was taken up in ether and dried over magnesium sulfate. Distillation gave 0.87 g. of colorless oil (odor like that of cyclopentanone), b.p. 50–58° at 100 mm., an intermediate fraction (0.22 g.), 0.77 g. of pale yellow oil, b.p. 83–102° at 9 mm. and 0.73 g. of residue. Distillation of like material from B gave 0.27 g., b.p. *ca.* 50° at 100 mm. The two fractions, 0.87 g. from A and 0.27 g. from B, were found to consist largely of ketone III. On treating such crude III with saturated aqueous sodium bisulfite, heat was evolved and the bulk of the material dissolved. After removing the small insoluble portion with ether, the ketone was regenerated from the soluble bisulfite compound by treatment with alkali. Following this purification, the ketone still slowly decolorized aqueous potassium permanganate (cyclopentanone stable in parallel experiment). Analyses[14] of crude III for alcohol were not conclusive but left open the possibility that these fractions contain 5–10% of alcohol calculated as C_5H_7OH. Attempts to prepare a *p*-nitrobenzal derivative gave an oil. A semicarbazone was obtained from crude III, tiny square plates with corners extended, m.p. 195.8–196.3° from ethanol.

Anal. Calcd. for $C_6H_{11}N_3O$: C, 51.04; H, 7.86; N, 29.77. Found: C, 51.22; H, 7.88; N, 29.43.

The 2,4-dinitrophenylhydrazone formed thin square orange-brown plates from methanol; m.p. 120.6–121.0°.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 50.22; H, 4.60; N, 21.52.

The boiling point (83–102° at 9 mm.) of the less-volatile neutral fraction corresponds roughly to that expected for aldol-type dimers[6] of III. The absence of appreciable amounts of an α,β-unsaturated ketone was indicated by the ultraviolet absorption spectrum which was devoid of peaks in the region 225–320 mμ. Attempts to prepare crystalline derivatives were generally unsuccessful; in one experiment with 2,4-dinitrophenylhydrazine, a small amount of yellow-brown crystals was obtained, m.p. *ca.* 184° from acetonitrile.

The bases which had been absorbed in dilute hydrochloric acid were liberated into ether by addition of sodium hydroxide and converted to picrates with ethereal picric acid. Fractionation of the crude picrate mixture gave only dimethylamine and trimethylamine picrates; a careful search for picrates of other bases was fruitless. In order to analyse the picrate mixtures, a melting point diagram was constructed from the following data obtained on mixtures of the two authentic picrates: 20.7 weight % dimethylamine picrate, final m.p. 210.7°; 40.4%, 186.2°; 50.3%, 176.4°; 68.2%, 146.2°; 75.8%, 149.4°; 87.2%, 154.3°; 92.5%, 157.3°; 97.4%, 159.8° (eutectic *ca.* 63%, 132°). Procedure A gave 11.1 g. of mixed picrates (*ca.* 50% dimethylamine picrate by weight) equivalent to a 67% yield of both bases, while the recovered picrates from B (*ca.* 35% dimethylamine picrate) corresponded to a 54% yield.

PASADENA 4, CALIFORNIA

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[14] J. W. Petersen, K. W. Hedberg and B. E. Christensen, *Ind. Eng. Chem., Anal. Ed.*, **15**, 225 (1943).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY (NO. 2072) AND THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. XV. Methylenecyclobutene and Related Substances[1]

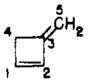
BY DOUGLAS E. APPLEQUIST[2a] AND JOHN D. ROBERTS[2b]

RECEIVED JANUARY 16, 1956

Methylenecyclobutene has been synthesized from diethyl methylenemalonate by way of 3-methylenecyclobutanecarboxylic acid and 3-methylenecyclobutylamine. The synthesis featured the use of anthracene as a blocking group for the exocyclic double bond during malonic-ester closure of the cyclobutane ring. 4,4-Dimethyl-3-methylenecyclobutene has been obtained by degradation of α-pinene and 1-phenyl-3-methylenecyclobutene by condensation of allene with phenylacetylene. Bromine addition and three types of polymerization of methylenecyclobutene have been found to proceed in accordance with predictions based on simple molecular-orbital theory. 3-Methylenetrimethylene oxide, of interest because of the possibility that it might have demonstrable π-bonding across the ring, has been prepared.

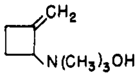
Introduction

Simple molecular-orbital (LCAO) calculations[3] indicate the substantial delocalization energy of 1.59 β for the cyclobutadienylcarbinyl radical, cation and anion. Cyclobutadienylcarbinyl intermediates could conceivably be obtained either from methylcyclobutadiene or from methylenecyclobutene (I), in the latter case by removal of a proton, hydrogen atom or hydride ion from the 4-position. Synthesis of methylcyclobutadiene appeared less promising than the synthesis of methylenecyclobutene,[4] and the objective of the present research was to find a practical synthesis of methylenecyclobutene (or simple derivatives thereof) and to test the validity of the predictions based on the molecular-orbital calculations.



I

The structure I was once tentatively assigned to pirylene, a hydrocarbon obtained by a degradation of piperidine, by von Braun in 1928.[5] However, more recent chemical[6] and electron diffraction[7] evidence has demonstrated that pirylene is methylvinylacetylene. Howton and Buchman have achieved the preparation of I, by pyrolysis of 2-methylenecyclobutyltrimethylammonium hydroxide (II)[4,8] (obtained from the previously described[9] corresponding quaternary bromide).



II

Synthesis of Methylenecyclobutenes.—The synthesis of methylenecyclobutene developed in the

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[1] Supported in part by the Petroleum Research Fund of the American Chemical Society and presented before the Meeting of the American Chemical Society at Minneapolis, September 16, 1955.

[2] (a) National Science Foundation Predoctoral Fellow, 1953–1955; (b) Gates and Crellin Laboratories, California Institute of Technology.

[3] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, THIS JOURNAL, **74**, 4579 (1952).

[4] E. R. Buchman, Abst. of A. C. S. meeting, Sept. 13, 1954, p. 9-O.

[5] J. von Braun and W. Teuffert, *Ber.*, **61**, 1092 (1928).

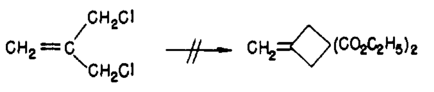
[6] H. Sargent, E. R. Buchman and J. P. Farquhar, THIS JOURNAL, **64**, 2692 (1942).

[7] R. Spurr and V. Schomaker, *ibid.*, **64**, 2693 (1942).

[8] D. R. Howton and E. R. Buchman, *ibid.*, **78**, 4011 (1956).

[9] E. R. Buchman and D. R. Howton, *ibid.*, **70**, 2517 (1948).

present research is analogous to Willstätter's classical synthesis of cyclobutene by degradation of cyclobutanecarboxylic acid to cyclobutylamine, exhaustive methylation, and Hofmann reaction.[10] Several preliminary attempts were made to prepare the required 3-methylenecyclobutanecarboxylic acid by condensation of the dichloride III with malonic ester, but the reaction primarily yielded polymolecular products instead of IV even at high dilution. The failure of the malonic ester reaction to produce ring closure probably was due to the unfavorably large bond angle (*ca.* 120°) at the central carbon of III. The synthesis was therefore 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.[11] The complete synthesis is outlined in Fig. 1.



III IV

The ester V was prepared by the method of Bachman and Tanner,[12] in which diethyl methylenemalonate was added to anthracene. The ester was reduced to the diol VI in 75–90% yields with lithium aluminum hydride in ether. Direct conversion of VI to the dibromide VII, with phosphorus tribromide gave mostly tar from which a trace of VII could be sublimed. However, 78% yields of VII were obtained by conversion of VI to its benzenesulfonate VIII with benzenesulfonyl chloride in pyridine and then treatment of the benzenesulfonate with a large excess of sodium bromide in diethylene glycol for 18 hr. at 165–170°. The conditions required for this step were unusually drastic[13] and appeared indicative of particularly large steric hindrance to displacement (SN2) reactions. The hindrance was further illustrated in the reaction of the benzenesulfonate VIII with base (described below in connection with the synthesis of 3-methylenetrimethylene oxide) and in the condensation of the dibromide VII with malonic ester, which was very slow. When the latter condensation was attempted in refluxing isoamyl alcohol (159 hr.), 60% of the dibromide was recovered unchanged and the malonic ester was converted to diisoamyl carbonate and isoamyl isoheptylate. Carbonate ester formation was effectively suppressed by using less-nucleophilic potassium *t*-amylate in *t*-amyl alcohol as the condensing agent, and after 171 hr. at reflux, a small yield of ester hydrolyzable to the diacid IX was obtained. Decarboxylation of IX to the monoacid X was effected in 70% yield at 155°, and pyrolysis of X at 350° gave an 87% yield of 3-methylenecyclobutanecarboxylic acid (XI). Curtius degradation of XI to the amine XIV followed standard procedures, the azide being prepared by the acid chloride–sodium azide method.[14] By exhaustive methylation of the amine XIV, the quaternary iodide XV 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°.

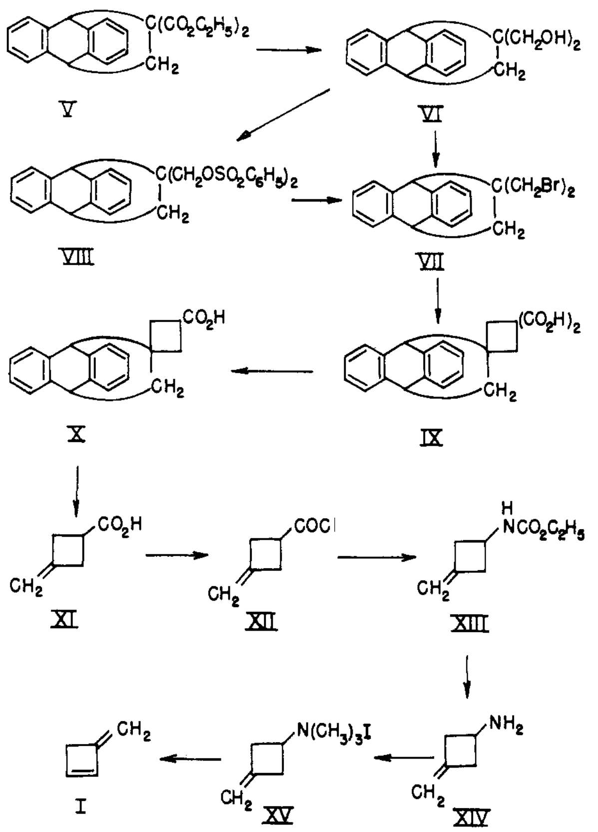


Fig. 1.—Synthesis of methylenecyclobutene.

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 (Fig. 3), which showed peaks characteristic of an exocyclic methylene group at 5.98 and 11.57 μ (almost exactly the same wave lengths absorbed by 4,4-dimethylmethylenecyclobutene and 1-phenyl-3-methylenecyclobutene, described below). There was no peak near 7.25 μ, as would be expected if a methyl group were present.[15a] The spectrum was nearly identical with that of a sample of Howton and Buchman's hydrocarbon,[4,8] establishing the identity of the materials made by different routes.

In order to determine whether the properties of methylenecyclobutene (I) are markedly dependent

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[10] R. Willstätter and W. von Schmaedel, *Ber.*, **38**, 1992 (1905).

[11] (a) P. D. Bartlett and F. A. Tate, This Journal, **75**, 91 (1953); (b) O. Diels and W. Friedrichsen, *Ann.*, **513**, 145 (1934); (c) O. Diels and W. E. Thiele, *Ber.*, **71**, 1173 (1938); (d) P. Baumgartner and G. Hugel, *Bull. soc. chim. France*, 1005 (1954).

[12] G. B. Bachman and H. A. Tanner, *J. Org. Chem.*, **4**, 493 (1939).

[13] (a) H. L. Herzog, *Org. Syntheses*, **31**, 82 (1951); (b) E. R. Buchman, D. H. Deutsch and G. I. Fujimoto, This Journal, **75**, 6228 (1953).

[14] P. A. S. Smith in "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 337.

[15] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York N. Y., 1954; (a) p. 19; (b) p. 49.

upon the presence of the hydrogens at the 4-position 4,4-dimethylmethylenecyclobutene (XXI) was prepared by the scheme outlined in Fig. 2.

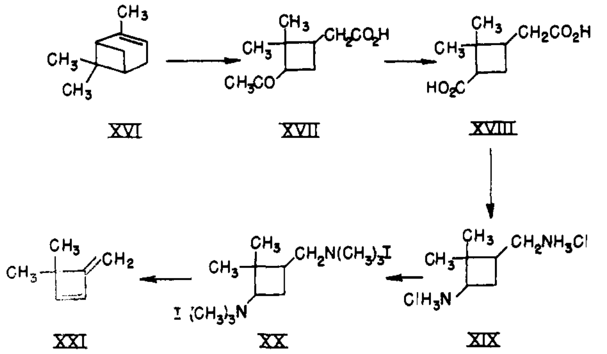
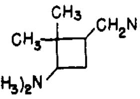


Fig. 2.—Synthesis of 4,4-dimethylmethylenecyclobutene.

The degradation of α-pinene (XVI) to *dl*-pinic acid (XVIII) followed a reported procedure,[16] but low yields in the permanganate oxidation of XVI to pinonic acid (XVII) prevented large-scale preparation of XVIII. Pinic acid was converted to the diamine XIX in 84% yield by the Schmidt reaction. Exhaustive methylation to the quaternary iodide XX was carried out directly with methyl iodide and potassium hydroxide or, preferably, in two steps with preparation of the ditertiary-amine XXII by the Eschweiler–Clarke procedure (74% yield) followed by quaternization with methyl iodide. The Hofmann reaction to form the diene XXI gave a yield of 52% from the ditertiary amine XXII when carried out at 160° and 40 mm. pressure. The quaternary hydroxide, which was not isolated, was prepared from the iodide XX by treatment with silver oxide.



XXII

The structure of the diene XXI rests primarily upon the method of synthesis and the spectra, which indicate conjugated double bonds ($\lambda_{\max}$ 229 mμ, ϵ 8600), an exocyclic methylene group (strong peaks at 5.97 and 11.57 μ) and *gem*-dimethyl groups (doublet at 7.22–7.31 μ).[15a] The infrared spectrum is shown in Fig. 3. Also, the chemical behavior was very similar to that of methylenecyclobutene.

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 cyclo-addition reactions to give four-membered rings.[17] The infrared spectrum showed peaks at 5.99 and 11.6 μ characteristic of the exocyclic methylene group in the previously described methylenecyclobutenes and provided no evidence for acetylenic, allenic or methyl groups (Fig. 3).[15b] The ultraviolet spectrum showed $\lambda_{\max}$ 291 mμ, ϵ 7250, which is in better agreement with a 1-phenylbutadiene than a 2-phenylbutadiene chromophore.[18] The structure 1-phenyl-3-methylenecyclobutene (XXIII) is therefore assigned to this substance. Variations in solvent and polymerization inhibitor failed to lead to satisfactory yields of XXIII, which was not obtained in sufficient quantity for detailed study.

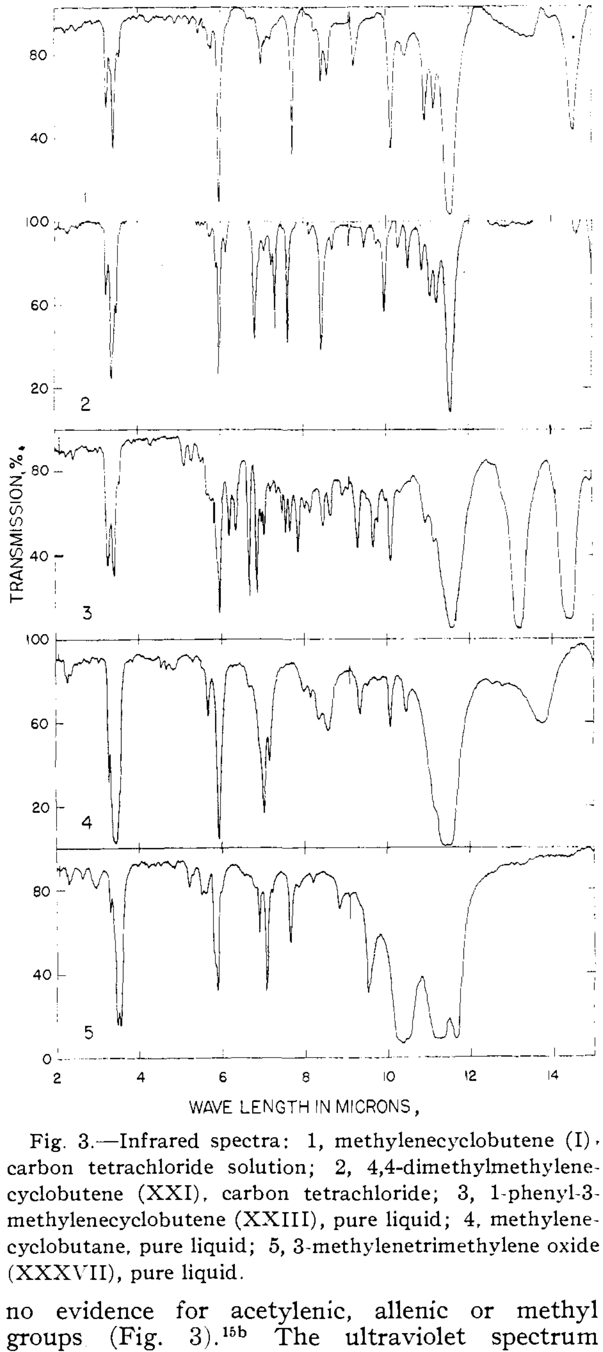
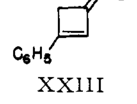


Fig. 3.—Infrared spectra: 1, methylenecyclobutene (I), carbon tetrachloride solution; 2, 4,4-dimethylmethylenecyclobutene (XXI), carbon tetrachloride; 3, 1-phenyl-3-methylenecyclobutene (XXIII), pure liquid; 4, methylenecyclobutane, pure liquid; 5, 3-methylenetrimethylene oxide (XXXVII), pure liquid.



XXIII

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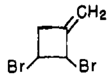
(16) M. Grandperrin, *Ann. Chim.*, **6**, 5 (1936).

(17) (a) S. V. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1390 (1913); *J. Chem. Soc.*, **104**, 1293 (1913); (b) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., This Journal, **75**, 4765 (1953).

(18) (a) B. Elpern and F. C. Nachod, *ibid.*, **72**, 3379 (1950); (b) E. A. Braude, *Ann. Reports*, **42**, 105 (1945).

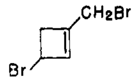
Properties of Methylenecyclobutenes.—Methylenecyclobutene (I) in carbon tetrachloride solution was titrated at 0° with a bromine solution in the same solvent and was found to take up just one mole of bromine. The product was fractionated, giving one isomer pure (b.p. 49° (5 mm.)) and a higher-boiling 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. 4).

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 and 11.16 μ. The former band was found at 5.90–5.95 μ in three other methylenecyclobutanes, 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[19] and 1,4-dibromo-2-butene react rapidly to give a deep red color and a white precipitate. The structure XXIV is assigned to the lower boiling dibromide on the basis of this information.

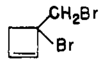


XXIV

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 stretching peak at 6.11 μ. 1-Methylcyclobutene has such a peak at 6.08 μ.[20] The ultraviolet spectrum indicated λ_{max} 208 mμ with ϵ 8100, whereas the lower-boiling XXIV appeared to have λ_{max} 206 mμ with ϵ 6300. These figures are slightly suggestive of the 1,4-adduct structure XXV rather than the 1,2-adduct XXVI



XXV



XXVI

for the higher-boiling isomer, since increasing bromine substitution in the positions allylic to a double bond increases the resemblance of the ultraviolet spectrum to that of a conjugated diene, although the principal effect is usually to increase λ rather than ϵ.[21] The high boiling point is likewise suggestive of structure XXV, since vicinal dibromides very commonly boil much lower than their isomers in which the bromines are further apart.[22] Finally, it may be argued that if the high-boiling isomer is either XXV or XXVI, then it is difficult to see how it could be XXVI, since XXV would almost necessarily have to be an intermediate in the isomerization of XXVI to XXIV, and as such it would have appeared in the infrared spectra as a third component unless XXV is quite unstable relative to both XXVI and XXIV, for which no reason is readily apparent. If, as is quite possible, the high-boiling dibromide is an equilibrium mixture of XXV and XXVI, then by analogy with other diene dibromides[23] XXV would be expected to predominate.

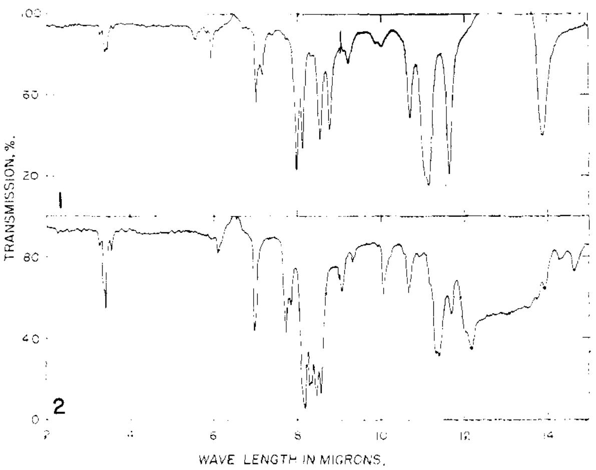
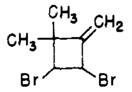


Fig. 4.—Infrared spectra: 1, rearranged dibromide of I (XXIV), carbon tetrachloride solution; 2, unrearranged dibromide of I (XXV?), carbon tetrachloride solution.

The dibromides were readily equilibrated by treatment with zinc bromide at 100° or by simply allowing them to stand for 4 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 (XXI) 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 and 11.13 μ, indicating that the dibromide XXVII was probably present. This substance



XXVII

must have been formed by isomerization during the distillation, since these bands were absent in the

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[19] D. E. Applequist and J. D. Roberts, THIS JOURNAL, **78**, 874 (1956).

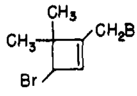
[20] E. F. Cox, Ph.D. Thesis, California Institute of Technology, 1955.

[21] Private communication from Professor H. J. Dauben, Jr., of the University of Washington.

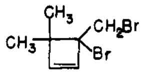
[22] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 120.

[23] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 670.

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 XXVIII, if the spectra of the methylenecyclobutene dibromides were correctly interpreted above. A new band at 5.80μ may represent compound XXIX. Only the band at 6.06 μ was strongly evident in the crude reaction mixture.

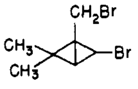


XXVIII



XXIX

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



XXX

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 weights. The infrared spectra (Fig. 5) showed strong bands at 5.95 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 XXXI.

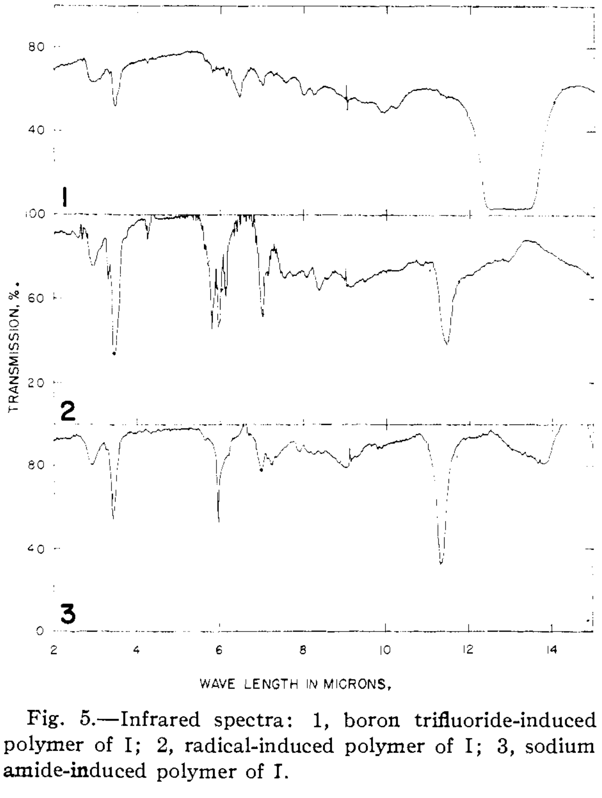
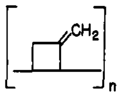


Fig. 5.—Infrared spectra: 1, boron trifluoride-induced polymer of I; 2, radical-induced polymer of I; 3, sodium amide-induced polymer of I.

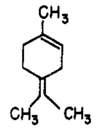


XXXI

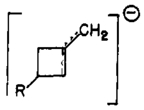
A single attempt to metalate 1-phenyl-3-methylenecyclobutene with sodium amide in benzene gave primarily tarry material. All three of the methylenecyclobutenes prepared in this research polymerized readily and spontaneously at room temperature. The behavior was not always reproducible in this respect, 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 and 11.46 μ, but they were smaller than in the product of the base-catalyzed polymerization. In addition, there were bands in the C=C stretching region at 5.81 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 is possibly not as stable as predicted. By contrast, terpinolene (XXXII) is apparently a good polymerization inhibitor.[24]

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 also seemed to have a high molecular weight as indicated by its insolubility in common solvents. It was more brittle and less elastic than the free-radical polymer and turned brown soon after preparation. The infrared spectrum showed the peaks at 5.8 and 6.13 μ found in the free-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-



XXXII



XXXIII

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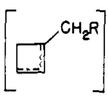
[24] D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, This Journal, 71, 490 (1949).

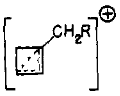
position and therefore that the cyclobutadienylcarbinyl cation is relatively unstable compared to the chain-carrying cation. However, this conclusion might be invalid since boron trifluoride could induce a high degree of cross-linking and reduced solubility of a short-chain polymer.[25]

It appears certain that anions attack methylenecyclobutene at the 1-position to give intermediates of the form XXXIII, which then attack another molecule preferentially to leave an exocyclic double bond rather than the more strained intracyclic double bond.

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



XXIV

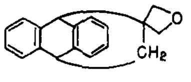


XXXV

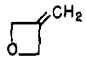
It seems possible that intermediates of type XXXIII should have smaller angle strain and be favored as products of both anion and cation attack on methylenecyclobutene. However, cation XXXIV appears to have special stabilization which might be due to inductive and hyperconjugative effects of the 4-methylene group although a more attractive explanation is that the geometry of the small-ring permits a substantial 1,3-π-bonding giving a cation which resembles the cyclopropenyl cation[3] and which can be represented as XXXV. Hydrogen hyperconjugation from the 4-position is probably not the major factor in stabilizing XXXIV, since 4,4-dimethylmethylenecyclobutene apparently adds bromine in the same manner.

The validity of arguments based upon stability of intermediates to explain orientation phenomena depends, of course, 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 XXXV,[26] but in the polymerization reactions, the intermediates XXXIII and XXXV 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 experimental results, since a simple LCAO calculation for 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 position 5 where cations attack and positive charges at the other three unsaturated positions. The greatest positive charge is at the 1-position where anions attack. The calculated free valences do not unambiguously predict the site of radical attack, nor does the "frontier electron" method.[27]

3-Methylenetrimethylene Oxide.—During the early work on the preparation of diacid IX (Fig. 1) by malonic ester condensation, an attempt was made to utilize the benzenesulfonate VIII, instead of using the dibromide VII. The main product was the trimethylene oxide XXXVI. XXXVI also was obtained by heating the benzenesulfonate VIII with sodium ethoxide in ethanol or sodium isoamylate in isoamyl alcohol. Since the reaction occurs in anhydrous media, sulfur–oxygen cleavage is necessarily involved, since alkyl–oxygen cleavage by an alkoxide ion would lead to a dialkyl ether of diol VI. Similar sulfur–oxygen cleavages have been observed in several cases where there is hindrance to alkyl–oxygen cleavage.[28]

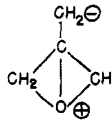


XXXVI



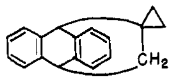
XXXVII

Pyrolysis of XXXVI at 350° gave 3-methylenetrimethylene oxide (XXXVII) (75% yields). A substance boiling 30° lower than XXXVII was assigned the same structure by Kleinfeller,[29] but his material was not well characterized. The structure of XXXVII was confirmed in the present work by addition of the compound to anthracene at 180–210°. The adduct was identical to the XXXVI from which XXXVII had been prepared.[30]



XXXVIII

Formation of Strained Double Bonds by Reverse Diels–Alder Reactions.—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 VII (Fig. 1) was debrominated with zinc to obtain the spirane XXXIX. Decomposition of XXXIX



XXXIX

would be expected to produce methylenecyclopropane, in which the double bond is probably highly strained. However, XXXIX proved to be unusually thermostable. It passed through a vertical

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(25) P. H. Plesch, M. Polanyi and H. A. Skinner, *J. Chem. Soc.*, 257 (1947).

(26) (a) Reference 23, p. 665; (b) G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

(27) K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954).

(28) (a) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949); (b) H. M. Walborsky, *ibid.*, **36**, 1251 (1953); (c) G. Stork, E. E. van Tamelen, L. J. Friedman and A. W. Burgstahler, THIS JOURNAL, **75**, 384 (1953).

(29) H. Kleinfeller, *Ber.*, **62B**, 1590 (1929).

(30) Further proof of the structure XXXVII has been obtained in an electron-diffraction investigation, carried out with V. Schomaker and E. Goldish to determine whether 1,3-π-bonding (of a type represented by structure XXXVIII) is sufficient to distort the ring. The details will be reported later when refinements are complete, but preliminary results show that the intracyclic ∠CCC is about 87°, too small to be considered demonstrative of 1,3-π-bonding, in the absence of suitable data for comparison.

tube at 450° unchanged and refluxed from the top for several minutes. By contrast, 3-methylenetrimethylene oxide (XXXVII) was formed rapidly when XXXVI was heated to 350°, and the preparation of 3-methylenecyclobutanecarboxylic acid (XI) from X was at least as easy.

The formation of compounds with completely unstrained double bonds by pyrolysis of the diester V and the diol VI occurred readily and vigorous decomposition took place when samples were heated to 300–330°. The products of these pyrolyses were not analyzed.

Experimental[31]

3-Chloro-2-chloromethyl-1-propene (III). A. **From Pentaerythritol.**—Following the procedure of Mooradian and Cloke,[32] III was prepared in 26% over-all yield from 136 g. (1 mole) of pentaerythritol; b.p. 134–137°, n^{24}D 1.4748.

B. **From Methallyl Chloride.**—Chlorine was bubbled rapidly into cooled, well-stirred methallyl chloride (181.0 g., 2 moles). For about 2.5 hr., 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.[33] 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., n^{26}D 1.4694, and a second at 59.6–60.8° (50 mm.), 48.4 g., 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 III prepared by method A. The yield of III was 19.4%. The lower-boiling isomer was 1,3-dichloro-2-methylpropene.[33]

Reaction of 3-Chloro-2-chloromethyl-1-propene with Malonic Ester.—To a stirred, refluxing solution of 8.6 g. (0.22 mole) of potassium in 140 ml. of anhydrous *t*-butyl alcohol 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 hr. and heating was continued for another hour. Neutralization (to phenolphthalein) with acetic acid required about 3.5 ml. (0.06 mole), 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 toward boiling alcoholic silver nitrate.

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

Diethyl 9,10-Ethano-9,10-dihydroanthracene-11,11-dicarboxylate (V).—Diethyl methylenemalonate was freshly prepared by the procedure of Bachman and Tanner[12] (18–23% yields, b.p. 203–210°). V had been synthesized by the same authors, but no experimental details were 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 hr. 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 V 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.

9,10-Ethano-9,10-dihydro-11,11-bis-(hydroxymethyl)-anthracene (VI).—To a slurry of 3.0 g. (0.079 mole) of lithium aluminum hydride in about 180 ml. of anhydrous ether was added slowly with stirring a suspension of 15.8 g. (0.045 mole) of V in 180 ml. of 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. of water added dropwise. Next was added a solution of 5 g. of concentrated sulfuric acid in 50 ml. of 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 V in ether, it was convenient to carry out larger scale runs with addition of V 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) (VIII).—The procedure was similar to one employed by Herzog.[13a] In a three-necked flask equipped with tantalum Hershberg stirrer, thermometer and dropping funnel was placed a solution of 139 g. (0.523 mole) of VI (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. of methanol, 930 ml. of water and 730 ml. of concd. hydrochloric acid and immediately worked vigorously with a large pestle to prevent the formation of large chunks. After the mixture had cooled, the solid was collected and washed with water. The crude VIII amounted to 272.9 g. (96% yield), 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.

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[31] All melting points are corrected. Boiling points are not corrected. Infrared spectra were obtained on a Perkin–Elmer Model 21 double-beam recording spectrophotometer with sodium chloride optics. Analyses are by Dr. S. M. Nagy and associates, Microchemical Laboratory, Massachusetts Institute of Technology, and Dr. A. Elek, Los Angeles, California.

[32] A. Mooradian and J. B. Cloke, THIS JOURNAL, **67**, 942 (1945).

[33] J. Burgin, G. Hearne and F. Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

9,10-Ethano-9,10-dihydro-11,11-bis-((bromomethyl)-anthracene (VII).—A mixture of 16.4 g. (0.03 mole) of VIII, 31.8 g. (0.3 mole) of sodium bromide, 0.318 g. (0.003 mole) of sodium carbonate and 60 ml. of reagent grade diethylene glycol was heated and stirred at 150° for 18 hr. The reaction mixture was poured into 180 ml. of water, and 11.1 g. of crude, nearly colorless VII, 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 VIII and the intermediate monobromobenzenesulfonate ester, 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 the formation of tar.

Reaction of the diol VI with phosphorus tribromide at 70° gave a dark, tarry solid from which only a trace of VII 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 (IX).—A mixture of 50 ml. of *t*-amyl alcohol (distilled from quicklime and from potassium) and 1.31 g. (0.0336 g.-atoms) of potassium was refluxed for 5.5 hr. until only a cloudy suspension remained. Next was added 5.40 g. (0.0336 mole) of redistilled malonic ester, which caused a heavier white precipitate to separate, and finally 4.40 g. (0.0112 mole) of the dibromide VII. The mixture was refluxed and stirred for 171 hr. 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 VII, m.p. 143.8–151.6°. An additional 0.30 g. of recovered VII, m.p. 144.5–150.2°, crystallized from the organic phase on standing. The total recovery of VII was 48%. A Volhard titration on the aqueous phase showed that it contained 0.00427 mole 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 semi-micro column and seemed to be a mixture of ethyl malonate and *t*-amyl malonates formed by ester interchange. To test this hypothesis, a few drops of the highest-boiling fraction 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 was evolved. The same treatment of malonic ester gave no such vapor.[34]

The non-volatile residue 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 IX, 183.2–190.0° with gas evolution. The product was recrystallized again to give 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 (X).—The residue from the mother liquor of the final recrystallization of the diacid IX sublimed at 155° (0.2 mm.) overnight, to give 0.026 g. (70% yield) of crude, yellowish X. Recrystallization of the product from cyclohexane gave 10 mg. of material, m.p. 151.8–168°, which was probably a mixture of *cis–trans* isomers. The infrared spectrum showed associated O–H (broad peak at 3.4 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 (XI).—In a 5-ml. distilling flask was placed 1.56 g. (0.0054 mole) of acid X. An ice-cooled receiver was attached, and a very slow stream of nitrogen 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, 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.), 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 (XII).—A solution of 5.49 g. (3.32 ml., 0.0461 mole) of thionyl chloride and 4.47 g. (0.0399 mole) of acid XI 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 XII, b.p. 71–90° (82 mm.) (90%), collected in four fractions.

An anilide was prepared[35] 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 (XIII).—To a cooled, swirled solution of 26 g. (0.2 mole) of XII in 100 ml. of reagent acetone was added 15.8 g. (0.243 mole) 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 mole) 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 XIII.

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 (XIV).—A solution of 50 g. (0.322 mole) of crude XIII and 144 g. (2.57 moles) of potassium hydroxide in 400 ml. of methanol was heated under reflux for 2 hr. The cooled reaction mixture was diluted with 1500 ml. of water and shaken with 200 ml. of 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. spiral-wire packed column gave 10 g. (37% yield) of XIV, b.p. 107–108°, 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 and 11.36 μ, but there was also a band in the C-methyl region (7.22 μ). However, the benzamide derivative was prepared[36] and found to show only the exocyclic methylene group (11.28 μ). The benzamide was

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[34] D. S. Breslow, E. Baumgarten and C. R. Hauser, THIS JOURNAL, **66**, 1286 (1944).

[35] N. D. Cheronis and J. B. Entriken, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 210.

[36] Reference 35, p. 258.

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.

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.

3-Methylenecyclobutyltrimethylammonium Iodide (XV).—To a solution of 13.5 g. (0.163 mole) of amine XIV in 30 ml. of methanol was added slowly with stirring 96 g. (0.68 mole) of methyl iodide dissolved in 100 ml. of methanol. Finally, 27.2 g. (0.485 mole) of potassium hydroxide in 130 ml. of 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 at gentle reflux for 3 hr. The solvent was removed *in vacuo* at 40°. The dry, solid residue was transferred to a Soxhlet thimble and extracted continuously with chloroform for 3 days to give 36.4 g. (89%) of XV, 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.

Methylenecyclobutane (I).—To a solution of 36.2 g. (0.143 mole) of quaternary salt XV 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 mole) of silver nitrate and 20.7 g. (0.37 mole) 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 phases were swirled briefly and the aqueous phase removed. The organic phase was dried over Drierite and distilled rapidly through a semi-micro 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 methylenecylobutenes (XXI and XXIII, see below).

An ultraviolet spectrum of I in isoöctane solution showed $\lambda_{\max}$ 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 semi-micro 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%). The infrared spectrum was essentially the same as the published spectrum of methylcyclobutane.[37]

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 (XIX).—To a stirred solution of 3.40 g. (0.0183 mole) of crude *dl*-pinic acid[16,38] (XVIII) (m.p. 80–96°) in 7 ml. of sulfuric acid was added 27.2 ml. (0.04 mole) 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 7 hr. At the end of this time, another 6 ml. (0.0088 mole) of hydrazoic acid solution was added, and the heating was continued for 3 hr. 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 XIX. 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,[36] 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 (XXII).—A mixture of 15 g. (0.0742 mole) of crude XIX, 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 hr. The reaction mixture was concentrated to a 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 XXII was collected at 114–117° (51 mm.), $n^{25}D$ 1.4482.

An infrared spectrum of XXII showed moderate absorption 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) (XX).—To a solution of 2.8 g. (0.02 mole) of methyl iodide in 1 ml. of methanol was added, with cooling, a solution of 0.73 g. (0.00396 mole) of XXII in 2 ml. of methanol. The mixture was allowed to stand for about 12 hr., after which the solvent was replaced with ethanol by the 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° dec. (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

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[37] J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 2482 (1949).

[38] A. Baeyer, *Ber.*, **29**, 3 (1896).

next step then carried out directly on the residual material on the assumption that the yield of methiodide XX was quantitative. XX was prepared also in 6% yield by direct exhaustive methylation of XIX.[39] The insolubility of XX in chloroform prevented convenient separation of the product from the accompanying potassium salts.

4,4-Dimethylmethylenecyclobutene (XXI).—The procedure was the same as that used in the preparation of methylenecyclobutene (I).

The quantities used were 6.78 g. (0.0368 mole) of freshly distilled ditertiary amine XXII, 26 g. (0.259 mole) of methyl iodide, 28.0 g. (0.164 mole) of silver nitrate and 10.9 g. (0.193 mole) of potassium hydroxide. The yield of dried, vacuum-distilled XXI was 1.81 g. (52% over-all from XXII). Of this material, 0.80 g. was distilled rapidly through a semi-micro column at 740 mm. from hydroquinone to give 0.73 g. of distillate, b.p. 65–65.7°, $n^{25}\text{D}$ 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.

The ultraviolet spectrum in ethanol showed λ_{max} 229 mμ, ϵ 8600.

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[40] 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 mole) of 2,3-dichloropropene at such a rate as to maintain refluxing. The mixture was heated under reflux for 45 min. after the addition of the dichloride was completed. The allene was passed through water and calcium chloride before condensation in a Dry Ice trap. The product amounted to 11.5 g. (96%). The infrared spectrum showed that the allene was nearly pure, though there was a small band at 8.44 μ not characteristic of allene.[41]

1-Phenyl-3-methylenecyclobutene (XXIII).—A mixture of 10.8 g. (0.106 mole) of phenylacetylene, 5 g. (0.125 mole) of allene and 50 mg. of 1,4-naphthoquinone was heated in a sealed tube for 24 hr. 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 semi-micro column to give 5.6 g. (51%) of phenylacetylene, b.p. 63–64° (50 mm.), and 0.07 g. of XXIII, b.p. 78–79° (4.5 mm.), m.p. 10–12°, $n^{25}\text{D}$ 1.5987.

Anal. 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 XXIII, 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.[42]

The ultraviolet spectrum in isoöctane showed maxima at 212 mμ, ϵ 4600; 219 mμ, ϵ 3760; 225 mμ, ϵ 3960; 233 mμ, ϵ 3640; 291 mμ, ϵ 7250.

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

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% solution of bromine in carbon tetrachloride. The end-point was fairly sharp, and 0.98 mole of bromine per mole of hydrocarbon was required. Very little hydrogen bromide was evolved. An infrared spectrum (Fig. 4) was taken of 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 at 5 mm. pressure. Fractions 1–3 (2.75 g., b.p. 49–50°, $n^{25}\text{D}$ 1.5487–1.5489) were shown by their infrared spectra to be the rearranged dibromide XXIV. The spectra of fractions 7 and 8 (3.42 g., b.p. 74°, $n^{25}\text{D}$ 1.5697–1.5688) were very much like that of the crude bromination product, although definite contamination by XXIV 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 4 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,[43] with the aid of the band at 5.94 μ characteristic of XXIV. The equilibrium mixture was 49% of XXIV and 51% of the other isomer (probably XXV). Rapid changes in the compositions 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 XXIV showed λ_{max} 206 mμ, ϵ 6260. The spectrum of the equilibrium mixture showed λ_{max} 207 mμ, ϵ 7170. It was calculated from these spectra and the equilibrium concentrations determined above that the spectrum of pure XXV would show λ_{max} *ca.* 208 mμ, ϵ 8130. A similar calculation from the infrared and ultraviolet spectra of a non-equilibrium mixture gave for XXV a λ_{max} *ca.* 208 mμ, ϵ 8200.

To confirm that the substances are isomeric dibromides, analyses were obtained on XXIV (a) and on a high-boiling fraction rich in XXV (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 (XXI) was carried out in the same manner as for methylenecyclobutene. A 0.1359-g. sample of XXI required 0.795 ml. of 1.94 *M* bromine (1.06 moles of bromine per mole of XXI) to reach the end-point. From 1.65 g. (0.0176 mole) of XXI was obtained 3.81 g. (81%) of dibromide, distilled through a semi-micro column and collected in five fractions, b.p. 75–89° (5 mm.), $n^{25}\text{D}$ 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 mmoles) of XXI 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.[44] 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 hr. in sealed ampules formed a colorless, transparent elastomer. 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

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[39] E. R. Buchman, M. J. Schlatter and A. O. Reims, THIS JOURNAL, **64**, 2701 (1942).

[40] (a) M. W. Tapley and P. M. Giesey, *J. Am. Pharm. Assoc.*, **15**, 173 (1926); *Chem. Zentr.*, **97**, **II**, 1941 (1926); (b) F. Smirnow, *J. Russ. Phys. Chem. Soc.*, **35**, 854 (1903); *Chem. Zentr.*, **75**, **I**, 575 (1904).

[41] R. C. Lord and P. Venkateswarlu, *J. Chem. Phys.*, **20**, 1237 (1952).

[42] Reference 22, p. 21.

[43] J. J. Heigl, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

[44] D. R. Howton, THIS JOURNAL, **69**, 2555 (1947), footnote 5.

that there was still liquid in the sample after two weeks at room temperature.[45] 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.[46] 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.

1-Phenyl-3-methylenecyclobutene (XXIII) also polymerized in a few hours to a few days at room temperature to a viscous, yellow material. 4,4-Dimethylmethylenecyclobutene (XXI), 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. XXI also showed less tendency to polymerize during distillation than did I.

Anionic Polymerization of Methylenecyclobutene.—About 0.24 g. (0.00354 mole) of methylenecyclobutene (I) was added to a solution of 0.00354 mole of sodium amide in 5 ml. of liquid ammonia. The brown color of the solution rapidly changed to 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 *p*H 2 and extracted with ether, but evaporation of the ether left no residue. The original ether phase (containing any basic and neutral materials) on evaporation left 0.22 g. (92%) of yellowish, sticky, non-volatile, chloroform-soluble polymer. The infrared spectrum of the polymer is shown in Fig. 5.

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 not enough was obtained for characterization.

When a sample of methylenecyclobutene was added to a solution of excess methyllithium[47] 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*-butyl alcohol 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.

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 (Fig. 5) was obtained by spreading the fragile film 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 and 13 μ.

Methylenecyclobutene gave no visible reaction with anhydrous aluminum bromide.

3'-Oxa-2,3,5,6-dibenz-spiro-(bicyclo[2.2.2]-octane-7,1'-cyclobutane) (XXXVI).—A solution of 101.1 g. (0.183 mole) of the benzenesulfonate VIII (m.p. 140.4–144.6°) and 1.1 moles of sodium ethoxide in 500 ml. of ethanol was heated under reflux for 26 hr. 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 XXXVI, 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 XXXVII. XXXVI was prepared also from the benzenesulfonate VIII by treatment with sodium isoamylate in isoamyl alcohol and through the reaction of VIII with sodiomalonic ester in isoamyl alcohol.

3-Methylenetrimethylene Oxide. (XXXVII).—Pure XXXVI (20 g., 0.0813 mole) was heated in a distilling flask for 105 min. at 340–355°. A slow stream of nitrogen 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.), $n^{25}\text{D}$ 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 an atmosphere of nitrogen. 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 mole) of XXXVII and 0.127 g. (0.00071 mole) of anthracene in 0.5 ml. of benzene was heated at 180° for 8.5 hr. and 210° for 12 hr. in a sealed tube. Fractional crystallization from ethanol of the non-volatile product gave 81 mg. of anthracene and 6 mg. of XXXVI (infrared spectrum).

2,3,5,6-Dibenz-spiro-(bicyclo[2.2.2]octane-7,1'-cyclopropane (XXXIX).—A mixture of 2.05 g. (0.00522 mole) of dibromide VII, 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.[48] 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 XXXIX, 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.

XXXIX boils without decomposition at about 300°. When a small sample was distilled into a vertical 0.4 × 15-cm. tube wound with a Chromel-wire heating element and heated to 450°, XXXIX refluxed at the top. No volatile product condensed in an attached Dry Ice trap, but the cooled solid showed slight purple fluorescence, which indicated that some anthracene was formed.

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(45) (a) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950); (b) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

(46) H. L. Dinsmore and D. C. Smith, *Anal. Chem.*, **20**, 11 (1948).

(47) H. Gilman, E. A. Zoellner and W. M. Selby, THIS JOURNAL, **55**, 1252 (1933).

(48) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **70**, 946 (1948).