sequent transformations without further purification. Its m.p. was not determined.

Pure 1,9-cyclohexadecanedione bis-ethylenedithioketal (VII) was obtained after two recrystallizations from chloroform–hexane of the fraction melting at 204–210°, m.p. 210.5–212°.

Anal. Calcd. for $C_{20}H_{36}S_4$: C, 59.35; H, 8.96; S, 31.69. Found: C, 59.69; H, 8.97; S, 32.06.

Reductive Desulfurization of the 1,9-Cyclohexadecanedione Dithioketals.—The 4.66 g. of crude V described above was added to a suspension of 15 g. of Raney nickel in 200 ml. of ethanol which had been refluxed previously for an hour with 5 ml. of acetone. The mixture was refluxed for 3 hr., cooled and filtered. The filtered Raney nickel was allowed to stand under methanol.

To the ethanolic filtrate was added a solution of 5 g. of semicarbazide hydrochloride and 10 g. of sodium acetate in 10 ml. of water. Although a white precipitate formed immediately, the mixture was allowed to stand 24 hr. before filtering. The methanolic solution obtained after removal of the Raney nickel was treated similarly and the resulting solid semicarbazone combined with that obtained above. The total semicarbazone precipitates were digested with 300-ml. and 250-ml. portions of boiling methanol. The insoluble material weighed 1.59 g. and showed m.p. 221–227° corresponding to that of I disemicarbazone. An additional quantity (0.29 g.) of impure disemicarbazone, m.p. 186–191°, separated when the methanolic filtrates stood at room temperature for one day. Concentration of the methanol solution gave three crystalline fractions of III semicarbazone: (1) 1.0 g. having m.p. 172–173°, (2) 0.77 g. having m.p. 168–172° and (3) 1.25 g. having m.p. 170–175°.

The 3.02 g. of III semicarbazone corresponds to a 47% conversion from I. The yield, adjusted for recoverable diketone derivatives, was 90%.

Similar reductive desulfurization of 730 mg. of VII using 6 g. of Raney nickel in 75 ml. of ethanol gave 170 mg. of IX, m.p. 60–60.2° (Ruzicka, *et al.*, give m.p. 61°[10]).

Hydrolysis of 1 g. of III semicarbazone with aqueous oxalic acid gave 0.62 g. (72%) of once sublimed III having an intense musk odor and repeated sublimation raised the melting point to 59.5–60.2° (Ruzicka, *et al.*, reported m.p.'s 63–64°,[11] 56°[12]). The infrared spectrum of the ketone in a Halocarbon mull showed carbonyl absorption at 5.87 μ and C–H absorption at 3.4, 6.9 and 7.2 μ.

Cyclization of Sebacyl Chloride.—Following the procedure outlined for cyclization of azelayl chloride, 245 g. (1.03 moles) of sebacyl chloride in 600 ml. of dry benzene was added over a 3-hr. period to a refluxing solution of 7 l. of benzene and 1 l. of triethylamine. Hydrolysis of the reaction mixture gave 33.4 g. (23.8%) of II which after crystallization from hexane showed m.p. 93–95° (Ruzicka, *et al.*, reported m.p. 96–97°[10]).

Conversion of (II) to its Ethylenedithioketals.—Following the procedure described earlier 2.26 g. (0.0094 mole) of II in 200 ml. of reagent grade benzene was treated with 0.758 g. (0.0094 mole) of ethanedithiol, 15 g. of anhydrous sodium acetate, and 5 g. of freshly fused and powdered zinc chloride. After working up the reaction mixture as previously described there was obtained 1.23 g. of crude bis-dithioketal VIII, m.p. 185–188°, and 1.43 g. of impure mono-dithioketal VI, m.p. 73–92°, contaminated with unreacted diketone.

After five recrystallizations from chloroform–hexane the bis-ethylenedithioketal of II showed m.p. 191.2–193.5°.

Anal. Calcd. for $C_{22}H_{40}S_4$: C, 61.05; H, 9.31. Found: C, 61.04, 61.34; H, 9.29, 9.47.

The crude mono-dithioketal VI was not purified prior to reductive desulfurization.

Reductive Desulfurization of 1,10-Cycloöctadecanedione Ethylenedithioketals.—The procedure used was identical with that given earlier for desulfurization of the I dithioketals. From 140 mg. of VIII there was obtained 40 mg. (66.6%) of X, m.p. 70–71° (Ruzicka, *et al.*, reported m.p. 72°[10]).

From 0.94 g. of the crude VI after desulfurization and treatment with semicarbazide reagent in the usual way there was obtained 0.78 g. of II disemicarbazone, m.p. 205–220°, and 0.56 g. of IV semicarbazone, m.p. 168–170°. Recrystallization of the latter from methanol raised the m.p. to 180–181° (Ruzicka, *et al.*, reported m.p. 184°[10]).

Anal. Calcd. for $C_{19}H_{37}N_3O$: C, 70.53; H, 11.53. Found: C, 70.65; H, 11.87.

The conversion of II to IV semicarbazone was 21% while the yield, adjusted for recoverable diketone derivatives, was 80%.

Hydrolysis of 200 mg. of IV semicarbazone with aqueous oxalic acid gave 90 mg. of once sublimed IV, m.p. 68–70° (Ruzicka, *et al.*, reported m.p. 71°[12]).

Ithaca, N. Y.

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(11) L. Ruzicka, *et al.*, *Helv. Chim. Acta*, **13**, 1152 (1930).

(12) L. Ruzicka, M. Stoll and H. Schinz, *ibid.*, **9**, 263 (1926).

[Contribution from the Baker Laboratory of Chemistry at Cornell University]

1,2-Dimethylenecyclobutane[1,2]

By A. T. Blomquist and Joseph A. Verdol

Received August 31, 1954

1,2-Dimethylenecyclobutane has been obtained by thermal decomposition of 1,2-bis-(dimethylaminomethyl)-cyclobutane dimethohydroxide. The latter was synthesized from diethyl 1,2-cyclobutanedicarboxylate by (1) lithium aluminum hydride reduction of the ester to a glycol, (2) bromination of the glycol with phosphorus tribromide, (3) aminolysis of the dibromide with trimethylamine and finally (4) hydrolysis of the bis-quaternary salt with moist silver oxide. That the diene was 1,2-dimethylenecyclobutane was confirmed by its chemical and physical properties, including its infrared and ultraviolet absorption spectra. Normal Diels–Alder adducts of the diene could be obtained only in the presence of a polymerization inhibitor. In their absence the diene polymerized. Treatment of the diene with sulfur dioxide also caused its polymerization, even in the presence of inhibitor. Persulfate initiated polymerization of the diene at 50° for 24 hr. gave a rubber-like soluble high polymer having *ca.* 80% 1,4-addition polymerization units as indicated by the perbenzoic acid method. Attempts to obtain the diene by pyrolysis of 1,2-bis-(acetoxymethyl)-cyclobutane were unsuccessful. 2-Vinyl-1,3-butadiene was the only isolable product of this thermal decomposition.

As part of an extensive program in this Laboratory concerned with an investigation of new conjugated diene systems which might be expected to show high reactivity in polymerization reactions, the synthesis and properties of 1,2-dimethylenecyclobutane (I) were studied. This particular hydrocarbon with two exocyclic double bonds conjugated through a cyclobutane ring was of especial interest because of its relationship to the conjugated exocyclic dienes in the cyclohexane series studied by Bailey[3] and by Wicklatz and Short.[4] Like the

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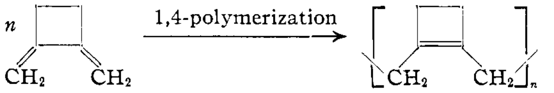
(1) Presented before the Division of Organic Chemistry at the National Meeting of the American Chemical Society at New York, N. Y., September 12–17, 1954.

(2) The work reported here was done as part of a research program at the Baker Laboratory of Chemistry, Cornell University, sponsored by the B. F. Goodrich Company.

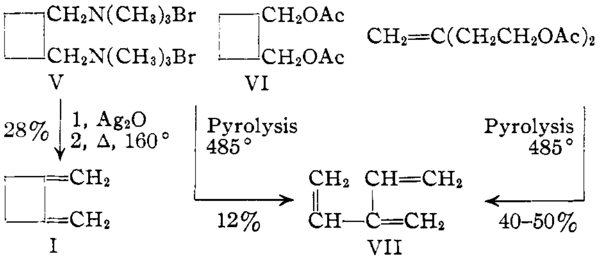
(3) (a) W. J. Bailey and H. R. Golden, Abstracts of the 117th Meeting of the American Chemical Society, March–April, 1950, p. 330; (b) W. J. Bailey and H. R. Golden, This Journal, **75**, 4780 (1953).

(4) J. E. Wicklatz and J. N. Short, U. S. Patent 2,600,454, June, 1952; *C. A.*, **46**, 11769b (1952).

1,2-dimethylenecyclohexanes, 1,2-dimethylenecyclobutane should afford an all-*cis* polymer on 1,4-addition polymerization. This polymer would correspond somewhat to an all-*cis*-poly-2,3-dimethyl-1,3-butadiene.



Further, as a consequence of the strain imposed upon the system by the cyclobutane ring, the diene might be expected to show a higher reactivity in addition polymerization reactions of all kinds. Synthesis of I was achieved as indicated



Lithium aluminum hydride reduction of diethyl 1,2-cyclobutanedicarboxylate (II) or the corresponding dimethyl ester gave 1,2-bis-(hydroxymethyl)-cyclobutane (III), a viscous, colorless liquid, in 80-85% yield. 1,2-Bis-(bromomethyl)-cyclobutane (IV) was obtained from III in 90% yield by treatment with phosphorus tribromide. Aminolysis of IV with trimethylamine in methanol gave the dimethobromide of 1,2-bis-(dimethylaminomethyl)-cyclobutane (V) in essentially quantitative yield. The conversion of V to the corresponding dimethohydroxide by treatment with silver oxide was also quantitative. Thermal decomposition (104-160°) under nitrogen of 1,2-bis-(dimethylaminomethyl)-cyclobutane dimethohydroxide containing a small amount of hydroquinone gave a 28% yield of crude I. Pure I was obtained as a colorless liquid, b.p. 73° (atm.), n^{20}_{D} 1.4721, d^{20}_{20} 0.7927.

Attempts to obtain I *via* the pyrolysis of 1,2-bis-(acetoxymethyl)-cyclobutane (VI) were unsuccessful. Extensive decomposition of the diacetate always occurred and the only isolable product was 2-vinyl-1,3-butadiene, obtained in very low yield. Thus cleavage of the cyclobutane ring accompanied the elimination reactions at temperatures of 475-500°. The VII obtained here was identical with a sample of VII prepared recently in this Laboratory.[5]

The diene I decolorized solutions of aqueous potassium permanganate and bromine in carbon tetrachloride. It absorbed 100.1% of two molar equivalents of hydrogen on quantitative hydrogenation using Adams catalyst. Oxidative ozonolysis of the diene gave a 53% yield of succinic acid. The latter was characterized by comparison of its m.p. and infrared spectrum with those of authentic succinic acid and by its *p*-bromophenacyl ester. Formaldehyde, as its dimedone derivative, was obtained in 38% yield upon reductive ozonolysis of I.

Conjugated unsaturation of I involving two exocyclic double bonds also was supported by the absorption spectra data. In the infrared (Fig. 1) the principal absorption maxima observed were at 3.25, 6.06 and 11.40 μ (all characteristic of $R_1R_2C{=}CH_2$) and at 3.40 μ (characteristic of the $>CH_2$ group).[6] The ultraviolet spectrum of I showed two principal absorption maxima: λ 237 mμ, log ε 3.99 and λ 246 mμ, log ε 4.01 with a shoulder at λ 255 mμ, log ε 3.81.

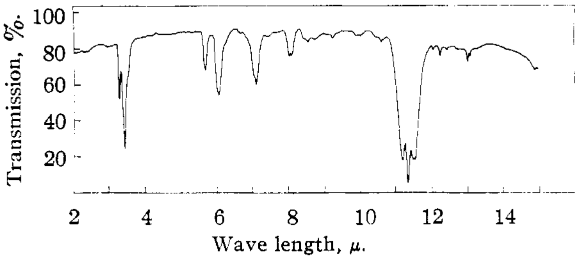
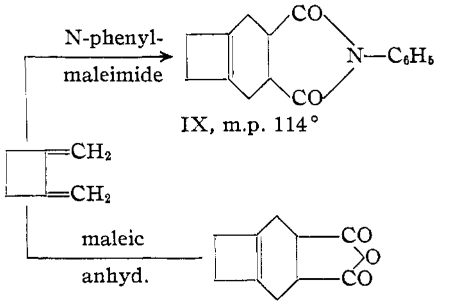


Fig. 1.—Infrared spectrum of 1,2-dimethylenecyclobutane, 10-cm. gas cell, 8 mm. pressure.

The diene I easily formed normal typical 1:1 Diels-Alder adducts with maleic anhydride and N-phenylmaleimide in benzene containing a small amount of hydroquinone. The addition of a polymerization inhibitor was necessary for in its absence only polymeric products were obtained. The Diels-Alder adducts are formulated as bicyclo [4,2,0]-1-octene derivatives as indicated



IX, m.p. 114°

X, m.p. 77-78°

Quantitative hydrogenation of the maleic anhydride adduct X and the hydrolyzed adduct XII showed the presence of one double bond.

That the diene I is most prone to undergo polymerization was indicated not only by the necessity of carrying out the Diels-Alder additions mentioned above in the presence of an inhibitor, but also by the failure to obtain a simple cyclic sulfone by reaction of I with sulfur dioxide. Even in the presence of hydroquinone or N-phenyl-β-naphthylamine only polymeric products were obtained. The resulting polymers were colorless crystalline solids softening *ca.* 170° and melting *ca.* 180-190°. They were insoluble in benzene, ether, and other common organic solvents. No sulfur dioxide was evolved when the polymers were pyrolyzed under a nitrogen atmosphere. This would seem to indicate that the diene I had undergone cationic polymerization.

The diene I formed tough, elastic rubber-like

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(5) A. T. Blomquist and J. A. Verdol, THIS JOURNAL, **77**, 81 (1955).

(6) H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, Vol. III, p. 143.

polymers after standing at room temperature for several months or when initiated with persulfate in an emulsion with water. The emulsion polymerization of I at 50° for 24 hours gave 100% yield of polymer. This polymer showed a static solubility in benzene greater than 0.5%. Its intrinsic viscosity in benzene at 30° was 175 cm.^{3} g.$^{-1}$. Infrared analysis of a transparent film of the polymer on a sodium chloride prism showed weak absorption at 11.40 μ indicative of the presence of some 1,2-units in the polymer chain. Analysis of the polymer by the perbenzoic acid method of Kolthoff and Lee[7] indicated that it comprised about 80% of 1,4-addition polymerization units and 20% of 1,2-units.

The high reactivity of I in polymerization was indicated further by comparing its behavior in this respect with 2,3-dimethyl-1,3-butadiene. Under identical conditions I gave a 96% yield of polymer, while the open-chain diene afforded only a 13% yield.

Experimental Part[8]

1,2-Bis-(hydroxymethyl)-cyclobutane (III).—To a stirred solution of 40.0 g. (1.06 moles) of lithium aluminum hydride in 3 l. of anhydrous ether, a solution of 107.0 g. (0.53 mole) of diethyl 1,2-cyclobutanedicarboxylate[9] in 200 ml. of anhydrous ether was added dropwise over a period of 3 hours. After the mixture had been stirred for another 12 hours it was hydrolyzed by the careful addition of 114.5 g. (6.36 moles) of water and filtered. From the dried combined ether filtrate and washings there was obtained 51.2 g. (82%) of III as a clear colorless viscous liquid, b.p. 107–108° (1.5 mm.), n^{20}_D 1.4736.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 62.22, 62.32; H, 10.34, 10.60.

The glycol III was converted to its diacetate VI by treatment with acetyl chloride or with acetic anhydride and pyridine; b.p. 79–80° (0.5 mm.), n^{20}_D 1.4456.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.03; H, 8.05. Found: C, 59.98, 59.95; H, 8.05, 8.02.

1,2-Bis-(bromomethyl)-cyclobutane (IV).—To 114.0 g. (0.42 mole) of phosphorus tribromide cooled to −10° there was added dropwise with stirring 49.4 g. (0.42 mole) of III over a 4-hr. period. The mixture was permitted to reach room temperature and then heated at 80–85° overnight. To the mixture, cooled in an ice-bath, was added 100 ml. of water and the lower organic layer separated. The aqueous layer was extracted with methylene chloride. The methylene chloride extracts were combined with the original organic layer, and the whole washed with dilute sodium carbonate solution and dried. Upon distillation there was obtained 91.6 g. (90%) of IV having b.p. 71–73° (1.8 mm.). Upon redistillation pure IV was obtained: b.p. 71° (1.8 mm.), n^{20}_D 1.5351, d^{20}_{20} 1.7331.

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.17; Br, 66.05; *MR*D 43.22. Found: C, 29.91, 29.93; H, 4.25, 4.12; Br, 66.00; *MR*D 43.46.

1,2-Bis-(dimethylaminomethyl)-cyclobutane Dimethobromide (V).—A mixture of 45 g. (0.76 mole) of trimethylamine, 22 g. (0.091 mole) of IV, and 15 ml. of methanol was heated in a Pyrex bomb at 85° for 24 hours. After evaporation of excess amine from the reaction mixture and final mild heating *in vacuo* crude V was obtained as a white crystalline solid. The crude solid was triturated with several portions of ethyl acetate and again dried *in vacuo*. There was obtained 33 g. (100%) of white crystalline V showing m.p. *ca.* 230–250°. V was extremely hygroscopic and no attempt was made to obtain it analytically pure. It was converted to the corresponding quaternary ammonium picrate by a standard procedure[10] and analyzed; m.p. 199–200°.

Anal. Calcd. for $C_{24}H_{32}O_{14}N_8$: C, 43.90; H, 4.91. Found: C, 43.85, 43.67; H, 5.13, 5.04.

1,2-Dimethylenecyclobutane (I).—An aqueous solution of 33 g. of V described above was treated with successive portions of freshly prepared moist silver oxide until the precipitation of yellow silver bromide was complete and the reaction mixture was brown in color. Careful evaporation of the filtrate from the reaction mixture by gentle heating to 60–70° *in vacuo* gave 21 g. (quantitative yield) of the crude quaternary base as a yellow liquid. This liquid was used directly in the subsequent pyrolysis step without further purification. Pyrolysis of the unpurified quaternary base was carried out in a pear-shaped flask having a capacity of at least three times the volume of liquid pyrolyzed. The flask was fitted with a capillary inlet tube extending to the bottom of the flask for the introduction of dry nitrogen during pyrolysis. It was also attached to a 6″ Vigreux column to minimize mechanical contamination of the pyrolysate as extensive foaming and bumping occurred during the heating. The pyrolysate was cooled by a water condenser and collected in a series of two Dry Ice traps. Hydroquinone was added to the pyrolysis flask and collecting traps to inhibit polymerization of the diene.

With nitrogen flowing through the system, 60.0 g. (0.267 mole) of unpurified bis-quaternary base containing 1 g. of hydroquinone was heated carefully with an oil-bath. Initial decomposition set in at 140° and proceeded smoothly as the temperature was raised gradually to 160°. Vapor temperature during the pyrolysis fluctuated between 67 and 75°. The pyrolysate was carefully washed with cold 10% hydrochloric acid and cold water. The separated organic layer was cooled in Dry Ice to freeze out most of the water. From this cold mixture 6.1 g. (28.4%) of impure diene I was pipetted as a clear yellow liquid. The crude I was dried further over magnesium sulfate and distilled three times. There was obtained 5.6 g. of pure I as a colorless mobile liquid showing b.p. 73° (atm.), n^{20}_D 1.4721, d^{20}_{20} 0.7927; *MR*D calcd. 27.3, found 28.3 (no correction for exaltation due to conjugation). The infrared absorption of I is shown in Fig. 1.

Anal. Calcd. for C_6H_8: C, 89.94; H, 10.05. Found: C, 89.90, 89.99; H, 10.20, 10.19.

Upon quantitative hydrogenation of 0.063 g. (0.00079 mole) of I in glacial acetic acid there was absorbed 39.5 ml. of hydrogen at 23.5° and 752 mm. (1.001 molar equivalents for two ethylenic bonds).

Ozonized oxygen was passed through a solution of 0.337 g. (0.0042 mole) of I in 35 ml. of chloroform cooled to Dry Ice temperature. Upon completion of the ozonolysis the mixture was heated with 10 ml. of 15% hydrogen peroxide for 1 hr. at 60°. Evaporation *in vacuo* of this solution gave 0.262 g. (53% yield of succinic acid) of a white crystalline solid having m.p. 186–187°. This acid after recrystallization from benzene–methyl ethyl ketone, m.p. 186–187°, did not depress the m.p. of authentic succinic acid but strongly depressed the m.p. of oxalic acid. The infrared spectrum of the ozonolysis product was identical with the spectrum of authentic succinic acid. Its di-*p*-bromophenacyl ester, m.p. 211°, was prepared by a standard procedure.[11] This derivative was identical with an authentic sample of the di-*p*-bromophenacyl ester of succinic acid.

An ozonized solution of 40 mg. of I in methylene chloride was heated for one hour with 40 mg. of zinc dust and 20 ml. of acetic acid. To the filtered solution was added 0.6 g. of methone and 2 drops of piperidine. After removal of methylene chloride by warming and addition of water to incipient turbidity and standing in the refrigerator overnight 0.11 g. (38%) of felt-like crystals were collected, m.p. 190–191°, which when mixed with an authentic sample of the formaldehyde derivative of methone also melted at 190–191°.

Diels–Alder Adduct of I with Maleic Anhydride.—From a solution of 1.57 g. (0.016 mole) of maleic anhydride, 0.5

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[7] I. M. Kolthoff and T. S. Lee, *J. Polymer Sci.*, **2**, 206 (1947).

[8] All m.p.'s were determined using a Nolge–Axelrod apparatus and are corrected. All b.p.'s are uncorrected. Infrared spectra were determined with a Perkin–Elmer double beam infrared spectrophotometer, model 21.

[9] The ester having n^{20}_D 1.4390–1.4398 was prepared according to the method of R. C. Fuson and T. Y. Kao, THIS JOURNAL, **51**, 1536 (1929).

[10] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, Ed. 3, p. 180.

[11] R. L. Shriner and R. C. Fuson, ref. 10, p. 157.

g. of hydroquinone and 1.27 g. (0.016 mole) of I in 25 ml. of benzene which had been allowed to stand at room temperature overnight and then refluxed for 5 hr. there was obtained, after evaporation to dryness *in vacuo*, a yellow oil which crystallized upon the addition of a small quantity of heptane. Sublimation of the dried crystals *in vacuo* gave a white crystalline material showing m.p. 65–75°. This upon recrystallization from heptane gave 2.69 g. (94%) of beautiful white needles of bicyclo[4,2,0]-1-octene-3,4-dicarboxylic anhydride (X) having m.p. 77–78°.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.57; H, 5.66.

Hydrogenation of 0.132 g. of X in ethyl acetate using Adams catalyst required 1.06 molar equivalents of hydrogen and gave bicyclo[4,2,0]octane-3,4-dicarboxylic anhydride (XI) as long white needles, from hexane, showing m.p. 108–109°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.77, 66.86; H, 6.67, 6.61.

Alkaline hydrolysis of X obtained from 0.27 g. (0.0034 mole) of I gave 0.61 g. (91%) of impure XII having m.p. 190–193°. Pure bicyclo[4,2,0]-1-octene-3,4-dicarboxylic acid (XII) was obtained after several recrystallizations from water; m.p. 206–207°.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.06, 60.93; H, 6.15, 6.06.

Catalytic hydrogenation of XII in acetic acid using Adams catalyst required 0.99 molar equivalent of hydrogen and afforded bicyclo[4,2,0]octane-3,4-dicarboxylic acid (XIII) showing m.p. 157° after several recrystallizations from water.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.43, 60.46; H, 7.09, 7.02.

XII, m.p. 157°, also was obtained by hydrolyzing XI with boiling water.

Attempts to prepare an adduct of I with maleic anhydride in the absence of hydroquinone gave only a white rubbery insoluble polymer in essentially quantitative yield. The polymer was insoluble in 20% sodium hydroxide, benzene, ethyl acetate, acetic anhydride and other common organic solvents. It swelled slightly in acetone.

Diels–Alder Adduct of I with N-Phenylmaleimide.—The slightly decolorized solution resulting after a mixture of 0.13 g. (0.00075 mole) of N-phenylmaleimide, 0.08 g. (0.001 mole) of I, and 0.3 g. of hydroquinone dissolved in 25 ml. of benzene had been allowed to stand at room temperature overnight was refluxed for 3 hr. Evaporation of the colorless solution gave a white residue which afforded, after recrystallization from hexane, 0.185 g. of bicyclo[4,2,0]-1-octene-3,4-dicarboxy-N-phenylimide (IX) having m.p. 111–113°. Pure IX, m.p. 114°, was obtained after several recrystallizations from hexane.

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97. Found: C, 75.79, 75.82; H, 6.17, 6.01.

Pyrolysis of VI (2-Vinyl-1,3-butadiene).—The pyrolysis apparatus and procedure used was similar to that described previously.[5] With dry nitrogen passing through the apparatus, 15 g. of VI was added at the rate of 1 drop every 3 seconds to the furnace at 500°. The furnace temperature was lowered to 475° after *ca.* one-third of the ester had been added because of the extensive carbonization which was occurring. Distillation of the crude pyrolysate over hydroquinone in a nitrogen atmosphere, as previously described,[5] gave 14 drops of a yellow liquid, b.p. 44–47°. This crude product had the characteristic odor of 2-vinyl-1,3-butadiene and decolorized solutions of aqueous potassium permanganate and bromine in carbon tetrachloride.

The crude hydrocarbon was treated with a solution of 1 g. of maleic anhydride in 15 ml. of benzene and gave 0.5 g. of a solid crystalline adduct. This adduct, after recrystallization from benzene, showed m.p. 238–239° and when mixed with an authentic sample of 2-vinyl-1,3-butadiene–maleic anhydride adduct[5] no depression in m.p. was observed. Further, the infrared spectra of this adduct and the previously prepared vinylbutadiene–maleic anhydride adduct[5] were identical.

Reaction of I with Sulfur Dioxide.—From a mixture of 10 g. of sulfur dioxide, 15 ml. of methanol, 2.5 g. of I and 1 g. of hydroquinone, which had been heated at 50° overnight in a Pyrex bomb, there was obtained 2.2 g. of insoluble polymeric material. Similarly when the reaction was carried out in the presence of N-phenyl-β-naphthylamine instead of hydroquinone, only a polymeric product was formed.

The polymer was a white brittle solid which softened at *ca.* 170° and melted at 180–190°. It was insoluble in benzene, ether and other common organic solvents. Heating of the polymer under nitrogen gave only carbonaceous material with no detectable evolution of sulfur dioxide.

Polymerization of I.—Emulsion polymerization of I at 50° was carried out using the following recipe: 1.0 g. of freshly distilled I, 0.1 g. of Ivory soap, 0.1 ml. of 3% potassium persulfate solution and 2.5 ml. of water. The mixture was sealed in a glass tube under nitrogen and rotated in a constant temperature bath for 24 hr. After addition of small amounts of hydroquinone and N-phenyl-β-naphthylamine the polymer was coagulated with 10 ml. of a solution of hydrochloric acid and alum. Drying of the coagulum *in vacuo* at 50° overnight gave 1.0 g. (100% conversion) of a very elastic rubber-like polymer showing a static solubility greater than 0.5% in benzene. The intrinsic viscosity of the polymer measured in benzene at 30° was 175 $cm.^3\ g.^{-1}$. The infrared spectrum of a transparent film of the polymer laid down on a sodium chloride prism showed weak absorption at 11.40 μ.

The amount of 1,4-addition which had occurred in forming this polymer was determined using the method of Kolthoff and Lee.[7] As shown in Fig. 2 about 80% of 1,4-addition had taken place.

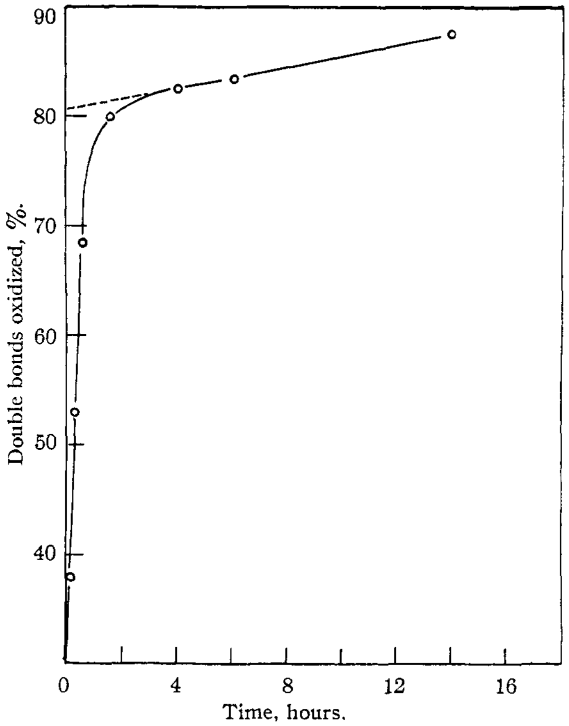

Fig. 2.—Determination of 1,4-addition in 1,2-dimethylenecyclobutane polymer; done at 0° in chloroform.

Simultaneous polymerization under identical conditions of 2,3-dimethyl-1,3-butadiene and I resulted in 12.9 and 96.5% conversions to polymers, respectively.

A sample of I which had been stored at room temperature under nitrogen for several months also was transformed to an extremely tough, elastic polymer similar to the emulsion polymer described above.

Ithaca, N. Y.