

[CONTRIBUTION NO. 511 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Chemistry of Cyclobutanes. III. Synthesis of Unsaturated Four-membered Ring Hydrocarbons

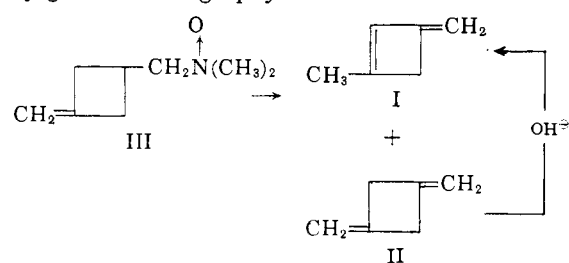
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RECEIVED JANUARY 26, 1959

1-Methyl-3-isopropylidenecyclobutene and 1,4,4-trimethyl-3-methylenecyclobutene have been prepared from 3-isopropylidenecyclobutanecarbonitrile and 2,2-dimethyl-3-methylenecyclobutanecarbonitrile, respectively. 1,3-Dimethylenecyclobutane has been shown to be one of the products formed by thermal dimerization of allene. A compound believed to be trimethylenecyclobutane also has been obtained from the pyrolysis of a bis-quaternary salt along with the isomeric triene 1-methyl-3,4-dimethylenecyclobutene. Evidence for the formation of this highly unsaturated compound rests upon isolation of a dimer.

A number of unsaturated four-membered ring hydrocarbons have been synthesized by routes analogous to Willstätter's¹ classical synthesis of cyclobutene by decomposition of cyclobutyltrimethylammonium hydroxide. Examples include the preparation of methylenecyclobutene,² 2,2-dimethylmethylenecyclobutene,² 1,2-dimethylenecyclobutane³ and recently 1-methyl-3-methylenecyclobutene.⁴ Discovery of a route to substituted alkylidenecyclobutanes⁵ that are converted readily to amine derivatives has made possible the preparation of a number of new unsaturated four-membered ring hydrocarbons.

The synthesis of 1-methyl-3-methylenecyclobutene (I) and 1,3-dimethylenecyclobutane (II), reported by Caserio, Parker, Piccolini and Roberts, has been confirmed independently in this Laboratory. Pyrolysis of N,N-dimethyl-(3-methylenecyclobutanemethyl)-amine oxide⁴ (III) gave a mixture containing 78% of II and 22% of I that was separated readily into the two pure hydrocarbons by gas chromatography.

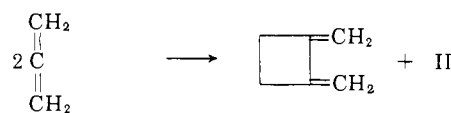


When the mixture composed of 78% 1,3-dimethylenecyclobutane and 22% 1-methyl-3-methylenecyclobutene was heated under reflux in contact with a 10% solution of potassium hydroxide in ethylene glycol it was converted to a mixture composed of only 4% 1,3-dimethylenecyclobutane and 96% 1-methyl-3-methylenecyclobutene.

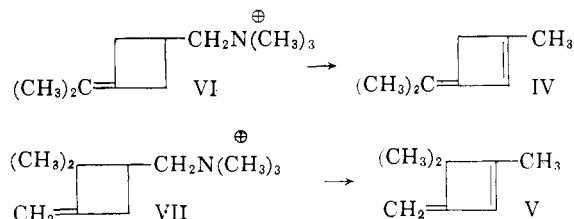
The preparation and characterization of pure 1,3-dimethylenecyclobutane led to detection of this compound in the product formed by dimerization of allene, which is reported to give 1,2-dimethylenecyclobutane.⁶ Dimerization of allene at 400° and atmospheric pressure⁷ gave two products in a ratio

- (1) R. Willstätter and W. von Schmaedel, *Ber.*, **38**, 1992 (1905).
- (2) D. E. Applequist and J. D. Roberts, *THIS JOURNAL*, **78**, 4012 (1956).
- (3) A. T. Blomquist and J. A. Verdol, *ibid.*, **78**, 109 (1956).
- (4) F. F. Caserio, Jr., S. H. Parker, R. Piccolini and J. D. Roberts, *ibid.*, **80**, 5507 (1958).
- (5) H. N. Cripps, J. K. Williams and W. H. Sharkey, *ibid.*, **80**, 757 (1958); **81**, 2723 (1959).

of 85:15. These compounds were separated by gas chromatography. The major component was 1,2-dimethylenecyclobutane. The minor component was identical to 1,3-dimethylenecyclobutane obtained by pyrolysis of I.



The route previously described⁴ for the preparation of III that culminates in a Hofmann pyrolysis has now been used to prepare more highly substituted alkylidene cyclobutenes. Dimethylallene upon cycloaddition to acrylonitrile forms two products, 3-isopropylidenecyclobutanecarbonitrile and 2,2-dimethyl-3-methylenecyclobutanecarbonitrile.⁵ These compounds were converted to 1-methyl-3-isopropylidenecyclobutene (IV) and 3-methylene-1,4,4-trimethylcyclobutene (V), respectively, by pyrolysis of the corresponding quaternary hydroxides VI and VII.



The infrared spectrum of IV showed a weak band at 5.83 μ for the isopropylidene double bond stretching vibration and at 6.26 μ for the stretching vibration of the endocyclic double bond. The infrared spectrum of V had bands at 5.99 and 6.27 μ for the stretching vibration of the exocyclic and endocyclic double bonds and a band at 11.78 μ for the out of plane bending vibration of the methylene hydrogens. The n.m.r. spectra⁸ of these compounds con-

(6) S. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913); *C. A.*, **8**, 320 (1914).

(7) We are indebted to the late Dr. C. Weaver who dimerized allene and first detected the 1,3-isomer in the product. Analysis of this product by vapor phase chromatography was done by Dr. B. C. Anderscn.

(8) We are indebted to Dr. W. D. Phillips of this Laboratory who determined and interpreted the n.m.r. spectra. N.m.r. spectra were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at 40 Mc. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of H₂O. Negative frequency displacements indicate resonances occurring at higher field relative to the reference.

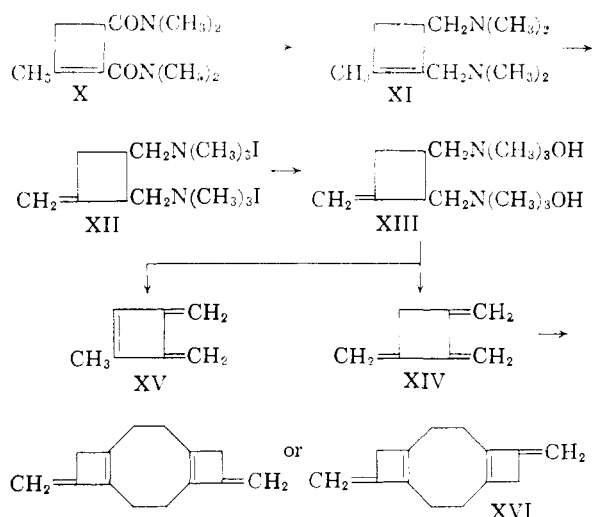
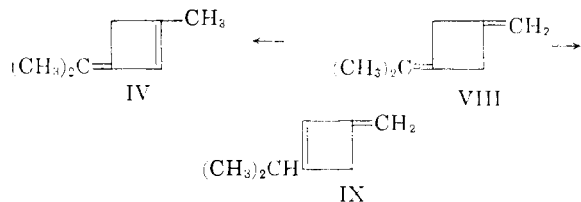


Fig. 1.—Preparation and reactions of trimethylenecyclobutane.

firmly the assigned structures. For IV resonance peaks occur at +33 c.p.s. corresponding to the hydrogen at position 2, at -101 c.p.s. for the two hydrogens at position 4, at -130 c.p.s. for the three hydrogens of the methyl group at position 1, and at -146 c.p.s. for the six hydrogens of the isopropylidene group. Similarly, the n.m.r. spectrum of V shows resonance at +23 c.p.s. for the hydrogen at position 2, at -37 c.p.s. for the two hydrogens on the exocyclic methylene group, at -140 c.p.s. for the three hydrogens of the methyl group at position 1, and at -164 c.p.s. for the hydrogens on the two methyl groups at position 4.

It is assumed that 1-isopropylidene-3-methylenecyclobutane (VIII) is the initial product in the reaction that gives IV; VIII could give both IV and IX, but IV was the only product isolated.



No evidence was obtained for the presence of either VIII or IX.

Bifunctional cyclobutenes⁹ are obtained readily by rearrangement of the 1:1 allene-maleic anhydride adduct, 3-methylenecyclobutane-1,2-dicarboxylic anhydride, and one of these derivatives, N,N,N',N'-tetramethyl-3-methyl-2-cyclobutene-1,2-biscarboxamide (X), served as a precursor to the triply unsaturated cyclobutane derivatives, trimethylenecyclobutane (XIV) and 1-methyl-3,4-dimethylenecyclobutene (XV). Trimethylenecyclobutane proved to be unstable and dimerized near room temperature to the cyclooctadiene derivative XVI. The reactions employed in the preparation of XIV and XV are outlined in Fig. 1.

Reduction of the bisamide X with lithium aluminum hydride proceeded normally to give

(9) H. N. Cripps, J. K. Williams, V. Tullio and W. H. Sharkey, in press.

the bisamine XI in good yield. Quaternization with methyl iodide was unusual in that the reaction was accompanied by migration of the double bond to the *exo* position. This was convincingly demonstrated by infrared analysis, which showed absorption at 3.31 and 11.25 μ for terminal methylene. These bands were not present in the infrared spectrum of XI.

Reaction of XII with silver oxide gave the quaternary hydroxide XIII, which was decomposed by mild heating to yield a volatile, water-insoluble hydrocarbon mixture. This product was caught in a trap cooled at -80°. In an attempt to isolate trimethylenecyclobutane (XIV) the pyrolysis product was allowed to warm to near room temperature where it evolved heat and obviously underwent spontaneous changes. When the pyrolysis product was allowed to stand at 25° in a solvent, and then distilled, the hydrocarbons XV and XVI were obtained.

Pure 1-methyl-3,4-dimethylenecyclobutene (XV) was obtained by gas chromatography and characterized by spectral studies. Its n.m.r. spectrum had peaks at +5 c.p.s. for the single hydrogen on the ring, at -32 c.p.s. for the four methylene hydrogens and at -145 c.p.s. for the methyl hydrogens. Infrared absorption of XV is shown in Fig. 2. The ultraviolet spectrum of XV in isoöctane showed two maxima which were at 210 $m\mu$ (ϵ 31,800) and at 245 $m\mu$ (ϵ 5800).

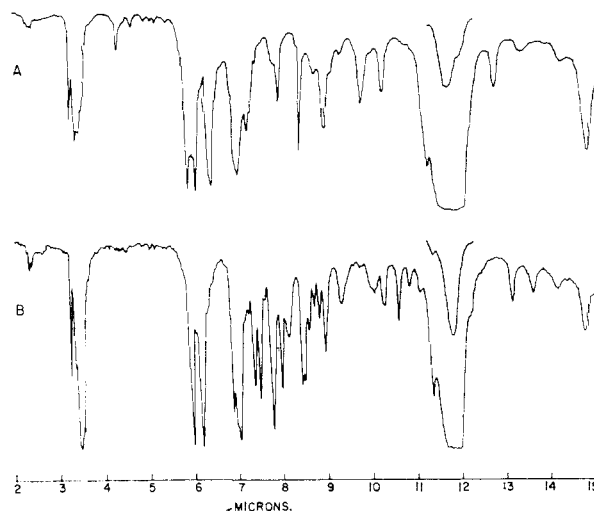


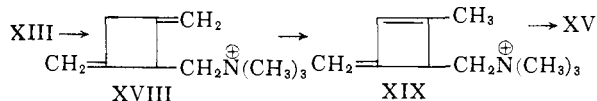
Fig. 2.—Infrared spectra: A, 1-methyl-3,4-dimethylenecyclobutene (XV); B, dimer XVI.

Characterization of the cyclooctadiene XVI is also based mainly on spectral studies. Its infrared spectrum (Fig. 2) is very similar to that of 1-methyl-3-methylenecyclobutene (I), with bands at 5.93, 6.17 and 11.75 μ . Of particular interest is its ultraviolet spectrum. Maximum absorption occurred at 225 $m\mu$ as compared to 224 $m\mu$ for I. At 225 $m\mu$ the extinction coefficient of XVI was 26,700, which is very nearly twice that of I⁴ as would be expected for the structure assigned. The n.m.r. spectrum of XVI was also consistent. Resonance was obtained at -22 and -29 c.p.s. for the four exocyclic methylene hydrogens and at -93, -107 and -114 c.p.s. for the twelve saturated hy-

drogens. No evidence has been obtained to differentiate between the two possible position isomers of XVI.

Although trimethylenecyclobutane is too reactive to be isolated and characterized by chemical methods, evidence was obtained indicating it to be a primary product formed by decomposition of XIII. When the organic material in the cold trap was dissolved in pentane, washed with cold, dilute acid to remove trimethylamine and quickly dried with magnesium sulfate and its infrared spectrum measured immediately, strong absorption at 5.64 and 11.37 μ was observed while bands ascribable to XV were of medium strength and those associated with the dimer XVI were weak. The bands at 5.64 and 11.37 μ diminished in intensity when this product was stored at 25°. At the same time the bands ascribable to the dimer XVI increased greatly and those associated with XV remained essentially unchanged.

The isolation of 1-methyl-3,4-dimethylenecyclobutene from the pyrolysis of XIII may be explained in several ways. The infrared spectral evidence indicates that dimerization is the process by which trimethylenecyclobutane stabilizes itself in neutral solution at 25°; nevertheless base-catalyzed rearrangement could take place under the highly alkaline pyrolysis conditions. Alternatively, analogy for the sequence involving rearrangement of the partial pyrolysis product XVIII to XIX is found in the formation of 1-methyl-3-alkylenecyclobutenes from N,N,N-trimethyl-(3-alkylenecyclobutanemethyl)-ammonium hydroxides.



Experimental¹⁰

1,3-Dimethylenecyclobutane (II).—The amine oxide prepared from 75 g. of N,N-dimethyl-(3-methylenecyclobutane)-methylamine⁴ was heated at 150–185° under 140–190 mm. pressure. Pyrolysis products were collected in a trap cooled at –80°. After pyrolysis was complete the material in the trap was allowed to warm to room temperature and the organic phase was separated and dried over magnesium sulfate. Distillation gave 28 g. of hydrocarbon, b.p. 68.5–69°, n_D^{25} 1.4486. Gas chromatography showed that the product was 78% 1,3-dimethylenecyclobutane and 22% 1-methyl-3-methylenecyclobutene. The 1-methyl-3-methylenecyclobutene, n_D^{25} 1.4598, was identified by comparison of the behavior of an authentic sample of this material on the same chromatographic column. Preparative gas chromatography of a sample of the hydrocarbon mixture afforded a pure sample of 1,3-dimethylenecyclobutane,¹¹ b.p. 68°, n_D^{25} 1.4466.

Rearrangement of 1,3-Dimethylenecyclobutane (II) to 1-Methyl-3-methylenecyclobutene (I).—A 5-ml. sample of the hydrocarbon mixture of 78% II and 22% I obtained in the previous experiment was heated under reflux with 2.5 g. of potassium hydroxide and 25 ml. of ethylene glycol. Over the course of 2.75 hours the refractive index changed from its original value of n_D^{25} 1.4486 to n_D^{25} 1.4564. Gas chromatography showed the hydrocarbon mixture was now composed of 96% 1-methyl-3-methylenecyclobutane and 4% 1,3-dimethylenecyclobutene.

3-Isopropylidenecyclobutanemethylamine.—A slurry of 100 g. of lithium aluminum hydride in 1 l. of absolute ether

was prepared under a nitrogen atmosphere. To it was added 242 g. (2 moles) of 3-isopropylidenecyclobutanecarbonitrile over a period of 3 hours. After stirring the reaction mixture at 25° for an additional 98 hr. the reduction was complete, and the metal salts were decomposed by addition of 46 g. of sodium hydroxide dissolved in 250 ml. of water. The ether solution was decanted from the solid inorganic salts, which were washed with additional portions of ether. The combined ether solutions were dried over potassium hydroxide, the ether was removed, and the residual oil distilled through a 24-inch spinning band column to yield 166 g. (66%) of 3-isopropylidenecyclobutanemethylamine, b.p. 114° (96 mm.), n_D^{25} 1.4748.

Anal. Calcd. for $\text{C}_8\text{H}_{15}\text{N}$: C, 76.74; H, 12.06. Found: C, 77.03; H, 11.98.

The phenylthiourea of this amine, purified by two recrystallizations from hexane, melted at 92–92.5°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{S}$: C, 69.18; H, 7.74; N, 10.76. Found: C, 69.28; H, 7.88; N, 10.70.

N,N,N-Trimethyl-(3-isopropylidenecyclobutanemethyl)-ammonium Iodide (VI).—3-Isopropylidenecyclobutanemethylamine (125 g., 1.0 mole) was added over 45 minutes to a mixture of 318 g. of sodium carbonate. 1.5 l. of absolute methanol and 270 g. (1.9 moles) of methyl iodide. The mixture was stirred at room temperature for 16 hours, filtered, and the filter cake washed with two 227-g. portions of hot absolute methanol. The filtrates were combined and evaporated to dryness under reduced pressure. A light-tan solid was obtained that was dried *in vacuo* at 30°. The quaternary salt was isolated from this solid by extraction with six 500-ml. portions of chloroform. Upon evaporation of the extracts to dryness, recrystallization of the residue from absolute alcohol and drying *in vacuo* at 60°, there was obtained 267 g. (90%) of N,N,N-trimethyl-(3-isopropylidenecyclobutanemethyl)-ammonium iodide, m.p. 208–210°. After recrystallization from a methanol–water mixture, this compound melted at 211–212°.

Anal. Calcd. for $\text{C}_{11}\text{H}_{22}\text{IN}$: C, 44.75; H, 7.51; N, 4.75. Found: C, 44.31; H, 7.41; N, 4.62.

1-Methyl-3-isopropylidenecyclobutene (IV).—The above quaternary iodide (155 g., 0.525 mole) dissolved in 1 l. of water was added to silver oxide prepared from 170 g. of silver nitrate. After stirring for 3 hours, the reaction mixture was filtered, and the filtrate concentrated at 40° under reduced pressure. The sirup obtained was heated in an oil-bath (bath temperature 120–130°) at 1–2 mm. and volatile products were collected in a trap cooled at –80°. After warming to room temperature, the upper, organic layer was separated, washed with cold water, and distilled. The portion boiling at 129–129.5° was washed with 10% aqueous acetic acid, then with saturated sodium bicarbonate, and dried over magnesium sulfate. Redistillation through a 12-inch packed column gave 14 g. of 1-methyl-3-isopropylidenecyclobutene, b.p. 130–130.5°, n_D^{25} 1.4742.

Anal. Calcd. for C_8H_{12} : C, 88.81; H, 11.19. Found: C, 88.71; H, 11.19.

2,2-Dimethyl-3-methylenecyclobutanemethylamine.—2,2-Dimethyl-3-methylenecyclobutanecarbonitrile (121 g., 1.0 mole) was reduced with 50 g. of lithium aluminum hydride by the same procedure described for 3-isopropylidenecyclobutanemethylamine. The crude amine was distilled through a 24-inch spinning band column to give 104 g. (83%) of 2,2-dimethyl-3-methylenecyclobutanemethylamine, b.p. 97° (102 mm.). This amine formed a phenylthiourea which, after two crystallizations from hexane, melted at 83–83.5°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{S}$: C, 69.18; H, 7.74; N, 10.76. Found: C, 69.05; H, 7.74; N, 10.62.

N,N,N-Trimethyl-(2,2-dimethyl-3-methylenecyclobutanemethyl)-ammonium Iodide (VII).—The procedure described for the preparation of IV afforded N,N,N-trimethyl-(2,2-dimethyl-3-methylenecyclobutanemethyl)-ammonium iodide, m.p. 249–250°, in 83% yield. Recrystallization from water gave crystals melting sharply at 256°.

Anal. Calcd. for $\text{C}_{11}\text{H}_{22}\text{IN}$: N, 4.75. Found: N, 4.32.

1,4,4-Trimethyl-3-methylenecyclobutene (V).—A slurry of silver oxide (prepared from 340 g. of silver nitrate) in 1 l. of distilled water was stirred with 148 g. (0.5 mole) of N,N,N-trimethyl-(2,2-dimethyl-3-methylenecyclobutanemethyl)-ammonium iodide (VII) at room temperature for 24 hours.

(10) Melting points and boiling points are uncorrected.

(11) Separation was accomplished readily on a 12 ft. \times 1/4 in. column at 25° packed with 1,5-dicyano-3-methyl-3-nitropentane on 40–60 mesh firebrick (3:7) with a helium flow rate of 545 ml./min. The retention time of I was 43 min. and of II was 64 min.

Silver salts were removed by filtration under nitrogen, and the filtrate was concentrated by distillation at atmospheric pressure. When the pot temperature reached 145°, the distillate began to distil in two phases. Pyrolysis was continued until the pot temperature reached 160°. The upper, organic layer of the distillate was separated and washed free of trimethylamine with water and then dried over potassium hydroxide. The crude product was distilled through a 12-inch packed column to give 31 g. (57%) of 1,4,4-trimethyl-3-methylenecyclobutene, b.p. 95°, n_D^{25} 1.4413.

Anal. Calcd. for C_8H_{12} : C, 88.81; H, 11.19. Found: C, 89.12; H, 11.29.

N,N,N',N'-3-Pentamethyl-2-cyclobutene-1,2-dicarboxamide (X).—A solution of 200 g. of anhydrous dimethylamine in 1 l. of benzene was cooled to 0° in a Morton flask. To it was added 100 g. of 3-methyl-2-cyclobutene-1,2-dicarbonyl chloride⁹ in 100 ml. of benzene with vigorous stirring over the course of 1.5 hours. During addition the temperature was maintained between 0 and 10°. Dimethylamine hydrochloride, 84 g. (100%), was removed from the reaction mixture by filtration. Benzene and excess dimethylamine were removed by distillation under reduced pressure. The dark brown oil that remained weighed 98 g. (90%). The crude amide was of sufficient purity for reduction to the more readily purified diamine XI.

3-Methyl-1,2-bis-(dimethylaminomethyl)-2-cyclobutene (XI).—The crude amide X, prepared as described above, was dissolved in 500 ml. of anhydrous ether and added to a slurry of 30 g. of lithium aluminum hydride and 640 ml. of anhydrous ether under nitrogen. The reaction mixture was stirred at room temperature for 18 hours and then under reflux for an additional 3 hours. The excess lithium aluminum hydride was decomposed by the cautious addition of 150 ml. of a solution of 100 g. of sodium hydroxide in 300 ml. of water. The ether solution was removed and the brown solid was washed with 640 ml. of ether. The combined ether solutions were reduced to a volume of 300 ml. by distillation on the steam-bath. The remaining ether was removed through a 30-inch spinning band column and the oil that remained was distilled under reduced pressure, b.p. 60–64° (3 mm.), 52.6 g. (62%), n_D^{25} 1.4569–1.4572. A heart cut, n_D^{25} 1.4572, was analyzed. The infrared spectrum of this diamine had no band at 3.25 or 11–11.75 μ , but did have a band at 5.91 μ (unconjugated C=C in four-membered ring).

Anal. Calcd. for $C_{11}H_{22}N_2$: N, 15.36. Found: N, 15.35.

3-Methylenecyclobutane-1,2-bis-(methyltrimethylammonium Iodide) (XII).—Over the course of one hour a solution of 182 g. of XI in 250 ml. of absolute ethanol was added to a stirred solution of 350 g. of methyl iodide in 1 l. of absolute ethanol while the temperature of the reaction mixture was maintained at 0–10°. The mixture then was allowed to stand at 5° for 16 hours. After the solid precipitate of bis-quaternary iodide XII was collected, washed with 200 ml. of cold absolute ethanol and dried in a vacuum oven at 45°, it weighed 437 g. (94%). After four recrystallizations from methanol, material was obtained that melted at 217–218° dec. The infrared spectra of both the crude product and the analytical sample showed bands at 3.31, 5.93 and 11.25 μ .

Anal. Calcd. for $C_{13}H_{28}N_2I_2$: C, 33.49; H, 6.05; N, 6.01. Found: C, 33.58; H, 6.30; N, 5.92.

1-Methyl-3,4-dimethylenecyclobutene (XV) and 5,11-(or 12 ?)-Dimethylenetricyclo[8.2.0.0^{4,7}]dodeca-1(10),4(7)-diene (XVI).—A mixture of 117 g. of XII, 750 ml. of water and the freshly prepared moist silver oxide from 128 g. of silver nitrate was stirred vigorously at 25° for 0.5 hour. At this point a filtered sample of the reaction mixture gave no precipitate with silver nitrate solution in dilute nitric acid. The solid was removed by filtration, and the filtrate was placed in a flask equipped with a stirrer and a 12-inch

Vigreux column. Water was removed by distillation at 5 mm. until decomposition of the quaternary hydroxide began, as evidenced by a change in the nature of the boiling. Then the product was collected in a receiver containing 100 ml. of ether and 0.25 g. of phenothiazine and cooled at –80°. Distillation was continued and the pot temperature was maintained at 20–40°. The contents of the receiver were allowed to warm to room temperature and were diluted with 200 ml. of ether. The ether layer was washed rapidly with two 200-ml. portions of water, two 200-ml. portions of 3% hydrochloric acid, and finally with two more 200-ml. portions of water and then dried over anhydrous potassium carbonate at 0°. The ether and more volatile materials were removed at 5 mm. and collected in a trap at –80°. Distillation of the residue gave 6.1 g. of the dimer XVI, b.p. 116–117° (5.5 mm.); XVI polymerized very rapidly when exposed to the air but could be stabilized by the addition of a trace of phenothiazine. It melted at about 5° and could be stored at that temperature, when protected from air, for several months without any apparent change. The infrared spectrum of XVI is reproduced in Fig. 2. The ultraviolet spectrum showed $\lambda_{max}^{isooctane}$ 225 m μ (ϵ 26,700).

Anal. Calcd. for $C_{14}H_{16}$: C, 91.23; H, 8.77; mol. wt., 184; quant. hydrogenation, 0.0439 g. H_2/g . Found: C, 91.00; H, 8.68; mol. wt., 188, 190; quant. hydrogenation, 0.0439 g. H_2/g .

The lower-boiling pyrolysis product that was collected in the cold trap during the initial distillation was redistilled to give 1.2 g. of XV, b.p. 44–45° (100 mm.). Gas chromatography afforded a specimen for characterization.¹²

The ultraviolet spectrum of XV had two maxima in iso-octane; λ_{max} 210 m μ (ϵ 31,800), λ_{max} 245 m μ (ϵ 5,800). The infrared spectrum is reproduced in Fig. 2.

Anal. Calcd. for C_7H_8 : C, 91.25; H, 8.75. Found: C, 91.63, 90.84; H, 8.59, 9.17.

Trimethylenecyclobutane (XIV).—In a separate pyrolysis conducted as described above, the pyrolysis product was collected in a trap at –80° without solvent. To the cold trap was added 100 ml. of pentane and enough calcium chloride to cause the aqueous phase to melt at about –40°. The pentane phase was collected and washed with a solution of 10 ml. of concentrated hydrochloric acid in 100 ml. of 29% calcium chloride solution at –40°. Pentane was removed by distillation at 30 mm. pressure until 8 ml. of material remained. From this residue, 4 ml. of material

TABLE I

Bands assignable to	μ	0 hr.	Absorbance 1 hr.	22 hr.
XIV	5.64	0.18	0.14	0.02
	6.08	.29	.26	.20
XV	5.87	.17	.19	.23
	6.03	.26	.26	.26
XVI	6.44	.90	.90	.90
	5.93	.10	.20	.45
	6.17	.24	.44	.95

was distilled into a receiver cooled at –80°. When a small portion of the distillate was allowed to warm to 25° a spontaneous, exothermic reaction took place. Another portion of distillate (0.5 ml.) was dissolved in 5 ml. of a 1:1 carbon tetrachloride–chloroform mixture at –80°. The infrared spectrum of this solution was measured as rapidly as possible in the 5–6.5 μ region. These measurements are summarized in Table I.

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(12) 12 ft. \times $\frac{3}{4}$ in. column at 140° packed with Dow-Corning 200 Fluid, 50 cs., on 40–60 mesh firebrick with helium flow rate of 265 ml./min. The retention time of XV was 31 min.