METHYLENECYCLOBUTENE AND RELATED SUBSTANCES

Thesis by

Douglas Einar Applequist

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ABSTRACT

Methylenecyclobutene was synthesized by a modification of the Willstätter cyclobutene synthesis, with the use of the Hofmann reaction to introduce the intracyclic double bond. A novel feature of the synthesis was the use of anthracene as a blocking group for the exocyclic double bond during the malonic-ester ring closure. 4,4-Dimethylmethylenecyclobutene was synthesized from pinene, and 3-phenylmethylenecyclobutene was obtained by condensation of allene and phenylacetylene.

The structures of the methylenecyclobutene dibromides and of the polymers formed by three different mechanisms were investigated. The results were shown to be consistent with the predictions of simple molecular orbital theory.

3-Methylenetrimethylene oxide was synthesized and its structure investigated by electron diffraction.

The structures of the dibromides of methylenecyclobutane were determined and found to be consistent with a carbonium-ion mechanism for bromine addition.

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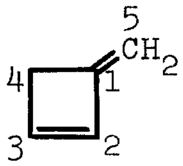
I. INTRODUCTION

The methylenecyclobutene system (I) provides opportunity to examine the behavior of an unusually and asymmetrically strained diene and of the conjugated intermediates derived by attack at the "allylic" 4-position. The system is sufficiently simple for interpretation of the experimental results in terms of molecular orbital theory, which has received very few experimental tests in the small-ring compounds.

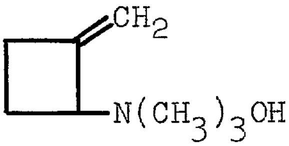


I

Methylenecyclobutene

The structure I was tentatively assigned to pirylene, a hydrocarbon obtained by a degradation of piperidine, by von Braun in 1928.[1] More recent chemical[2] and electron diffraction[3] evidence, however, has demonstrated that pirylene is methylvinylacetylene.

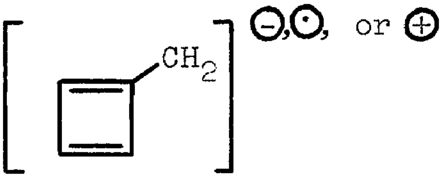
Buchman has reported the preparation of a hydrocarbon, probably I, by pyrolysis of 2-methylenecyclobutyltrimethylammonium hydroxide (II).[4,5] II was prepared from the corresponding quaternary bromide, which had been previously



II

described.[6] The optimum reaction conditions for pyrolysis of II were 310-325° on powdered Pyrex glass and gave as high as 13% yields of hydrocarbon. The reaction was complicated by formation of 2-methylcyclobutanone and condensation products thereof. The hydrocarbon was found to polymerize rapidly, even at 0°, to a yellow, resinous material. It boiled at 37°, and showed an ultraviolet absorption maximum at 221 mμ (ϵ = *ca.* 10,000) in *n*-hexane. It failed to react with maleic anhydride at 0°, but at room temperature a polymeric material was formed. The hydrocarbon took up one mole of bromine in benzene solution, to give a dibromide only one of whose bromines was displaced on treatment with trimethylamine in benzene. The resulting bromoquaternary ammonium bromide was converted to the picrate (m.p. 133.6-133.8°), which gave a good analysis for $C_{14}H_{17}O_7N_4Br$.

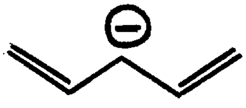
Simple molecular orbital calculations (LCAO) on the cyclobutadienylcarbinyl system (III) predicted that



III

it would have substantial delocalization energy (resonance energy) in the anion, radical, and cation.[7] The energy calculated was 1.59β (<u>ca</u>. 29 kcal.) for each of the three species. This stood in striking contrast with the predicted delocalization energy of cyclobutadiene as zero, in agreement with the observed difficulty in preparing this substance,[4] and with the predicted alternating stabilities of monocyclic anions and cations, according to which the cyclopropenyl cation, cyclopentadienyl anion, and cycloheptatrienyl cation should be stable and the corresponding cyclopropenyl anion, cyclopentadienyl cation, and cycloheptatrienyl anion, respectively, should be relatively unstable.[7] These predicted alternating stabilities have received some striking experimental confirmations.[8]

The cyclobutadienylcarbinyl system (III) could conceivably be obtained either from methylcyclobutadiene (and derivatives) or from methylenecyclobutene (and derivatives), in the latter case by removing a proton, hydrogen atom, or hydride ion from the 4-position. A proton might be removable with a strong base like sodamide in ammonia, which metalates open-chain 1,4-dienes,[9] or Grignard reagents, which react with cyclopentadiene, but are inert to 1,4-pentadiene.[10] However, the anion (IV) derived from 1,4-pentadiene is predicted



IV

to have somewhat more resonance stabilization relative to 1,4-pentadiene than III relative to I (1.46β and 1.12β, respectively; see Appendix), so it would not be expected that the weaker metalating agents would attack I. However, the effects of π-bonding between nonadjacent atoms and of strain, which are particularly important in four-membered rings, have been neglected in these calculations.

If anion III could be obtained, methylenecyclobutenes variously substituted in the 4-position could presumably be prepared by the usual reactions of metallo-organic compounds. Thus, reaction with iodine might give an iodo compound, and reaction with oxygen might furnish an alcohol, either of which might be used to study the behavior of cation III. Alternatively, attack at the 4-position of I by a less stable cation than III, such as an allyl cation, might remove a hydride ion directly. Such a reaction would be demonstrable if it could be shown that there is a high degree of chain transfer in the cation induced polymerization of I. The stability or instability of radical III might be demonstrated analogously.

Since the synthesis of methylcyclobutadiene appeared much less promising than the synthesis of methylenecyclobutene, the objective of the present research was to find a practical synthesis of methylenecyclobutene and to carry out experiments to test the validity of the above-described molecular orbital calculations. The synthesis of I due to

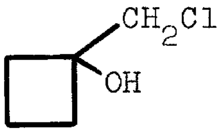
Buchman (p. 1) did not appear promising for large-scale preparation of the hydrocarbon because of low yields in two steps.

Methylenecyclobutane Dibromides

The "dibromide" of methylenecyclobutane was first prepared by Gustavson,[11] both by direct addition of bromine to the olefin and by treating the glycol from permanganate oxidation of the olefin with concentrated hydrobromic acid. He reported boiling points of 105-108° (50 mm.) and 185-190° for the respective samples. The first material was heated with lead dioxide and water to give an aldehyde (oxidized with silver oxide to an acid $C_5H_8O_2$) and a ketone, later shown to be cyclopentanone.[12] He also found that treatment of the dibromide with zinc in alcohol gave back methylenecyclobutane (which he considered to be vinylcyclopropane).

Fecht[13] found that treatment of the dibromide (physical constants not given) with potassium cyanide in 50% ethanol in the presence of iodide ion gave a dinitrile (with displacement of both bromine atoms), but he failed to determine the structure of the nitrile.[14,15]

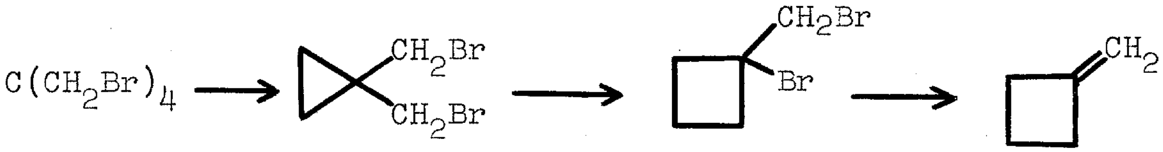
Demjanow and Dojarenko[16] repeated Gustavson's lead dioxide oxidation of the dibromide at lower temperatures and likewise obtained mainly cyclopentanone. They also added hypochlorous acid to methylenecyclobutane and assigned structure V to the product. This material gave an epoxide with



V

concentrated aqueous potassium hydroxide, cyclopentanone and a trace of cyclobutanecarboxaldehyde with lead dioxide in water, and glutaric acid with nitric acid. The boiling point was different from that of cyclopentene chlorohydrin (64.5° (20 mm.) vs. 81-82° (15.5 mm.), respectively).

Structures which are reasonable possibilities for methylenecyclobutane dibromides have been proposed as reaction intermediates in the conversion of pentaerythrityl tetrabromide (VI) to methylenecyclobutane (IX) with zinc in alcohol.[17] Stepwise syntheses of IX



VI VII VIII IX

have in fact been carried out from VII (?), prepared from the corresponding diol and phosphorus tribromide, by Zelinsky and Krawetz[18] and by Slobodin and Shokhor.[19] These workers gave the properties of the dibromide as b.p. 72-74° (13 mm.), $n^{20}D$ 1.5340, and b.p. 83-87° (20 mm.), $n^{20}D$ 1.53643, respectively. Slobodin and Shokhor suspected from Raman evidence that some rearrangement to the 4-membered ring had occurred in the preparation of the dibromide.

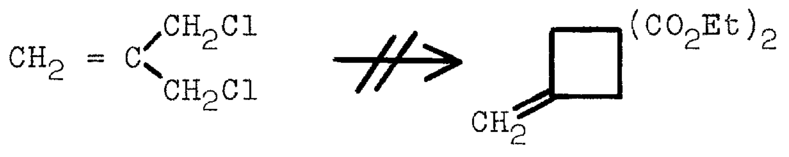
Buchman and Howton[5,6] prepared samples of methylenecyclobutane dibromide by direct bromination and by Ziegler bromination of the hydrocarbon. The reported physical properties were b.p. 41-45° (2.2 mm.) and 43-50° (3 mm.), and $n^{25}D$ 1.532. It was found that material from either source was unsaturated to permanganate and reacted with dimethylamine or trimethylamine to give both saturated (permanganate) and unsaturated products in which both bromines had been displaced by the amines, analogously to the aforementioned results of Fecht.

Taken as a whole, the above information seems strongly indicative that the "dibromide" is a mixture containing at least two compounds (one saturated and one unsaturated) in addition to VIII, the normal bromine adduct (if, indeed, there is any VIII present). Confirmation of this conclusion and elucidation of the structures of the component dibromides is described later in this thesis.

II. RESULTS AND DISCUSSION

Synthesis of Methylenecyclobutene

The synthesis of methylenecyclobutene developed in this research is essentially analogous to Willstätter's classical synthesis of cyclobutene by degradation of cyclobutanecarboxylic acid to cyclobutylamine, exhaustive methylation, and Hofmann reaction.[20] Several preliminary attempts were made to prepare the required 3-methylenecyclobutanecarboxylic acid by first condensing the dichloride X with malonic ester to give XI, but the reaction primarily yielded polymolecular condensation products when ethoxide or *t*-butoxide was used as condensing agent, even under high dilution conditions. An attempt to use sodium hydride in dioxane as the condensing agent resulted in reduction of X to a volatile unsaturated substance, presumably isobutylene.[21] The failure of the alkoxide-catalyzed reactions to produce ring closures was probably due to the unfavorably large bond angle (*ca.* 120°) at the central carbon of X. The synthesis was therefore



X

XI

modified to include a blocking group for the double bond, the group selected being the anthracene molecule, which is known to be thermolytically removable to regenerate unsaturated compounds.[22-25] The complete synthesis is outlined in Fig. 1.

The ester XII was prepared by the method of Bachman and Tanner,[54] in which diethyl methylenemalonate was added to anthracene. The ester was reduced to the diol XIII in 75-90% yields with lithium aluminum hydride in ether. Direct conversion of XIII to the dibromide XIV with phosphorus tribromide gave mostly tar from which a trace of XIV was sublimed. However, 78% yields of XIV were obtained by conversion of XIII to its benzenesulfonate (XV) with benzenesulfonyl chloride in pyridine and then treatment of the benzenesulfonate with a large excess of sodium bromide in diethylene glycol for 18 hrs. at 165-170°. The conditions in the last step were unusually drastic for a reaction of this type,[26,27] but less drastic conditions gave incomplete reaction. The slowness of the reaction appeared indicative of a particularly high steric hindrance to displacement (S_N2) reactions in this system. The hindrance was further illustrated in the reaction of the benzenesulfonate (XV) with base (described later in connection with the synthesis of 3-methylenetrimethylene oxide) and in the condensation of the dibromide XIV with malonic ester, which was particularly slow. When the latter condensation was attempted in reflux-

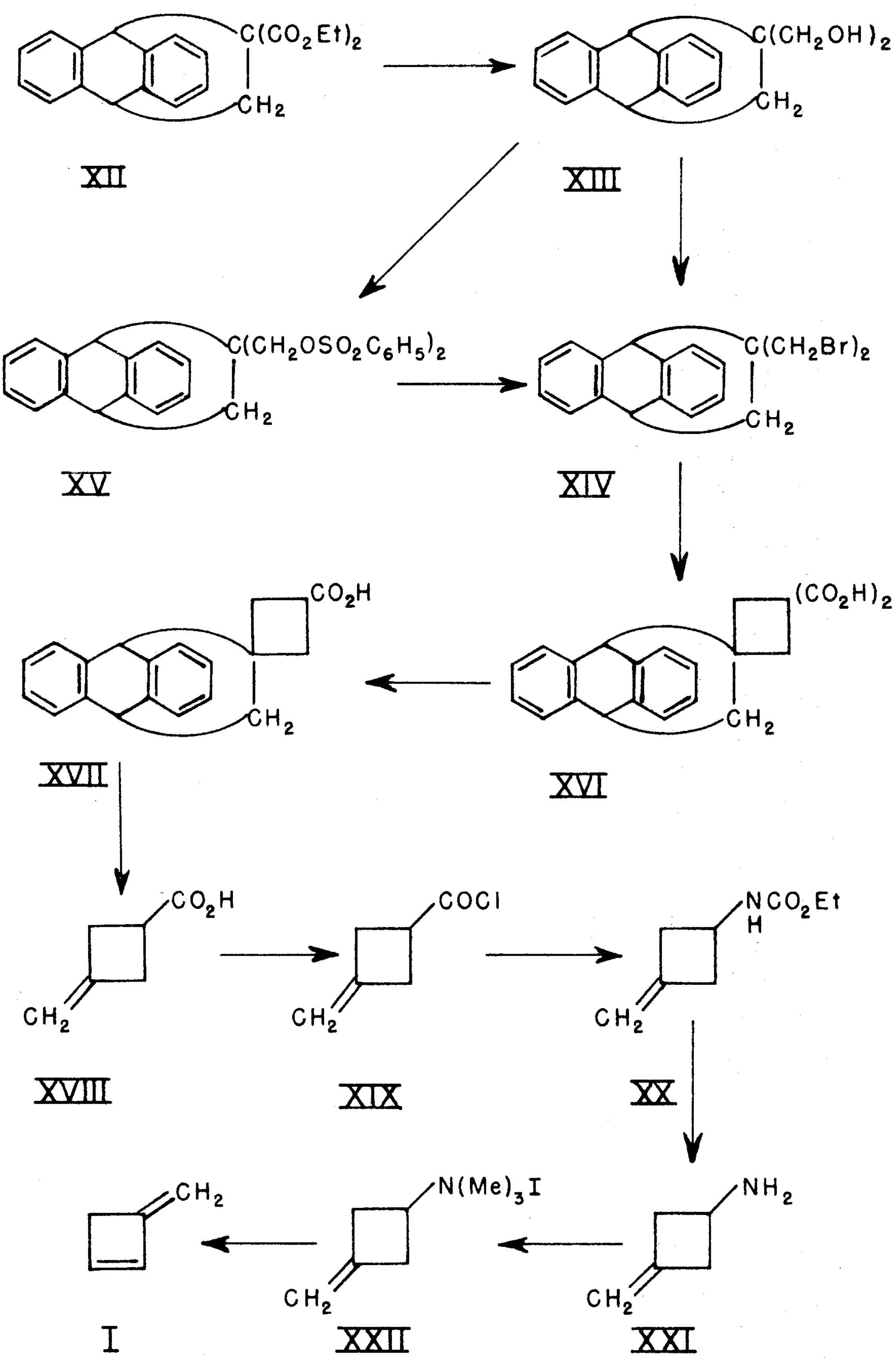

C(CO2Et)2
CH2
XII
C(CH2OH)2
CH2
XIII
C(CH2OSO2C6H5)2
CH2
XV
C(CH2Br)2
CH2
XIV
CO2H
CH2
XVII
(CO2H)2
CH2
XVI
CO2H
CH2
XVIII
COCl
CH2
XIX
NCO2Et
H
CH2
XX
CH2
I
N(Me)3I
CH2
XXII
NH2
CH2
XXI

Fig.1

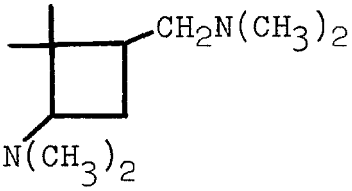
ing isoamyl alcohol (159 hrs.), 60% of the dibromide was recovered unchanged and the ester was converted to diisoamyl carbonate and isoamyl isoheptylate. The carbonate formation was effectively suppressed by using the less nucleophilic potassium _t_-amylate in _t_-amyl alcohol as condensing agent, which gave, after 171 hrs. heating under reflux, a small yield of ester hydrolyzable to the diacid XVI. Decarboxylation to the monoacid XVII was effected in 70% yield at 155°, and pyrolysis of XVII at 350° gave an 87% yield of 3-methylenecyclobutanecarboxylic acid (XVIII). Curtius degradation of XVIII to the amine XXI followed standard procedures, the azide being prepared by the acid chloride-sodium azide method.[28] By exhaustive methylation of the amine XXI, the quaternary iodide XXII was obtained in one step (89% yield). The Hofmann reaction gave methylenecyclobutene (I) with surprising ease, the odor of the hydrocarbon being noticeable as soon as the quaternary hydroxide solution was prepared. The yield was 68% when the decomposition was carried out at 160°.

The structure of methylenecyclobutene was established by hydrogenation to methylcyclobutane (infrared spectrum identical to that of an authentic sample), 96% of the theoretical hydrogen being taken up. Methylcyclobutadiene was eliminated as a possible structure by the infrared spectrum, which showed peaks characteristic of an exocyclic methylene group at 5.98 μ and 11.57 μ (almost exactly the same wavelengths absorbed by 4,4-dimethylmethylenecyclobutene and 3-phenylmethylenecyclobutene, see Fig. 12). There was no peak near 7.25 u, as would be expected if a methyl group were present.[29] The spectrum was nearly identical with that of a sample of Buchman's hydrocarbon (p. 1), which was remarkably preserved in carbon tetrachloride solution after standing several years.

Synthesis of 4,4-Dimethylmethylenecyclobutene

In order to determine whether the properties of methylenecyclobutene (I) are markedly dependent upon reactivity of the hydrogens at the 4-position, the derivative in which these hydrogens are replaced by methyl groups (XXVIII) was prepared by the scheme outlined in Fig. 2.

The degradation of α-pinene (XXIII) to pinic acid (XXV) followed the reported procedure,[30] but low yields in the permanganate oxidation of XXIII to pinonic acid (XXIV) prevented large-scale preparations of XXV. Pinic acid was degraded in 84% yield to the diamine XXVI by the Schmidt reaction. Exhaustive methylation to the quaternary iodide XXVII was carried out directly with methyl iodide and potassium hydroxide or, preferably, in two steps with preparation of the ditertiary amine (XXIX) by the Eschweiler-Clarke procedure (74% yield) followed by quaternization with



XXIX

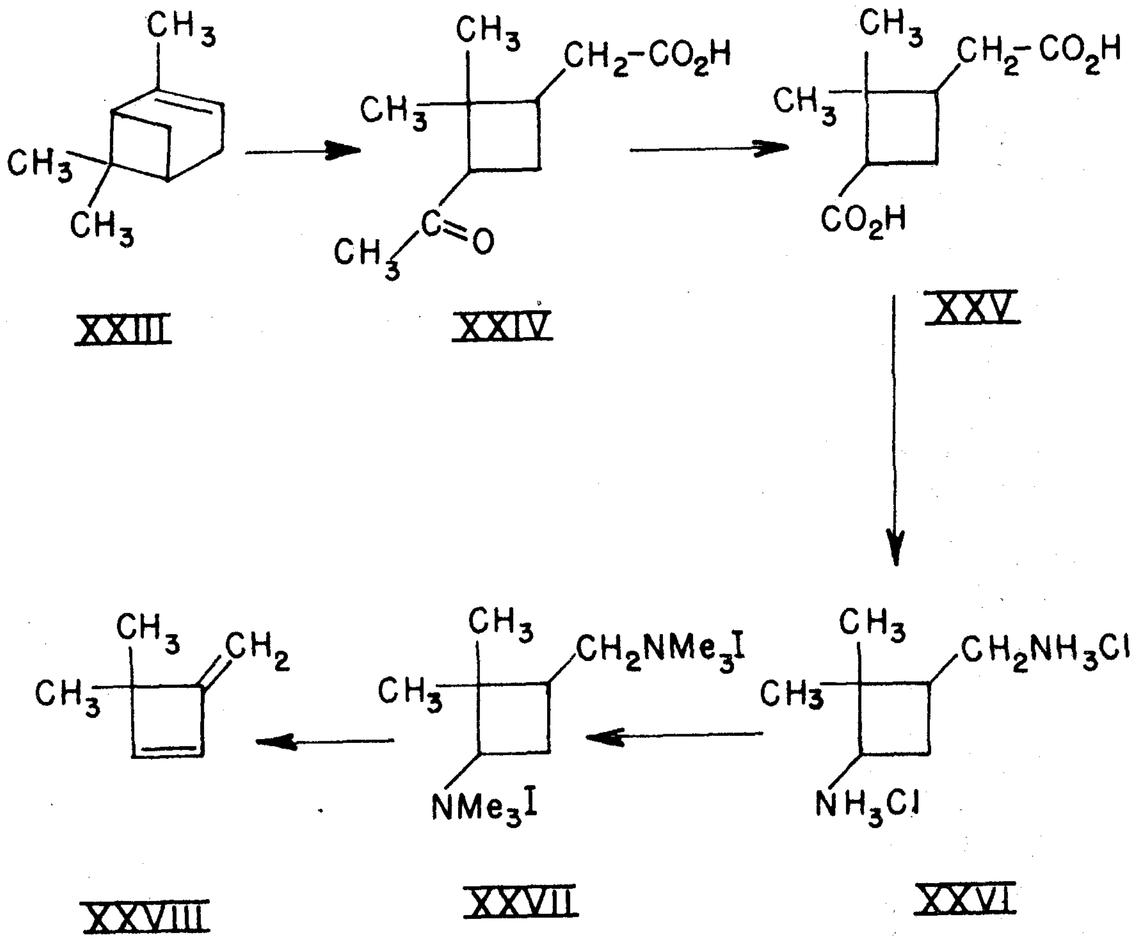

CH3
CH3
CH3
XXIII
CH3
CH2-CO2H
CH3
CH3
C=O
XXIV
CH3
CH2-CO2H
CH3
CO2H
XXV
CH3
CH2NH3Cl
CH3
NH3Cl
XXVI
CH3
CH2NMe3I
CH3
NMe3I
XXVII
CH3
CH2
CH3
XXVIII

Fig. 2

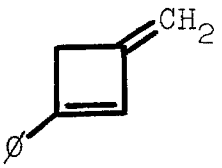
methyl iodide. The Hofmann reaction to form the diene XXVIII gave 52% yield overall from the ditertiary amine XXIX when carried out at 160° and 40 mm. pressure. The quaternary hydroxide, which was not isolated, was prepared from the iodide XXVII by treatment with silver oxide.

The structure of the diene XXVIII rests upon the method of synthesis and the spectra, which indicate conjugated double bonds (λ_{max} 229 mμ, $\epsilon = 8600$), an exocyclic methylene group (strong peaks at 5.97 μ and 11.57 μ) and *gem*-dimethyl groups (doublet at 7.22-7.31 μ).[29] The infrared spectrum is illustrated in Fig. 12. Also, the behavior on bromination is very similar to that of methylenecyclobutene (to be discussed later under Properties of Methylenecyclobutenes).

3-Phenylmethylenecyclobutene

Condensation of allene with phenylacetylene at 130° in sealed tubes gave small yields (*ca.* 1%) of a hydrocarbon boiling at 69-73° (3 mm.). The C/H ratio determined by combustion was close to that of a 1:1 adduct of allene and phenylacetylene, and the boiling point was reasonable for such an adduct. Phenylacetylene and allene have both been reported to undergo cycloaddition reactions to give four-membered rings.[31,32] The infrared spectrum showed the peaks at 5.99 μ and 11.6 μ characteristic of the exocyclic methylene group in the previously described methylenecyclobutenes and showed no evidence for acetylenic, allenic, or methyl groups (Fig.12).[29,33] The ultraviolet spectrum showed λ_{max} 291 mμ,

ϵ = 7250, which is in good agreement with a 1-phenylbutadiene chromophore rather than a 2-phenylbutadiene.[34,35] The structure 3-phenylmethylenecyclobutene (XXX) is therefore assigned



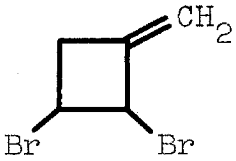
XXX

to this substance. Variations in solvent and polymerization inhibitor failed to give satisfactory yields of XXX, which was therefore not obtained in sufficient quantity for detailed study.

Properties of Methylenecyclobutenes

Methylenecyclobutene (I) in carbon tetrachloride solution was titrated at 0° with a bromine solution in the same solvent and was found to take up just one mole of bromine. The product was fractionated, giving one isomer pure (b.p. 49° (5 mm.)) and a higher-boiling second isomer (b.p. 74° (5 mm)) contaminated with the first, even though the boiling points were far enough apart to get clean separations normally with the column used. Infrared spectra revealed that the lower-boiling isomer was in fact not present in the undistilled bromination mixture, which contained only the higher-boiling form (Fig.13).

The lower-boiling isomer reacted instantly with alcoholic silver nitrate but only very slowly with sodium iodide in acetone to give a red solution and a slight precipitate. The infrared spectrum indicated an exocyclic methylene group, with strong bands at 5.94 μ and 11.16 μ. The former band was found at 5.90-5.95 μ in three other methylenecyclobutanes encountered in this research, while the latter was observed at 11.25-11.5 μ in eight methylenecyclobutanes (the first band being obscured by a carbonyl group in five of these). An authentic sample of cyclobutene dibromide did not react on standing overnight with sodium iodide in acetone, while 1-bromo-1-bromomethylcyclobutane (whose preparation is described later in this thesis) and 1,4-dibromo-2-butene* react rapidly to give a deep red color and a white precipitate. The structure XXXI is assigned to the lower-boiling dibromide on the basis of this information.



XXXI

The higher-boiling dibromide reacted rapidly with sodium iodide in acetone to give a red color and a white precipitate. The infrared spectrum showed a smaller C=C

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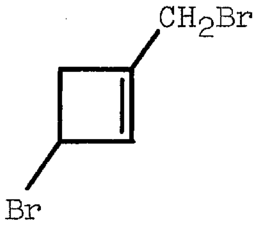
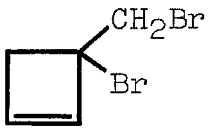
* A sample was kindly provided by Dr. E. R. Buchman.

stretching peak at 6.11 u. 1-Methylcyclobutene has such a peak at 6.08 μ.[36] The ultraviolet spectrum showed λ_{max} 208 mμ with $\epsilon = 8100$, whereas the lower-boiling XXXI showed λ_{max} 206 mμ with $\epsilon = 6300$. These figures are slightly suggestive of the 1,4-adduct structure (XXXII) rather than the 1,2-adduct XXXIII for the higher-boiling isomer, since increasing bromine substitution in the positions allylic to a double bond increase the resemblance of the ultraviolet spectrum to that of a conjugated diene, although the principal effect is usually to increase λ rather than ϵ.[37] The high boiling point is likewise suggestive of structure XXXII, since vicinal dibromides very commonly boil much lower than their isomers in which the bromines are further apart.[38] Finally, it may be argued that if the high-boiling isomer is either XXXII or XXXIII, then it is difficult to see how it could be XXXIII, since XXXII would almost necessarily have to be an intermediate in the isomerization of XXXIII to XXXI, and as such it would have appeared in the infrared spectra as a third component unless XXXII is quite unstable relative to both XXXIII and XXXI, for which no reason is readily apparent. If, as is quite possible, the high-boiling di-



XXXII

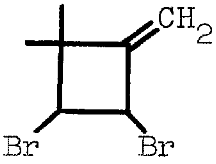


XXXIII

bromide is an equilibrium mixture of XXXII and XXXIII, then by analogy with other diene dibromides[39] XXXII would be expected to predominate.

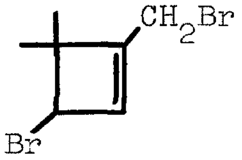
The dibromides were readily equilibrated by treatment with zinc bromide at 100° or simply by allowing them to stand for four days. The equilibrium mixture at room temperature (reached from both sides) contained the two apparent isomers in very nearly a 1:1 ratio.

4,4-Dimethylmethylenecyclobutene (XXVIII) likewise took up just one mole of bromine on bromination in carbon tetrachloride. Treatment of the crude product with trimethylamine in benzene gave a quaternary bromide in which only one of the bromines had been displaced. Fractional distillation was not successful in effecting separation of pure components, and it was evident from the change of infrared spectra with boiling point that there were at least three components in the mixture. The lowest boiling fraction had strong bands at 5.92 μ and 11.13 μ, indicating that the dibromide XXXIV was probably present. This substance was

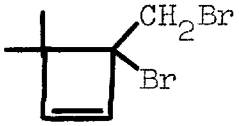


XXXIV

formed by isomerization during the distillation since these bands were absent in the spectrum of the crude bromination product. In the various fractions there was also a C=C stretching band at 6.06 μ, probably corresponding to the 1,4-adduct XXXV if the spectra of the methylenecyclobutene



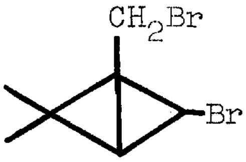
XXXV



XXXVI

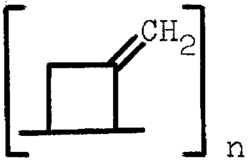
dibromides were correctly interpreted above. A new band at 5.80 μ may represent compound XXXVI. Only the band at 6.06 μ was strongly evident in the crude reaction mixture.

The ultraviolet spectrum of a typical sample of the dibromide mixture was very similar to that of the mixed methylenecyclobutene dibromides (λ_{max} 213 mμ, ε = 7680) tending to eliminate the possibility that a primary constituent of the dibromide mixture in the present case was saturated, such as structure XXXVI.



XXXVI

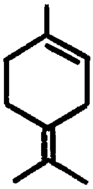
Attempts to metalate methylenecyclobutene with sodium amide and potassium amide in liquid ammonia gave nearly quantitative yields of polymeric materials in the form of yellowish, sticky, non-volatile gums. These were readily soluble in ether and chloroform, suggesting low molecular weight. The infrared spectrum showed strong bands at 5.95 μ and 11.34 μ, typical of methylene groups exocyclic to a four-membered ring. There were no other bands in the C=C stretching region. The structure assigned to the polymer is therefore XXXVII.



XXXVII

A single attempt to metalate 3-phenylmethylenecyclobutene with sodium amide in benzene gave primarily tarry material. All three of the methylenecyclobutenes prepared in this research polymerize readily and spontaneously at room temperature. The behavior was not always reproducible in this respect, but marked polymerization usually occurred in a few hours. On one occasion, however, the 4,4-dimethyl derivative stood for several days without visible change. This diene was easily distilled at atmospheric pressure (b.p. 65.7°) without serious polymer formation, whereas methylenecyclobutene itself formed large amounts of a tough, white polymer, insoluble in all common solvents, on distillation at 35°.

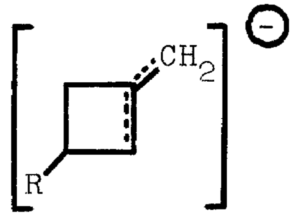
Methylenecyclobutene polymerized on standing to a clear, colorless, tough elastomer. The polymerization was partially inhibited with 2,2-diphenyl-1-picrylhydrazyl, but not very effectively, if at all, with hydroquinone or 1,4-naphthoquinone. The infrared spectrum of the polymer showed exocyclic methylene peaks at 5.97 μ and 11.46 μ, but they were smaller than in the base-catalyzed polymer. In addition, there were bands in the C=C stretching region at 5.81 μ and 6.14 μ, suggesting that all types of 1,2- and 1,4-polymerization had occurred. The molecular weight of the polymer was probably high, since it was not soluble in any common solvents. This fact indicates that there was not much chain transfer and therefore that the cyclobutadienylcarbinyl radical (III) is possibly not as stable as predicted. In contrast, terpinolene (XXXVIII) is apparently a good polymerization inhibitor.[40]



XXXVIII

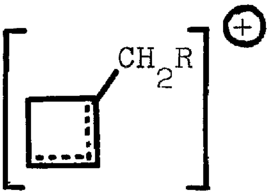
Treatment of methylenecyclobutene with boron trifluoride caused extremely rapid polymerization to a third type of polymer, presumably involving carbonium ions as the chain carriers. This polymer was again high molecular weight as indicated by insolubility in common solvents. It was more brittle and less elastic than the radical polymer, and turned brown soon after preparation. The infrared spectrum showed the peaks at 5.8 μ and 6.13 μ found in the radical polymer, but the peaks characteristic of exocyclic methylene groups were absent. The high molecular weight of the polymer might again be interpreted as an indication that there was no chain transfer by extraction of a hydride ion at the 4-position and therefore that the cyclobutadienylcarbinyl cation (III) is also unstable. However, this conclusion might be invalid since boron trifluoride might easily induce a high degree of cross-linking in a short-chain polymer, resulting in high molecular weight.[41]

It appears certain that anions attack methylenecyclobutene at the 3-position to give intermediates of the form XXXIX, which then attack another molecule preferentially to leave an exocyclic double bond rather than the more strained intracyclic double bond.



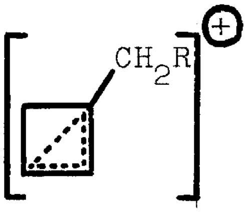
XXXIX

On the other hand, from the fact that the cationic polymer and the initial bromination product contain no exocyclic double bonds, it appears highly likely that initial attack by electrophilic reagents is at the 5-position to give intermediates of the form XL.



XL

One explanation is that intermediates of the type XXXIX have less angle strain and would be preferred for both anion and cation attack except that there is particular stabilization of type XL in the cation case due to 1,3-π-bonding across the ring, giving a cation resembling the highly stable cyclopropenyl cation.[7] The intermediate may be represented as XLI. The validity of this argument depends upon the extent to which these intermediates resemble the transition states for the reactions. The approximation may be very good in the case of bromination, where the rate-determining step would be the exothermic dibromide formation from XLI,[42,43] but in the polymerization reactions, the intermediates XXXIX and XLI are necessarily formed in exothermic reactions, and the transition states for their formation would be best approximated by the structures of the reactants. It may be shown here also that 1,3-π-bonding can account for the results, since a simple molecular orbital calculation on methylenecyclobutene with assignment of a small resonance integral between the 1 and 3 positions suggests that the molecule should be polarized with a small negative charge at

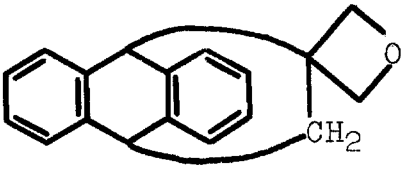


XLI

position 5, where cations attack, and positive charges at the other three positions. The greatest positive charge is at the 3-position, where anions attack (see Appendix). The calculated free valences do not unambiguously predict the site of radical attack, nor does the "frontier electron" method.[51]

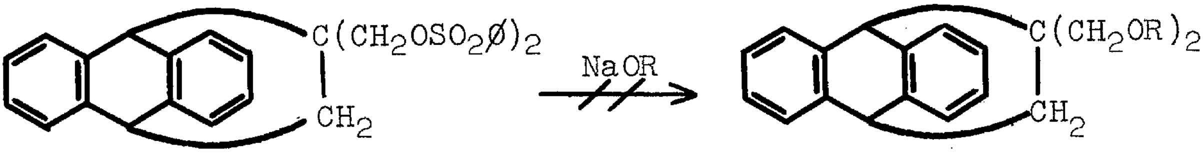
Synthesis and Structure of 3-Methylenetrimethylene Oxide

During the early work on the preparation of diacid XVI (Fig. 1) by malonic ester condensation, an attempt was made to carry out the condensation directly on the benzenesulfonate XV, instead of using the dibromide XIV.[44] The main product isolated was the trimethylene oxide XLII. XLII was



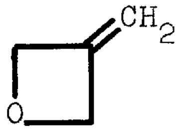
XLII

obtained also by heating the benzenesulfonate XV with sodium ethoxide in ethanol or sodium isoamylate in isoamyl alcohol. Since the reaction occurs in anhydrous media, a sulfur-oxygen cleavage is necessarily involved, since alkyl-oxygen cleavage by an alkoxide ion would lead to a dialkyl ether of diol XIII. Similar sulfur-oxygen cleavages have been ob-



served in several cases where there is hindrance to alkyl-oxygen cleavage.[45-47]

Pyrolysis of XLII at 350° gave 3-methylene trimethylene oxide (XLIII) (75% yields). A substance boiling 30° lower



XLIII

than XLIII was assigned the same structure by Kleinfeller,[48] but his material was not well characterized. The structure of XLIII was confirmed in the present work by heating the compound with anthracene at 180-210°. The adduct was identical to the XLII from which XLIII had been prepared.

It was considered possible that 3-methylenetrimethylene oxide would provide an example of 1,3-π-bonding, in the ground state, of the type used to explain the chemical behavior of methylenecyclobutene. In an effort to demonstrate such bonding by measuring the interatomic distances in the molecule, an electron diffraction investigation was carried out cooperatively with Mr. Elihu Goldish and Prof. Verner Schomaker. Final refinements have not yet been made, and will be reported in Mr. Goldish's thesis, but the parameters of the molecule have been determined with high probable accuracy (± 0.02 Å in distances, ± 2° in angles) to be as shown in Fig. 3. Important details of the analysis are recorded in the Appendix.

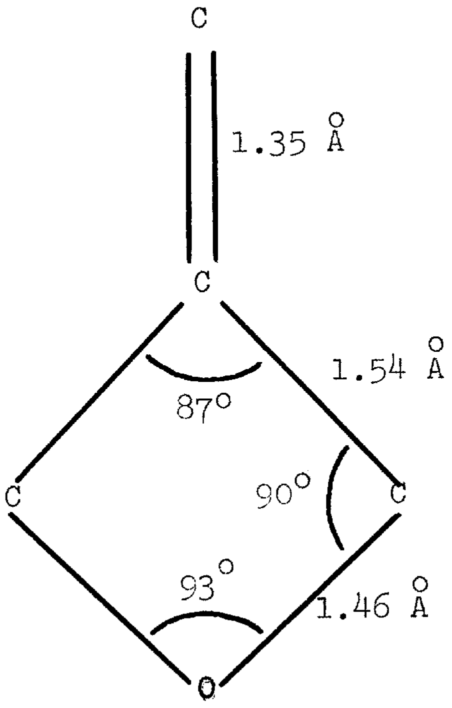
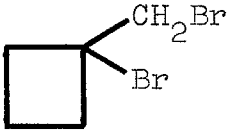


Fig. 3

It was thought that the bonding interaction between the oxygen and the opposite carbon atom (C_3) might be sufficiently large to make the intracyclic angle at C_3 substantially larger than 90°, in which case the bonding would have been clearly indicated, but in the absence of suitable data for comparison,[55] the present results cannot be interpreted as evidence for or against 1,3-π-bonding. The electron diffraction study does, however, provide additional proof of the structure of XLIII and confirmation of the structures of the intermediates leading to its preparation.

Methylenecyclobutane Dibromides

A synthesis of methylenecyclobutene which appeared attractive for its simplicity was treatment of methylenecyclobutane dibromide (XLIV) with strong base, which might

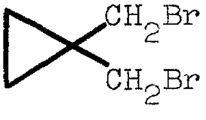


XLIV

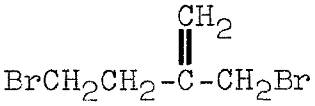
cause successive 1,2- and 1,4-eliminations of hydrogen bromide, giving methylenecyclobutene (I). Heating the crude dibromide, obtained by addition of bromine to methylenecyclobutane, with powdered potassium hydroxide or potassium t-butoxide in t-butanol did in fact give trace amounts of a volatile hydrocarbon having conjugated double bonds (λ_{max} 222 mμ), infrared indication of an exocyclic double bond (11.53 μ peak; solution too dilute for other bands to appear), and the property of polymerizing rapidly, even in dilute t-butanol solution.

The synthesis was clearly impractical, but, as indicated in the Introduction, there was some doubt that the dibromide actually had structure XLIV, and it seemed desirable to clarify the structure before abandoning the approach.

Fractional distillation of the crude dibromide and infrared analysis of the various fractions showed that there were four constituents in the mixture, none of which was obtained pure by distillation. These four were assigned the structures XLIV-XLVII.

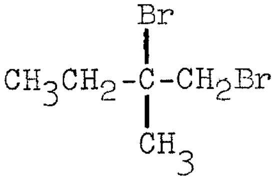


XLV



$\mathrm{BrCH_2CH_2\text{-}\overset{CH_2}{\overset{\|}{C}}\text{-}CH_2Br}$

XLVI



$\mathrm{CH_3CH_2\text{-}\overset{Br}{\underset{CH_3}{C}}\text{-}CH_2Br}$

XLVII

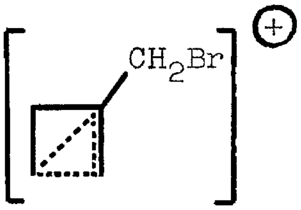
Compound XLV, which was about 32% of the total, was obtained pure by treatment of the mixture with powdered potassium hydroxide, toward which XLV alone is inert due to the impossibility of elimination of hydrogen bromide. XLV is inert toward permanganate in acetone, reacts readily with sodium iodide in acetone on warming to give a white precipitate, reacts rapidly with alcoholic silver nitrate, and shows no double bonds or methyl groups in the infrared.

From the properties of a fraction containing both XLV and XLVI it was deduced that XLVI (about 6% of the total) is readily oxidized by permanganate in acetone, reacts rapidly with sodium iodide in acetone to give a white precipitate, is a strong lachrymator (as are many allylic bromides), and shows a strong C=C stretching band at 6.05 µ in the infrared. *The infrared shows no methyl groups.*

Compound XLIV, the unrearranged adduct, comprised about 61% of the total and was obtained in about 93% purity by a second fractional distillation of the fractions containing it. From the properties of fractions containing some XLV it was shown that XLIV is saturated toward permanganate, reacts rapidly with sodium iodide in acetone to give a red color and a white precipitate, and shows no double-bond or methyl-group absorptions in the infrared.

The structure of XLVII is assigned tentatively and is based on the facts that it is saturated toward permangante and shows methyl groups in the infrared (7.23 μ), and that 2-methyl-1-butene (from which it arose) is known to contaminate methylenecyclobutane prepared by the zinc debromination of pentaerythrityl tetrabromide. XLVII constituted only about 1% of the total.

General support can be inferred for the assignment of structures XLIV, XLV, and XLVI, since these are the products expected if the addition of bromine goes by way of a carbonium-ion intermediate,[36,49] which in this case might be represented as XLVIII. That the three dibromides are indeed anionotropically related was proved by isomerization studies with zinc bromide. By treatment of mixtures having widely different compositions with zinc bromide at room temperature, it was



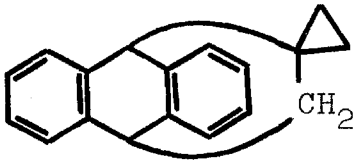
XLVIII

found that the equilibrium constant between the normal adduct XLIV and the 3-ring dibromide XLV is about 5.7 ± 2 in favor of XLIV, as expected from the greater strain in XLV.[36] The concentration of the open chain dibromide XLVI increased in every run, however, so its relative free energy was not determined. The fact that the concentration of XLVII was invariant in these experiments confirms the conclusion that it is not an anionotropic relative of the other three, but merely a contaminant.

The structures of the 3-ring and 4-ring dibromides (XLV and XLIV) were finally confirmed by a study of the nuclear magnetic resonance spectra, carried out by C. A. Reilly of the Shell Development Corp. (see Appendix). By this method it is possible to distinguish and estimate quantitatively the methylene hydrogens of types $C-CH_2-C$ and $C-CH_2-Br$. The ratios of the former to the latter were 0.985 and 2.94 for XLV (theoretical 1.00) and XLIV (theoretical 3.00) respectively.

Miscellany

It was of interest to determine whether strain would have an influence on the ease of removal of anthracene in reverse Diels-Alder reactions. To this end, the dibromide XIV (Fig. 1) was debrominated with zinc to obtain the spirane XLIX. Decomposition of XLIX would be expected to produce



XLIX

methylenecyclopropane, in which the double bond is probably highly strained.[50] However, XLIX proved to be unusually thermostable. It passed through a vertical tube at 450° unchanged and refluxed from the top for several minutes. By contrast, 3-methylenetrimethylene oxide (XLIII) was formed rapidly when XLII was heated to 350°, and the preparation of 3-methylenecyclobutanecarboxylic acid (XVIII) from XVII was at least as easy.

The formation of compounds with completely unstrained double bonds by pyrolysis of the diester XII and the diol XIII was particularly easy. There was vigorous decomposition when samples were heated to 300-330°. The products of these pyrolyses were not analyzed.

III. EXPERIMENTAL

All melting points are corrected and were determined in a Hershberg apparatus using National Bureau of Standards calibrated thermometers. Boiling points are not corrected. Analyses are by S. M. Nagy and his staff, Microchemical Laboratory, Massachusetts Institute of Technology, and Dr. A. Elek, Los Angeles, California

3-Chloro-2-chloromethyl-1-propene (*X*). *A*. *From Pentaerythritol*.--Following the procedure of Mooradian and Cloke,[52] X was prepared in 26% overall yield from 136 g. (1 mole) of pentaerythritol; b.p. 134-137°, n^{24}D 1.4748.

B. *From methallyl chloride*.--Methallyl chloride (181.0 g., 2 moles) was placed in a 500-ml. three-necked flask fitted with a glass, mechanical stirrer. Chlorine was bubbled rapidly into the cooled, well-stirred liquid. For about 2.5 hours, no chlorine escaped from the solution (vapor tested for bleaching action on wet litmus paper) and the solution increased in weight by 70 g. (approximately the theoretical expectation). The product, 247 g., was distilled from a modified Claisen flask at 50 mm. After a small fore-run of about 0.5 g., two main fractions were collected: (1) 141.0 g., b.p. 58-68°; (2) 35.5 g., b.p. 68-85° (mostly 82-85°). The first fraction was primarily dichloro compounds and the second 2-methyl-1,2,3-trichloropropane.[53] The residue was

60.0 g.

The first fraction was fractionally distilled through a 120-cm. column packed with glass helices and fitted with a total reflux head. Two isomers were separated, one boiling at 54-55° (50 mm.)(36.1 g., $\underline{n}^{26}D$ 1.4694) and a second at 59.6-60.8° (50 mm.)(48.4 g., $\underline{n}^{26}D$ 1.4735). There was a 17.7 g. intermediate fraction, but infrared spectra showed no cross contamination in the narrow-boiling fractions described. The spectrum of the higher-boiling isomer was identical with that of X prepared by method A. The yield of X was 19.4%. The lower-boiling isomer was 1,3-dichloro-2-methylpropene.[53]

Diethyl 3-Methylenecyclobutane-1,1-dicarboxylate (XI) (attempts).--To a stirred, refluxing solution of 8.6 g (0.22 moles) of potassium in 140 ml. of anhydrous *t*-butanol was added dropwise a mixture of 12.5 g. (0.1 mole) of 3-chloro-2-chloromethyl-1-propene and 16.0 g. (0.1 mole) of redistilled malonic ester. The mixture turned yellow and a precipitate began to form as soon as the addition was started. After about a third of the halide-ester solution had been added, the reaction mixture turned a brick red-brown color. The addition required about 3.5 hrs. and heating was continued for another hour. Neutralization (to phenolphthalein) with acetic acid required about 3.5 ml. (0.06 moles), indicating that the reaction was 80% complete. The main part of the solvent (about 100 ml.) was distilled, and 80 ml. of water was added to dissolve the solid. Benzene was also added to make the separation cleaner. The organic layer was distilled _in vacuo_. After removal of the solvent, 9.0 g. of material boiling at 35-100° (0.2 mm.) was collected. The residue of dark viscous liquid, undistillable at 200° (0.2 mm.), weighed 14.0 g. The distillate was redistilled through a semi-micro column to give approximately a 37% recovery of malonic ester and 0.85 g. of material boiling at 142-144° (11.2 mm.)(n^{25}D 1.4628) which showed no terminal methylene group in the infrared (11.2-11.5 μ) and which contained chlorine in a form unreactive with boiling alcoholic silver nitrate. XLX is a pos-

$$ClCH{=}C(CH_3){-}CH_2{-}CH(CO_2Et)_2$$

XLX

sible structure for this material.

Attempts to use sodium ethoxide as a condensing agent gave similar products, and an attempt to use sodium hydride failed due to reduction of the dihalide (also observed in experiments with trimethylene bromide).

Diethyl 9,10-Ethano-9,10-dihydroanthracene-11,11-dicarboxylate (_XII_).--Diethyl methylenemalonate was freshly prepared by the procedure of Bachman and Tanner[54] (18-23% yields, b.p. 203-210°). XII had been synthesized by the same authors, but experimental details were not given.

To 228.6 g. (1.33 moles) of freshly-distilled diethyl methylenemalonate was added 187 g. (1.05 moles) of anthracene. The mixture was heated under reflux for 9 hours. The temperature of the solution increased from 205° to 224° during this period. The liquid darkened and was fuming at the end of the reaction. The hot solution was poured into 1200 ml. of benzene and the whole allowed to cool. A precipitate of 20 g. of crude anthracene, m.p. 204-212°, was obtained. Excess absolute ethanol was then added to the benzene filtrate and the solution was boiled until all benzene had been removed. When the final solution (about 400 ml.) was cooled, 314.2 g. (85%) of crude VIII separated, m.p. 110-124°. A pure product could be obtained by several recrystallizations, but the consequent reduction in yield made such purification wasteful. The crude diester gave only slightly poorer yields in the following step.

<u>9,10-Ethano-9,10-dihydro-11,11-bis(hydroxymethyl)-anthracene</u> (<u>XIII</u>).--To a slurry of 3.0 g. (0.079 moles) of lithium aluminum hydride in about 180 ml. of anhydrous ether contained in a three-necked flask fitted with a mercury-sealed, Hershberg stirrer, a dropping funnel, and reflux condenser was added slowly a suspension of 15.8 g. (0.045 moles) of XII in 180 ml. ether. The reaction mixture, from which a light-colored sludge separated, was heated and

stirred under reflux overnight. At the end of this time, there was still considerable undissolved sludge. The mixture was cooled to room temperature and 15 ml. water added dropwise. Next was added a solution of 5 g. of concentrated sulfuric acid in 50 ml. water. Two colorless liquid phases resulted. The layers were separated, the ether layer was washed with water and the water layer was washed with ether. The combined ether layers were taken nearly to dryness in vacuo with gentle warming. The residual white moist solid was recrystallized once from benzene (about 300 ml.) to give 10.5 g. (88%) of white crystals, m.p. 169-171°.

A sample of the product was recrystallized again from benzene and dried overnight at 100° and 0.2 mm. pressure. It melted at 171.0-172.2°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.29; H, 6.99.

When a sample of the compound was heated above 300°, bubbles were given off, the decomposition becoming violent at about 330°. The contents of the melting point tube had a strong purple fluorescence after this treatment, indicating the presence of anthracene.

Due to the limited solubility of XII in ether, it was convenient to carry out larger scale runs with addition of XII by Soxhlet extraction, although efficient reflux condensers were required in this procedure.

9,10-Ethano-9,10-dihydro-11,11-bis(hydroxymethyl)-anthracene Bis(benzenesulfonate) (XV).--The procedure was similar to one employed by Herzog.[26] In a three-necked flask equipped with tantalum Hershberg stirrer, thermometer, and dropping funnel was placed a solution of 139 g. (0.523 moles) of XIII (m.p. 170.4-171.6°) in 600 ml. of dry pyridine. Next was added dropwise 224 g. (1.27 moles) of benzenesulfonyl chloride, at such a rate as to maintain the temperature at 30°. A white solid precipitated from the solution when the addition was nearly complete (about 40 minutes). The mixture was stirred overnight at room temperature.

The reaction mixture was poured into a porcelain crock containing 1850 ml. methanol, 930 ml. water, and 730 ml. conc. hydrochloric acid, and immediately worked vigorously with a large pestle to prevent the formation of large chunks. After the mixture had cooled, it was filtered and washed with water to obtain 272.9 g. (96% yield) of XV, m.p. 140-143.5° with shrinking at 139°.

A sample was recrystallized once from methanol, once from ethanol, and once from acetone-ethanol, and dried *in vacuo* at 100°; m.p. 144.5-145.9°.

Anal. Calcd. for $C_{30}H_{26}O_6S_2$: C, 65.91; H, 4.80. Found: C, 66.00; H, 4.82.

9,10-Ethano-9,10-dihydro-11,11-bis(bromomethyl)-anthracene (XIV).--A mixture of 16.4 g. (0.03 moles) of XV, 31.8 g. (0.3 moles) of sodium bromide, 0.318 g. (0.003 moles) of sodium carbonate, and 60 ml. of reagent grade diethylene glycol was heated and stirred at 150° for 18 hrs. The reaction mixture was poured into 180 ml. of water, and 11.1 g. of crude, nearly colorless XIV, m.p. 130-148° precipitated. The product was recrystallized from ethanol to give 9.49 g. (81%) of white crystals, m.p. 149.9-151.5° with shrinking at 147°. A sample was recrystallized again from ethanol and dried overnight at 100° and 1 mm. The m.p. was then 150.0-150.8°.

Anal. Calcd. for $C_{18}H_{16}Br_2$: C, 55.13; H, 4.11. Found: C, 55.28; H, 4.05.

Shorter reaction times or lower sodium bromide concentrations gave incomplete reaction,and unreacted XV and the intermediate monobromo benzenesulfonate, m.p. 173.6-175.4° (from benzene-ethanol) were isolated.

Anal. Calcd. for $C_{24}H_{21}O_3BrS$: C, 61.41; H, 4.51. Found: C, 61.27; H, 4.55.

Omission of the sodium carbonate resulted in tar formation.

Reaction of the diol XIII with phosphorus tribromide at 70° gave a dark, tarry solid from which only a trace of XIV could be isolated by sublimation. A mixed melting point with the material prepared above showed no depression.

2,3,5,6-Dibenz-spiro[bicyclo(2.2.2)octane-7,1'-cyclobutane]-3',3'-dicarboxylic acid (XVI).--In a 100-ml. three-necked flask equipped with reflux condenser and stirrer were placed 50 ml. of *t*-amyl alcohol (distilled from quicklime and from potassium) and 1.31 g. (0.0336 g.-atoms) of potassium. After the mixture had refluxed for 5.5 hrs., only a cloudy suspension remained. Next was added 5.40 g. (0.0336 moles) of redistilled malonic ester, which caused a heavier white precipitate to separate, and finally 4.40 g. (0.0112 moles) of the dibromide XIV. The mixture was refluxed and stirred for 171 hrs. and then was neutralized with acetic acid. Water (30 ml.) was added and two liquid phases and a white solid separated. The solid amounted to 2.91 g. and was recrystallized from ethanol to give 1.83 g. of white crystals of XIV, m.p. 143.8-151.6°. An additional 0.30 g. of recovered XIV, m.p. 144.5-150.2°, crystallized from the organic phase on standing. The total recovery of XIV was 48%. A Volhard titration on the aqueous phase showed that it contained 0.00427 moles of ionic bromine, which represented 19.1% of the starting halide.

The volatile and non-volatile esters in the remaining organic phase were separated by distillation *in vacuo* (0.2 mm., bath temp. up to 100°). The volatile esters were redistilled through a semimicro column:

Frac.	Temp.	Press.	Wt., g.	$n^{25}D$
1	26-87°	15.1 mm.	0.01	-
2	90-95	"	0.42	1.4118
3	95-103	"	0.56	1.4143
4	103-105.5	"	0.57	1.4164
5	105-107	"	0.31	1.4184
Residue			0.01	

The infrared spectrum of Frac. 2 was substantially the same as that of malonic ester. That of Frac. 5 was still very similar to that of malonic ester, but showed a few significant differences in the relative intensities and frequencies of bands. It seemed likely that the higher-boiling esters were *t*-amyl malonates formed by ester interchange. To test this hypothesis, a few drops of Frac. 5 was heated under reflux with 1 ml. of a saturated solution of *p*-toluenesulfonic acid in benzene. An unsaturated vapor (presumably pentenes) which decolorized moist permanganate paper, came out of the condenser. The same treatment of malonic ester gave no such vapor.[56]

The non-volatile ester product from the first distillation was heated under reflux for 2 days with 10 ml. of 6 *N* hydrochloric acid. The solvent was then distilled. The residue was dissolved in excess 10% sodium hydroxide and the solution was washed twice with ether. The aqueous phase was decolorized and filtered twice with Norit, but remained quite dark. It was acidified with hydrochloric acid to precipitate 0.18 g. of a tan solid which on recrystallization from benzene gave a dark, insoluble residue (60 mg.) and 57 mg. (1.5%) of white, crystalline XVI, m.p. 183.2-190.0° with gas evolution. The product was recrystallized again to give 14 mg., m.p. 188.7-189.8° with gas evolution.

Anal. Calcd. for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 74.46; H, 5.78.

2,3,5,6-Dibenz-spiro(bicyclo(2.2.2)octane-7,1'-cyclobutane)-3'-carboxylic acid (XVII).--The residue from the mother liquor of the final recrystallization of the diacid XVI sublimed at 155° (0.2 mm.) overnight, to give 0.026 g. (70% yield) of crude, yellowish XVII. Recrystallization of the product from cyclohexane gave 10 mg. of m.p. 151.8-168°, which was probably a mixture of cis-trans isomers. The infrared spectrum showed associated O-H (broad peak at 5.8 μ), carbonyl stretching at 5.84 μ, and no double bonds or methyl groups.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.77; H, 6.34.

3-Methylenecyclobutanecarboxylic Acid (XVIII).--In a 5-ml. distilling flask was placed 1.56 g. (0.0054 moles) of the acid XVII. An ice-cooled receiver was attached, and a very slow nitrogen stream was allowed to pass through the flask to the receiver. Immersion of the flask in a salt bath at 350° caused immediate decomposition (vigorous boiling). After 35 minutes at this temperature, a distillate of 0.52 g. (87% yield) of yellowish liquid containing a small amount of white solid had collected. The infrared spectrum of the crude product was not changed by redistillation. The purified acid had b.p. 102.5-103° (11 mm.), $\underline{n}^{25}D$ 1.4664. The infrared spectrum showed typical, strong, exocyclic methylene absorption at 11.32 μ, and no methyl absorption near 7.25 μ.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.26; H, 7.15.

3-Methylenecyclobutanecarbonyl Chloride (XIX).--A solution of 5.49 g. (3.32 ml., 0.0461 moles) of thionyl chloride and 4.47 g. (0.0399 moles) of acid XVIII in 20 ml. of chloroform (dried over calcium chloride) was heated under reflux overnight. The colorless reaction mixture was distilled through a semi-micro column, to give 4.72 g. of crude XIX, b.p. 71-90° (82 mm.)(90%), collected in four fractions.

An anilide was prepared[57] and recrystallized from alcohol-water; m.p. 146.7-147.8° with shrinking at 145.5°.

Anal. Calcd. for $C_{12}H_{13}ON$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.80; H, 6.85; N, 7.61.

Ethyl N-(3-Methylenecyclobutyl)carbamate (XX).--To a cooled, swirled solution of 26 g. (0.2 moles) of XIX in 100 ml. of reagent-grade acetone was added 15.8 g. (0.243 moles) of sodium azide dissolved in 45 ml. of water. The mixture was poured into 300 ml. of water, and the colorless liquid azide separated with the aid of 50 ml. of benzene. The organic layer was added to a 2-l. flask containing 400 ml. of refluxing anhydrous ethanol and fitted with a reflux condenser, a pressure-equalized dropping funnel, and an azotometer. No heat was supplied during the addition, which required only a few minutes. The reaction was then completed by heating under reflux for 30 min. This process was repeated by addition of four more batches of azide to the same ethanol solution. A total of 122.3 g. (0.938 moles) of acid chloride XIX and 74 g. (1.14 moles) of sodium azide was used. In all, 19.45 l. (82.4%) of nitrogen was collected (over water). The solvent was removed *in vacuo* to leave 147.3 g. (101% yield) of crude, partly solidified XX.

Most of the crude material was hydrolyzed to the amine without purification, but a small sample was recrystallized from cyclohexane for analysis; m.p. 58.0-59.0°.

Anal. Calcd. for $C_8H_{13}O_2N$: C, 61.91; H, 8.44. Found: C, 61.85; H, 8.38.

3-Methylenecyclobutylamine (*XXI*).--A solution of 50 g. (0.322 moles) of crude XX and 144 g. (2.57 moles) of potassium hydroxide in 400 ml. of methanol was heated under reflux for 2 hours. The cooled reaction mixture was diluted with 1500 ml. water and shaken with 200 ml. methylene chloride. The aqueous layer was removed and extracted with four more

100-ml. portions of methylene chloride. The methylene chloride fractions were combined and extracted with a solution of 3 moles of 3 N hydrochloric acid. The acidic solution was basified with 140 g. of sodium hydroxide in 300 ml. of water (slowly, with ice cooling) and extracted with 600 ml. of ether in five portions. The ether extracts were combined and dried over sodium sulfate followed by barium oxide. Distillation through a 61-cm. Podbielniak (spiral wire) column gave 10 g. (37% yield) of XXI, b.p. 107-108°, $\underline{n}^{24}D$ 1.4662.

Anal. Calcd. for C_5H_9N: C, 72.24; H, 10.91. Found: C, 71.64; H, 10.83.

The infrared spectrum showed typical exocyclic methylene bands at 5.93 μ and 11.36 μ, but there was also a band in the C-methyl region (7.22 μ). However, the benzamide derivative was prepared[58] and found to show only the exocyclic methylene group (11.28 μ). The benzamide was recrystallized from ethanol-water; m.p. 145.5-146.4° with shrinking at 144°.

Anal. Calcd. for $C_{12}H_{13}ON$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.77; H, 6.94; N. 7.53.

Attempts to discover the fate of the urethane not converted to XXI revealed only that it was not present in a form which could be extracted from aqueous solution, acidic or basic. The possibility that XXI was lost as an azeotrope during solvent removal was ruled out.

When the diluted reaction mixture was extracted with ether instead of methylene chloride, large amounts of alcohols were removed with the amine. Direct distillation of the methylene chloride extract, on the other hand, proved impractical due to a tar-producing reaction of methylene chloride with the amine when the solution was heated.

<u>3-Methylenecyclobutyltrimethylammonium Iodide</u> (<u>XXII</u>).--In a three-necked flask fitted with reflux condenser, stirrer, and dropping funnel was placed a solution of 13.5 g. (0.163 moles) of the amine XXI in 30 ml. of methanol. To this solution was added slowly 96 g. (0.68 moles) of methyl iodide dissolved in 100 ml. methanol. Finally, 27.2 g. (0.485 moles) of potassium hydroxide in 130 ml. methanol was added dropwise with stirring at such a rate as to maintain the temperature between 30 and 35°. The addition required about 10 minutes. The solution turned cloudy a few minutes after the addition was begun. The mixture was then heated under gentle reflux for 3 hours. The solvent was removed *in vacuo* at 40°. The dry, solid residue was transferred to a Soxhlet thimble and extracted continuously with chloroform for three days to give 36.4 g. (89%)of XXII, m.p. 201.9-207.3°. A sample was recrystallized from absolute ethanol for analysis; m.p. 207.6-208.1° with shrinking at 205°.

Anal. Calcd. for $C_8H_{16}NI$: C, 37.96; H, 6.37; N, 5.53. Found: C, 37.87; H, 6.45; N, 5.62.

<u>Methylenecyclobutene</u> (<u>I</u>).--To a solution of 36.2 g. (0.143 moles) of the quaternary salt XXII in the minimum

amount of water was added a suspension of the freshly prepared silver oxide made by mixing aqueous solutions of 53.0 g. (0.312 moles) of silver nitrate and 20.7 g. (0.37 moles) of potassium hydroxide. The precipitated silver oxide had been washed with distilled water by decantation ten times. The reaction mixture was shaken until the supernatant solution was clear, then filtered rapidly with suction in a nitrogen atmosphere. The filtrate was concentrated to a volume of about 50 ml. in vacuo at 30°. A two-necked flask fitted with a dropping funnel and connected to a vacuum pump by way of a large Dry-Ice trap was evacuated to 46 mm. and heated in an oil bath at 160°. The concentrated solution of quaternary hydroxide was then added dropwise. The reaction was rapid and there was no appreciable non-volatile residue. To the cold distillate was added 200 ml. of 1 N hydrochloric acid. As soon as the ice had melted, the two liquid phases were swirled briefly and the aqueous phase removed. The organic phase was dried over Drierite and distilled rapidly through a semimicro column from hydroquinone. The yield of I was 5.82 g. (68%), b.p. 35.0-35.2°, $n^{25}D$ 1.4482. During the distillation, considerable tough, rubbery polymer formed in the column. The polymer was insoluble in common solvents.

A sample of I was dried and redistilled in vacuo for analysis.

Anal. Calcd. for C_5H_6: C, 90.85; H, 9.15. Found: C, 90.87, 90.74; H, 9.12, 9.16.

Combustion of I was very difficult because the polymer, which formed rapidly on warming, burned slowly. Low analyses were obtained under routine conditions on I and on the other methylenecyclobutenes (XXVIII and XXX; see p.51 and p.52).

An ultraviolet spectrum of I in isooctane solution showed λ_{max} 221 mμ, ϵ = 11,400.

Methylcyclobutane. A. From Methylenecyclobutane.--A 0.6272 g. sample of methylenecyclobutane was weighed in a sealed ampule. The ampule was broken in the flask of a semimicro atmospheric pressure hydrogenation apparatus, which already contained 0.0553 g. of platinum oxide and 20 ml. of acetic acid, and the mixture was frozen with Dry Ice. The system was degassed, filled with hydrogen and the flask warmed to room temperature for the hydrogenation reaction. The sample absorbed 250 ml. (104% of theory for one double bond, corrected for catalyst) of hydrogen in 115 min., at which point the reaction was complete.

The reaction mixture was put in a test tube with a side-arm and a slow nitrogen stream passed through the liquid. The exit gases were then passed through concentrated sodium hydroxide solution, through a drying tube containing calcium chloride and sodium hydroxide, and finally condensed in a weighed vial at Dry-Ice temperature. The yield of clear, liquid hydrocarbon was 0.44 g. (68%). An infrared spectrum was essentially the same as the published spectrum of methylcyclobutane.[59]

B. From Methylenecyclobutene (I).--When methylenecyclobutene was hydrogenated by the same procedure, 0.5056 g. of I with 0.0550 g. of platinum oxide absorbed 378 ml. of hydrogen (96% of theoretical for two double bonds) in 100 minutes and no additional hydrogen in 20 minutes more. The isolated methylcyclobutane amounted to 0.32 g. (60%) and had an infrared spectrum virtually identical with that of the product from methylenecyclobutane.

1-Amino-2,2-dimethyl-3-(aminomethyl)cyclobutane Dihydrochloride (XXVI).--To a stirred solution of 3.40 g. (0.0183 moles) of crude dl-pinic acid[30,60] (XXV)(m.p. 80-96°) in 7 ml. sulfuric acid was added 27.2 ml. (0.04 moles) of 1.47 M hydrazoic acid in chloroform, at such a rate as to maintain the temperature below 45°. The mixture was stirred and kept at 45-47° for seven hours. At the end of this time, another 6 ml. (0.0088 moles) of hydrazoic acid solution was added, and the heating was continued for three hours. A total of 1600 ml. (87%) of gas was evolved.

The cooled reaction mixture was diluted with ice and the chloroform layer removed. The aqueous layer was washed with ether and basified with sodium hydroxide. Continuous extraction with ether for two days followed by extraction of the ether with 50 ml. of 2.4 N hydrochloric acid and evaporation of the acidic extract to dryness in vacuo gave 3.0 g. (82%) of crude XXVI. A sample recrystallized from methanol-ethanol decomposed slowly between 250 and 300°, with no definite melting.

Anal. Calcd. for $C_7H_{18}N_2Cl_2$: Cl, 35.25. Found: Cl, 35.56.

A benzamide was prepared,[58] but several recrystallizations from benzene and ethyl acetate-cyclohexane gave material which melted at 147.4-154.7° and was probably a mixture of stereoisomers.

Anal. Calcd. for $C_{21}H_{24}O_2N_2$: C, 74.97; H, 7.19. Found: C, 75.41; H, 7.31.

2,2,N,N,N',N'-Hexamethyl-1-amino-3-(aminomethyl)cyclobutane (XXIX).--A mixture of 15 g. (0.0742 moles) of crude XXVI, 107 ml. (1.29 moles) of 36% formaldehyde, and 44.7 ml. (53.8 g., 1.05 moles) of 90% formic acid was heated under reflux for 4 hrs. The reaction mixture was concentrated to small volume on a steam bath and the amine was liberated with excess 40% sodium hydroxide. The oil was taken up in ether, dried over barium oxide, and distilled from barium oxide in a modified Claisen apparatus. After a small forerun, 10.1 g. (74%) of XXIX was collected at 114-117° (51 mm.), $n^{25}D$ 1.4482.

An infrared spectrum of XXIX showed a medium band in the carbonyl region (5.58 μ); in spite of precautions to prevent contamination by carbon dioxide.

Anal. Calcd. for $C_{11}H_{24}N_2$: C, 71.67; H, 13.13. Found: C, 69.81; H, 12.69.

A picrate was prepared and recrystallized twice from aqueous ethanol. The maximum temperature at which a fresh sample survived decomposition for 20 seconds was 218°.

Anal. Calcd. for $C_{23}H_{30}N_8O_{14}$: C, 42.99; H, 4.71 Found: C, 43.21; H, 4.84.

2,2,N,N,N',N'-Hexamethyl-1-amino-3-(aminomethyl)cyclobutane Bis(methiodide) (*XXVII*).--To a solution of 2.8 g. (0.02 moles) of methyl iodide in 1 ml. methanol was added, with cooling, a solution of 0.73 g. (0.00396 moles) of XXIX in 2 ml. methanol. The mixture was allowed to stand for about 12 hours, after which the solvent was replaced with ethanol by addition of excess ethanol and concentration of the resulting solution. The cooled concentrate deposited 1.31 g. (70%) of a colorless, neutral, hygroscopic solid. A sample was recrystallized from absolute ethanol and had m.p. 272°d. (the highest temperature at which a fresh sample survived decomposition for 20 sec.).

Anal. Calcd. for $C_{13}H_{30}N_2I_2$: C, 33.35; H, 6.46. Found: C, 33.08; H, 6.33.

In other runs, the solvent was removed *in vacuo* and the next step then carried out directly on the residual material on the assumption that the yield of methiodide (XXVII) was quantitative. XXVII was prepared also in 6%

yield by direct exhaustive methylation of XXVI.[61] The insolubility of XXVII in chloroform prevented convenient separation of the product from the accompanying potassium salts.

4,4-Dimethylmethylenecyclobutene (XXVIII).--The procedure was the same as that used in the preparation of methylenecyclobutene (p. 45).

The quantities used were 6.78 g. (0.0368 moles) of freshly-distilled di-tertiary amine XXIX, 26 g. (0.259 moles) of methyl iodide, 28.0 g. (0.164 moles) of silver nitrate and 10.9 g. (0.193 moles) of potassium hydroxide. The yield of dried, vacuum-distilled product was 1.81 g. (52% overall from XX). Of this material, 0.80 g. was distilled rapidly through a semimicro column at 740 mm. from hydroquinone to give 0.73 g. of distillate, b.p. 65-65.7°, $n^{25}D$ 1.4284.

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71; C/H ratio, 8.34. Found: C, 88.36; H, 10.56; C/H ratio, 8.37. (See p. 47).

An ultraviolet spectrum showed λ_{max} 229 mμ, $\epsilon = 8600$, in ethanol.

Allene.--Part of the allene used in this investigation was generously provided by the Union Carbide and Carbon Corp., and the rest was prepared by a modification of a reported procedure[63,64] as follows: To a boiling, stirred suspension of 45.6 g. (0.7 g.-atoms) of zinc dust in 70 ml. of 80% ethanol was added 33.3 g. (0.3 moles) of 2,3-dichloropropene at such a rate as to maintain refluxing. The mixture was heated under reflux for 45 min. after addition had been completed. The allene was passed through water and calcium chloride before condensation in a Dry-Ice trap. The product was 11.5 g. (96%). An infrared spectrum showed that the allene was nearly pure, though there was one small band at 8.44 µ not characteristic of allene.[65]

<u>3-Phenylmethylenecyclobutene</u> (<u>XXX</u>).--A mixture of 10.8 g. (0.106 moles) of phenylacetylene, 5 g. (0.125 moles) of allene, and 50 mg. of 1,4-naphthoquinone was heated in a sealed tube for 24 hrs. at 150°, giving a clear, red liquid. When the tube was opened, about 4 g. (80%) of allene (infrared spectrum) boiled out. The viscous residue (11.2 g.) was distilled at 0.2 mm., bath temp. up to 200°, to give 6.1 g. of distillate and 5.0 g. of undistillable residue. The distillate was redistilled through a semimicro column to give 5.6 g. (51%) of phenylacetylene, b.p. 63-64° (50 mm.), and 0.07 g. of XXX, b.p. 78-79° (4.5 mm.), m.p. 10-12°, $\underline{n}^{25}$D 1.5987.

<u>Anal</u>. Calcd. for $C_{11}H_{10}$: C, 92.91; H, 7.09. Found: C, 88.75; H, 7.12.

The C/H ratio is 12.47 compared with 13.10 calculated for XXX, 8.94 for allene, 15.89 for phenylacetylene, and

11.91 for a compound from one phenylacetylene and two allene molecules. The boiling point would appear too low for the last, which would be a fourteen-carbon hydrocarbon,[66] however.

An ultraviolet spectrum in isooctane showed maxima at 212 mμ, $\epsilon = 4600$; 219 mμ, $\epsilon = 3760$; 225 mμ, $\epsilon = 3960$; 233 mμ, $\epsilon = 3640$; 291 mμ, $\epsilon = 7250$.

The use of solvents (chloroform, benzene), other polymerization inhibitors (trinitrobenzene, hydroquinone), or lower reaction temperature (130°) failed to improve the yield of XXX.

Bromination of Methylenecyclobutene.--A solution of 3.26 g. of methylenecyclobutene (I) in 25 ml. of carbon tetrachloride was titrated at 0° with a 10% (1.94 M) solution of bromine in carbon tetrachloride. The endpoint was fairly sharp and 25.00 ml. (0.98 moles per mole of hydrocarbon) of bromine solution was required. Very little hydrogen bromide was evolved. An infrared spectrum (see Appendix) was taken on the reaction mixture after it had been concentrated slightly *in vacuo* to remove hydrogen bromide.

The dibromide was distilled through a 61-cm. Podbielniak (spiral-wire) column with total reflux head.

Frac.	Temp.	Press.,mm.	Wt., g.	$n^{25}D$
1	49.0-50.0°	5.0	1.32	1.5487
2	49.0-49.0	5.0	1.29	1.5489
3	49.0-49.0	5.0	0.14	1.5488
4	58.0-70.0	5.0	0.63	1.5514
5	70.0-73.2	5.0	0.72	1.5608
6	73.2-74.0	5.0	0.57	1.5662
7	74.0-74.0	5.0	1.86	1.5697
8	73.0-74.0	5.0	1.56	1.5688

Fractions 1-3 were shown by their infrared spectra to be the rearranged dibromide XXXI. The spectra of fractions 7 and 8 were very much like that of the crude bromination product, although definite contamination by XXXI was evident. Fraction 2 reacted very slowly with sodium iodide in acetone to give a yellow solution and, after several hours, a slight precipitate. Fraction 7 reacted rapidly with the same reagent to give a white precipitate and a red solution. Both fractions reacted rapidly with alcoholic silver nitrate and with potassium permanganate in acetone.

Rearrangement occurred when the distilled dibromides were allowed to stand for four days (generally in a refrigerator) and, at the end of this interval, Fractions 2 and 7 were found to have identical infrared and ultraviolet spectra. The infrared spectra of the pure liquids in a 0.05-mm. cell were analyzed by the base-line optical density method,[67] with the aid of the band at 5.94 μ characteristic of XXXI. The equilibrium mixture was 49% of XXXI and 51% of the other isomer (probably XXXII). Rapid changes in the composition of non-equilibrium mixtures were induced by treatment of the mixtures with zinc bromide at 100° for a few minutes.

An ultraviolet spectrum of freshly-distilled XXXI showed λ_{max} 206 mμ, $\epsilon = 6260$. The spectrum of the equilibrium mixture showed λ_{max} 207 mμ, $\epsilon = 7170$. It was calculated from these spectra and the equilibrium concentrations determined above that the spectrum of pure XXXII would show λ_{max} ca. 208 mμ, $\epsilon = 8130$. A similar calculation from the infrared and ultraviolet spectra of a non-equilibrium mixture gave for XXXII a λ_{max} ca. 208 mμ, $\epsilon = 8200$.

To confirm that the substances are isomeric dibromides, analyses were obtained on XXXI (a) and on a high-boiling fraction rich in XXXII (b).

Anal. Calcd. for $C_5H_6Br_2$: C, 26.58; H, 2.68. Found: (a), C, 26.54; H, 2.67. (b), C, 26.53; H, 2.60.

Bromination of 4,4-dimethylmethylenecyclobutene (XXVIII) was carried out in the same manner as for methylenecyclobutene. A 0.1359 g. sample of XXVIII required 0.795 ml. of 1.94 M bromine (1.06 moles of bromine per mole of XXVIII) to reach the endpoint. From 1.65 g. (0.0176 moles) of XXVIII was obtained 3.81 g. (81%) of dibromide, distilled through a semimicro column and collected in five fractions, b.p. 75-89° (5 mm.), n^{25}D 1.5298-1.5440. The infrared spectra of the fractions revealed that there were several substances in the distillate, and that none of the fractions was pure. The middle fraction was analyzed.

Anal. Calcd. for $C_7H_{10}Br_2$: C, 33.10; H, 3.97. Found: C, 33.12; H, 4.00.

To a sample of crude dibromide from 0.1359 g. (1.445 millimoles) of XXVIII was added 2 ml. of benzene followed by 1 ml. of a 20% solution of trimethylamine in benzene. A white precipitate formed immediately. The mixture was allowed to stand overnight, after which the solvent and excess trimethylamine were removed in vacuo to leave 0.17 g. of white solid. A portion of the solid was recrystallized twice from ethanol-benzene to give white crystals which decomposed at 182° (maximum temperature at which a fresh sample survived decomposition for 20 sec.).

Anal. Calcd. for $C_{10}H_{19}NBr_2$: C, 38.36; H, 6.12. Found: C, 38.73; H, 6.26.

A small amount (ca. 50 mg.) of the quaternary bromide was converted to the picrate by addition of warm, aqueous sodium picrate to an aqueous solution of the quaternary bromide.[68] The precipitate was recrystallized from methanol to give first a very small amount of amorphous solid, m.p. 153-200°, followed by radial clusters of elongate prisms, m.p. 128.3-128.7°. The latter substance was analyzed.

Anal. Calcd. for $C_{16}H_{21}N_4O_7Br$: C, 41.66; H, 4.59. Found: C, 42.09; H, 4.48.

Radical Polymerization of Methylenecyclobutene.--Samples of methylenecyclobutene (I) allowed to stand at room temperature for 12-36 hrs. in sealed ampules formed colorless, transparent, rubbery polymers. Attempts to inhibit the polymerization with hydroquinone or naphthoquinone failed, but addition of 2,2-diphenyl-1-picrylhydrazyl to a sample of I inhibited the polymerization to such an extent that there was still liquid in the sample after two weeks at room temperature.[69,70] Polymerized I was insoluble in carbon tetrachloride, chloroform, ethylene dichloride, and m-cresol. The insolubility prevented infrared-spectrum determination by the conventional methods used on rubbers.[71] To obtain a spectrum, a partially polymerized sample (a clear, viscous fluid) was spread quickly on a salt block. A hard film formed rapidly as the unreacted monomer evaporated.

3-Phenylmethylenecyclobutene (XXX) also polymerized in a few hours to a few days at room temperature to form a viscous, yellow material. 4,4-Dimethylmethylenecyclobutene (XXVIII), by contrast, on one occasion stood for several days at room temperature without visible change, though a white polymer precipitated in one day from another sample. XXVIII also showed less tendency to polymerize during distillation than did I.

Anionic Polymerization of Methylenecyclobutene.--About 0.24 g. (0.00354 moles) of methylenecyclobutene (I) was added to a solution of 0.00354 moles of sodium amide in 5 ml. of liquid ammonia. The brown color of the solution rapidly changed to a light green, and a green solid precipitated. The ammonia was allowed to evaporate, and to the multicolored residue was added 8 ml. of anhydrous ether and 4 g. of pulverized Dry Ice. After the mixture had warmed to room temperature, 10 ml. of water was added and the layers were separated. The aqueous phase was acidified to pH 2 and extracted with ether, but evaporation of the ether left no residue. The original ether phase (containing any basic and neutral materials) was evaporated to leave 0.22 g. (92%) of yellowish, sticky, non-volatile polymer. The polymer was soluble in chloroform so it was possible to take an infrared spectrum (see Appendix) in solution.

A similar product was obtained through the reaction of I with potassium amide in liquid ammonia (106% yield of crude polymer, non-volatile at room temperature and 1 mm.). A small amount of a bright-blue solid (possibly an inorganic iron compound) precipitated on acidification of the aqueous portion of the reaction, but there was not enough for characterization.

When a sample of methylenecyclobutene was added to a solution of excess methyllithium[72] in 80% xylene-20% ether, there was no evolution of methane, and unreacted I was detected in ether solution by the infrared spectrum). Under the same conditions, a sample of t-butanol reacted with methyllithium to produce 100% of the theoretical methane in 15 min. and crude cyclopentadiene gave 67% of the theoretical methane (for one active hydrogen) in 18 min. The gas evolution was measured in a semimicro hydrogenation apparatus.

Cationic Polymerization of Methylenecyclobutene.--A tiny stream of boron trifluoride was introduced through a capillary tube into a centrifuge tube containing 0.1 ml. of methylenecyclobutene. A brownish, translucent, filmy polymer deposited immediately when the boron trifluoride vapor came in contact with the liquid. The polymer was insoluble in carbon tetrachloride and in chloroform, but an infrared spectrum (see Appendix) was obtained from some of the fragile film spread between two salt blocks. The air space between the blocks was filled with carbon tetrachloride to reduce light scattering, and carbon tetrachloride bands therefore appear in the spectrum at 6.47 μ and 13 μ.

An attempt to induce polymerization of methylenecyclobutene with anhydrous aluminum bromide gave no visible reaction.

Methylenecyclobutane Dibromides.--The dibromide mixture was prepared by addition of 73.6 g. (0.46 moles) of bromine in 50 ml. of carbon tetrachloride to a stirred solution of

34 g. (0.5 moles) of methylenecyclobutane[73] (b.p. 41.0-42.0° (739 mm.)) in 100 ml. of carbon tetrachloride. The temperature of the reaction mixture was kept between -5° and -2° with an ice-salt bath. There was slight hydrogen bromide evolution. The reaction mixture was first distilled through a modified Claisen apparatus to give a forerun, b.p. 28-48° (3.4 mm.), 6.2 g.; the dibromide mixture, b.p. 48-59° (3.4 mm.), 72.3 g. (69%); and a dark residue, 12.3 g. The dibromide fraction was unsaturated to permanganate in acetone.

Part of the crude dibromide mixture was used in reactions with bases (p. 27) and the rest was kept in a refrigerator for eight months before it was distilled through a 61-cm. Podbielniak column with total reflux head:

Frac.	Temp.	Press.,mm.	Wt.,g.	$\underline{n}^{25}D$
1	53-54°	4.1-4.2	1.19	1.5339
2	54.5-56.6	4.4-4.9	2.90	1.5358
3	56.6-57.0	4.9-5.1	2.60	1.5366
4	57.0-57.6	5.1-5.0	1.76	1.5369
5	57.6-58.3	5.1	2.67	1.5370
6	58.9-60.7	5.2	2.90	1.5371
7	61.0-61.5	5.3	1.96	1.5371
8	60.2-60.7	5.1	2.57	1.5370
9	60.7-61.8	5.1-4.8	1.38	1.5367
10	61.9-65.0	4.9-5.4	1.09	1.5362
11	65.0-65.0	5.3-5.2	3.01	1.5362
12	65.0-65.0	5.3	0.49	1.5362
13	65.0-65.0	5.3-5.1	1.23	1.5364
14	64.6-50	5.3-5.1	0.27	1.5369
Residue (dark, tarry)			0.20	

Infrared spectra were taken of Fractions 1, 5, 7, 11, and 14 as pure liquids in a 0.054-mm. cell, and the spectra were analyzed by the base-line method for the four component dibromides, XLIV-XLVII. It was qualitatively evident from the spectra and was therefore assumed for the analysis that Fraction 5 contained only XLIV and XLV, Fraction 7 contained only XLIV, XLV, and XLVI, and Fraction 14 contained only XLV and XLVI. A spectrum of pure XLV was also available. The bands used for analysis were as follows: XLIV, 14.45 μ; XLV, 7.5 μ and 12.07 μ; XLVI, 6.05 μ; and XLVII, 8.85 μ and 10.17 μ. The bands used for XLVII were weak and otherwise unsatisfactory, and the analyses for XLVII are consequently less reliable than those for the other dibromides, which were probably determined to within 5%. The analyses are recorded in Table I. The figures in parentheses are values assumed in accordance with the foregoing assumptions.

Table I

Compositions of Methylenecyclobutane Dibromide Fractions

Compound	Percent Composition by Fractions				
	1	5	7	11	14
XLIV	79.0	(86.4)	68.4	7.7	0.0
XLV	6.7	13.6	28.6	71.3	48.9
XLVI	0.0	0.0	2.6	14.2	(51.1)
XLVII	(14.3)	0.0	0.0	0.0	0.0
Totals	(100.0)	(100.0)	99.6	93.3	(100.0)

Fractions 1-5 were redistilled through the same column in order to obtain a purer sample of XLIV:

Frac	Temp.	Press.,mm.	Wt.,g.	$\underline{n}^{25}D$
1	55.5-55.8°	5.1	0.91	1.5336
2	55.9-56.0	5.2-5.1	1.24	1.5352
3	56.1-56.1	5.1	1.17	1.5367
4	56.1-56.6	5.1	1.30	1.5370
5	56.6-56.7	5.1	1.18	1.5372
6	56.7-56.7	5.1	0.68	1.5372
7	56.7-56.9	5.1	0.91	1.5372
8	58.5-59.8	5.1	0.89	1.5371
9	60.0-61.5	5.1	0.55	1.5367

Residue--negligible

Fractions 1, 3, 4, 6, and 9 were analyzed by infrared, and the results are recorded in Table II.

Table II

Compositions of Methylenecyclobutane Dibromide Fractions

(Second Fractional Distillation)

Compound	Percent Composition by Fractions				
	1	3	4	6	9
XLIV	80.4	89.0	93.0	84.9	57.7
XLV	2.5	4.0	5.5	11.6	38.3
XLVI	0.0	0.0	0.0	0.0	3.2
XLVII	(17.1)	4.7	4.3	0.0	0.0
Totals	(100.0)	97.7	102.8	96.5	99.2

The analytical data from the first distillation (Table I) were plotted against total distillate and the curves were integrated graphically to obtain the approximate overall composition of the dibromide mixture: XLIV, 61%; XLV, 32%; XLVI, 6%; and XLVII, 1%.

Chemical tests on the various fractions from the first fractional distillation (Table I) showed that Fraction 4 was nearly inert to permanganate in acetone, while Fraction 13 reacted rapidly with the same reagent. Fraction 4 reacted with sodium iodide in acetone to give a white precipitate and a red color, both at a moderate rate. Fraction 7 reacted with the same reagent to give a white precipitate readily and a red solution slowly, while Fraction 13 gave a white precipitate rapidly but no red solution. Fractions 4 and 13 reacted rapidly with alcoholic silver nitrate.

An analysis was obtained on Fraction 13.

Anal. Calcd. for $C_5H_8Br_2$: C, 26.34; H, 3.54. Found: C, 26.41; H, 3.58.

Isolation of 1,1-Bis(bromomethyl)cyclopropane (XLV).--A mixture of 8.74 g. of mixed methylenecyclobutane dibromides (over 50% XLV from infrared analysis) and 13.1 g. of powdered potassium hydroxide was heated at 100° for 2.5 hours. The reaction mixture was diluted with ether and filtered. Distillation of the filtrate through a semimicro column gave 2.06 g. of XLV, b.p. 63.7-64.0° (5.1 mm.), $\underline{n}^{25}D$ 1.5346. There was a viscous residue (0.5 g.) and a substantial forerun of lower-boiling, unsaturated material, which was not further investigated. Dibromide XLV was unreactive to permanganate in acetone. It reacted with sodium iodide in acetone at 50° and with alcoholic silver nitrate at room temperature to give precipitates of sodium and silver bromides, respectively.

Anal. Calcd. for $C_5H_8Br_2$: C, 26.34; H, 3.54. Found: C, 26.48; H, 3.55.

Isomerization of Methylenecyclobutane Dibromides.--Fraction 11 of the first fractional distillation (p. 60)(a) and fraction 3 of the second distillation (p.62) (b) were selected for isomerization studies because they contained high concentrations of XLV and XLIV, respectively. In each experiment, a few drops of dibromide mixture was treated with a small amount of powdered zinc bromide at room temperature for 17 hrs. The volatile material was removed *in vacuo* with gentle warming. A very small amount of undistillable tar was formed in each reaction. The spectra of the products were analyzed as previously described (p. 61), and the results are shown in Table III.

Table III

Isomerization of Methylenecyclobutane Dibromides with Zinc Bromide at Room Temperature

Compound	Dibromide Mixtures, Percent Composition (a)		(b)	
	Before $ZnBr_2$	After $ZnBr_2$	Before $ZnBr_2$	After $ZnBr_2$
XLIV	7.7	36.6	89.0	60.9
XLV	71.3	19.2	4.0	8.4
XLVI	14.2	38.2	0.0	20.3
XLVII	0.0	0.0	5.1	5.0
Totals	93.3	94.0	98.1	94.6

If it is assumed that the interconversions of XLIV and XLV are fast relative to the isomerization of either to the open-chain form, XLVI,[49] and that the former interconversions are first-order reactions, then the equilibrium constant for the interconversion of the cyclic dibromides XLIV and XLV is calculated from the data in Table 3 to be 5.7 ± 2.1 in favor of XLIV, the four-membered-ring dibromide. The error was estimated from maximum errors in the infrared analysis and does not include any error inherent in the foregoing assumptions.

3'-Oxa-2,3,5,6-dibenz-spiro[bicyclo(2.2.2)-octane-7,1'-cyclobutane] (XLII).--A solution of 101.1 g. (0.183 moles) of the benzenesulfonate XV (m.p. 140.4-144.6°) and 1.1 moles of sodium ethoxide in 500 ml. of ethanol was heated under reflux for 26 hours. The mixture was poured into about 1.5 l. of water, neutralized with acetic acid, and stirred to prevent formation of large lumps. The white precipitate was collected by filtration and recrystallized twice from ethanol to give 36.1 g. (77%) of XLII, m.p. 130.2-132.6°.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.23; H, 6.55.

Shorter reflux periods gave impure products, unsuitable for preparation of XLIII. XLII was prepared also from the benzenesulfonate XV by treatment with sodium isoamylate in isoamyl alcohol and through the reaction of XV with sodio-malonic ester in isoamyl alcohol.

3-Methylenetrimethylene Oxide (XLIII).--Pure XLII (20 g., 0.0813 moles) was heated in a distilling flask for 105 min. at 340-355°. A slow nitrogen stream was used to sweep the product (3.97 g., 76%) into a Dry-Ice-cooled receiver. Distillation of the combined products from several runs through a 61-cm. Podbielniak column gave material boiling at 70.0° (745 mm.), $n^{25}D$ 1.4306. There were no volatile impurities, but a very small amount of white solid was present in the crude reaction product and appeared in the top of the column during distillation. The solid was identified as a peroxide from the observations that it turned sodium iodide solution red and had a high proportion of oxygen. The peroxide was formed in spite of efforts to carry out all transfers and distillations in nitrogen atmosphere. Analyses on the distilled ether were always low and there was a persistent band, never completely eliminated, in the O-H stretching region of the infrared spectra. These facts were also explained by oxygen absorption.

Anal. Calcd. for C_4H_6O: C, 68.54; H, 8.63. Found: Pure liquid, C, 67.65; H, 8.83. Solid peroxide, C, 40.65; H, 6.79.

One sample of the liquid 3-methylenetrimethylene oxide exploded violently during a combustion, but the heated peroxide just melted and sublimed (125-160°).

A solution of 0.056 g. (0.00080 moles) of XLIII and 0.127 g. (0.00071 moles) of anthracene in 0.5 ml. of benzene was heated at 180° for 8.5 hrs. and 210° for 12 hrs. in a sealed tube. Fractional crystallization from ethanol of the non-volatile product gave 81 mg. of anthracene and 6 mg. of XLII (infrared spectrum).

2,3,5,6-Dibenz-spiro[bicyclo(2.2.2)octane-7,1'-cyclopropane] (XLIX).--A mixture of 2.05 g. (0.00522 moles) of dibromide XIV, 1.32 g. (0.0204 g.-atoms) of zinc dust, and 30 ml. of 85% ethanol was stirred and heated under reflux for 24 hours.[74] Most of the alcohol was distilled, and the residue was diluted with water and extracted with ether. Evaporation of the ether gave 1.15 g. (95%) of crude XLIX, m.p. 110.1-114.1°. Two recrystallizations from ethanol gave material of m.p. 114.6-115.1°.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.84; H, 7.06.

XLIX boils without decomposition at about 300°. When a small sample was distilled into a 6-in. column of 4 mm. tubing, wound with a Chromel-wire heating element and heated to 450°, the XLIX refluxed from the top of the column. No volatile product condensed in an attached Dry-Ice trap, but the cooled solid showed slight purple fluorescence, which indicated that some anthracene was present.

IV. APPENDIX

Electron Diffraction Study of 3-Methylenetrimethylene Oxide (XLIII)

The electron diffraction photographs were taken in an apparatus similar to that described by Brockway.[75] The radial distribution curve (Fig. 4, R) was calculated from the visual curve of E. Goldish, which was similar in its essential features to that of V. Schomaker (Fig. 4, V).[76,77] The theoretical intensity curves (Fig. 4, A-E) were calculated[76] for the models defined by the parameters in Table IV (see Fig. 3).

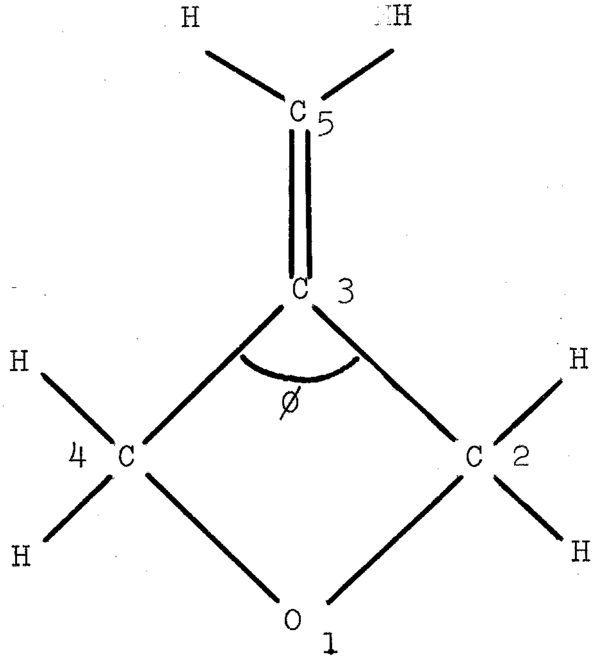


Fig. 3

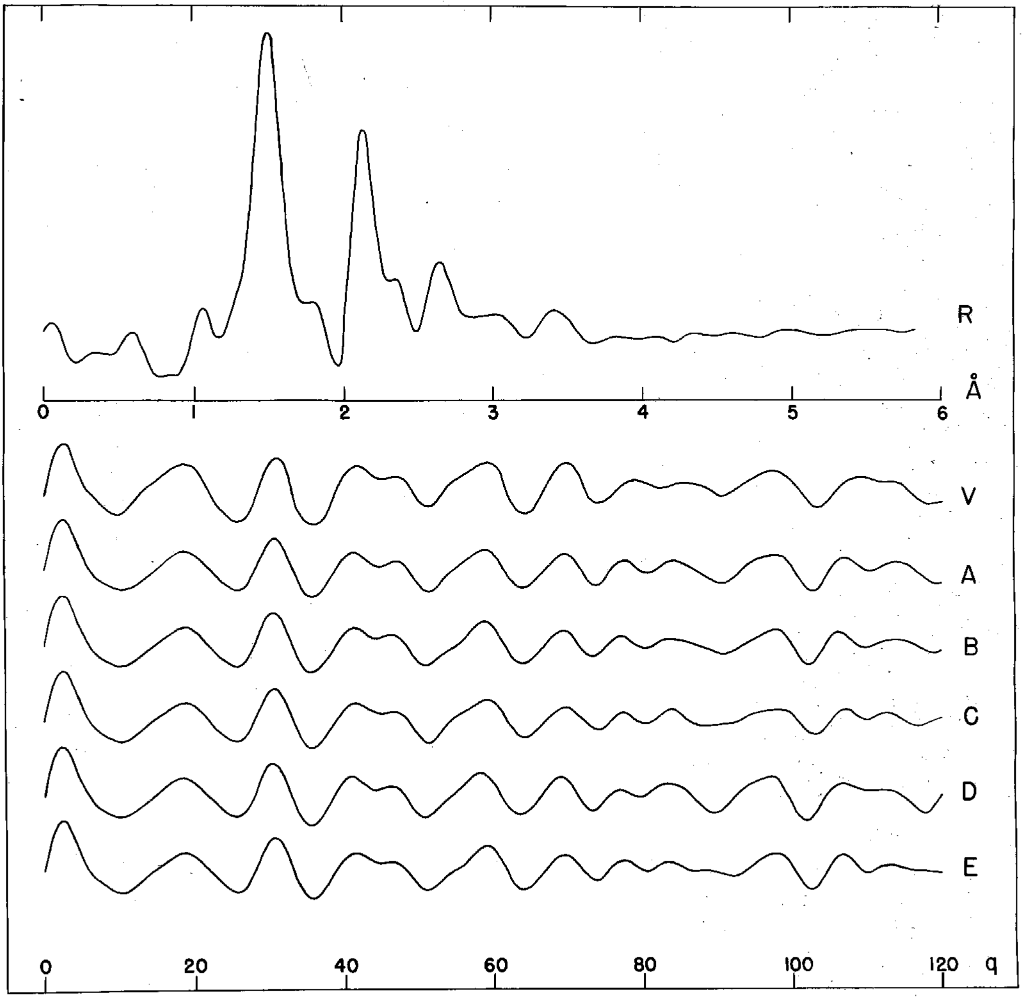


Fig. 4

Table IV

Models of 3-Methylenetrimethylene Oxide Represented in Fig. 4

Model[a]	C_2-C_3(Å)	C_3-C_5(Å)	∅ (°)	C_2-O(Å)	C-H(Å)
A	1.54	1.33	87	1.46	1.09
B	1.54	1.35	87	1.46	1.09
C	1.54	1.35	89	1.46	1.09
D	1.54	1.35	87	1.48	1.09
E[b]	1.54	1.35	87	1.46	1.09

[a] Models A-D are planar except for the hydrogens at C_2 and C_4, where ∠HCH is taken to be 114°,[76] and the hydrogens are assumed to lie on the plane which is perpendicular to the ring and passes through C_2 and C_4. ∠HCH at C_5 is taken to be 120° in every case. [b] Model E is like B except that the oxygen is fixed 0.3 Å above the plane determined by the carbon atoms.

Models A and B were considered the most acceptable planar models. Models C and D illustrate the effects of varying and C_2-O, while E indicates the magnitude of the improvements obtainable by the use of non-planar models or by consideration of out-of-plane bending vibrations. Variations in C-H had very little effect on the theoretical curves. C_2-C_3 was fixed at 1.54 Å in all curves and all other distances were determined relative to this value. A constant scale factor will be computed after final refinements have been made, and the absolute distances will then be calculable. The angle ϕ , of primary interest in the present research, is independent of the scale factor.

Nuclear Magnetic Resonance Data on Methylenecyclobutane Dibromides

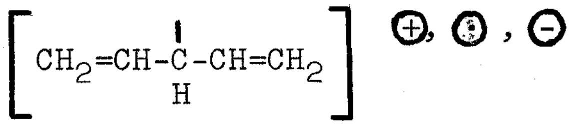
The nuclear magnetic resonance spectra of the two saturated methylenecyclobutane dibromides XLIV and XLV were obtained by C. A. Reilly of the Shell Development Corp., Emeryville, Calif. Also studied as standards were trimethylene dibromide, tetramethylene dibromide, and isobutylene dibromide. All samples were pure except that of XLIV, which was approximately 93% pure (Table II, Frac. 4). Peaks in the spectra due to hydrogens on bromine-bearing carbon atoms were shifted relative to hydrogen peaks due to non-halogenated methylene groups, and relative intensities of the peaks (products of peak intensity and halfwidth) provided a measure of the relative numbers of hydrogens of the two types. The spectra are shown in Fig. 5 and C. R.'s interpretation in Table V. Shielding numbers used for resonance identification are defined according to

$$N = 100 + \frac{\Delta H}{H_R} \times 10^7$$

where ΔH is the difference $(H_C - H_R)$ required to bring nuclei of any particular compound C and of the reference R (water) into resonance.

Molecular Orbital Calculations

All calculations were done by the usual simple LCAO method and with the usual assumptions.[7] In some cases, the calculations were carried only as far as the energies (DE = delocalization energy), but where the charges, bond orders, and free valences were computed, they are shown on the diagrams (Figs. 6-11).



$$\left[\mathrm{CH_2{=}CH{-}\overset{|}{\underset{H}{C}}{-}CH{=}CH_2}\right]^{\oplus,\ \odot,\ \ominus}$$

DE = 1.464β

Fig. 6

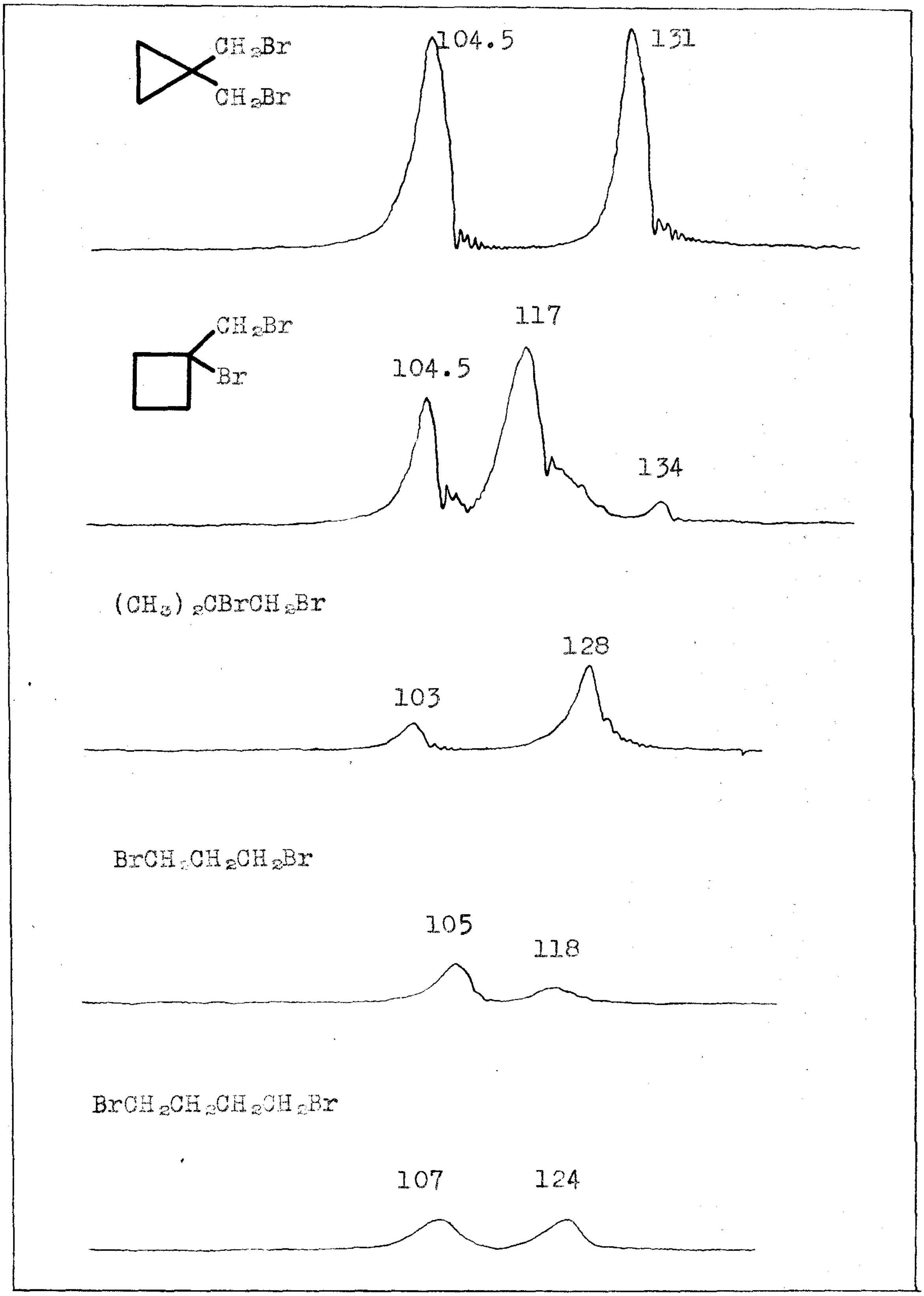
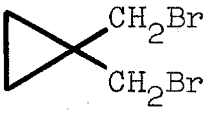
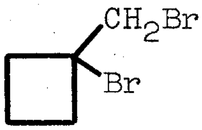
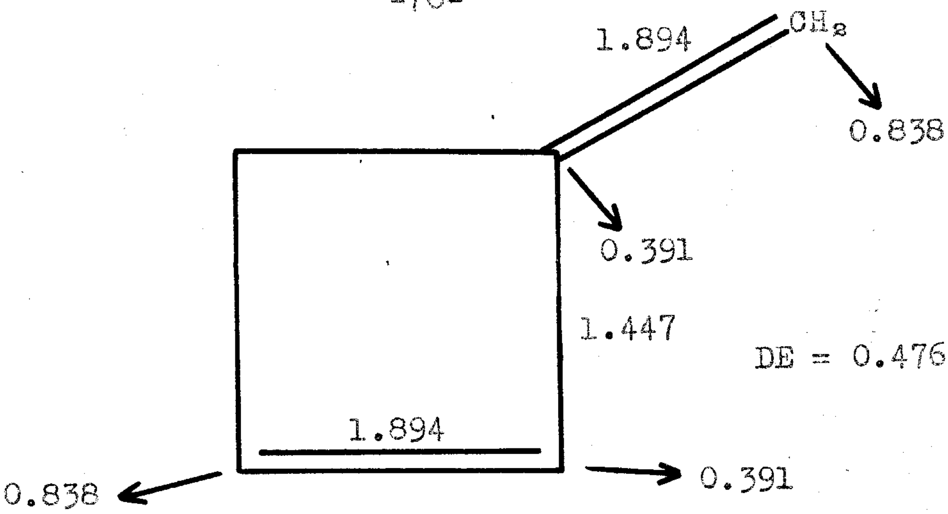

CH₂Br
CH₂Br
104.5
131
CH₂Br
Br
104.5
117
134
(CH₃)₂CBrCH₂Br
103
128
BrCH₂CH₂CH₂Br
105
118
BrCH₂CH₂CH₂CH₂Br
107
124

Fig. 5

Table V

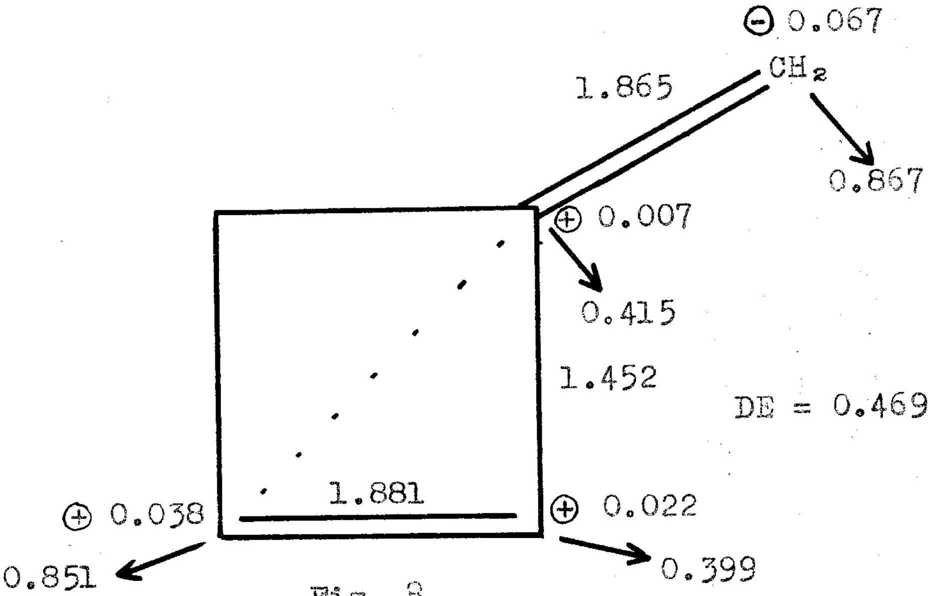
Summary of Nuclear Magnetic Resonance Data

Compound	Shielding No.	Assignment	Relative Intensity	
			Expected	Observed
$(CH_3)_2CBrCH_2Br$	103	$-CH_2Br$	1	4.5
	128	$-CH_3$	3	14.0
$BrCH_2CH_2CH_2Br$	105	$-CH_2Br$	2	6.5
	118	$-CH_2-$	1	2.5
$BrCH_2CH_2CH_2CH_2Br$	107	$-CH_2Br$	1	46
	124	$-CH_2$	1	40
	104.5	$-CH_2Br$	1	192
	131	$-CH_2-$	1	189
	104.5	$-CH_2Br$	1	95
	110	Impurity	?	
	112			
	117	$-CH_2-$	3	279
	(121)			
	134	Impurity	?	16



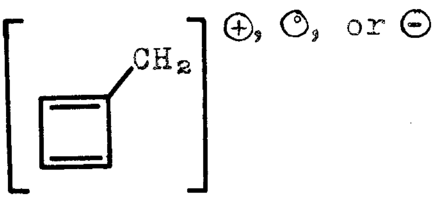
DE = 0.476β

Fig. 7



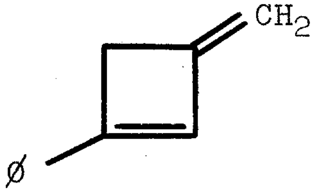
DE = 0.469β

Fig. 8



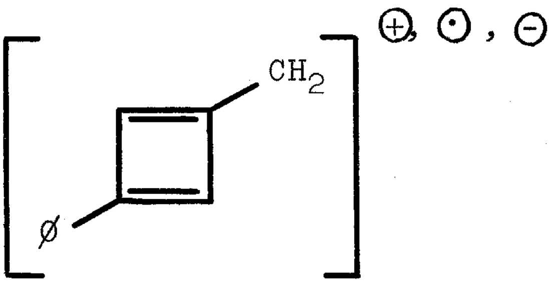
DE = 1.59β

Fig. 9[7]



DE = 2.930β

Fig. 10



DE = 4.014β

Fig. 11

Fig. 7 represents a calculation for methylenecyclobutene neglecting C_1-C_3 interaction, and is therefore the same as 1,3-butadiene in the LCAO treatment. A resonance integral of 0.1β between C_1 and C_3 (Fig. 8) introduces charges into the molecule and alters the free valences, bond orders, and energies slightly.

The molecular-orbital wave equations corresponding to

Fig. 8, which were used in the "frontier electron" predictions of site of attack,[51] are as follows, in increasing order of energy:

$$\psi_{I} = 0.3859\phi_3 + 0.5964\phi_2 + 0.6026\phi_1 + 0.3636\phi_5$$

$$\psi_{II} = 0.5761\phi_3 + 0.3650\phi_2 - 0.3655\phi_1 - 0.6335\phi_5$$

$$\psi_{III} = 0.6267\phi_3 - 0.3775\phi_2 - 0.3784\phi_1 + 0.5670\phi_5$$

Subscripts on the atomic wave functions refer to the usual numbering of methylenecyclobutene (I).

<u>Infrared Spectra</u>

Fig. 12

Curve	Compound	State and Thickness
1	Methylenecyclobutene (I)	10% CCl_4 soln., 0.1 mm.
2	4,4-Dimethylmethylenecyclobutene (XXVIII)	10% CCl_4 soln., 0.1 mm.
3	3-Phenylmethylenecyclobutene (XXX)	Pure liq., 0.028 mm.
4	Methylenecyclobutane	Pure liq., 0.05 mm.
5	3-Methylenetrimethylene Oxide (XLIII)	Pure liq., 0.028 mm.

Fig. 13

6	Boron Trifluoride-Induced Polymer of I	Film suspended in CCl_4
7	Radical Induced Polymer of I	Film
8	Sodium Amide-Induced Polymer of I	ca. 10% $CHCl_3$ soln., 0.1 mm.

9	Dibromide of I, Rearranged (XXXI)	10% CCl_4 soln., 0.1 mm.
10	Dibromide of I, Unrearranged (XXXII ?)	10% CCl_4 soln., 0.1 mm

The infrared spectra were obtained on a Model 21 Perkin-Elmer double-beam recording spectrophotometer with sodium chloride optics.

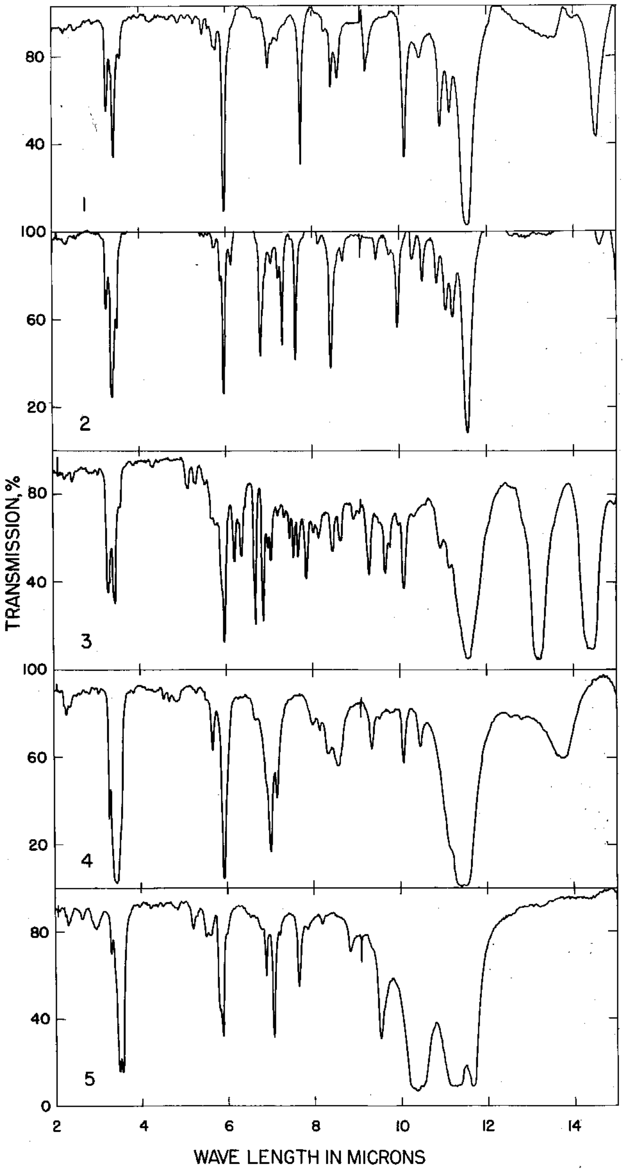
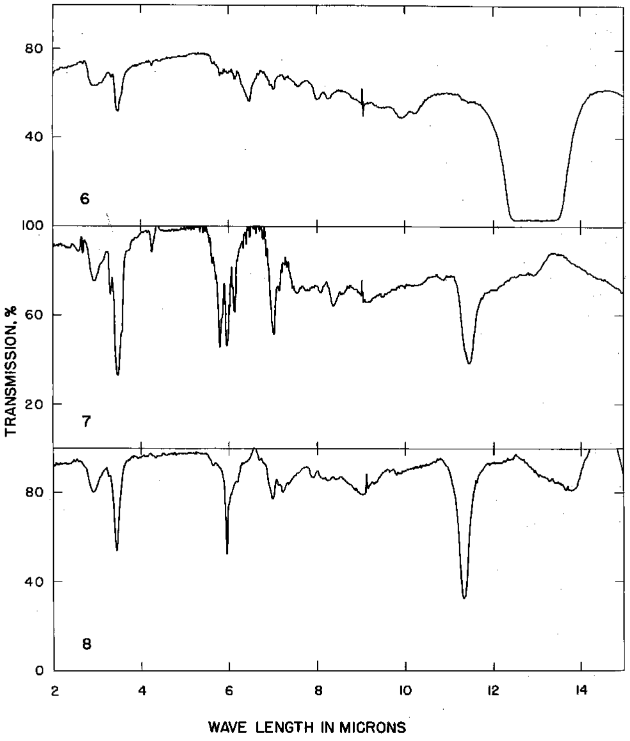

80
40
1
100
60
20
2
80
40
3
100
60
20
4
80
40
5
0
TRANSMISSION,%
2
4
6
8
10
12
14
WAVE LENGTH IN MICRONS

Fig. 12


80
40
6
100
60
20
7
80
40
8
0
TRANSMISSION, %
2
4
6
8
10
12
14
WAVE LENGTH IN MICRONS

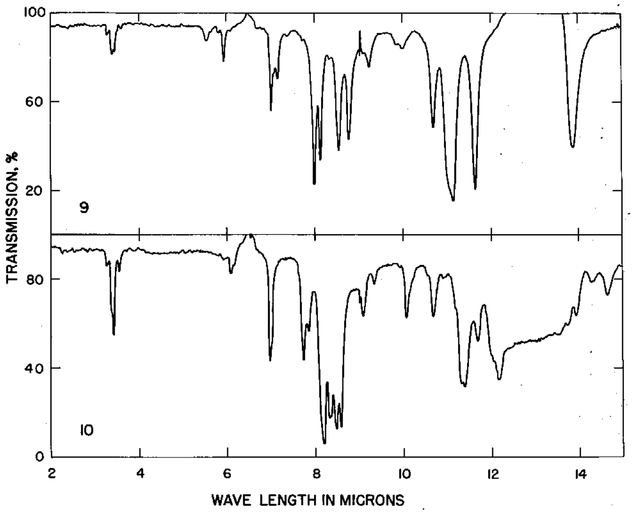

100
60
20
9
80
40
10
0
TRANSMISSION, %
2
4
6
8
10
12
14
WAVE LENGTH IN MICRONS

Fig. 13

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VI. PROPOSITIONS

1. The two mechanisms which have been proposed for the low-temperature, liquid-phase, allylic chlorination of olefins[1,2] could be distinguished by examination of the products of chlorination of 3-chloro-2-methyl-1-propene-3-^{14}C.
2. A structural, as opposed to chemical, demonstration of π-bonding between non-adjacent atoms might be obtained by electron diffraction study of 3-oxacyclobutanone and comparison of the results with the known dimensions of 3-methylenetrimethylene oxide.[3]
3. A logical synthesis of bicyclo[2.2.0]hexane, which has resisted previous synthetic efforts,[4] would be the reaction of cis-1,2,-bis(bromomethyl)cyclobutane with phenyllithium.[5]
4. Some possible intermediates in the Hunsdiecker degradation of silver succinates could be confirmed or rejected by a study of the bromination of optically active silver trans-cyclobutane-1,2-dicarboxylate or silver trans-cyclopentane-1,2-dicarboxylate.
5. The method of Heilbronner[6] can be used to simplify the LCAO calculation of energy levels in molecules having C_2 symmetry by considering the simple structural equivalents of the factored secular determinants obtained by group-theory operations.

6. Despite the instability of bridgehead carbonium ions in small bridged-ring systems, such ions are not known to rearrange. 1-Amino-4,7,7-trimethylbicyclo[2.2.1]-heptadiene-2,5, for which a synthesis is proposed, could be used to generate a carbonium ion in which rearrangement would be particularly favorable. It might thus be possible to demonstrate that rearrangement in these systems is not stereoelectronically impossible, but just kinetically unfavorable.
7. It should be possible to synthesize tricyclo[$4.2.2.2^{2,5}$]-dodecene-1, whose existence would help clarify the electronic basis of Bredt's rule and which would be useful in studies of the stereochemistry of reactions of double bonds.
8. The available data on the thermal decomposition of ammonium nitrate to water and nitrous oxide[7-9] seem best explained by a mechanism in which combination of ammonia and the conjugate acid of nitric acid is the rate determining step, a mechanism more consistent with other chemical facts than the "dehydration mechanism."[7,9] It is suggested that the reaction should proceed in concentrated aqueous solutions under pressure, and that studies of reaction kinetics and nitrogen isotope effects under these conditions would further clarify the mechanism.

9. The condensation of 1,3-dienolates with gem-dihalides could be made a practical synthesis of certain 1,3-disubstituted cyclobutanes otherwise relatively difficult to prepare.[10]

10. Development of ovaries in worker bees is inhibited by a substance, soluble in acetone and alcohol, on the surface of the queen bees.[11] Although chemical identification would probably be impractical due to the small quantities involved, the substance might be characterized and perhaps identified by chromatographic RF values, using bio-assay technique to follow the chromatography.

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