stoppered and allowed to remain in an ice-bath overnight. The reaction mixture was then poured into ice-water and extracted with ether. The ether solution was washed with 5% aqueous sodium hydroxide, water and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure yielded an oil which was crystallized from ethanol, yielding 0.3 g. (25%) of the bis-diethylmercaptal, m.p. 147–151°. Recrystallization from absolute ethanol furnished an analytical sample, m.p. 151–153°.

Anal. Calcd. for $C_{28}H_{48}O_8S_4$: C, 52.48; H, 7.55; S, 20.01. Found: C, 52.35; H, 7.51; S, 19.94.

3,3,7,7-Tetracarbethoxybicyclo[3.3.0]octane-1,5-diamine Dihydrochloride (VIII). A. Reduction of the Dioxime of VI.—3,3,7,7-Tetracarbethoxycycloöctane-1,5-dione dioxime (1.96 g.) in 100 ml. of absolute ethanol containing 0.94 g. of concentrated hydrochloric acid was hydrogenated in the presence of 1.1 g. of 10% palladium-on-Norit for 37 hr. at 60°. The catalyst was removed by filtration and washed with hot absolute ethanol. Concentration of the filtrate to 20 ml. under reduced pressure and the addition of anhydrous ether caused turbidity. Chilling then resulted in the separation of the diamine dihydrochloride, 1.57 g. (73%), m.p. 223–224° dec. An analytical sample was prepared by recrystallization from absolute ethanol, m.p. 223–224° dec.

Anal. Calcd. for $C_{20}H_{32}N_2O_8 \cdot 2HCl$: C, 47.91; H, 6.83; N, 5.59; Cl, 14.14. Found: C, 47.62; H, 7.01; N, 5.60; Cl, 14.03.

B. Reduction of the Nitrogen Tetroxide III Adduct.[10]—Nitrogen tetroxide was passed with stirring at 0° into 50 ml. of an ether solution containing 0.5 g. of III. The reactants were stirred for 2 hr. at 0° and 1 hr. at room temperature. The solution was washed with water and dried over anhydrous sodium sulfate. Filtration of the solution and concentration of the filtrate under reduced pressure yielded an oil that was dissolved in 10 ml. of glacial acetic acid and hydrogenated in the presence of 0.3 g. of prereduced platinum oxide. The catalyst was removed by filtration and the solvent was evaporated. The residue was acidified with dilute hydrochloric acid, washed with ether and the aqueous phase made alkaline with a 10% solution of sodium carbonate. The aqueous solution was extracted four times with ether and the combined ether extracts were dried over anhydrous magnesium sulfate. After filtration, dry hydrogen chloride was passed into the ether solution and 0.10 g. (17%) of VIII was obtained, m.p. 217.2–217.8° dec. A mixed melting point determination with the diamine dihydrochloride obtained by procedure A was undepressed, m.p. 216.4–217° dec.

3,3,7,7-Tetracarbethoxybicyclo[3.3.0]octane-1,5-diamine.—The diamine dihydrochloride VIII prepared by reduction of the dioxime (0.5 g.) was dissolved in 25 ml. of water and 0.08 g. of sodium hydroxide in 10 ml. of water was added. The solution was extracted once with benzene and three times with methylene chloride. The combined extracts were dried over anhydrous sodium sulfate, filtered, and the filtrate was concentrated under reduced pressure. The residue was triturated with petroleum ether and solidified on concentration under reduced pressure. Recrystallization of the crude product from methylcyclohexane gave 0.27 g. (62%) of 3,3,7,7-tetracarbethoxybicyclo[3.3.0]octane-1,5-diamine, m.p. 67–69°. An analytical sample was prepared by recrystallization from methylcyclohexane, m.p. 67.5–69.0°.

Anal. Calcd. for $C_{20}H_{32}N_2O_8$: C, 56.06; H, 7.53; N, 6.54. Found: C, 55.79; H, 7.75; N, 6.37.

A purified sample of the diamine prepared from III *via* the nitrogen tetroxide adduct melted at 67.6–68.2°.[10] A mixed melting point determination with the diamine prepared as described above from the dioxime derived from VI was not depressed. Infrared absorption spectra of the two samples of the diamine were superimposable.

3,3,7,7-Tetracarbethoxybicyclo[3.3.0]octane-1,5-bis-(dimethylamine) Monopicrate.—To 0.35 g. of VIII in 10 ml. of dioxane and enough water to dissolve the salt was added 1.0 g. of methyl sulfate and 0.5 g. of sodium carbonate. The reaction mixture was allowed to remain at room temperature for 4 days. The mixture was acidified with 5 ml. of 6 *N* hydrochloric acid and concentrated under reduced pressure until a white solid separated. The solid was dissolved in water and the resultant solution extracted with ether. The aqueous phase was treated with 10% sodium hydroxide to *p*H 11–12, extracted with ether and the ether extracts dried over anhydrous sodium sulfate. To the filtered ether solution was added 0.33 g. of picric acid in ethanol. The yellow solid which precipitated amounted to 0.2 g., m.p. 195–204° dec. Recrystallization from absolute ethanol yielded 0.16 g. (32%) of the monopicrate, m.p. 205–210° dec. An analytical sample was prepared by recrystallization from absolute ethanol, m.p. 209–211° dec.

Anal. Calcd. for $C_{30}H_{45}N_5O_{15}$: C, 50.34; H, 6.34; N, 9.79. Found: C, 50.36; H, 6.08; N, 10.09.

CAMBRIDGE, MASS.

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[10] We are indebted to Dr. W. J. Keller who performed this experiment.

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

Cyclic Polyolefins. XLIII. Derivatives of Bicyclo[3.3.0]oct-1(5)-ene[1]

BY ARTHUR C. COPE AND WILLIAM J. KELLER[2]

RECEIVED APRIL 1, 1958

Bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxylic acid (II) has been prepared and separated into its *cis* and *trans* isomers Ozonolysis of II formed cycloöctane-3,7-dione-1,5-dicarboxylic acid (III). Catalytic hydrogenation of the dicarboxylic acid II yielded bicyclo[3.3.0]octane-3,7-dicarboxylic acid (V). The dicarboxylic acid II has been converted into the corresponding diamide VI, the dimethyl ester IX (97%), the dihydrazide X (90%) and the diazide XI (93%). From the diazide XI, bicyclo[3.3.0]oct-1(5)-ene-3,7-diamine dihydrochloride (XII) and the corresponding bis-ethyl carbamate XIII (88%) were prepared. Methylation of XII gave 3,7-bis-dimethylaminobicyclo[3.3.0]oct-1(5)-ene (XIV), from which the dimethiodide XV was obtained.

The preceding paper[3] describes the synthesis of 3,3,7,7-tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene and its utilization as a precursor to compounds in the cycloöctane and bicyclo[3.3.0]octane series. The present paper is an extension of the previous work and describes the preparation of a number of disubstituted bicyclo[3.3.0]oct-1(5)-ene derivatives.

Decarboxylation of bicyclo[3.3.0]oct-1(5)-ene-3,3,7,7-tetracarboxylic acid (I) in pyridine gave bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxylic acid (II) in 97% yield. The separation of II into its *cis* (IIa) and *trans* (IIb) isomers was accomplished by repeated recrystallization from water. The isomer with the lower melting point and greater solubility in water was tentatively assigned the *cis*

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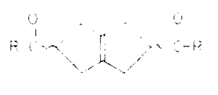
[1] This work was supported in part by the Office of Naval Research under Contract N5ori-07822, Project NR-055-96.

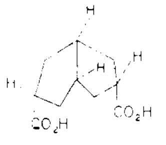
[2] Abstracted from the Ph. D. Thesis of William J. Keller, Massachusetts Institute of Technology, 1951.

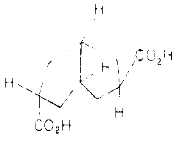
[3] A. C. Cope and F. Kagan, THIS JOURNAL, **80**, 5499 (1958).

configuration. The thermal conversion of the *cis* isomer to the other form provided support for this assignment.

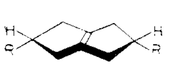
Ozonolysis of II formed cyclooöctane-3,7-dione-1,5-dicarboxylic acid (III), isolated as the disemicarbazone IV in an over-all yield of 72%. On the reduction of II (a mixture of the *cis* and *trans* forms) or the pure *cis* and *trans* isomers in the presence of a platinum catalyst, one equivalent of hydrogen was absorbed and bicyclo[3.3.0]octane-3,7-dicarboxylic acid (V) was obtained. Two isomers are theoretically possible for the reduced *cis*-dicarboxylic acid Va; however, the melting range of the product, which was obtained in high yield, indicated that one isomer was formed predominantly. The structure of Va probably corresponds to the isomer in which the hydrogen atoms have become attached to the unhindered side of IIa.



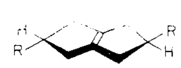

Va


Vb

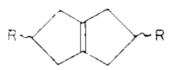
II, R = -OH
VI, R = $-NH_2$
VII, R = -OAg
IX, R = $-OCH_3$
X, R = $-NHNH_2$
I, R = $-N_3$



IIa, R = $-CO_2H$
VIIa, R = $-CO_2Ag$
IXa, R = $-CO_2Me$



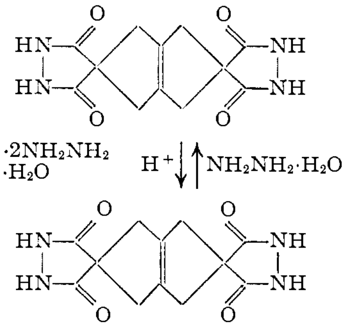
IIb
VIIb
IXb



XII, R = $-NH_2{\cdot}HCl$
XIII, R = $-NHCO_2Et$
XIV, R = $N(CH_3)_2$
XV, R = $-N(CH_3)_3I^{\ominus}$

The diammonium salt of II decomposed to the dicarboxylic acid and ammonia at 100°. Bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxamide (VI) was prepared in low yield, however, by treatment of II with thionyl chloride followed by ammonium hydroxide. The dicarboxylic acid II was converted quantitatively to 3,7-dicarbomethoxybicyclo[3.3.0]-oct-1(5)-ene (IX) either by treatment of the disilver salt of bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxylic acid (VII) with methyl iodide or by reaction of II with diazomethane. The latter method yielded a purer product.

The pure *cis* and *trans* isomers of the disilver salt VII, 3-carbomethoxybicyclo[3.3.0]oct-1(5)-ene-7-carboxylic acid (VIII), and the dimethyl ester IX were obtained from the corresponding isomers of II. Treatment of IX with hydrazine hydrate in ethanol furnished bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarbohydrazide (X). The action of nitrous acid on X formed bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxazide (XI) in high yield. When XI was heated with absolute ethanol, bicyclo[3.3.0]oct-1(5)-ene-3,7-bis-ethyl carbamate (XIII) was obtained. The hydrolysis of XIII in dilute potassium hydroxide was unsuccessful for the bicyclo[3.3.0]oct-1(5)-ene-3,7-diamine formed was very unstable; therefore the diazide XI was converted directly in dilute hydrochloric acid and dioxane to bicyclo-[3.3.0]oct-1(5)-ene-3,7-diamine dihydrochloride (XII). The reaction of the dihydrochloride XII with dilute potassium hydroxide and treatment of the crude free amine thus produced with formic acid and formaldehyde yielded 3,7-bis-(dimethylamino)-bicyclo[3.3.0]oct-1(5)-ene (XIV). The reaction of the dihydrochloride XII with methyl iodide and sodium bicarbonate in methanol resulted in the formation of the dimethiodide XV. The dimethohydroxide prepared from XV and silver hydroxide was concentrated and heated from room temperature to 210° at 1 mm. The products were a saturated amine, presumably trimethylamine, and a non-volatile polymeric solid; no triene could be isolated.



XVI

XVII

The preparation of a tetrahydrazide derivative by treatment of 3,3,7,7-tetracarbethoxybicyclo[3.3.0]-oct-1(5)-ene with hydrazine hydrate in ethanol was unsuccessful. The product obtained was the hydrated dihydrazine salt XVI of the bis-diacylated hydrazine derivative. The addition of an excess of hydrochloric acid to an aqueous solution of XVI caused the precipitation of the bis-diacylated hydrazine XVII in 92% yield along with hydrazine dihydrochloride (88%). Treatment of XVII with hydrazine hydrate in ethanol resulted in the re-formation of XVI.

Experimental[4]

Bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxylic Acid (II).—Bicyclo[3.3.0]oct-1(5)-ene-3,3,7,7-tetracarboxylic acid (I) was prepared by a modification of the previously described procedure,[3] by addition of saponified 3,3,7,7-tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene to excess hydrochloric acid, which formed a purer product in 98.5% yield. A mixture of 18.05 g. of I and 80 ml. of pyridine was heated under reflux for 1 hour, and the reaction mixture was filtered. The filtrate was poured into 500 ml. of water, and the solution evaporated on a steam-bath until precipitation occurred. Chilling resulted in precipitation of 12.02 g. (97%) of crystalline bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxylic acid, m.p. 228–274°.[5] An analytical sample was prepared by recrystallization from water and then drying, and melted at 273–276° dec.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17; neut. equiv., 98.1. Found: C, 61.31; H, 6.14; neut. equiv., 98.0.

Repeated recrystallization of 2.0 g. of the dicarboxylic acid II from water yielded 0.57 g. of *trans*-bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxylic acid (IIb), m.p. 283.8–286.2°.[5]

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 60.93; H, 6.08.

Concentration of the mother liquor from the first crystallization described above and recrystallization of the resulting solid from water yielded 0.50 g. of *cis*-bicyclo[3.3.0]-oct-1(5)-ene-3,7-dicarboxylic acid (IIa), m.p. 229–231°.[5]

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(4) Melting points are corrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

(5) Melting point determined in a sealed capillary under nitrogen.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 60.98; H, 6.42.

A sample that was heated in a sealed tube under nitrogen at 232° for 20 minutes and cooled remelted at 265–275°,[5] indicating partial conversion to the *trans*-dicarboxylic acid IIb.

Cyclooöctane-3,7-dione-1,5-dicarboxylic Acid (III).—A suspension of 1.00 g. of II in 50 ml. of glacial acetic acid was cooled to 17° and 320 mg. of ozone in a stream of oxgen was introduced during a period of 32 minutes. Water (50 ml.) was added, and the mixture was heated under gentle reflux for 1.3 hours. The solvent was removed under reduced pressure and the residual solid was dried in an oven at 100° for 3 hours. The product was recrystallized twice from a small amount of water as thick rods, and dried at 25° (0.3 mm.) for 2 hours giving the dicarboxylic acid III, presumably as a mixture of *cis* and *trans* isomers, m.p. 283–285.5° dec.

Anal. Calcd. for $C_{10}H_{12}O_6$: C, 52.63; H, 5.30; neut. equiv., 114.1. Found: C, 52.47; H, 5.47; neut. equiv., 115.1.

Cyclooöctane-3,7-dione-1,5-dicarboxylic Acid Disemicarbazone (IV).—To a solution of the crude diketone III (obtained by ozonolysis of 1.00 g. of II) in 10 ml. of water was added 2.0 g. of semicarbazide hydrochloride and 1.5 g. of sodium acetate. The reaction mixture was heated for 30 minutes on a steam-bath. Precipitation occurred on cooling and 1.28 g. (72%) of cyclooöctane-3,7-dione-1,5-dicarboxylic acid disemicarbazone (presumably a mixture of *cis* and *trans* isomers) was obtained. After five recrystallizations from water, the product foamed vigorously at 235.4° when placed in a melting point bath at 224° and heated rapidly. An analytical sample was dried for 17 hours at 25° (0.3 mm.) over phosphorus pentoxide.

Anal. Calcd. for $C_{12}H_{18}O_6N_6 \cdot {}^1/_2H_2O$: C, 41.02; H, 5.45; N, 23.92; neut. equiv., 175.7. Found: C, 40.94; H, 5.43; N, 23.34; neut. equiv., 173.2.

Bicyclo[3.3.0]octane-3,7-dicarboxylic Acid (V).—Catalytic hydrogenation of 0.51 g. of II (a mixture of the *cis* and *trans* isomers) in 10 ml. of glacial acetic acid in the presence of 0.10 g. of prereduced platinum oxide resulted in the absorption of one molar equivalent of hydrogen. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. The residue amounted to 0.52 g. (100%) of bicyclo[3.3.0]octane-3,7-dicarboxylic acid, m.p. 159–184°. An analytical sample of the mixture of *cis* and *trans* isomers was prepared by sublimation at 140–150° (0.3 mm.), m.p. 164–181°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.60; H, 7.18.

Reduction of the *trans*-dicarboxylic acid IIb and of the *cis*-dicarboxylic acid IIa under similar conditions yielded the saturated *trans*-dicarboxylic acid Vb, m.p. 169.6–170.6°, and a saturated *cis*-dicarboxylic acid Va, m.p. 194–202°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12; neut. equiv., 99.1. Found: *trans* isomer, C, 60.78; H, 7.08; *cis* isomer, C, 60.66; H, 7.36; neut. equiv., 98.0.

Bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxamide (VI).—A mixture of 0.5 g. of II and 4.0 ml. of thionyl chloride was heated under reflux for 1.3 hours. Part of the excess thionyl chloride was removed by distillation. The residual liquid was added to 10 ml. of ammonium hydroxide cooled in a Dry Ice-bath. The precipitated diamide VI (0.26 g., 53%) on recrystallization from water yielded 0.08 g. (16%) of the diamide VI, a mixture of *cis* and *trans* isomers, m.p. 290–305° dec.

Anal. Calcd. for $C_{10}H_{14}O_2N_2$: C, 61.84: H, 7.27; N, 14.42. Found: C, 61.84; H, 7.23; N, 14.48.

Bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxylic Acid Disilver Salt (VII).—Dilute ammonium hydroxide was added to a suspension of 0.5 g. of II in 10 ml. of water until the solution was neutral to phenolphthalein. To this solution was added 0.87 g. of silver nitrate in 10 ml. of water. The precipitated disilver salt of II was collected by filtration, washed with water, dried in a steam heated oven and weighed; 0.95 g. (91.3%). An analytical sample was dried over phosphorus pentoxide at 100° (0.15 mm.) for 4 hours.

Anal. Calcd. for $C_{10}H_{10}O_4Ag_2$: C, 29.30; H, 2.46; Ag, 52.63. Found: C, 29.46; H, 2.73; Ag, 52.57.

Analytically pure samples of the silver salts of the *trans*-acid IIb and of the *cis*-acid IIa were prepared in the above manner in 99 and 97% yields, respectively.

***cis*-3-Carbomethoxybicyclo[3.3.0]oct-1(5)-ene-7-carboxylic Acid (VIIIa).**—A mixture of 136 mg. of the *cis*-monosilver salt, 5 ml. of methanol and 0.3 ml. of methyl iodide was heated under reflux for 3 hours. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. Sublimation of the residual solid at 110–140° (0.15 mm.) and extraction of the sublimate with ether partially removed the monomethyl ester from the dicarboxylic acid IIa. Resublimation then gave 36.3 mg. (31%) of *cis*-3-carbomethoxybicyclo[3.3.0]oct-1(5)-ene-7-carboxylic acid, m.p. 84.0–87.4°. An analytical sample, recrystallized from an ether–pentane mixture and dried at 25° (0.25 mm.) for 1 hour, melted at 86.0–87.8°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.83; H, 6.76.

***trans*-3-Carbomethoxybicyclo[3.3.0]oct-1(5)-ene-7-carboxylic Acid (VIIIb).**—The *trans*-disilver salt VII (2.505 g.) was heated with 3.0 ml. of methyl iodide in 20 ml. of methanol under reflux for 1 hour. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in ether and the solution was washed with dilute sodium thiosulfate solution, a small amount of 5% sodium bicarbonate solution and water. The acid IIb (25%) was recovered from the alkaline extract. The ether was removed from the ethereal solution under reduced pressure and the residue was purified by sublimation and then crystallization from carbon tetrachloride to separate *trans*-3-carbomethoxybicyclo[3.3.0]oct-1(5)-ene-7-carboxylic acid, m.p. 133.6–134.2°, from the dimethyl ester IXb.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71; neut. equiv., 210.2. Found: C, 62.78; H, 6.75; neut. equiv., 204.

3,7-Dicarbomethoxybicyclo[3.3.0]oct-1(5)-ene (IX). A. **From the Disilver Salt VII.**—A mixture of 4.03 g. of VII, 40 ml. of methanol and 6.0 ml. of methyl iodide was heated under reflux for 1 hour. The isolation procedure described above for VIIIb was used. Sublimation of the product at 70° (0.1 mm.) provided 2.09 g. (95%) of the dimethyl ester IX, a mixture of *cis* and *trans* isomers, m.p. 40–78°. Resublimation yielded an analytical sample, m.p. 55–81°.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.52; H, 7.26.

B. **From the Dicarboxylic Acid II.**—An excess of diazomethane in ether solution was added to a suspension of 250 mg. of II in 4 ml. of ether at 0° in an ice-bath. After 10 minutes the evolution of nitrogen was slow and the mixture was allowed to warm to room temperature and stand for 1 hour. On removal of solvent and sublimation at 55° (0.17 mm.), 278 mg. (97%) of the dimethyl ester IX, a mixture of *cis* and *trans* isomers, m.p. 41.2–91.4°, was obtained. The infrared absorption spectrum of this material was identical with that of the dimethyl ester obtained from the disilver salt VII.

Treatment of the *cis*-dicarboxylic acid IIa and the *trans*-dicarboxylic acid IIb with diazomethane in a similar manner furnished analytically pure samples of the *cis*-dimethyl ester IXa, m.p. 34.4–36.0°, and the *trans*-dimethyl ester IXb, m.p. 88–91°, in 98 and 88% yields, respectively.

Bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarbohydrazide (X).—A solution of 500 mg. of IX in 0.34 ml. of 85% hydrazine hydrate and 1.5 ml. of absolute ethanol was heated under reflux for 3.3 hours. The reaction mixture was chilled and the crude dihydrazide (448 mg., 90%) was removed by filtration, washed with ether and dried. A recrystallization from water yielded an analytical sample of X, a mixture of *cis* and *trans* isomers, m.p. 306–307° dec.

Anal. Calcd. for $C_{10}H_{16}N_4O_2$: C, 53.55; H, 7.19; N, 24.99. Found: C, 53.76; H, 7.33; N, 25.30.

Bicyclo[3.3.0]oct-1(5)-ene-3,7-dicarboxazide (XI).—One gram of sodium nitrite in 3 ml. of cold water was added to a stirred solution of 500 mg. of X in 10 ml. of 40% acetic acid at 0°. The reaction temperature was maintained at 0° for 45 minutes. The precipitated diazide was removed by filtration, washed with cold water and dried at 0° (0.3 mm.) for 2 hours. The yield of the diazide XI, a mixture of *cis* and *trans* isomers, m.p. 50–60° dec., was 502 mg. (93%). A sample washed several times with cold water and dried at 0° (0.3 mm.) for 3 hours, m.p. 52–60.5° dec., was analyzed.

Anal. Calcd. for $C_{10}H_{10}N_6O_2$: C, 48.78; H, 4.09; N, 34.13. Found: C, 48.92; H, 4.09; N, 34.13.

Bicyclo[3.3.0]oct-1(5)-ene-3,7-diamine Dihydrochloride (XII).—Freshly prepared, moist diazide XI obtained from 1.0 g. of the dicarbohydrazide X, was suspended in 20 ml. of dioxane, 5 ml. of water and 3 ml. of concentrated hydrochloric acid. The reaction mixture was heated under reflux for 2 hours. The solvent was removed under reduced pressure. Recrystallization of the solid residue from acetone–methanol yielded 0.39 g. (42%) of the diamine dihydrochloride XII, a mixture of *cis* and *trans* isomers, m.p. >300°. Further recrystallization from acetone–methanol followed by drying provided an analytical sample, m.p. 395° (darkened at 350°).

Anal. Calcd. for $C_8H_{14}N_2 \cdot 2HCl$: C, 45.51; H, 7.64; N, 13.27; Cl, 33.59. Found: C, 45.43; H, 7.63; N, 13.40; Cl, 33.25.

Bicyclo[3.3.0]oct-1(5)-ene-3,7-bis-ethylcarbamate (XIII).—A suspension of 471 mg. of the diazide XI in 5 ml. of absolute ethanol was warmed until evolution of nitrogen ceased and then was heated to boiling. Crystallization occurred on cooling. The product was separated by filtration and dried. The yield of XIII, a mixture of *cis* and *trans* isomers, was 473 mg. (88%). An analytical sample was prepared by recrystallization from ethanol–water, m.p. 180–212° (dec., sintered and darkened at 170–180°).

Anal. Calcd. for $C_{14}H_{22}N_2O_4$: C, 59.55; H, 7.86; N, 9.92. Found: C, 59.86; H, 8.02; N, 9.85.

3,7-Bis-(dimethylamino)-bicyclo[3.3.0]oct-1(5)-ene (XIV).—Freshly prepared, moist diazide XI obtained from 2.0 g. of the dihydrazide X was suspended in a solution of 2 ml. of concentrated hydrochloric acid and 10 ml. of water. The reaction mixture was warmed on a water-bath maintained at 60° for 1 hour and then filtered. The filtrate was treated with 1.5 g. of potassium hydroxide and extracted with chloroform. Concentration of the combined chloroform extracts under reduced pressure yielded 0.84 g. (68%) of crude bicyclo[3.3.0]oct-1(5)-ene-3,7-diamine. The diamine was treated with 8 ml. of 85% formic acid and 4 ml. of 40% formaldehyde. The resultant solution was heated under reflux for 18 hours, treated with 4 ml. of 4 *N* hydrochloric acid, and concentrated under reduced pressure. The residue was dissolved in 5 ml. of water. The solution was made alkaline with 1 g. of potassium hydroxide and extracted with ether and chloroform. The solvent was removed from the combined organic extracts. Purification by sublimation at 90–110° (30 mm.) yielded 0.37 g. (31%) of the diamine XIV, a mixture of *cis* and *trans* isomers, m.p. 61.4–70.2°.

Anal. Calcd. for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.16; H, 11.29; N, 14.71.

3,7-Bis-(dimethylamino)-bicyclo[3.3.0]oct-1(5)-ene Dimethiodide (XV).—The diamine dihydrochloride XIV obtained from 2.0 g. of the dihydrazide X was immediately heated with 40 ml. of methanol, 4.56 g. of sodium bicarbonate and 15.34 g. of methyl iodide under reflux for 17 hours. The reaction mixture was filtered and the filtrate was concentrated to a small volume. The addition of acetone caused the precipitation of 2.24 g. (53%) of the dimethiodide XV, a mixture of *cis* and *trans* isomers. Recrystallization from methanol and from methanol–acetone furnished an analytical sample, m.p. 280–310° dec.

Anal. Calcd. for $C_{14}H_{28}I_2N_2$: C, 35.17; H, 5.88; I, 53.09; N, 5.86. Found: C, 35.53; H, 5.97; I, 53.12; N, 5.93.

The Hydrated Dihydrazine Salt of the Bis-diacylated Hydrazine Derived from 3,3,7,7-Tetracarbethoxybicyclo[3.3.0]-oct-1(5)-ene (XVI).—Hydrazine hydrate (8.0 ml.) was added to a solution of 1.5 g. of 3,3,7,7-tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene[3] in 30 ml. of absolute ethanol at room temperature. After 4 days, 1.2 g. (89%) of the hydrated dihydrazine salt XVI had separated, m.p. 204.5° dec. When washed with absolute ethanol and dried, an analytical sample melted at 206.5° dec.

Anal. Calcd. for $C_{12}H_{12}N_4O_4 \cdot 2N_2H_4 \cdot H_2O$: C, 40.22; H, 6.19; N, 31.27. Found: C, 39.98; H, 6.41; N, 31.51.

The Bis-diacylated Hydrazine Derived from 3,3,7,7-Tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene (XVII).—A solution of 0.52 g. of XVI in 15 ml. of water was treated with excess hydrochloric acid. The precipitated diacylated hydrazine XVII, 0.36 g. (92%), was removed by filtration, washed with water and dried. A sample was washed with absolute ethanol, dried at 80° (0.5 mm.), and analyzed; m.p. >300°.

Anal. Calcd. for $C_{12}H_{12}N_4O_4$: C, 52.17; H, 4.38; N, 20.29. Found: C, 51.84; H, 4.62; N, 20.02.

Evaporation of the mother liquor from XVII to dryness at 100° yielded 0.23 g. (88%) of impure hydrazine dihydrochloride, m.p. 140–190° dec. Recrystallization from ethanol–water gave hydrazine monohydrochloride, m.p. 91–92°. A mixed melting point determination with an authentic sample of hydrazine monohydrochloride was undepressed.

Recrystallization of 0.71 g. of XVII from ethanol which contained hydrazine hydrate gave 0.85 g. (92%) of the hydrated dihydrazine salt XVI, m.p. 206° dec. A mixed melting point determination with XVI prepared from the tetracarboxylic ester and hydrazine as described above was 205.5° dec.

CAMBRIDGE, MASS.

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

Cyclic Polyolefins. XLIV. The Structure of Cycloöctatetraene Oxide

BY ARTHUR C. COPE, PHYLIS T. MOORE[1] AND WILLIAM R. MOORE

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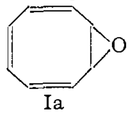
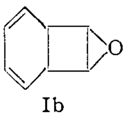
Cycloöctatetraene oxide has been shown to be a 1,2- rather than a 1,4-oxide by chemical means, and to contain an unbridged eight-membered ring by its nuclear magnetic resonance spectrum.

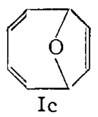
Three structures (Ia, Ib and Ic) have been proposed for cycloöctatetraene oxide (I). The formation of cycloöctanol from the catalytic hydrogenation of I led Reppe, Schlichting, Klager and Toepel[2] to propose structure Ia. Friess and Boekelheide[3] have proposed structure Ib which they believed to be in agreement both with the ultraviolet absorption spectrum of I (λ_{max} 241 mμ, log ε 3.60) and the absorption of only one mole of hydrogen by the maleic anhydride adduct of I. Cope and Tiffany favored structure Ia for I,[4] and pointed out that the absorption of only one mole of hydrogen by the maleic anhydride adduct of I does not exclude structure Ia since bridging as well as addition could occur in the formation of the



Ia



Ib



Ic

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[1] National Science Foundation Fellow, 1955–1957.

[2] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

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[4] A. C. Cope and B. D. Tiffany, *ibid.*, **73**, 4158 (1951).