TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	Proton chemical shifts, cycles/sec. Vinyl (a, Fig. 1)	Allylic (b, Fig. 1)	Paraffinic (c, Fig. 1)	Area ratios Calcd.	Obsd.
VII	39	−98		a:b = 3:2	a:b = 3:2
VIII	32	−96.5	−74	a:b:c = 2:1:2	a:b:c = 2:1:2
Ia	48	−56		a:b = 3:1	a:b = 3:1

placed inside the 5-mm. Pyrex tube containing the sample. The proton chemical shifts were measured by the method of superimposing audio-frequency sidebands from a calibrated Hewlett Packard 200-I oscillator, giving a precision of about ±2 c.p.s. The chemical shifts were determined for 1, 5 and 20% (by volume) solutions of the compounds in carbon tetrachloride and extrapolated to infinite dilution. The observed area ratios were determined with a precision of about 10%. We are indebted to Professor John S. Waugh for the determination of the nuclear magnetic resonance spectra.

Maleic Anhydride Adduct of Cycloöctatetraene Oxide (II). A. Epoxidation of Maleic Anhydride Adduct of Cycloöctatetraene (III).—To a solution of 0.50 g. of III[2] in 7 ml. of dry chloroform at 5° was added a solution of 0.44 g. of perbenzoic acid in 13.3 ml. of benzene. The reaction flask was swirled briefly and then placed in a refrigerator (5°) for the entire reaction period.

The progress of the reaction was followed by titration. Aliquots (0.50 ml.) were removed from the reaction flask periodically and treated with 2 ml. of an aqueous solution of potassium iodide to which an excess of glacial acetic acid had been added. The amount of iodine which was liberated by the peracid in each aliquot was determined by titration with a standard solution of sodium thiosulfate. The epoxidation proceeded very slowly and was stopped after 400 hours when 102% of one equivalent of perbenzoic acid had been consumed.

The white crystalline solid which had precipitated during the reaction period was collected and washed with a small amount of cold chloroform. The product thus obtained weighed 0.27 g. (m.p. 207-208°). The filtrate and washings from this solid were placed in a separatory funnel and washed with two 5-ml. portions of a saturated aqueous solution of sodium bisulfite followed by two 5-ml. portions of a saturated aqueous solution of sodium bicarbonate and finally with 5 ml. of water. The organic layer was dried over anhydrous sodium sulfate. Distillation of the organic solvent under reduced pressure afforded an additional 0.17 g. of product (m.p. 185–202°) as the crystalline residue. The total yield of crude product was 0.44 g. or 91% (yield corrected for aliquots removed for titration). Recrystallization of the crude product from a benzene–ligroin mixture (2:1) afforded 0.31 g. (66%) of II as white needles (m.p. 208.5–209.5°).

B. **Addition of Maleic Anhydride to Cycloöctatetraene Oxide.**—This preparation was carried out as described by Reppe, Schlichting, Klager and Toepel[2]; the product obtained melted at 209.5–210.0°. No depression in melting point was observed when a sample of II prepared by this method was mixed with II prepared by method A. The infrared spectrum of II (in potassium bromide) from this method was identical with that of II prepared by method A.

Nuclear Magnetic Resonance Samples.—Cycloöctatetraene oxide (I) was prepared by the method described in ref. 4 and had $n^{25}D$ 1.5380 (lit.[4] $n^{25}D$ 1.5383). 1,3,5-Cycloöctatriene (VII) was prepared by the procedure given in ref. 5, and had $n^{25}D$ 1.5243 (lit.[5] $n^{25}D$ 1.5249). Bicyclo[4.2.0]octa-2,4-diene (VIII) was prepared as described in ref. 5 and had $n^{25}D$ 1.5041 (lit.[5] $n^{25}D$ 1.5035). The purity of these hydrocarbons was ascertained by gas chromatography on a column (200 × 0.6 cm.) containing 25% (by weight) tetrahydroxyethylethylenediamine on 48–100 mesh firebrick. The column temperature was 60° and the preheater temperature was kept at 65° to avoid thermal isomerization. Helium at 10.1 p.s.i.g. and a flow rate of 100 ml. per min. was employed as the carrier gas; a thermal conductivity cell was used as a detector. By increasing the preheater temperature it was possible to obtain mixtures of bicyclo[4.2.0]octa-2,4-diene and 1,3,5-cycloöctatriene from pure 1,3,5-cycloöctatriene. The maximum amount of diene (20%) was obtained with a preheater temperature of 250° (column temperature 60°, flow rate 100 ml./min.). The presence of a small amount (less than 1%) of a thermally stable compound, probably 1,3,6-cycloöctatriene, in the samples of 1,3,5-cycloöctatriene ($n^{25}D$ 1.5243) was detected in these studies.

CAMBRIDGE, MASS.

[CONTRIBUTION No. 2316 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Small-ring Compounds. XX. 1,3-Dimethylenecyclobutane and Related Compounds[1]

BY FREDERICK F. CASERIO, JR., STUART H. PARKER,[2] RICHARD PICCOLINI AND JOHN D. ROBERTS

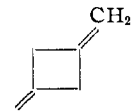
RECEIVED MAY 2, 1958

1,3-Dimethylenecyclobutane and 1-methyl-3-methylenecyclobutene have been synthesized by way of 3-methylenecyclobutanecarboxylic acid and (3-methylenecyclobutylcarbinyl)-dimethylamine. No clear experimental evidence was obtained for π-type electronic interaction across the ring of 1,3-dimethylenecyclobutane.

Introduction

The simple molecular-orbital (LCAO) method predicts a delocalization energy of about 0.066 β for cross-ring π-type electronic interaction in the 1,3-dimethylenecyclobutane (I) molecule if the 1,3-resonance integral is taken to be $\beta/3$. The objective of the present research was to synthesize I to see if evidence for such cross-ring interaction could be gained from studies of its chemical behavior and physical properties.

Synthesis of 1,3-Dimethylenecyclobutane and 1-Methyl-3-methylenecyclobutene.—A one-step synthesis of I through dimerization of allene is theoretically possible, but in practice only the 1,2-dimethylenecyclobutane appears to be formed.[3] However, 3-substituted methylenecyclobutanes such as would be appropriate for conversion to I and related compounds, are readily available by the elegant cycloadditions of monosubstituted alkenes to allene developed by Cripps and co-



I

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[1] Supported in part by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the Donors of this Fund.

[2] Fellow of the Foreign Research Scientists Program, 1954–1956.

[3] S. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913); *Chem. Zentr.*, **85**, 1402 (1914).

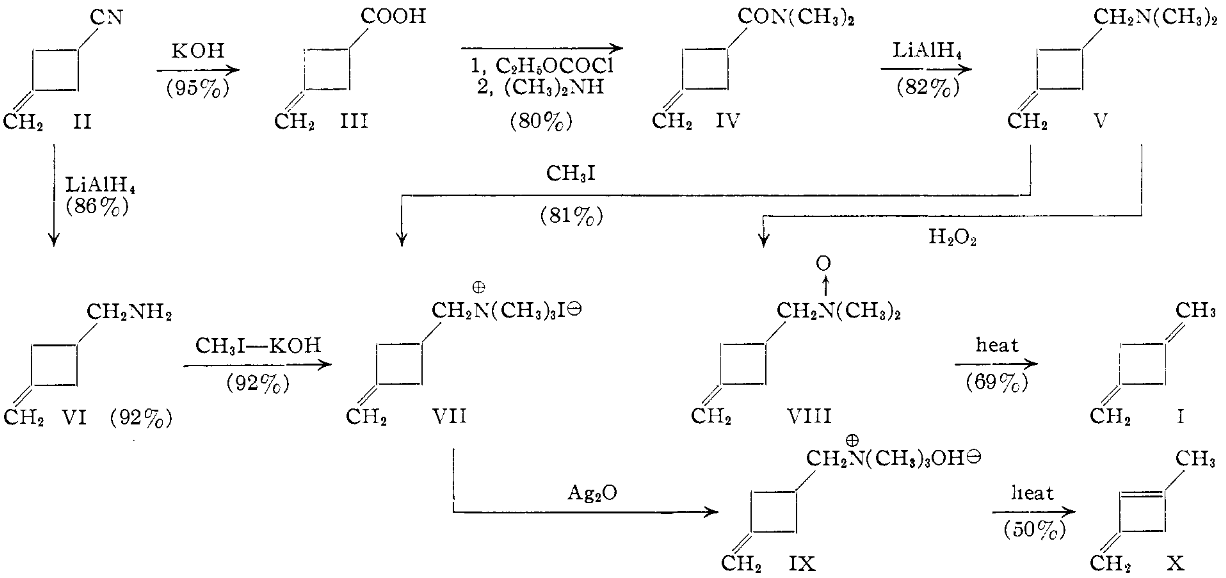

Fig. 1.—Syntheses of 1,3-dimethylenecyclobutane and 1-methyl-3-methylenecyclobutene.

workers.[4] Of particular interest in this connection is 3-methylenecyclobutanecarbonitrile (II) obtainable from allene and acrylonitrile. Use of II in syntheses of I and X is outlined in Fig. 1.

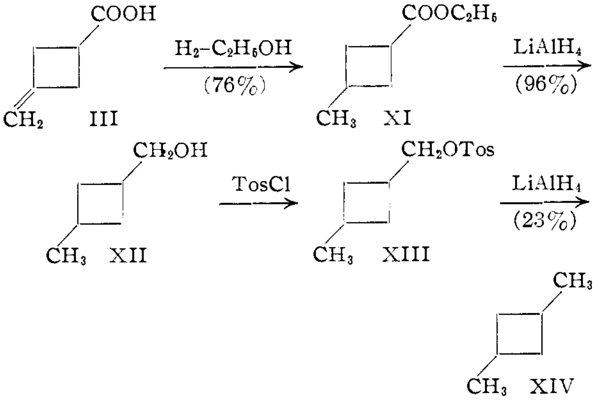

Fig. 2.—Synthesis of 1,3-dimethylcyclobutane.

3-Methylenecyclobutanecarboxylic acid (III) was prepared in 95% yield by alkaline hydrolysis of the nitrile II and was found to be identical in every respect to the material prepared by an independent method.[5] The primary amine VI was prepared in 74 and 86% yields by reduction of II with lithium aluminum hydride according to the procedure described by Amundsen and Nelson.[6] The quaternary iodide VII was obtained from VI with methyl iodide in the presence of base. Methylation of VI according to standard procedures failed to give the pure dimethylamine V and therefore V was prepared from the dimethylamide IV which was obtained from III by a modification of the amide preparations described by Wieland[7a] and Boissonnas.[7b] Reduction of IV with lithium aluminum hydride in ether gave V in an average yield of 83%. The product was converted to the quaternary iodide VII with methyl iodide in benzene and to the corresponding N-oxide VIII with 10% aqueous hydrogen peroxide; VII and VIII were not purified but were used directly for the next synthetic steps. Treatment of VII with silver oxide gave (3-methylenecyclobutylcarbinyl)-trimethylammonium hydroxide (IX). Decomposition of IX at 160° produced the conjugated diene X in 50% yield. Pyrolysis of the N-oxide VIII at 220° produced I in 69% yield. The yields of both I and X were based on V.

The structures of I and X were proved by physical methods and an independent synthesis of their common hydrogenation product, 1,3-dimethylcyclobutane (XIV) which was prepared for comparison as diagrammed in Fig. 2.

The ester XI was prepared in 76% crude yield by hydrogenation of III over palladium followed by esterification. The crude ester was reduced to XII with lithium aluminum hydride in 96% yield. Treatment of XII with *p*-toluenesulfonyl chloride afforded XIII as a yellow oil which failed to crystallize. Displacement of the tosylate group by hydrogen was accomplished with lithium aluminum hydride and produced XIV in 23% yield.

Hydrogenation of I and X resulted in a hydrogen uptake of 97 and 98%, respectively, of the theoretical amount required for two double bonds and both starting materials appeared to give the same saturated hydrocarbon or *cis–trans* mixture of hydrocarbons as was produced by the route of Fig. 2.

The infrared spectra (Fig. 3) of I and X are consistent with the assigned structures in that X has a doublet at 1598 and 1672 cm.$^{-1}$ and I has a singlet at 1661 cm.$^{-1}$ in the double-bond stretching region. Both compounds have an out-of-plane deformation absorption with that for X at 857 cm.$^{-1}$ and that for I at 880 cm.$^{-1}$. The lower energy absorption for X is evidence for conjugation of the two double bonds. Of special interest is the ease with which I and X can be distinguished by their respective nuclear magnetic resonance (n.m.r.) spectra (Fig.

[4] H. N. Cripps, J. K. Williams and W. H. Sharkey, THIS JOURNAL, **80**, 751 (1958).

[5] D. E. Applequist and J. D. Roberts, *ibid.*, **78**, 4012 (1956).

[6] L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 242 (1951).

[7] (a) T. Wieland, W. Schäfer and E. Bokelmann, *Ann.*, **573**, 99 (1951); (b) R. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951).

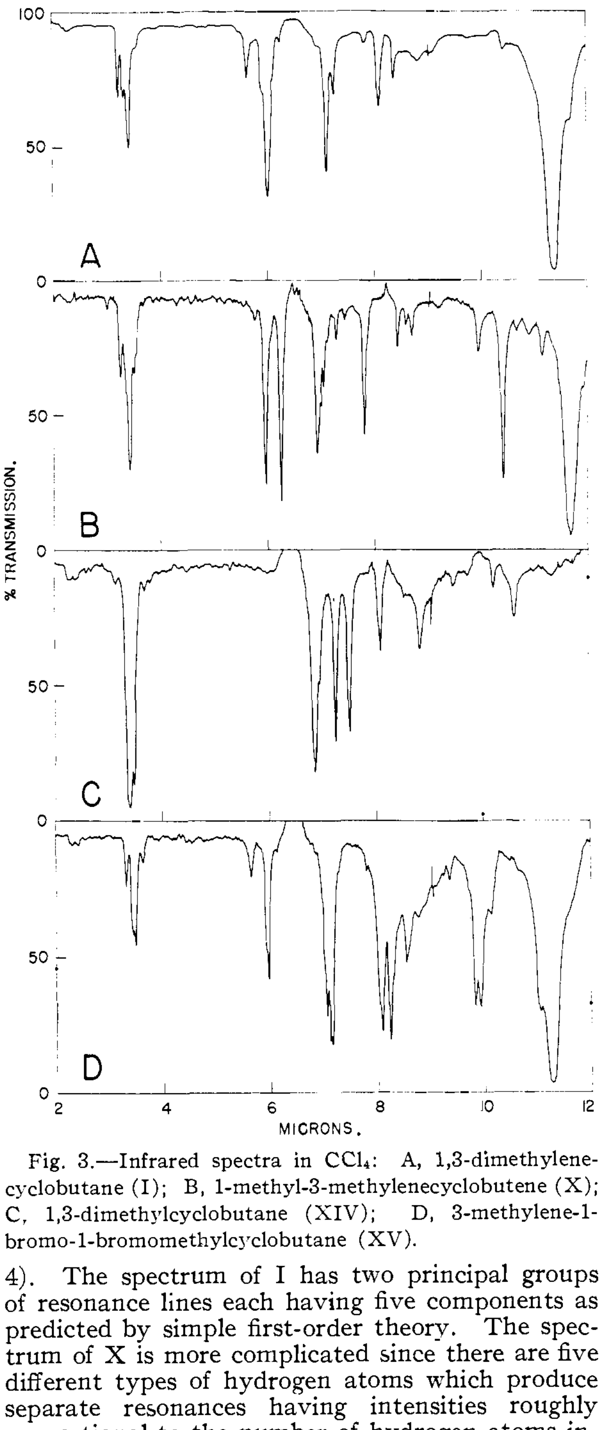

Fig. 3.—Infrared spectra in CCl_4: A, 1,3-dimethylenecyclobutane (I); B, 1-methyl-3-methylenecyclobutene (X); C, 1,3-dimethylcyclobutane (XIV); D, 3-methylene-1-bromo-1-bromomethylcyclobutane (XV).

4). The spectrum of I has two principal groups of resonance lines each having five components as predicted by simple first-order theory. The spectrum of X is more complicated since there are five different types of hydrogen atoms which produce separate resonances having intensities roughly proportional to the number of hydrogen atoms involved. The resonances were tentatively identified by comparison with the n.m.r. spectrum of methylenecyclobutene.[5] Some X always appeared to be present in even the purest samples of I as shown by the methyl resonance of X at 220 c.p.s. relative to benzene in the n.m.r. spectrum and the shoulder at 857 cm.$^{-1}$ in the infrared spectrum.

Properties and Reactions of 1,3-Dimethylenecyclobutane.—Evidence for 1,3-π-type electronic interaction in I could not be discerned from its ultraviolet spectrum. No absorption maximum was observed before the cutoff at 206 and 200 mμ in methylcyclohexane solution and in the gas phase, respectively. Fine structure in the form of three shoulders at 202, 207 and 214 mμ appeared in the vapor spectrum. The ultraviolet spectrum of X in ethanol had a maximum at 223.5 mμ (ε 19,000) which is consistent with a conjugated diene structure.

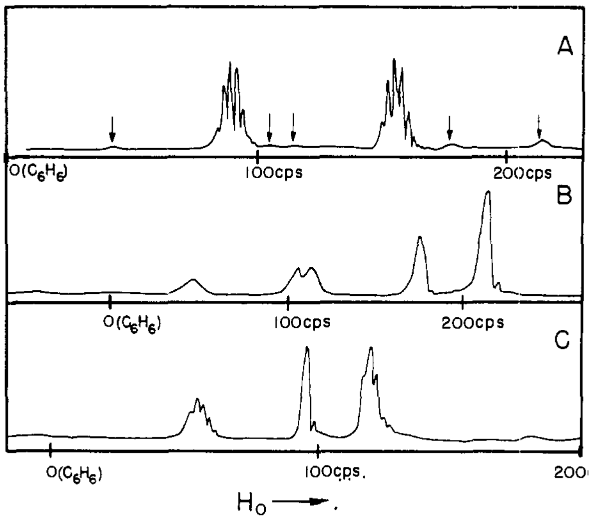

Fig. 4.—N.m.r. spectra: A, 1,3-dimethylenecyclobutane (I), liquid containing some 1-methyl-3-methylenecyclobutene as indicated by peaks marked with arrows; B, 1-methyl-3-methylenecyclobutene (X), pure liquid; C, 3-methylene-1-bromo-1-bromomethylcyclobutane (XV), pure liquid; C, 3-methylene-1-bromo-1-bromomethylcyclobutane (XV), pure liquid, taken with Varian Associates high resolution nuclear magnetic resonance spectrometer at 40 mc. with 12-in. magnet equipped with super stabilizer.

An electron diffraction study has been made of I and X.[8] Both substances turn out to be planar (±5°) with nearly square four-membered rings. The 1 and 3 carbons of I were found to be 2.11 ±0.02 Å. apart which is only 0.04 Å. less than the distance calculated for a perfectly square four-membered ring having 1.52 Å. sides in accord with the electron diffraction results for the distance between ring carbon atoms. As with methylenetrimethylene oxide,[5] the cross-ring distance of I provides no evidence for significant 1,3-bonding.

Heats of hydrogenation of I, X, methylenecyclobutane (XV) and 1-methylcyclobutene (XVI) have been measured[9] in acetic acid at 25° by Dr. R. B. Turner and his associates and are listed in Table I.

Comparison of the data listed in Table I with

TABLE I

HEATS OF HYDROGENATION[9]

	ΔH, kcal./mole
1,3-Dimethylenecyclobutane	−60.03 ± 0.08^{a,b}
1-Methyl-3-methylenecyclobutene	−54.95 ± .11^{b}
Methylenecyclobutane	−29.43 ± .06^{b}
1-Methylcyclobutene	−28.48 ± .01^{b}

[a] Corrected for the presence of 10 % of X estimated from infrared and n.m.r. spectra. [b] Unpublished data of Professor R. B. Turner.

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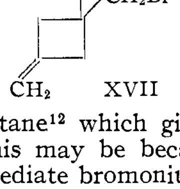
(8) J. P. McHugh and V. Schomaker, unpublished results.

(9) The procedure is described by R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

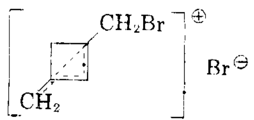
similar data for 1-methylcyclohexene, methylenecyclohexane, 1-methylcyclopentene and methylenecyclopentane[10] permit no conclusion concerning stabilization of I by 1,3-bonding. A more definite conclusion with regard to resonance energy is provided by the result for X. A minimum stabilization of 3.0 kcal. can be estimated from the data for methylenecyclobutane (XV) and 1-methylcyclobutene (XVI) by ignoring the unknown contribution to the strain energy of X introduced by having exocyclic and endocyclic double bonds in the same molecule. This minimum amount of resonance energy for X is as high or higher than the resonance energies of other conjugated dienes and may be evidence for some extra stabilization from 1,3-π-interaction of the type suggested earlier for the methylenecyclobutene system.[5]

The hydrogenation data for XV and XVI reveal that XVI might be thermodynamically more stable than XV. In an attempt to check this inference, both XV and XVI were treated with acid in carbon tetrachloride and chloroform solutions. No isomerization of either compound was observed after 24 hr. at room temperature. Treatment of XV with acid produced 1-methylcyclobutyl acetate in glacial acetic acid solution and a substance appearing to be 1-methylcyclobutylethyl ether in absolute ethanol solution. The latter two compounds probably result from a common tertiary carbonium ion[11] which preferentially reacts with solvent rather than lose a proton and revert to the unsaturated compounds.

Titration of I in carbon tetrachloride with bromine in the same solvent resulted in a rapid uptake of only one mole of bromine. A single dibromide was isolated in 54% yield along with a small amount of what appeared to be a mixture of di-, tri- and tetrabromides. The dibromide reacted instantly with potassium permanganate, alcoholic silver nitrate, and with sodium iodide in acetone to give a red solution and a white precipitate. Treatment of the dibromide with zinc bromide gave a dark solution from which the starting material was recovered unchanged upon distillation. Debromination of the dibromide with zinc dust gave I in 60% yield which was identical in all respects with an authentic sample. The infrared and n.m.r. spectra of the dibromide are shown in Figs. 3 and 4, respectively. The above data led to the conclusion that the dibromide is the simple 1,2-addition product and accordingly is assigned structure XVII. The straightforward reaction of I with bromine is in striking contrast to the behavior of methylenecyclobutane[12] which gives extensive rearrangement. This may be because of stabilization of the intermediate bromonium ion XVIII by cross-ring interaction and/or destabilization by the methylene double bond of the type of non-classical intermediate[13] which could lead to rearrangement.



XVII



XVIII

With maleic anhydride, compound I afforded a polymeric material which melted above 360° and was not soluble in common organic solvents or dilute acid or base. The analysis of the product indicated a 2:1 ratio of I to anhydride.

Compound I was found to isomerize smoothly to X in the presence of a catalytic amount of sodium amide in liquid ammonia. Weaker bases such as triethylamine and sodium hydroxide at room temperature did not cause isomerization to occur. Formation of X by the Hofmann degradation from IX thus is suggested to proceed by way of I as an intermediate which then rearranges at elevated temperatures in the presence of the strong base IX.

The possibility that either I or X might rearrange and react with metals to form cyclobutadiene–metal compounds[14] similar to ferrocene or dibenzenechromium was tested both with ferrous iron and nickel carbonyl as reagents. For ferrous iron, standard methods for the preparation of ferrocene[15] were followed and with nickel carbonyl both gas-phase and liquid-phase interactions were tried. No metal–organic products were isolated.

Acknowledgments.—We are much indebted to Professors V. Schomaker and R. B. Turner for their respective determinations of the electron diffraction and heat of hydrogenation data on I and X.

Experimental[16]

3-Methylenecyclobutanecarbonitrile (II) was prepared from allene and acrylonitrile in a 1-l. stainless-steel Parr bomb. The temperature was commonly 260–270° which is higher than that employed by Cripps.[4] After two rather violent decompositions under these conditions, one of which caused the copper gasket to be extruded from the bomb head, toluene was added as a diluent and no further difficulty was encountered. The maximum yield of II was 50%. A purified sample had b.p. 74–76° (31 mm.) and n^{25}_D 1.4590. Cripps reports b.p. 64–65° (21 mm.) and n^{25}_D 1.4595.

3-Methylenecyclobutanecarboxylic Acid (III).—Twenty grams (0.215 mole) of II was added to a solution of 56 g. (0.86 mole) of 85% potassium hydroxide pellets in 400 ml. of 50% aqueous ethanol and the mixture was heated on a steam-bath. After about 2 hr., the ammonia evolution had ceased and the solvent was evaporated under water aspirator vacuum. The residual solid was dissolved in 150 ml. of water and the solvent was evaporated again. This process was repeated once more in order to remove all the ethanol. The salts then were dissolved in 150 ml. of water, cooled in an ice-bath, and strongly acidified to congo red paper with concentrated hydrochloric acid. The resulting upper layer was separated and the aqueous, lower layer was extracted with four 50-ml. portions of ether. The organic layers were combined and dried over anhydrous magnesium sulfate.

Hydrolyses were performed as above in two batches on larger amounts of II and combination of the ether solutions afforded a 95% yield of III after distillation, b.p. 99–101° (9 mm.) and n^{25}_D 1.4653. An infrared spectrum of the product was identical with that obtained by Applequist and

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(10) R. B. Turner and R. H. Garner, This Journal, **79**, 253 (1957).

(11) E. F. Cox, Ph.D. Thesis, California Institute of Technology, 1955.

(12) D. E. Applequist and J. D. Roberts, This Journal, **78**, 874 (1956).

(13) Formula V of ref. 12.

(14) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

(15) G. Wilkinson, *Org. Syntheses*, **36**, 34 (1957).

(16) All melting and boiling points are uncorrected. Analyses are by Dr. A. Elek, Los Angeles, California.

Roberts[5] from a sample of III prepared by an independent synthesis.

N,N-Dimethyl-3-methylenecyclobutanecarboxamide (IV).—The procedure was based on those of Wieland[7a] and Boissonnas.[7b] A solution of 7.9 (0.07 mole) of III and 7.2 g. (0.07 mole) of triethylamine in 100 ml. of chloroform was cooled in an ice–salt-bath and 7.8 g. (0.07 mole) of ethyl chlorocarbonate dissolved in 10 ml. of chloroform was added rapidly with agitation. Twenty-five minutes later, 6.2 g. (0.14 mole) of anhydrous dimethylamine was added in small portions while the flask was swirled. The clear solution was removed from the cooling bath and was allowed to stand at room temperature overnight.

The chloroform and excess amine were distilled from the reaction mixture at atmospheric pressure. The brown crystalline residue was dissolved in 40 ml. of water and extracted with 30 ml. of benzene. The aqueous layer was saturated with sodium chloride and extracted with three 30-ml. portions of benzene and two 30-ml. portions of ether. The organic layers were combined, dried over anhydrous magnesium sulfate and, after removal of the drying agent, distilled at atmospheric pressure to remove the solvents. The concentrate then was distilled under reduced pressure and 7.8 g. (80%) of IV was obtained, b.p. 62–67° (1 mm.). The last fraction, b.p. 67° (1 mm.), had n^{25}_D 1.4880. An analytical sample was prepared by two distillations of the last fraction, n^{25}_D 1.4877.

Anal. Calcd. for $C_8H_{13}ON$: C, 69.03; H, 9.41. Found: C, 69.10; H, 9.43.

(3-Methylenecyclobutylcarbinyl)-dimethylamine (V).—To an ice-cooled stirred suspension of 2.0 g. (0.053 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether was added, over a period of 20 min., 5.8 g. (0.042 mole) of IV dissolved in 100 ml. of ether. The mixture was refluxed for 3 hr., cooled in an ice-bath and then the excess hydride was destroyed by slow, careful addition of a large excess of water (the destruction of the excess reagent is unnecessary but desirable for the ultimate disposal of the reaction residues). The ether solution was poured off and was combined with three 50-ml. ether rinses of the residue. The ether solution was dried over anhydrous magnesium sulfate and concentrated by distillation through a 30-cm. Vigreux column. The yellow concentrate was distilled under reduced pressure through a short Vigreux column and yielded 4.2 g. (82%) of V, b.p. 82–83° (99 mm.). The average yield of three preparations was 83%.

Three reduced pressure distillations of a small sample gave the analytical sample having n^{25}_D 1.4480.

Anal. Calcd. for $C_8H_{15}N$: C, 76.79; H, 12.08. Found: C, 76.71; H, 12.11.

A picrate was formed from V in ether solution and after recrystallization from 95% ethanol had m.p. 136.5–137°.

Anal. Calcd. for $C_{14}H_{18}N_4O_7$; C, 47.46; H, 5.12. Found: C, 47.38; H, 5.09.

3-Methylenecyclobutylcarbinylamine (VI).—The procedure of Amundsen and Nelson[6] was used except that the quantities of ether were halved. Two preparations gave VI in yields of 74 and 86%, b.p. 132–133° (744 mm.), n^{25}_D 1.4668.

Anal. Calcd. for $C_6H_{11}N$: C, 74.16; H, 11.4; N, 14.42. Found: C, 74.19; H, 11.3; N, 14.45.

(3-Methylenecyclobutylcarbinyl)-trimethylammonium Iodide (VII). A. From (3-Methylenecyclobutylcarbinyl)-dimethylamine.—A mixture of 2.0 g. (0.016 mole) of V and 5.0 g. (0.035 mole) of methyl iodide in 60 ml. of benzene was allowed to stand 2 hr. at room temperature. The solid was recrystallized from absolute alcohol and gave 3.5 g. (81%) of VII, m.p. 233° dec. with charring at 225°. An earlier sample prepared in the absence of benzene from V gave m.p. 218.8–220° dec. After storage for about a year, the same sample had m.p. 234.5–235° dec. and gave no depression of melting point when mixed with the first sample.

Anal. Calcd. for $C_9H_{18}NI$: C, 40.46; H, 6.79. Found: (material with m.p. 220° dec.) C, 40.44; H, 6.77; (material with m.p. 235° dec.) C, 40.63; H, 6.80.

B. **From 3-Methylenecyclobutylcarbinylamine.**—A solution containing 494 g. (3.48 moles) of methyl iodide in 330 ml. of absolute methanol was added slowly to a stirred solution of 74 g. (0.76 mole) of VI in 460 ml. of absolute methanol. A solution of 140 g. (2.50 moles) of potassium hydroxide in 660 ml. of absolute methanol then was added and the reaction mixture was refluxed for 2 hours. Removal of the solvent by distillation at 40–50° (30 mm.) followed by extraction of the solid residue with chloroform in a Soxhlet apparatus gave 186.9 g. (92%) of VII, m.p. 218.5–219° dec. The melting point of the product when admixed with the lower melting material obtained in A above was not depressed.

Anal. Calcd. for $C_9H_{18}NI$: C, 40.46; H, 6.77; N, 5.24. Found: C, 40.53; H, 6.69; N, 5.21.

(3-Methylenecyclobutylcarbinyl)-trimethylammonium Hydroxide (IX).—Silver oxide, freshly prepared from 146 g. (0.88 mole) of silver nitrate and 58.0 g. (1.04 mole) of potassium hydroxide, was shaken for 2.5 hr. with a suspension of 85.0 g. (0.35 mole) of VI in 200 ml. of water. The filtered solution was concentrated to a viscous yellow sirup using a rotary film evaporator. The material thus obtained was not purified but was used directly for the preparation of X.

1-Methyl-3-methylenecyclobutene (X).—The sirupy hydroxide IX formed from 63 g. (0.24 mole) of VII was decomposed by slowly dripping it into a 100-ml. flask maintained at 160° and 50 mm. pressure and connected to a Dry Ice trap. The decomposition was completed in about 45 min. The contents of the trap were then allowed to warm to room temperature and the resulting two liquid phases were shaken with 25 ml. of 1 *N* hydrochloric acid. The layers were separated and the upper, organic layer was extracted with three 20-ml. portions of 1 *N* hydrochloric acid, two 10-ml. portions of 5% sodium bicarbonate solution and two 10-ml. portions of saturated sodium chloride solution. All washings were carried out using ice-cold solutions in order to minimize loss of the volatile product. The crude yield was 11.6 g. (62%). Distillation through a short Vigreux column gave 9.4 g. (50%, based on VII) of purified X, b.p. 69–70°, n^{25}_D 1.4588. The product polymerizes in the presence of air, but can be stored at least a year under its own vapor pressure without change.

Anal. Calcd. for C_6H_8: C, 89.94; H, 10.06. Found: C, 89.88; H, 10.04.

(3-Methylenecyclobutylcarbinyl)-dimethylamine Oxide (VIII).—Fourteen grams (0.12 mole) of V was added dropwise during 30 min. to 100 ml. of a 10% solution (0.28 mole) of hydrogen peroxide in a 200-ml. flask immersed in an ice-bath and stirred with a Teflon covered magnetic stirring bar. After the addition was completed, the solution was allowed to warm to room temperature and stirred overnight (about 16 hours). The next morning, the reaction was shown to be complete by the failure of the solution to cause pink coloration of phenolphthalein indicator. A small amount of catalase was then added to destroy the excess peroxide.

The slightly cloudy solution was filtered and the water was removed at room temperature using a rotary film evaporator. A yellow, extremely hygroscopic, crystalline solid was obtained which was not further purified. The yield of crude product was 15 g. (95%). In some preparations, a sirup was obtained which crystallized very slowly in storage at 0°. A melting point of 150–155° (subl.) was determined in one of the decomposition experiments described below.

The picrate was formed in absolute ethanol and was recrystallized three times from this solvent, m.p. 127.2–128°. The melting point of the product was depressed more than 28° on admixture with picric acid.

Anal. Calcd. for $C_{14}H_{18}O_8N$: C, 45.37; H, 4.90. Found: C, 45.38; H, 4.95.

1,3-Dimethylenecyclobutane (I).—Forty-six grams (0.33 mole) of VIII contained in a 200-ml. flask connected to a Dry Ice trap (reversed to minimize plugging) and evacuated to 1 mm. was decomposed in a Woods metal-bath at a temperature of 210 ± 20°. All glass connections were used between the flask and trap since use of rubber tubing appeared to lower the yield of I. The decomposition proceeded smoothly and appeared to be over in 6 minutes.

The material trapped at −78° was washed with seven 5-ml. portions of 1 *N* hydrochloric acid, two 5-ml. portions of water and once with 5 ml. of saturated sodium chloride solution. The solutions were all maintained at about 0° to avoid loss of volatile material. The crude I was dried over anhydrous magnesium sulfate and amounted to 17.1 g. (69%, based on V). An analytical sample was prepared by careful distillation through a 30-cm. Holzman column,[17]

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[17] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

b.p. 68.0° (742 mm.), $n^{25}_{\rm D}$ 1.4465. The infrared spectrum showed a weak absorption at 858 cm.$^{-1}$ which is indicative of the presence of a small amount of the conjugated isomer X.

Anal. Calcd. for C_6H_8: C, 89.94; H, 10.06. Found: C, 89.93; H, 10.03.

Ethyl 3-Methylcyclobutylcarboxylate (XI).—A solution containing 20.3 g. (0.18 mole) of III in 200 ml. of absolute ethanol was hydrogenated over palladium. After the theoretical amount of hydrogen had been absorbed, the catalyst was removed, 0.5 ml. of concentrated hydrochloric acid was added and the solution allowed to stand overnight at room temperature. The ethanol was fractionated from the crude ester through a 30-cm. Holzman column. The hydrochloric acid was neutralized with 1 ml. of triethylamine and the hydrochloride was removed by filtration with the aid of 20 ml. of benzene. Fractional distillation of the benzene solution through the Holzman column gave 19.2 g. (76%) of XI, b.p. 99–100° (100 mm.), 74–74.8° (30 mm.), $n^{25}_{\rm D}$ 1.4222. This material was used without further purification for the preparation of XII.

3-Methylcyclobutylcarbinol (XII).—An ether solution of 19.2 g. (0.137 mole) of XI was added dropwise to an ice-cooled mixture of 5.0 g. (0.137 mole) of lithium aluminum hydride and 200 ml. of ether during 20 min. The mixture was allowed to stand at room temperature for 24 hr. and then heated under reflux for 1.5 hr. It was cooled in an ice-bath and carefully hydrolyzed by slow addition of 20 ml. of water. The ether layer was decanted from the residue, combined with five 50-ml. ether extracts of the residue, dried over anhydrous magnesium sulfate and the ether distilled through a 30-cm. Vigreux column. The residue was distilled through a 30-cm. Holzman column and gave 13.4 g. (96%) of XII, b.p. 84° (50 mm.), $n^{25}_{\rm D}$ 1.4362.

Anal. Calcd. for $C_6H_{12}O$: C, 71.96; H, 12.08. Found: C, 71.68; H, 12.23.

3-Methylcyclobutylcarbinyl *p*-Toluenesulfonate (XIII).—To a solution of 27.0 g. (0.14 mole) of *p*-toluenesulfonyl chloride in 150 ml. of pyridine maintained at −10° was added 13.2 g. (0.132 mole) of XII in 1 min. The resulting yellow solution was kept at −10° for 15 min. and then was placed in a refrigerator for 2 hr. The mixture containing some pyridine hydrochloride was allowed to warm to room temperature, then poured into 300 ml. of ice-water containing 100 ml. of concentrated hydrochloric acid, and extracted with four 50-ml. portions of chloroform and the extracts dried over a magnesium sulfate–Norite mixture. The solution was filtered and the chloroform was removed by distillation under reduced pressure. The yellow viscous oil amounted to 30.4 g. (91%) and was not further purified.

1,3-Dimethylcyclobutane (XIV). A. From 1,3-Dimethylenecyclobutane (I).—A 0.105-g. (1.31 mmoles) sample of I in 15 ml. of glacial acetic acid was hydrogenated over platinum in a semi-micro apparatus at atmospheric pressure. A total of 65.6 ml. of hydrogen gas was absorbed which was 97% of the theoretical amount required for two double bonds. Corrections were made for temperature, pressure and the vapor pressure of acetic acid. No correction was made for the vapor pressure of the starting material or product. In order to obtain an isolable amount of product, 1 ml. more of I and a small amount of catalyst were added to the solution and hydrogenation was continued. After the hydrogen uptake ceased, the catalyst was removed and the saturated hydrocarbon caused to separate by addition of 25 ml. of water. The product was dissolved in 5 ml. of *m*-xylene and the xylene solution was washed with dilute sodium permanganate solution and then several portions of water. The xylene solution was dried over sodium hydroxide and then fractionated through an 8-mm. × 30-cm. concentric tube column. About 0.4 ml. of XIV was obtained in three fractions. The third fraction had b.p. 56.5–57° (742 mm.) and n^{25} 1.3868. An analytical sample was prepared by passing the combined fractions through a short column of activated alumina followed by simple distillation.

Anal. Calcd. for C_6H_{12}: C, 85.62; H, 14.38. Found: C, 85.51; H, 14.29.

B. **From 3-Methylcyclobutylcarbinyl *p*-Toluenesulfonate (XIII).**—A solution of 25.4 g. (0.10 mole) of XIII in 20 ml. of dry ether was added dropwise to a stirred, cooled mixture of 5.0 g. (0.13 mole) of lithium aluminum hydride and 40 ml. of ether. After 1 hr. at room temperature, another 4.5 g. (0.12 mole) of hydride was added. The mixture remained at room temperature 48 hr., then was refluxed for 1 hr. and finally flash distilled under reduced pressure into a Dry Ice-cooled flask. The residue was stirred with 50 ml. of ether and the ether was removed as before. The combined distillates contained a small amount of colloidal matter which was removed by filtration. The ether solution was carefully fractionated through the 30-cm. concentric tube column. Four fractions above the boiling point of ether were obtained, the last of which had b.p. 56.5–57° (740 mm.). The four fractions were combined and extracted with three 5-ml. portions of concentrated sulfuric acid and were then distilled three times, b.p. 56–58°, $n^{25}_{\rm D}$ 1.3870. The total yield of pure XIV after recovery of some material in the distillation residue was 1.9 g. (23%).

Anal. Calcd. for C_6H_{12}: C, 85.62; H, 14.38. Found: C, 85.65; H, 14.36.

C. **From 1-Methyl-3-methylenecyclobutene (X).**—A 0.0515-g. (0.643 mmole) sample of X was quantitatively hydrogenated in the same manner as described in A above. The hydrogen uptake was 98% of the theoretical value for two double bonds.

A slow stream of nitrogen was passed through the acetic acid solution of the hydrogenation product. Acetic acid was removed from the gas stream by a bubbler containing concentrated sodium hydroxide solution. A small amount (less than 0.1 g.) of a colorless liquid collected in a trap cooled to −70°. The liquid was dissolved in 1 ml. of chloroform and an infrared spectrum was taken. The spectrum obtained was virtually identical to the completely superimposable spectra of carbon tetrachloride solutions of the product from procedures A and B.

It would appear that these products are mixtures of *cis* and *trans* isomers since vapor-phase chromatography resolves analytically pure material into two components in a ratio of about 3 to 1. The configuration of the predominant isomer is not known.

Bromination of 1,3-Dimethylenecyclobutane. A.—The bromide–bromate titration of olefins of Johnson and Clark[18] was used to obtain quantitative bromination data on I. The published procedure was followed closely except that the concentrations of reagents were half of those recommended. The average equivalent weight from three determinations was 20.8 which corresponds to 96.5% of the theoretical amount of bromine required for two double bonds. A blank showed no corrections to be necessary. The method is reported to be accurate to ±3% for simple monoalkenes.

B.—A solution of 2.0 g. (0.025 mole) of I in 10 ml. of carbon tetrachloride was titrated with 19.7 ml. (0.025 mole) of 1.27 *M* bromine in carbon tetrachloride. Decolorization was slow at first and a small amount of hydrogen bromide was evolved which appeared to catalyze subsequent bromine absorption.

The hydrogen bromide was removed under reduced pressure and the infrared spectrum of the residual solution showed strong absorptions at 887 and 1680 cm.$^{-1}$ characteristic of an exocyclic methylene group. The carbon tetrachloride was removed and the crude bromide mixture separated into two fractions by vacuum distillation. The first fraction had b.p. 54–67° (1 mm.) and amounted to 2.7 g. (44% yield of dibromide).

The first fraction was purified by repeated vacuum distillations and finally had b.p. 69–70° (1 mm.) and $n^{25}_{\rm D}$ 1.5460

Anal. Calcd. for $C_6H_8Br_2$: C, 30.07; H, 3.37; Br, 66.70. Found: C, 30.01; H, 3.34; Br, 66.60.

The second fraction which was a mixture of higher bromination products had b.p. 67–120° (1 mm.) and amounted to 1.6 g. It was distilled under reduced pressure but could not be obtained colorless. The final distillation yielded a product with a long boiling range and $n^{25}_{\rm D}$ 1.5827.

Anal. Calcd. for $C_6H_7Br_3$: Br, 75.19; for $C_6H_8Br_4$: Br, 79.94. Found: Br, 73.87.

Both bromide fractions reacted instantaneously with ethanolic silver nitrate and potassium permanganate in aqueous acetone but did not react with 5% bromine in carbon tetrachloride. Also, both bromides reacted instantaneously with sodium iodide in acetone to give a red solution and a white precipitate.

In an attempt to isomerize the dibromide,[5] a small amount of anhydrous zinc bromide was added to about 0.3 ml. of the

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[18] H. L. Johnson and R. A. Clark, *Anal. Chem.*, **19**, 869 (1944).

purified material and the mixture was allowed to stand at room temperature. A dark color was produced immediately. After 21 hr. at room temperature, the mixture was distilled at 1 mm. and gave about 0.1 ml. of product having n^{25}D 1.5465. The infrared spectrum of the distillate in carbon tetrachloride solution was identical with that of the starting dibromide.

Debromination of the Dibromide of I with Zinc.—To a stirred mixture of 5.0 g. (0.077 mole) of zinc powder and 5 ml. of 95% ethanol was added dropwise 3.2 g. (0.0136 mole) of the dibromide of I. The mixture was refluxed during the addition and each drop of dibromide caused a momentary increase in reflux rate. After 10 min., all of the dibromide had been added and the pressure on the system was reduced slightly and about 4 ml. of volatile product (and solvent) was collected in a Dry Ice trap. The trap was allowed to warm to room temperature and 5 ml. of distilled water was added. Two phases appeared and the upper layer was separated and washed with four 3-ml. portions of distilled water. The aqueous layer of the last wash was frozen and the organic layer was removed carefully. Distillation of the organic layer gave 0.6 g. (60%) of I, b.p. 67° and n^{25}D 1.4470. The infrared spectrum of a carbon tetrachloride solution of the distillate was identical to that of an authentic sample of I. The identity of the product was also confirmed by its n.m.r. spectrum.

Isomerization of 1,3-Dimethylenecyclobutane.—Sodium amide was prepared from 0.035 g. (0.0016 mole) of sodium dissolved in about 5 ml. of liquid ammonia containing a trace of ferric chloride as catalyst and then the ammonia was allowed to evaporate until only about 1 ml. remained. Compound I (1.0 g., 0.0125 mole) (containing about 10% X) was added rapidly. The resulting dark mixture was allowed to reflux for 1.5 hr. and at the end of this time the ammonia was allowed to distil from the flask; 12 ml. of 1 *N* hydrochloric acid was added to the residue and the organic layer was removed after first freezing the aqueous layer. The slightly yellow organic phase amounted to 0.86 g. (86%) and had b.p. 68–69°. The infrared spectrum of the product was identical to that of an authentic sample of X.

In several experiments in which triethylamine and sodium hydroxide were used as the base, no isomerization occurred at room temperature.

Reaction between 1,3-Dimethylenecyclobutane (I) and Maleic Anhydride.—A mixture of 1.2 g. (0.0125 mole) of I, 1.0 g. (0.0125 mole) of maleic anhydride and 15 ml. of *m*-xylene was heated for 10 hr. at 100° in a sealed tube. Solid and liquid phases were obtained. Fractionation of the liquid phase yielded no starting materials except the solvent. The solid amounted to 0.6 g. of a white powder, m.p. >360°, which could not be dissolved in any common organic solvent or 1 *N* acid or base. The analysis corresponds to a polymeric substance made up of molecules of maleic anhydride and I in the ratio of 2 to 1, respectively.

Anal. Found: C, 60.94; H, 5.25.

Attempted Preparation of Iron and Nickel Complexes from 1,3-Dimethylenecyclobutane (I).—An olive-drab colored mixture of 0.013 mole of sodium amide, 1.0 g. (0.013 mole) of I and 15 ml. of tetrahydrofuran was added to a mixture of 0.013 mole of ferrous chloride in 40 ml. of tetrahydrofuran prepared according to the directions of Wilkinson.[15] The resulting brown mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the resultant residue was extracted with four 20-ml. portions of boiling *n*-hexane. Removal of the solvent from the combined extracts by distillation yielded about 0.1 ml. of a dark yellow liquid which contained no iron.

Another attempt to prepare an iron compound in which I was mixed directly with a solution of ferrous chloride containing diethylamine resulted only in the isolation of diethylamine hydrochloride.

Attempts to prepare nickel compounds of I and X by reaction with nickel carbonyl in both the gas and liquid phases at various temperatures resulted in the isolation of nickel, nickel oxide and polymeric substances containing no nickel.

Attempts to Interconvert Methylenecyclobutane (XV) and 1-Methylcyclobutene (XVI).—A mixture of 0.8 g. of XV, 0.1 g. of 96% sulfuric acid and 1.6 g. of glacial acetic acid was shaken mechanically in a sealed tube for 1 hr. at room temperature. The brown one-phase solution then was flash distilled at room temperature (1 mm.) and the distillate was mixed with 5 ml. of water which caused two phases to form. The upper phase was isolated, washed with 5% sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Distillation from sodium yielded about 0.5 ml. of colorless sweet-smelling liquid, b.p. 100–130°, n^{25}D 1.4180, which did not react with bromine in carbon tetrachloride solution. The infrared spectrum of the product was almost identical with that of 1-methylcyclobutyl acetate, b.p. 54.7–54.8° (40 mm.), n^{25}D 1.4162, prepared previously.[11] A vapor-phase chromatogram showed the product to be 90% pure. The above procedure was repeated using absolute ethanol in place of glacial acetic acid with subsequent isolation of a compound, b.p. 107°, n^{25}D 1.4100, which appears to be ethyl 1-methylcyclobutyl ether.

Solutions of XV and XVI in carbon tetrachloride and chloroform saturated with dry hydrogen chloride were allowed to stand at room temperature about 24 hr. No change in the infrared spectra of the solutions occurred during the stated reaction time. The solutions then were heated 3 hr. at 100° in sealed tubes after which the infrared spectra of the solutions were different but could not be interpreted.

In an attempt to interconvert XV to XVI under basic conditions, a mixture of 0.004 mole of sodium amide in 1 ml. of liquid ammonia and 1.7 g. (0.025 mole) of XV was allowed to reflux for 2 hr. The mixture then was treated with dilute hydrochloric acid and the organic layer was distilled to yield 0.9 g. of the starting material XV.

PASADENA, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Condensation Product of 9,10-Phenanthrenequinone and Ethyl Acetoacetate

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The condensation product of 9,10-phenanthrenequinone and ethyl acetoacetate and the isomer into which it is converted by acids have been shown to be III and IV, respectively, rather than I and II as originally proposed by Japp, Klingemann and Streatfeild. Ultraviolet and infrared spectra provided the information essential for the new structural assignments. A number of compounds derived from III and IV that were prepared by earlier workers but for which no structures were proposed have been re-synthesized and assigned structures (V-XIII) that are in accord with all of the chemical and spectral data obtained for them.

The preparation of several derivatives of 1H-cyclopenta(*l*)phenanthrene from the condensation product of 9,10-phenanthrenequinone and ethyl acetoacetate has been described recently.[2] This condensation product was first prepared by Japp and Streatfeild,[3] who used aqueous ethanolic potassium hydroxide as the condensing agent, and later by Lachowicz,[4] who effected the condensation with piperidine in ethanol. Japp and Streatfeild as-

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[1] Visking Corporation Fellow, 1953–1954.

[2] A. C. Cope, L. Field, D. W. H. MacDowell and M. E. Wright, THIS JOURNAL, **78**, 2547 (1956).

[3] F. R. Japp and F. W. Streatfeild, *J. Chem. Soc.*, **43**, 27 (1883).

[4] B. Lachowicz, *Monatsh.*, **17**, 344 (1896).