complex; 2.68 δ (2H) broad band (C-1, C-5), 4.16 δ (1H) doublet, J = 2.8 c.p.s. with ∼1 c.p.s. fine splitting (C-4); 6.10 δ (1H) doublet, J = 7.0 c.p.s. with ∼1 c.p.s. fine splitting (C-2).

Anal. Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.30; H, 5.66; Cl, 40.32.

3-Bromobicyclo[3.2.1]octene-2 (**3**).—Dibromide **2** (2.35 g.) was added dropwise to a stirred mixture of 1.10 g. of lithium aluminum hydride in 300 ml. of ether. After the addition was completed the mixture was refluxed for 24 hr. The excess hydride was destroyed and the mixture was worked up in the usual way. Short-path distillation gave 1.03 g. (63%) of **3**; n^{25}D 1.5336. Infrared: 3020, 1633, and 665 cm.$^{-1}$. N.m.r.: 1.1–3.0 δ (10 H) complex; 6.12 δ (1H) broad doublet, J ∼ 7 c.p.s. (C-2).

Anal. Calcd. for $C_8H_{11}Br$: C, 51.36; H, 5.93. Found: C, 51.09; H, 6.08.

Reduction of **3** with excess sodium in liquid ammonia followed by the usual work-up gave bicyclo[3.2.1]octene-2-(**4**)[22] in *ca.* 90% yield. Infrared: 3015, 2940, 1640 cm.$^{-1}$. N.m.r.: 1.1–2.1 δ (7H) complex; 2.25 δ (3H) broad band (C-1, C-4); ∼5.24 δ (1H) broad doublet, J ∼ 9 c.p.s. of unresolved multiplets (C-3); ∼5.77 δ (1H) broad quartet, J_1 ∼ 9 c.p.s., J_2 ∼ 7 c.p.s. (C-2).

Anal. Calcd. for C_8H_{12}: C, 88.88; H, 11.12. Found: C, 88.50; H, 11.42.

Microhydrogenation of **4** over palladium on charcoal in ethanol proceeded with the uptake of 0.99 mole of hydrogen. Isolation of the product by gas chromatography gave a very volatile white solid, m.p. 133–135° (sealed capillary), with an infrared spectrum identical to that of bicyclo[3.2.1]octane[23] (**5**); lit. m.p. 133°[24]; m.p. 139.5–141°.[25]

Bicyclo[3.2.1]octanone-3 (**6**).—Vinyl bromide **3** (0.72 g.) was stirred for 6 hr. with 100 ml. of 80% aqueous sulfuric acid. Then ice was added and the mixture was extracted with ether (leaving some insoluble tar). The ether extract was concentrated and gas chromatographed (C20M, 200°) giving a 4% recovery of the starting material and a 38% yield of ketone **6**[26]; m.p. 137–139°; infrared: 1708 cm.$^{-1}$; there are no clear maxima in the far-ultraviolet, but in heptane it appears that there may be a maximum just below the accessible range of the instrument, λ_{end} mμ 186 (ε 715). N.m.r.: ∼1.65 δ (6H) broad complex band; 2.25 δ (4H) sharp band (C-2, C-4); 2.50 δ (2H) band (C-1, C-5).

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.83; H, 10.07.

The 2,4-dinitrophenylhydrazone prepared in the usual way and repeatedly recrystallized from ethanol had m.p. 165–166.2°.

Anal. Calcd. for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30. Found: C, 55.54; H, 5.44.

When 13.7 mg. of **3** was shaken with 2 ml. of concentrated sulfuric acid at 0° for 15 min. followed by hydrolysis with ice and extraction with ether, gas chromatographic analysis (C20M, 200°, naphthalene internal standard) indicated a 64% yield of **6** and a 2% recovery of **3**.

Addition of Dibromocarbene to Bicyclo[2.2.1]heptadiene.—Bromoform (118 g.) was added dropwise to a stirred pentane slurry of 42.5 g. of bicyclo[2.2.1]heptadiene and 0.385 mole of potassium *t*-butoxide at −15°. The mixture was then warmed to room temperature, hydrolyzed, and extracted with pentane

(22) A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960).

(23) American Petroleum Institute Infrared Spectrum no. 2037.

(24) J. W. Barrett and R. P. Linstead, *J. Am. Chem. Soc.*, **58**, 611 (1936).

(25) W. von E. Doering and M. Tarber, *ibid.*, **71**, 1514 (1949).

(26) K. Alder and R. Reubke, *Ber.*, **91**, 1525 (1958), reported isolation of a mixture of **6** and bicyclo[2.2.2]octanone.

Volatile materials were removed at reduced pressures (ultimately 0.05 mm.) without heating. Infrared and n.m.r. spectra of the residue established that the subsequent distillation did not materially change the ratios of **13**, **14**, and **15**. Rapid distillation gave 35.6 g. (35% based on potassium *t*-butoxide) of a colorless liquid, b.p. 77° (0.05 mm.), $n^{25}D$ 1.5964, which gave an immediate precipitate with silver nitrate in aqueous alcohol. This material underwent extensive decomposition on the gas chromatography columns at hand. Infrared: 3040, 1608, 738, 690 cm.$^{-1}$. N.m.r.: 1.04 δ weak doublet, J = 12 c.p.s. (**15**, *syn*-C-8); 1.6–2.6 δ complex; ~2.9 δ multiplet (**13** and **14**, probably C-5); 3.30 δ multiplet (**13** and **14**, probably C-1); 3.65 δ weak singlet (**15**, C-6); 4.44 δ doublet, J = 2.0 c.p.s. (**13**, C-4); 4.89 δ weak doublet, J = 5.0 c.p.s. (**14**, C-4); 5.86 δ quartet, J_1 = 5.5 c.p.s., J_2 = 3 c.p.s. (**13**, C-6) superimposed on weaker signals (the 5.97 δ quartet of **15** and, by differences, a signal due to **14**); 6.37 δ weak quartet, J_1 = 5.5 c.p.s., J_2 = 3 c.p.s. (**14**, C-7); 6.5–6.7 δ a complex pattern which appears to arise from overlapping of a perturbed doublet at ~6.57 δ (**13**, C-2) with a quartet at 6.62 δ, J_1 = 5.5 c.p.s., J_2 = 3 c.p.s. (**13**, C-7), and, by differences, a signal due to **14**. The integrals from the 3.65-δ, 4.44-δ, and 4.89-δ signals give the ratios **13**:**14**:**15** = 83:11:6. The area obtained from the signals in the 1.5–3.0-δ region appeared to be a little too high for a mixture of only **13**, **14**, and **15** indicating that one or more isomers with no –CHBr– groups and no olefinic protons might be present in small amounts.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.32; H, 3.05. Found: C, 36.59; H, 3.21.

In a second preparation employing 1.1 moles of bromoform, 1.2 moles of potassium *t*-butoxide, and 1.46 moles of bicyclo[2.2.1]heptadiene, after two slow distillations, a total of 96 g. (33% based on bromoform) of a dibromide fraction was obtained b.p. 90° (0.1 mm.). The n.m.r. spectrum was similar to that above and indicated ratios of **13**, **14**, and **15** to be 62:14:24. Again the integral of the signals in the 1.5–3-δ region was somewhat higher than would be expected for these three compounds alone.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.32; H, 3.05. Found: C, 36.42; H, 3.21.

Upon standing for six weeks at *ca.* −10°, the composition changed to **13**:**14**:**15** = 20:10:70.

Reduction of $C_8H_8Br_2$ Mixtures with Lithium Aluminum Hydride.—A mixture (32.9 g.) of **13**, **14**, and **15** (62:14:24) was added dropwise to a stirred mixture of 4.7 g. of lithium aluminum hydride in 1.5 l. of refluxing ether. After the addition was completed, refluxing was continued for 8 hr. then the mixture was worked up in the usual way. Distillation gave 17.6 g. (76%) of 3-bromobicyclo[3.2.1]octadiene (**16**); b.p. 63° (5 mm.); $n^{25}D$ 1.5453; no reaction with alcoholic silver nitrate. Infrared: 3040, 1625, 725, 675 cm.$^{-1}$. N.m.r.: 1.5–2.9 δ (6H) complex; 5.64 δ (1H) quartet, J_1 ~ 5.6 c.p.s., J_2 ~ 2.8 c.p.s. (C-6); 6.10 δ (1H) quartet, J_1 ~ 5.6 c.p.s., J_2 ~ 2.6 c.p.s. (C-7) superimposed on ~6.17 δ broad doublet, J ~ 7 c.p.s (C-2). The mass spectrum established the molecular formula C_8H_9Br based on equally intense peaks due to isotopic molecular ions at mass numbers 184 and 186.

Anal. Calcd. for C_8H_9Br: C, 51.92; H, 4.90. Found: C, 51.46; H, 4.94.

From the distillation above 1.4 g. (4%) of a higher boiling fraction, b.p. 74–75° (0.3 mm.), was obtained which n.m.r. analysis showed was mainly **14** and **15**.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.32; H, 3.05. Found: C, 36.67; H, 3.28.

Reduction of 15.6 g. of **13**, **14**, and **15** (20:10:70) with 2.6 g. lithium aluminum hydride in 300 ml. of ether for 37 hr. gave 6.6 g. (61%) of **16** and 4.2 g. (27%) of a higher boiling fraction, b.p. 65° (0.1 mm.) which n.m.r. analysis showed was nearly pure **15**. Infrared: 3060, 1620, 1190, 1165, 1020, 970 cm.$^{-1}$. N.m.r.: 1.04 δ (1H) doublet, J = 12 c.p.s. (*syn*-C-8); 2.29 δ (1H) octet, J_1 = 12 c.p.s., J_2 = 4.6 c.p.s., J_3 = 2 c.p.s. (*anti*-C-8) included in a complex pattern from 1.6–2.5 δ; ~2.73 (1H) broad quartet, J_1 ~ 7.7 c.p.s., J_2 ~ 4.6 c.p.s. (C-5); 3.65 δ (1H) singlet (C-6); 5.97 δ (1H) sharp quartet, J_1 = 7.7 c.p.s., J_2 = 2.5 c.p.s. (C-4). Weak signals at 2.97 δ triplet, 4.13 δ quartet, and 5.67 δ singlet indicated the presence of minor amounts of presumably isomeric impurities.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.32; H, 3.05. Found: C, 36.80; H, 3.27.

Addition of 0.56 g. of this sample of (predominantly) **15** to 1 g. of sodium in liquid ammonia gave a 43% yield (isolated by gas chromatography) of **18** (below), identified by comparison of retention times and infrared spectra. Reversal of this procedure, *i.e.*, addition of sodium to a solution of **15** in liquid ammonia, afforded only traces of hydrocarbons.

A solution of 15 mg. of **15** (above) in 68 mg. of *n*-tributyl tin hydride was heated at *ca.* 100° under nitrogen in a sealed glass tube for 20 hr. Ammonia was then passed through the solution until no further precipitate formed.

Then the mixture was extracted with pentane, naphthalene was added as an internal standard and the solution was analyzed by gas chromatography (C20M, 213°), indicating a 98% yield of a compound shown to be **16** and 0.5% of **18**.

Bicyclo[3.2.1]octadiene (18).—Reduction of **16** with excess sodium in liquid ammonia gave **18** in about 85% yield; b.p. 50° (120 mm.); $n^{24}D$ 1.4918. Infrared: 3040, 3020, 1625, 1587, 725, 675 cm.$^{-1}$. N.m.r.: 1.5–2.7 δ (6H) complex; 5.03 δ (1H) very broad perturbed doublet (C-3); 5.53 δ (1H) sharp quartet, J_1 ~ 5.3 c.p.s., J_2 ~ 2.8 c.p.s. (C-6); 5.86 δ (1H) very broad perturbed doublet (C-2); 6.07 δ (1H) sharp quartet, J_1 ~ 5.3 c.p.s., J_2 ~ 2.8 c.p.s. (C-7).

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.71; H, 9.43.

Microhydrogenation of **18** over 30% palladium on charcoal in ethanol resulted in the absorption of 99% of two equivalents of hydrogen giving bicyclo[3.2.1]octane, m.p. 133.5–135° (sealed capillary), lit. m.p. 133°,[24] m.p. 139.5–141°,[25] which had an infrared spectrum identical with the published[23] spectrum of bicyclo[3.2.1]octane.

Hydrolysis of 16.—Vinyl bromide **10** (2 g.) was shaken with 80% sulfuric acid (300 ml.) at 0° for 1.5 min. and then the mixture was hydrolyzed with ice. The hydrolysate was partially neutralized with sodium bicarbonate and then was extracted with ether. The extract was washed with bicarbonate solution, dried and analyzed by gas chromatography C20M, 200°, with naphthalene as an internal standard, collecting the following products: **16** (21%) t_R = 0.52, **17** (17%) t_R = 0.65, an unidentified ketone (0.4%; assuming a molecular weight of 122; infrared, 1745 cm.$^{-1}$) t_R = 0.72, and **19** (22%) t_R = 1.28.[27] In a similar experiment employing a reaction time of 5 min. the per cents were **16** (5%), **17** (12%), unidentified ketone (2.7%), and **19** (25%). Physical constants for **17** and **19** are given subsequently.

3-Bromotricyclo[3.2.1.0^{2,7}]octene-3 (17).—**17** has $n^{25}D$ 1.5471. Infrared: 3040, 1612, 850, 833, 695 cm.$^{-1}$. N.m.r.: 0.92 δ (2H) doublet, J = 11.8 c.p.s. (*syn*-C-6, -C-8); 1.4–1.8 δ (4H) complex; 1.93 δ (1H) multiplet (C-2); 2.55 δ (1H) multiplet (C-5); 5.97 δ (1H) sharp quartet, J_1 = 7.3 c.p.s., J_2 = 2.9 c.p.s. (C-4).

Anal. Calcd. for C_8H_9Br: C, 51.92; H, 4.90. Found: C, 51.68; H, 4.89.

Bromide **17** (10 mg.) was shaken with 2 ml. of 80% sulfuric acid for 5 min.; then the mixture was hydrolyzed and processed as before. Analysis by gas chromatography (C20M, 212°, with naphthalene as an internal standard) established the following yields: **16** (3%), **17** (56%), and **19** (21%).

Tricyclo[3.2.1.0^{2,7}]octanone-3 (19).—This compound appeared to be free of impurities (gas chromatography) but did not solidify upon standing. It is very hygroscopic; $n^{25}D$ 1.5074. Infrared: 3030, 2920, 2860, 1710, 1450, 1410, 1340, 1325, 860 cm.$^{-1}$. Ultraviolet (heptane): λ_{max} 192 mμ (ϵ 7090). N.m.r.: 1.35–2.3 δ complex, no signals at lower field. The mass spectrum showed a molecular ion peak at mass number 122 in agreement with the indicated molecular formula.

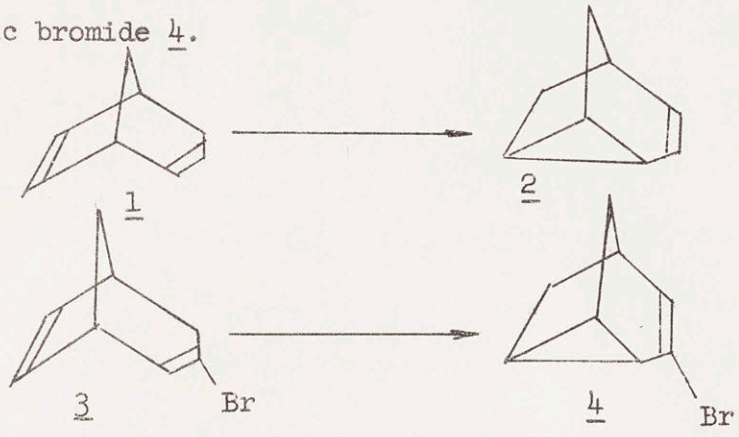
Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 79.20, H, 8.41.

The 2,4-dinitrophenylhydrazone of **19** melted at 210–211° (recrystallized from alcohol).

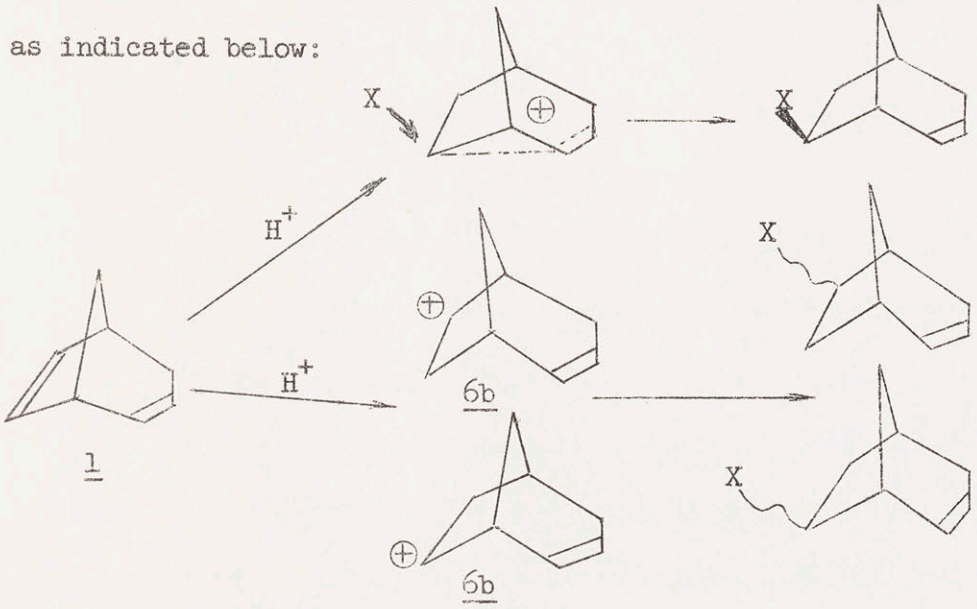
Anal. Calcd. for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.67. Found: C, 55.59; H, 4.69.

(27) Retention times relative to naphthalene = 1.00, C20M, 218°; **6** has t_R = 0.61.

Several studies were conducted in an attempt to convert the bicyclic hydrocarbon 1 to the tricyclic hydrocarbon 2 and the bicyclic monobromide 3 to the tricyclic bromide 4.



Acid-catalyzed rearrangement of 1 was attempted utilizing p-toluenesulfonic acid. Treatment of olefin 1 with p-toluenesulfonic acid in acetic acid at room temperature afforded a 42% yield of acetate A. Attempted rearrangement with 50% aq. sulfuric acid at 0° afforded a 31% yield of alcohol B as the only product. In neither reaction could starting material or tricyclic olefin 2 be obtained. The mechanism of the formation of these products could follow eigher the "non-classical" or the "classical" approach as indicated below:



5a X= OAc

5b X= OH

The fact that the hydroxyl and acetoxy groups were located on the two-membered bridge in the products A and B was shown by comparing the olefin regions of the n.m.r. spectra of these compounds with the same region in the spectra of bicyclo[3.2.1]octadiene. These spectra show that the olefin protons in the three-membered bridge appear as two clusters of broad multiplets. Whereas, the olefinic hydrogens on the two-membered bridge appear as two clusters of four sharp lines. The olefinic region of alcohol B and acetate A showed a splitting pattern that was nearly identical to the pattern in bicyclo[3.2.1]octene-2. The major difference in the two regions was in the magnitude of the separation of alcohol B and the acetate A was not defined, although the groups would be expected to enter exo-oriented if the "non-classical" structure 6a correctly describes the carbonium ion intermediate. If the reactive intermediate was the "classical" structure 6b, the choice of exo or endo attack is not completely clear and the steric hindrance to approach of the entering group may be about the same from either the exo ($-CH_2-CH_2-$) or endo ($-CH=CH-CH_2-$) side of the molecule.

From the data at hand, one cannot firmly assign the structure of the alcohol B and acetate A to any one of the four possible isomers (arising from exo and endo addition to both of the 6- and 7- positions of 1. Based on the "non-classical" mechanism one would expect that only the exo-7-positioned alcohols or acetates would be formed, whereas the "classical" representation (no homoallylic stabilization) would seem to predict the formation of both the 6- and 7-oriented compounds. Since gas chromatographic analyses and the n.m.r. spectra of the alcohol and acetate were consistent with isomer-free material, some preference for the struc-

ture of the compounds as being 5a and 5b is obtained.

Attempted sealed tube thermal isomerization of diene 1 utilizing a range of temperatures and reaction times afforded mainly a recovery of starting material or polymeric material. In several cases unidentified materials in yields of 1 to 9% were observed by gas chromatographic analysis.

An attempted base-catalyzed isomerization of the diene utilizing sodium hydride[63] in dimethyl sulfoxide afforded a quantitive recovery of the starting material

Attempted rearrangement of the bicyclic bromide 3 to the tricyclic bromide 4 using zinc bromide in ether afforded a complete recovery of the starting material. Allowing the bicyclic bromide to stand in the presence of p-toluenesulfonic acid and a little ether for 6 hr. afforded a 38% recovery of starting material. No other volatile components could be detected by gas chromatographic analysis. When the same mixture was heated at 100° for a short time a 36% recovery of starting material was observed in addition to a 6% yield of a material with a gas chromatographic retention time identical to that of the tricyclic bromide 4. Heating the mixture at 200° for 6 hr. afforded mainly tars. Attempted isomerization of the bicyclic bromide 3 with aluminum bromide utilizing varying ratios of catalyst to olefin and a variety of contact times resulted in 1 to 71% recovery of the starting material. The highest yield of the tricyclic bromide 4 was 1.9%. Attempted base-catalyzed isomerization of the bromide 3 with sodium hydride in dimethyl sulfoxide[63] afforded no volatile products by gas chromatographic analysis.

(63) E.J.Corey and M.Chaykovsky, J.Am.Chem.Soc., 84, 866 (1962).

Pyrolysis of the bicyclic bromide 3 at 261°, 359°, and 480° over acidic glass wool and over acidic alumina at 200° afforded starting material only. However, a ratio of 0.07:1.00 of benzene to bromobenzene was obtained over alumina at 300°. The same treatment at 458° afforded a 0.37:0.91:1.00 ratio of benzene to diene 1 to bromobenzene. Pyrolysis of diene 1 at 350° afforded a 26% yield of ethylbenzene and a 28% yield of benzene.

The pyrolysis of 1,4-cyclohexadiene, 1,3-cyclohexadiene and cyclohexene over alumina at 350°, resulted in varying yields of benzene, 1-methylcyclopentene, cyclohexene, and cyclohexane. Cyclohexane was inert to these conditions.

Experimental

Acetolysis of diene 1 from attempted acid catalyzed rearrangement in acetic acid. - Diene 1 (0.0379 g., 0.358 mmole) was added to a solution of 0.1 molar p-toluenesulfonic acid in 10 ml. of glacial acetic acid. The mixture was stirred at room temperature under nitrogen for 14 hr. and then the product was worked up as usual and extracted with pentane. Gas chromatographic analysis (S-710, 110°) showed that no starting material or other isomeric materials were present. Gas chromatographic analysis (C-20M, 200°, naphthalene as internal standard) showed a compound in 42% yield with a retention time that was 0.70 times that of naphthalene. This material was collected. Infrared (PL): 3015 (0.63), 2920 (0.81), 2840 (0.57), 1735 (1.0), 1375 (0.98), and 695 cm^{-1} (0.60). Its mass

spectrum showed a molecular ion at m/e 166. The n.m.r. showed bands at 5.28 - 6.08δ ((2H, multiplet, -CH=CH-); 4.8 - 5.1δ (1H multiplet, -CH-OH); 1.4 - 2.7δ (11H multiplet).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.93 H, 8.63.

Hydration of diene 1 from attempted sulfuric acid isomerization. - Diene 1 (0.0288 g., 0.271 mmole) was added to 2 ml. of 50% aqueous sulfuric acid at 0° and shaken for 10 minutes. After ice was added, the product was worked up in the usual way and extracted into ether. Gas chromatographic analysis of the product (S-710, 170°, naphthalene as internal standard) showed a compound, formed in 31% yield, with a retention time 0.61 times that of naphthalene. The sample was collected by gas chromatography. Infrared (CS_2): 3600 (0.12), 3340 (broad, 0.55), 3020 (0.31), 2930 (0.62), 2880 (shoulder), 2820 (shoulder), 1635 (0.12) and 695 cm^{-1} (0.53). The mass spectrum of the alcohol showed a molecular ion at m/e 124. N.m.r.: 5.2 - 6.0δ (2H, multiplet -CH=CH-); 4.0 - 4.3δ (1H, multiplet, -CH-$OCOCH_3$); 3.56δ (1H, singlet, -O-CO-CH_3); and 1.3 - 2.8δ (8H, multiplet).

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.17; H, 9.93.

Several unsuccessful attempts were made to improve the yield of alcohol B. 1) Diene 1 (43.7 mg., 0.406 mmole) was treated with 2 ml. of 80% aqueous sulfuric acid at 0° for 5 minutes. This reaction produced only polymeric material. 2) Diene 1 (37.6 mg., 0.354 mmole) was treated with 2 ml. of 50% aqueous sulfuric acid for 1 minute at 0°. Gas chromatographic analysis (S-710, naphthalene as internal standard) showed a 2.4% yield of the alcohol and a 50% recovery of starting materials (S-710, 110°, benzene as internal standard.) 3) Diene 1 (27.2 mg.,

0.256 mmole) was treated with 2 ml. of 60% aq. dicxane for 8 hr. Gas chromatographic analysis of the product showed only a 65% recovery of starting material.

Attempted thermal (sealed tube) isomerization of diene 1. - All reactions were run in capillary tubes into which the samples had been drawn, followed by thorough nitrogen flushing. All product mixtures were analyzed by gas chromatography using benzene as an internal standard. Only three products were observed on a 12% TEG-12% Carbowax 400 column at 61° and their retention times relative to benzene (1.00) are as follows: starting material, 1.83; peak I, 1.44; peak II, 2.56. 1) Diene 1 (12.9 mg.) was heated at 284° for one hour and 88% of the starting material was recovered along with 3.1% yield of compound I and a 1.4% yield of compound II. 2) Diene 1 (13.8 mg.) was heated at 284° for two hours and 42% of starting material was recovered along with a 5% yield of compound I and a 9.2% yield of compound II. 3) Diene 1 (13.8 mg., was heated at 284° for 4.5 hr. and a 12% recovery of starting material was obtained along with a 6.5% yield of compound I and a 5.4% yield of compound II. 4) Heating diene 1 (13.5 mg.) at 402° for 30 minutes allowed the recovery of 3.8% of starting material, 5.3% of compound I and no compound II.

Attempted base catalyzed[63] isomerization of diene 1. - Diene 1 (0.0501 g., 0.473 mmole) was added to 10 ml. of a 3.4 molar solution of sodium methylsulfinylcarbanion in dimethylsulfoxide. After the solution was allowed to stir at room temperature for 18 hours, the mixture was hydrolyzed and the product was extracted with pentane. Gas chromatographic analysis (S-710, 110° benzene as internal standard) showed a quantitative

recovery of starting material.

Attempted rearrangement of monobromide 3. -

a.) Vinyl bromide 3 (1.86 g., 10.1 mmole) was added to a mixture of 100 ml. of anhydrous ether and 0.94 g. of zinc bromide. After 10 days the infrared spectrum of the product was identical with that of the starting material, indicating no rearrangement.

b.) Vinyl bromide 3 (48 mg., 0.26 mmole) 2 mg. of p-toluenesulfonic acid and ether (just enough to dissolve acid) were added to a glass tube which was then sealed and kept at room temperature for 6 hours. Gas chromatographic analysis of the product (C-20M, 207°, naphthalene as internal standard) showed a 38% recovery of starting material.

c.) Vinyl bromide 3 (48 mg., 0.26 mmole) 2 mg. of p-toluenesulfonic acid and ether were added to a glass tube which was then sealed and heated at 100°. Gas chromatographic analysis of the product (as above) showed a 36% recovery of starting material and a 6% yield of a compound with the same retention time (C-20M, 207°) as tricyclic bromide 4.

d.) Vinyl bromide 3 (48 mg., 0.26 mmole) and 2 mg. of toluenesulfonic acid were treated as above except the temperature was maintained at 200° for 6 hours. Except for tars, the only products found were starting material 3, 9% recovery, and rearranged bromide 4 (by retention time) in 7% yield.

e.) Vinyl bromide 3 (0.1374 g., 0.742 mmole) was added to a flask containing 50 mg. of aluminum bromide in 10 ml. of carbon disulfide and this mixture was allowed to stir at room temperature for 5 hours. After the product was washed with water and worked up as usual, gas chromatographic analysis (C-20M, 202°, naphthalene as internal standard) showed a

1.0% recovery of starting material and a 1.9% yield of a compound with the same retention time as compound 4.

f.) Vinyl bromide 3 (64.9 mg., 0.348 mmole) was added to a mixture of 15 mg. of aluminum bromide in 25 ml. of carbon disulfide. After one minute water was added and the product worked-up as usual. Gas chromatographic analysis (C-20M, 204°, naphthalene as internal standard) showed an 11% recovery of starting material and a 1.1% yield of a compound with the same retention time as compound 4.

g.) Vinyl bromide 3 (63.8 mg., 0.345 mmole) was added to a stirred mixture of 15 mg. of aluminum bromide in 25 ml. of anhydrous ether and this mixture was allowed to stir for 30 minutes. Gas chromatographic analysis of the product showed only a 71% recovery of starting material.

Attempted pyrolytic isomerization of monobromide 3. - The apparatus employed was a pyrolysis chamber attached at the inlet of a gas chromatographic unit. In each case the sample was injected into the pyrolysis chamber and directly analyzed, after a contact time of ca. 2 sec.

a.) Acidified glass wool utilized as chamber packing. - This pyrolysis resulted in unchanged starting material at pyrolysis chamber temperatures of 261°, 359°, and 480°.

b.) Acidic alumina utilized as chamber packing. - Pyrolysis at 220° resulted in unchanged starting material. Similar treatment at 300° formed benzene to bromobenzene in a ratio of 0.07:1.00. Pyrolysis with a chamber temperature of 458° afforded benzene, diene 1 and bromobenzene in a ratio of 0.37:0.91:1.00. All compounds were identified by

comparing infrared spectra and gas chromatographic retention times with those of authentic materials.

Attempted base-catalyzed[63] isomerization of monobromide 3. - Monobromide 3 (0.0749 g., 0.404 mmole) was added to a solution of 0.65 g. sodium hydride in 20 ml. of dimethylsulfoxide . After stirring at room temperature for 3 days the mixture was hydrolyzed and extracted with pentane. Gas chromatographic analysis (S-710,110° and 170° showed no volatile materials were present.

Hydrocarbon pyrolysis on acidic alumina. - All pyrolyses were carried out by injecting the material to be studied into a pyrolysis chamber which was located at the inlet to a gas chromatographic column (12% TEG-12% carbowax 400 at 61°). The pyrolytic chamber was packed with acidic alumina and the flow rate through the chamber was adjusted to a contact time of about 2 seconds.

1.) Pyrolysis of diene 1 at 350° formed a 26% yield of ethylbenzene and a 28% yield of benzene.

2.) Pyrolysis of 1,4-cyclohexadiene at 350° resulted in a 61% yield of benzene, 2.1% yield of cyclohexene, 9.6% yield of 1-methylcyclopentene and a 3.1% yield of cyclohexane.

3.) Pyrolysis of 1,3-cyclohexadiene at 350° formed benzene in 59% yield, cyclohexene in 2.7% yield, 1-methylcyclopentene in 14% yield and cyclohexane in 4.5% yield.

4.) Pyrolysis of cyclohexene at 342° formed benzene in 18% yield, cyclohexene in 16% yield, 1-methylcyclopentene in 34% yield and cyclohexane in 15% yield.

5.) Cyclohexane was inert to the pyrolysis at 350°.

BIOGRAPHICAL NOTE

The author, the son of Edgar V. and Ophelia L. Moser, was born on August 3, 1935 in Old Hickory, Tennessee. After graduation from Murfreesboro Central High School in 1954, he attended Georgia Institute of Technology, Vanderbilt University, and received a B.S. degree from Middle Tennessee State College in August, 1959. He entered the graduate school at the Massachusetts Institute of Technology in September of 1959 and came under the thesis supervision of Professor William R. Moore in December of 1960, and has held a National Institutes of Health Fellowship between September, 1960 and January, 1964.

On June 26, 1960, the author married the former Eleanor Theresa Sullivan. They have two sons, William R. II, born on March 17, 1962, and Edgar Alexander, born on July 21, 1963.

The author is a member of the American Chemical Society and the Society of the Sigma Xi. He is the co-author of a paper describing a part of this work, published in the Journal of Organic Chemistry [28, 2200 (1963)].