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

Cyclic Polyolefins. XLII. 3,3,7,7-Tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene and 3,3,7,7-Tetracarbethoxycycloöctane-1,5-dione

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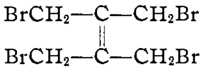
RECEIVED APRIL 1, 1958

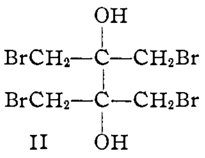
Alkylation of diethyl malonate with tetrabromomethylethylene (I) yielded 3,3,7,7-tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene (III, 19%). Saponification of III formed bicyclo[3.3.0]oct-1(5)-ene-3,3,7,7-tetracarboxylic acid (IV, 85%). Oxidation of III with performic acid followed by hydrolysis furnished *trans*-3,3,7,7-tetracarbethoxybicyclo[3.3.0]octane-1,5-diol (V, 61%). Ozonolysis of III or lead tetraacetate cleavage of V yielded 3,3,7,7-tetracarbethoxycycloöctane-1,5-dione (VI, 37 and 69%, respectively). Catalytic reduction of the diketone VI has been shown to result in bridging forming *cis*-3,3,7,7-tetracarbethoxybicyclo[3.3.0]octane-1,5-diol (VII, 68%) which also was prepared by *cis*-hydroxylation of III. The *cis*-glycol VII was reconverted to the diketone VI by lead tetraacetate cleavage.

In a search for synthetic routes to substituted cycloöctanes and cycloöctatetraenes, the utilization of bicyclo[3.3.0]oct-1(5)-ene derivatives was investigated. Previously Wawzonek[2] had demonstrated that cleavage of a bicyclo[3.3.0]oct-1(5)-ene derivative offered a convenient route to the corresponding 1,5-cycloöctanedione derivative. The present paper describes the synthesis of a bicyclo-[3.3.0]oct-1(5)-ene with carbethoxyl substituents and its subsequent cleavage to a correspondingly substituted 1,5-cycloöctanedione.

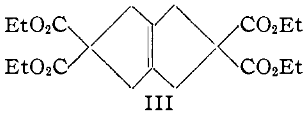
Addition of one molar equivalent of bromine to 2,3-dimethylbutadiene followed by treatment of the intermediate 1,4-dibromo-2,3-dimethyl-2-butene (not isolated) with N-bromosuccinimide formed tetrabromomethylethylene (I) in 60% yield. Hydroxylation of the tetrabromide I with potassium permanganate yielded tetrabromomethylethylene glycol (II). Cleavage of II with lead tetraacetate furnished the known *sym*-dibromoacetone in 79% yield. A 2,4-dinitrophenylhydrazone derivative prepared from this ketone exhibited no melting point depression upon mixture with an authentic sample. These transformations establish the structure of the tetrabromide I.


$$\begin{array}{c} BrCH_2-C-CH_2Br \\ \| \\ BrCH_2-C-CH_2Br \end{array}$$

I


$$\begin{array}{c} OH \\ | \\ BrCH_2-C-CH_2Br \\ | \\ BrCH_2-C-CH_2Br \\ | \\ OH \end{array}$$

II



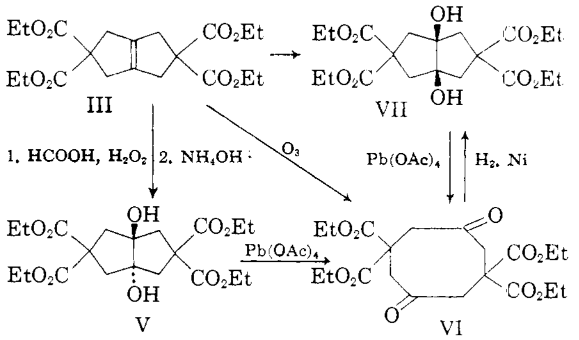
III

Attempts to convert I to a nitrile with cuprous or potassium cyanide under a variety of conditions were unsuccessful. However, alkylation of diethyl malonate with I resulted in the formation of 3,3,7,7-tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene (III), isolated in 19% yield. A saponification equivalent of III indicated the presence of four ester groups, and the absorption of 1 molar equivalent of hydrogen was observed on catalytic hydrogenation. Molecular weight determinations on the alkylation product also were in agreement with the formula III.

Saponification of III resulted in formation of bicyclo[3.3.0]oct-1(5)-ene-3,3,7,7-tetracarboxylic acid (IV, 85%). Recently Yates and Bhat[3] reported the synthesis of bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic acid, which has the same carbon skeleton as IV.

The action of performic acid on III followed by selective cleavage of the resultant formate ester with ammonium hydroxide yielded *trans*-3,3,7,7-tetracarbethoxybicyclo[3.3.0]octane-1,5-diol (V, 61%), m.p. 184-186°. Subsequent treatment of this glycol with lead tetraacetate formed 3,3,7,7-tetracarbethoxycycloöctane-1,5-dione (VI) in 69% yield.

cis-Hydroxylation of III with osmium tetroxide and hydrogen peroxide[4] did not proceed at room temperature, but was successful at higher temperatures. The crude *cis*-3,3,7,7-tetracarbethoxybicyclo[3.3.0]octane-1,5-diol (VII) thus obtained was converted to VI by lead tetraacetate cleavage in 43% over-all yield. The pure *cis*-glycol, m.p. 73-76°, was obtained from potassium permanganate oxidation of III. Lead tetraacetate cleavage of pure VII gave the diketone VI in 74% yield. As would be expected from stereochemical considerations, the lead tetraacetate cleavage of the *cis*-glycol VII was fast and exothermic while the cleavage of the *trans*-glycol V was slower. An additional route to VI in 37% yield was provided by ozonolysis of III.



Catalytic reduction of VI with hydrogen and Raney nickel resulted in the absorption of only one molar equivalent of hydrogen. The product, isolated in 68% yield, was the *cis*-glycol VII. A mixed melting point determination with the product obtained from permanganate oxidation of III was undepressed. Bridging in this manner has been

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[1] Abstracted from the Ph. D. Thesis of Fred Kagan, Massachusetts Institute of Technology, 1949.

[2] S. Wawzonek, THIS JOURNAL, **65**, 839 (1943); **62**, 745 (1940).

[3] P. Yates and G. Bhat, *Chemistry & Industry*, 1237 (1954).

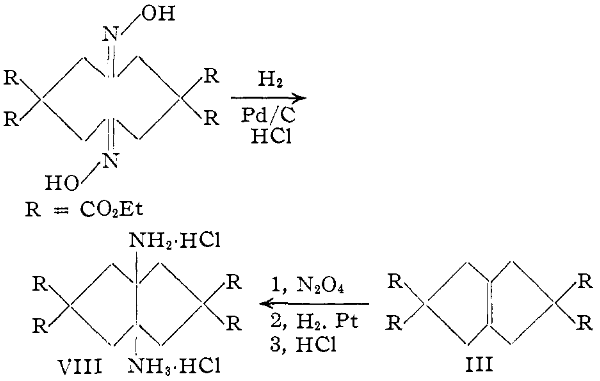
[4] N. A. Milas and S. Sussman, THIS JOURNAL, **58**, 1302 (1936).

observed previously for eight- and ten-membered cyclic diketones.[2,5]

Carbonyl derivatives of VI which were prepared include the dioxime, disemicarbazone, the bis-2,4-dinitrophenylhydrazone and the bis-diethylmercaptal.

Catalytic hydrogenation of the dioxime of VI in ethanol containing hydrochloric acid in the presence of 10% palladium-on-Norit catalyst formed 3,3,7,7-tetracarbethoxybicyclo[3.3.0]octane-1,5-diamine dihydrochloride (VIII) in 73% yield. This diamine dihydrochloride was independently synthesized by the addition of nitrogen tetroxide to III followed by reduction of the dinitro compound, which was not isolated. The product obtained by this method was identical with that prepared from the dioxime, proving that bridging had occurred on reduction of the dioxime. The free amines prepared from the two hydrochlorides also were identical. 3,3,7,7-Tetracarbethoxybicyclo[3.3.0]octane-1,5-bis-(dimethylamine) was prepared by methylation of VIII, and isolated as the monopicrate.

The stereochemistry of VIII cannot be assigned with complete certainty because the mechanism of the addition of nitrogen tetroxide to olefins has not been elucidated completely. However, the analogous reduction of the diketone VI to the *cis*-glycol VII, and the fact that the *cis*-bicyclo[3.3.0]-octane ring system is more stable than the corresponding *trans* structure strongly suggest that the diamine VIII has the *cis* configuration.



VIII III

Experimental[6]

Tetrabromomethylethylene (I).—A solution of 41 g. (0.5 mole) of freshly distilled 2,3-dimethylbutadiene in 500 ml. of carbon tetrachloride was maintained at 0° while a solution of 80 g. (0.5 mole) of bromine in 200 ml. of carbon tetrachloride was added dropwise over a 4-hr. period. To this solution 178 g. (1.0 mole) of N-bromosuccinimide, 4 g. of benzoyl peroxide and 250 ml. of carbon tetrachloride were added and the mixture was heated to reflux on a steam-bath. After completion of the vigorous exothermic reaction, controlled by cooling the reaction vessel, the mixture was heated under reflux for 1 hr. The hot mixture was filtered to remove precipitated succinimide. The filtrate then was cooled to 0° and the precipitated tetrabromomethylethylene was removed by filtration (123 g., m.p. 150–155°). An additional 9.0 g. of crystals was obtained from the mother liquors, m.p. 148–156°. Recrystallization of the total amount of crude product from ethyl acetate yielded 120 g. (60%) of tetrabromomethylethylene, m.p. 157–159°. Recrystallization from cyclohexane yielded an analytical sample, m.p. 158–159°.

Anal. Calcd. for $C_6H_8Br_4$: C, 18.02; H, 2.02; Br, 79.96. Found: C, 18.16; H, 2.03; Br, 80.18.

Tetrabromomethylethylene Glycol (II).—Twenty grams of the tetrabromide I dissolved in 1 l. of acetone was oxidized at 5–12° by the dropwise addition over a 7-hr. period of a solution of 8 g. of potassium permanganate and 6 g. of magnesium sulfate in 300 ml. of water. Excess permanganate and manganese dioxide were then decomposed by the addition of dilute sulfuric acid to *p*H 3 followed by decolorization of the solution with aqueous sodium bisulfite. The acetone was removed under reduced pressure and the aqueous solution was extracted with ether. The ether solution was dried over anhydrous sodium sulfate, concentrated under reduced pressure, and the residual solid was washed with 1:1 ether–petroleum ether. Recrystallization of this product (11 g., m.p. 85–95°) from ligroin–benzene (2:1) and methylcyclohexane yielded 5.6 g. (26%) of tetrabromomethylethylene glycol, m.p. 105.0–107.5°. A sample recrystallized to a constant melting point of 107.0–109.5° from ethanol was analyzed.

Anal. Calcd. for $C_6H_{10}O_2Br_4$: C, 16.61; H, 2.32. Found: C, 16.90; H, 2.41.

A solution of 5.6 g. of II and 7 g. of lead tetraacetate in 100 ml. of chloroform and 5 ml. of glacial acetic acid was allowed to stand at room temperature for 8 hr. Excess lead tetraacetate was destroyed by the addition of ethylene glycol. The solution was washed with water, dried over anhydrous sodium sulfate, and the solvent removed under reduced pressure. Distillation of the residual oil yielded 4.4 g. (79%) of *sym*-dibromoacetone in two fractions: 1.5 g., b.p. 90–94° (16 mm.), m.p. 19–20°; and 2.9 g., b.p. 94–96° (16 mm.), m.p. 24°.[7] A 2,4-dinitrophenylhydrazone of the ketone melted at 119–120°.[8] A mixed melting point determination with an authentic sample of *sym*-dibromoacetone 2,4-dinitrophenylhydrazone was not depressed.

3,3,7,7-Tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene (III).—Diethyl malonate (80 g.) was added rapidly to a boiling solution of sodium ethoxide prepared from 23 g. of sodium and 700 ml. of absolute ethanol, and the resulting mixture was transferred to a 1-l. separatory funnel. In a 5-l. flask equipped with a stirrer, condenser and the separatory funnel containing the diethyl sodiomalonate was placed a suspension of 100 g. of I in 2.5 l. of anhydrous ether. The diethyl sodiomalonate mixture was added to the refluxing ether suspension of I under a nitrogen atmosphere over a 5-hr. period. The reaction mixture was heated under reflux for 1 hr. after the addition was complete, and the cooled reaction mixture was poured into a separatory funnel containing cracked ice and 200 ml. of 3 *N* hydrochloric acid. The ether layer was separated and washed successively with water, dilute sodium carbonate solution and water, and dried over anhydrous sodium sulfate. The ether solution was concentrated under reduced pressure until crystallization occurred. Chilling caused further precipitation, and after removal of the product by filtration and washing it with cold absolute ethanol and petroleum ether–methylcyclohexane, the yield of III amounted to 19.5 g., m.p. 112–114°. Recrystallization from methylcyclohexane yielded 19 g. (19%) of 3,3,7,7-tetracarbethoxybicyclo-[3.3.0]oct-1(5)-ene, m.p. 115–116°. An analytical sample was prepared by recrystallization from absolute ethanol, m.p. 115.5–116.5°.

Anal. Calcd. for $C_{20}H_{28}O_8$: C, 60.59; H, 7.12; sapn. equiv., 99.1; mol. wt., 396.4. Found: C, 60.47; H, 7.11; sapn. equiv., 98.2; mol. wt., 433 (cryoscopic in benzene).

The reduction of 0.40 g. of 3,3,7,7-tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene in 15 ml. of dioxane with hydrogen in the presence of 0.1 g. of 10% palladium-on-Norit catalyst was complete in 2 hr. with the absorption of 0.98 molar equivalent of hydrogen.

Bicyclo[3.3.0]oct-1(5)-ene-3,3,7,7-tetracarboxylic Acid (IV).—A solution of 3.5 g. of III and 5 g. of sodium hydroxide in 25 ml. of ethanol and 100 ml. of water was heated under reflux for 16 hr. and, after cooling, the reaction mixture was extracted with ether. The aqueous layer was

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[5] Pl. A. Plattner and J. Hulstkamp, *Helv. Chim. Acta*, **27**, 211 (1944).

[6] Melting points are corrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[7] O. Völker, *Ann.*, **192**, 97 (1878).

[8] W. Boekmüller and L. Pfeuffer, *ibid.*, **537**, 195 (1939), report m.p. 120–121°.

treated with dilute hydrochloric acid to *p*H 3. Concentration under reduced pressure yielded 2.2 g. of the acid III as a crystalline solid, m.p. 230–232° dec. Recrystallization from water yielded 2.1 g. (85%) of bicyclo[3.3.0]oct-1(5)-ene-3,3,7,7-tetracarboxylic acid, m.p. 232–233° dec.

Anal. Calcd. for $C_{12}H_{12}O_8$: C, 50.71; H, 4.26; neut. equiv., 71.1. Found: C, 50.75; H, 4.32; neut. equiv., 69.9.

***trans*-3,3,7,7-Tetracarbethoxybicyclo[3.3.0]octane-1,5-diol (V).**—Ten grams of the bicycloöctene derivative III was suspended in 100 ml. of 87% formic acid and 4 ml. of 35% hydrogen peroxide was added. The resulting solution was heated at 45° for 1 hr. with stirring and permitted to stand at room temperature for 19 hr. After concentration of the solution under reduced pressure to a small volume, the addition of water yielded a solid which was washed free of formic acid with water. The solid was suspended in a solution of 35 ml. of ethanol and 100 ml. of concentrated ammonium hydroxide and agitated for 2 hr. The solution was diluted with an equal volume of water and the white solid (7.4 g., m.p. 180.0–182.5°) was removed by filtration. Recrystallization of the solid from absolute ethanol yielded 6.6 g. (61%) of *trans*-3,3,7,7-tetracarbethoxybicyclo[3.3.0]-octane-1,5-diol, m.p. 183–185°. An analytical sample, m.p. 184–186°, was obtained by further recrystallization from absolute ethanol.

Anal. Calcd. for $C_{20}H_{30}O_{10}$: C, 55.80; H, 7.03. Found: C, 55.62; H, 7.08.

3,3,7,7-Tetracarbethoxycycloöctane-1,5-dione (VI). A. Lead Tetraacetate Cleavage of the *trans*-Glycol V.—A solution of 3.8 g. of the glycol V and 3.9 g. of lead tetraacetate in 200 ml. of methylene chloride containing 10 drops of glacial acetic acid was heated under reflux for 1.5 hr. and left at room temperature overnight. Excess lead tetraacetate was destroyed by the addition of ethylene glycol and the precipitated lead acetate was removed by filtration. The filtrate was washed with water, dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Crystallization of the residue from ether–petroleum ether (6:1) yielded 2.6 g. (69%) of 3,3,7,7-tetracarbethoxycycloöctane-1,5-dione, m.p. 108.5–110.5°. An analytical sample was prepared by recrystallization from absolute ethanol, m.p. 109.5–110.5°.

Anal. Calcd. for $C_{20}H_{28}O_{10}$: C, 56.07; H, 6.59; mol. wt., 428. Found: C, 55.77; H, 6.55; mol. wt., 453 (cryoscopic in benzene).

B. Lead Tetraacetate Cleavage of *cis*-3,3,7,7-Tetracarbethoxybicyclo[3.3.0]octane-1,5-diol.—The bicyclic ester III (3.0 g.) and 2 ml. of a 0.5% solution of osmium tetroxide in *t*-butyl alcohol[4] were added to a solution (dried for 3 hr. over anhydrous sodium sulfate) of 3 ml. of 88% hydrogen peroxide in 50 ml. of *t*-butyl alcohol. The resulting solution was heated under reflux for 18 hr. Excess hydrogen peroxide was destroyed by heating the reaction mixture for 3 hr. on a steam-bath in the presence of platinum foil. Solvent was removed under reduced pressure and the residual oil was dissolved in methylene chloride. This solution was washed with ammonium hydroxide and water and dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure and further drying of the residue by distillation with benzene yielded the crude *cis*-glycol, which was treated with 3.5 g. of lead tetraacetate in 75 ml. of methylene chloride containing 10 drops of glacial acetic acid. The solution was allowed to stand for 40 hr. at room temperature. The product was isolated as described above and yielded 1.4 g. (43% over-all) of 3,3,7,7-tetracarbethoxycycloöctane-1,5-dione, m.p. 109–110°.

C. Ozonolysis of 3,3,7,7-Tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene.—Oxygen containing ozone was passed through a solution of 1.0 g. of III in 15 ml. of ethyl acetate for 2.5 hr. at −20°. The ethyl acetate was removed under reduced pressure and the resulting sirup was treated with 15 ml. of glacial acetic acid and 15 ml. of water and heated on a steam-bath for 3 hr. The solution was concentrated under reduced pressure and the residual oil was triturated with 95% ethanol until crystallization occurred, yielding 0.45 g. of 3,3,7,7-tetracarbethoxycycloöctane-1,5-dione, m.p. 103–107°. Recrystallization from absolute ethanol yielded 0.4 g. (37%), m.p. 108–110°.

***cis*-3,3,7,7-Tetracarbethoxybicyclo[3.3.0]octane-1,5-diol (VII). A. Reduction of 3,3,7,7-Tetracarbisthoxycyclooctane-1,5-dione (VI)**—Reduction of a 1.0-g. sample of VI in 25 ml. of dioxane in the presence of 0.3 g. of W-7 Raney nickel[9] was complete in 4 hr. and 78% of one molar equivalent of hydrogen was absorbed. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was crystallized at room temperature from methylcyclohexane. Recrystallization of the crude glycol from 95% ethanol yielded 0.6 g. (68%) of *cis*-3,3,7,7-tetracarbethoxybicyclo[3.3.0]octane-1,5-diol, m.p. 75–76°. A sample purified to a constant melting point of 75–76° by recrystallization from methylcyclohexane was analyzed.

Anal. Calcd. for $C_{20}H_{30}O_{10}$: C, 55.80; H, 7.03. Found: C, 55.66; H, 7.04.

B. Permanganate Oxidation of 3,3,7,7-Tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene.—Potassium permanganate (0.4 g.) in 30 ml. of water was added with stirring to a solution of 1.0 g. of III in 50 ml. of ethanol and 10 ml. of acetone over a 1-hr. period. Excess permanganate and manganese dioxide were destroyed by the addition of dilute hydrochloric acid to *p*H 3 and decolorization by the dropwise addition of a solution of sodium bisulfite. The solution was chilled in an ice-bath and 0.45 g. of the starting material III, identified by melting point and mixed melting point, was recovered. Concentration of the solution under reduced pressure resulted in separation of 0.25 g. of the crystalline *cis*-glycol. Recrystallization of this sample from methylcyclohexane yielded 0.2 g. of the glycol, m.p. 73–76°. A mixed melting point determination with the glycol (m.p. 74.0–76.5°) prepared by catalytic reduction of VI was undepressed, m.p. 74.0–76.5°.

A solution of 0.68 g. of the *cis*-glycol VII in 25 ml. of methylene chloride and 1 ml. of glacial acetic acid was treated with a solution of 1 g. of lead tetraacetate in 25 ml. of methylene chloride containing 1 ml. of glacial acetic acid. The reaction mixture was allowed to remain at room temperature for 4 hr. By the previously described isolation procedure there was obtained 0.5 g. (74%) of 3,3,7,7-tetracarbethoxycycloöctane-1,5-dione (VI), m.p. 107–110°. A mixed melting point determination of this product with an authentic sample of VI was not depressed.

Derivatives of 3,3,7,7-Tetracarbethoxycycloöctane-1,5-dione (VI). A. Dioxime.—A solution of 1.0 g. of VI and 1.0 g. of hydroxylamine hydrochloride in 5 ml. of pyridine and 5 ml. of absolute ethanol was heated under reflux for 3 hr. Evaporation of the solvent in a stream of air left an oil. The oil was triturated with water and dissolved by addition of 95% ethanol. Chilling the solution caused the precipitation of 0.9 g. (84%) of the dioxime, m.p. 157–160°. Recrystallization from dilute ethanol furnished an analytical sample, m.p. 164.2–165.2°.

Anal. Calcd. for $C_{20}H_{30}N_2O_{10}$: C, 52.39; H, 6.60; N, 6.11. Found: C, 52.37; H, 6.78; N, 5.96.

B. Disemicarbazone.—A solution of 0.6 g. of VI in 15 ml. of ethanol and sufficient water to cause turbidity was treated with a drop of ethanol, 1.0 g. of semicarbazide hydrochloride and 1.2 g. of sodium acetate trihydrate. The mixture was heated on a steam-bath for 30 min. Upon cooling, 0.76 g. (100%) of the disemicarbazone was obtained, m.p. 216–218° dec. Recrystallization from methyl Cellosolve–water provided an analytical sample, m.p. 226–227° dec.

Anal. Calcd. for $C_{22}H_{34}N_6O_{10}$: C, 48.70; H, 6.32; N, 15.49. Found: C, 48.76; H, 6.61; N, 15.34.

C. Bis-2,4-dinitrophenylhydrazone.—To a solution of 100 mg. of VI in 25 ml. of 95% ethanol was added a solution of 110 mg. of 2,4-dinitrophenylhydrazine in 0.5 ml. of concentrated sulfuric acid, 1 ml. of water and 2.5 ml. of 95% ethanol. The reaction mixture was heated on a steam-bath for 1 hr. and then cooled in ice. The yellow 2,4-dinitrophenylhydrazone obtained amounted to 0.15 g. (84%), m.p. 244.5–246.5° dec. An analytical sample was prepared by recrystallization from chloroform–petroleum ether, m.p. 244.5–245.5° dec.

Anal. Calcd. for $C_{32}H_{36}N_8O_{16}$: C, 48.73; H, 4.60; N, 14.21. Found: C, 48.56; H, 4.81; N, 14.28.

D. Bis-diethylmercaptal.—Hydrogen chloride was bubbled through an ice-cold mixture of 0.8 g. of VI, 1.0 g. of anhydrous sodium sulfate, 0.5 g. of freshly fused zinc chloride and 15 ml. of ethyl mercaptan for 5 hr. The reaction flask was

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(9) H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 698 (1948).

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.

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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).