sure in the presence of 15 g. of ruthenium dioxide. From the reduced hydrocarbon mixture, ethylcyclohexane (2355 g.) was removed at 130–131°, or 68–69° (100 mm.), n^{25}D 1.4312. The residue was rapidly distilled through a short-path still to remove the hydrocarbon from *p*-butylcatechol. This distillate was separated by distillation through a 10-inch helices-packed column into the following fractions: (D) b. p. 135–142°, n^{25}D 1.4480, 18.5 g.; (E) b. p. 143–150°, n^{25}D 1.4531, 30.8 g.; (F) b. p. 151–153°, n^{25}D 1.4551, m. p. 6–7°, 1.1 g. On the basis of refractive indices and infrared data, these fractions contain: (D) 66% cycloöctane; (E) 86% cycloöctane; (F) 94% cycloöctane. The total yield of cycloöctane amounted to approximately 1%. Fractionation and infrared analyses of smaller preparations indicated cycloöctane yields of 3–5%. Fraction F was conclusively identified by nitric acid oxidation to a solid acid, m. p. 140–141°, which showed no depression in melting point when mixed with an authentic sample of suberic acid.

Dimerization of 2,3-Dichloro-1,3-butadiene.—A mixture of 91.3 g. of 2,3-dichloro-1,3-butadiene,[3] 3 g. of phenothiazine, and 5 g. of Darco (Grade S-51) was agitated in a pressure bottle at 80° for one hundred and twenty hours. The resulting solid mass was extracted with several 200-ml. portions of ethanol. The alcohol was removed through a Vigreux column and the tarry solid was distilled at reduced pressure to give 11.3 g. (12.5%) of a solid, b. p. 140–146° (3.6 mm.). This was the only distillable product, and on crystallization from an acetone–alcohol–water mixture (5:5:1, by volume) gave white plates, m. p. 98–99°. The material appeared to be a very stable compound.

Anal. Calcd. for $C_8H_8Cl_4$: Cl, 57.66; mol. wt., 246. Found: Cl, 57.0, 56.8; mol. wt., 241, 241 (ebullioscopic method in benzene).

This material was hydrogenated in acetic acid solution in the same manner as that described for the dimer from 2-chloro-1,3-butadiene. The reduction mixture was added to water, and the hydrocarbon was isolated by extraction with benzene. The organic solution was dried and distilled, and the fraction boiling at 140–150° was shown to be approximately 80% cycloöctane by comparison of its infrared absorption curve with that of an authentic sample of cycloöctane.

The Removal of Chlorine from Dichloro-1,5-cyclooctadiene.—The action of sodium in liquid ammonia was found to effect the removal of the halogens from dichloro-1,5-cycloöctadiene without simultaneous reduction of the carbon–carbon double bonds.

Thirty-six grams of dichloro-1,5-cycloöctadiene was mixed with 200 ml. of liquid ammonia and approximately 100 ml. of absolute ether was added to effect homogeneity. Ten grams of sodium was added in small pieces and the mixture was stirred and allowed to reflux under a Dry Ice condenser until the sodium had dissolved. This required about two hours. The ammonia was then allowed to evaporate and the residue was filtered. There was obtained 43.4 g. of black solid (theory for NaCl is 23.2 g.), suggesting that considerable polymerization of the product had occurred. The filtrate was dried and distilled; the product boiling at 149–160° weighed 3.9 g., which corresponded to a 19% yield of cycloöctadiene. This was redistilled, and the pure material boiling at 150–152° was presumed to be 1,5-cycloöctadiene.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.78, 88.99; H, 10.94, 11.11.

Cope and Bailey[5] have found conditions for this reaction which give a 56% yield of the product.

Acknowledgment.—The authors are indebted to Dr. J. W. Stillman, under whose supervision the microanalyses were carried out, and to Miss Doris Huck for the infrared curves.

Summary

The dimerization of chloroprene to a mixture of 6- and 8-membered ring compounds has been confirmed. This unusual dimerization to 8-membered ring compounds has been extended to 1,3-butadiene and 2,3-dichloro-1,3-butadiene.

WILMINGTON, DELAWARE RECEIVED FEBRUARY 28, 1948

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

Cyclic Polyolefins. II. Synthesis of Cycloöctatetraene from Chloroprene[1]

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

Cycloöctatetraene has been prepared by the thirteen-step Willstätter synthesis from pseudopelletierine,[3,4] and by a catalytic process from acetylene.[5] We have continued an investigation of synthetic routes to cycloöctatetraene in a search for a reasonably short synthesis which could be adapted to the preparation of functional derivatives of cycloöctatetraene, which are not accessible through any reactions reported for the hydrocarbon.[5] This paper describes a seven-step synthesis of cycloöctatetraene from chloroprene (2-chloro-1,3-butadiene).

A method for the preparation of a cyclic dimer of chloroprene containing an eight-membered ring (previously isolated from chloroprene distillation residues[6]) has been developed by Foster and Schreiber.[7] By a modification of their procedure, chloroprene was heated in the presence of phenothiazine as a polymerization inhibitor and converted into a mixture of dimers. The eight-membered ring dimer (I) was separated from six-membered ring dimers by fractional distillation, treatment with alcoholic alkali to remove a dimer containing reactive chlorine which otherwise was difficult to separate, and refractionation. The eight-membered ring structure of I is established by its hydrogenation to cycloöctane,[6,7] which we have

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[1] Presented at the Tenth National Organic Chemistry Symposium, Boston, Massachusetts, June 13, 1947.

[2] Arthur D. Little Postdoctorate Fellow, 1946–1947.

[3] Willstätter and Waser, *Ber.*, **44**, 3423 (1911); Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913).

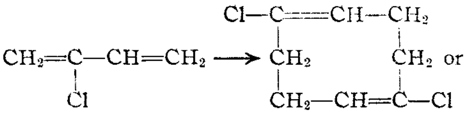
[4] Cope and Overberger, THIS JOURNAL, **70**, 1433 (1948).

[5] Described in Department of Commerce reports of German technological developments, including a translation of a paper by W. J. Reppe reprinted in "German Synthetic Fiber Developments," p. 631, Textile Research Institute, New York, N. Y., 1946 (P. B. 7416).

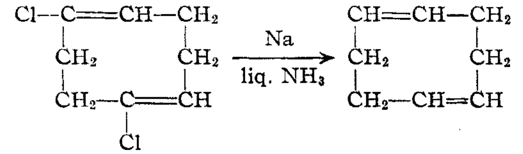
[6] Brown, Rose and Simonsen, *J. Chem. Soc.*, 101 (1944).

[7] Foster and Schreiber, THIS JOURNAL, **70**, 2303 (1948).

confirmed. The chloroprene units in the dimer may be joined head to tail (Ia) or head to head (Ib), or both structures may be present. These possibilities were not investigated, because the chlorine was replaced by hydrogen and the possibility for isomerism removed in the next step of the synthesis. The dehalogenation was accomplished by reaction of I with sodium in liquid ammonia.[7] Highest yields (56%) of 1,5-cycloöctadiene (II) were obtained with a low reaction temperature (−75 to −50°) and a short reaction time (three minutes), after which sodium compounds were neutralized and excess sodium decomposed by adding solid ammonium nitrate. These conditions minimized the polymerization which occurred as a side reaction. Titration showed that 90% of the chlorine in I was removed as ionic chlorine under these conditions. The structure of II was established by quantitative hydrogenation to cycloöctane, and by ozonization followed by oxidation with hydrogen peroxide, which gave succinic acid.



Ia



Ib II

Reaction of an excess of II with N-bromosuccinimide in the presence of benzoyl peroxide[8] gave a stable monobromo substitution product (III) in 45–57% yield. Although the methylene groups in 1,5-cycloöctadiene are equivalent, rearrangement could occur either during the substitution reaction (through an intermediate free radical) or through an allylic shift of the bromo compound. Consequently the product may have structure IIIa, IIIb or be a mixture of the two. Reaction of III with dimethylamine gave a 61% yield of a dimethylaminocycloöctadiene (IV), which likewise may have structure IVa or IVb; the displacement reaction presents an added possibility for an allylic rearrangement.

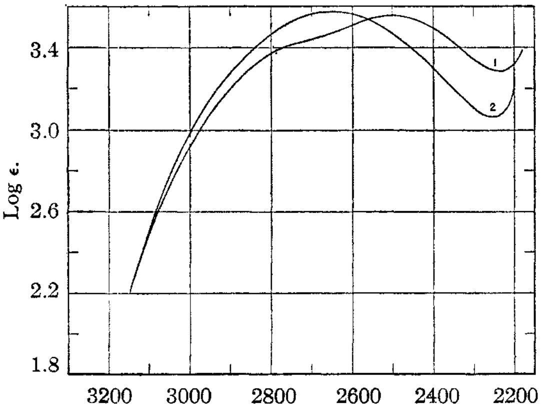
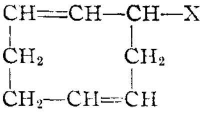
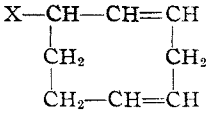


Fig. 1.—Curve 1, absorption spectrum of cycloöctatriene (VI); curve 2, absorption spectrum of 1,3,5-cyclooctatriene (ref. 4).

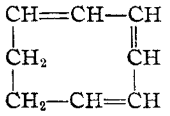


IIIa, X = Br
IVa, X = $N(CH_3)_2$
Va, X = $N(CH_3)_3I$

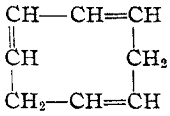


IIIb, X = Br
IVb, X = $N(CH_3)_2$
Vb, X = $N(CH_3)_3I$

IV was proved to be a dimethylaminocycloöctadiene by quantitative hydrogenation to dimethylaminocycloöctane, which was identified as the methiodide. IV reacted with methyl iodide to give a methiodide, V, which was converted to the quaternary base and distilled to give a cyclooctatriene, VI. VI differed in index of refraction, density and ultraviolet absorption spectrum (Fig. 1) from 1,3,5-cycloöctatriene (prepared from pseudopelletierine).[4] Comparison of the ultraviolet absorption curves of VI and 1,3,5-cycloöctatriene (also shown in Fig. 1) indicates that VI probably is a mixture of 1,3,5-cycloöctatriene (VIa) and 1,3,6-cycloöctatriene (VIb), such as might be formed from a mixture of quaternary salts (Va and Vb). The ultraviolet absorption curve for 1,3,5-cycloöctatriene has a maximum at 2650 Å.[4] In VI the maximum is displaced to 2500 Å., while for structure VIb the maximum would be expected to fall nearer 2200 Å.



VIa



VIb

The possibility of conducting a similar sequence of reactions beginning with a dibromo derivative of cycloöctadiene was next investigated. 1,5-Cycloöctadiene (II) reacted with two molar equivalents of N-bromosuccinimide in the presence of benzoyl peroxide to give a dibromo compound, which was treated directly with an excess of dimethylamine. In this way a bis-(dimethylamino)-cycloöctadiene (VII) was obtained in an over-all yield of 34% from II. VII might be expected to be a mixture from its method of preparation, but proved to be practically homogeneous and identical with the compound believed to be 1,6-bis-(dimethylamino)-2,4-cycloöctadiene which is an intermediate in the Willstätter synthesis of cyclooctatetraene. Identity of the diamines from the two syntheses was established by correspondence

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[8] Ziegler, Späth, Schaaf, Schumann and Winkelmann, *Ann.*, **551**, 80 (1942); Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

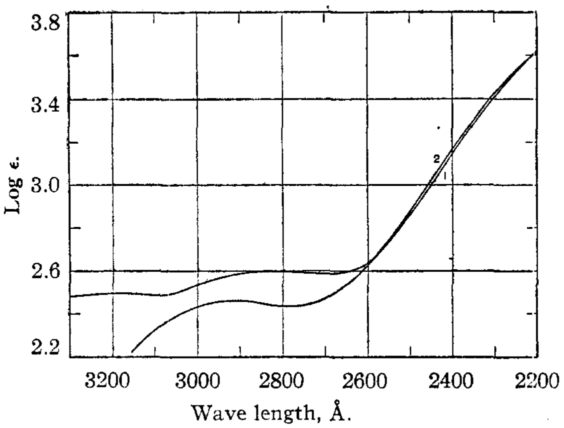
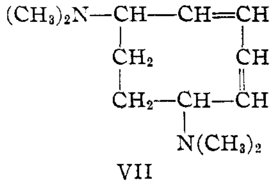


Fig. 2.—Curve 1, absorption spectrum of 1,6-bis-(dimethylamino)-2,4-cycloöctadiene (VII) derived from 1,5-cycloöctadiene; curve 2, absorption spectrum of 1,6-bis-(dimethylamino)-2,4-cycloöctadiene prepared from pseudopelletierine (ref. 4).

in melting points of the dipicrates and dimethiodides, and comparison of ultraviolet absorption spectra (Fig. 2). Also VII was hydrogenated to 1,4-bis-(dimethylamino)-cycloöctane, which was identified as the dipicrate and dimethiodide. The formation of VII from II can be explained by rearrangement during the bromination of II, yielding 1,6-dibromo-2,4-cycloöctadiene, or by formation of 3,4-dibromo-1,5-cycloöctadiene followed by a double allylic rearrangement either before or during the displacement reaction with dimethylamine. The tendency of the double bonds to become conjugated undoubtedly accounts for the formation of VII, regardless of the step at which the rearrangements occur.



VII

The remaining steps in the synthesis of cycloöctatetraene followed the sequence of reactions used by Willstätter. VII was converted to the dimethiodide, which with silver hydroxide gave the quaternary base. Very slow distillation of the latter at 0.15–1 mm. gave a 15.5% yield of cycloöctatetraene, which was established as identical with a sample prepared from acetylene by correspondence in index of refraction, melting point, mixed melting point, ultraviolet (Fig. 3) and infrared[9] absorption spectra. The spectra indicated the presence of approximately 8% of styrene in this sample of cycloöctatetraene, presumably formed by rearrangement during decomposition of the quaternary base.

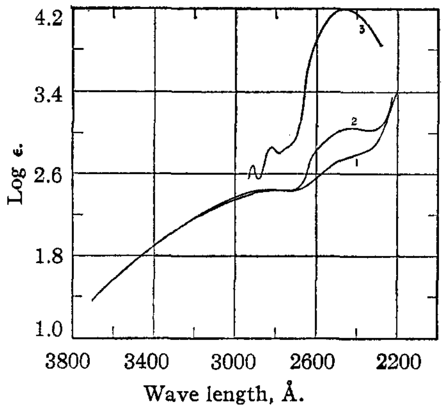


Fig. 3.—Curve 1, absorption spectrum of cycloöctatetraene prepared from acetylene; curve 2, absorption spectrum of cycloöctatetraene (containing approximately 8% of styrene) prepared from chloroprene; curve 3, absorption spectrum of styrene.[12]

Experimental[10]

Dichloro-1,5-cycloöctadiene (I).—A stabilized 50% solution of chloroprene in xylene[11] was distilled rapidly in a nitrogen atmosphere without appreciable fractionation to obtain chloroprene containing 10–12% xylene. This distillate (2.5 kg.) and 45 g. of phenothiazine were placed in a 3-liter three-necked flask equipped with a thermometer, a mercury-sealed stirrer and a reflux condenser which was connected to a nitrogen cylinder through a line containing a mercury pop-valve. Air in the system was displaced with nitrogen, and the mixture was stirred slowly under nitrogen and heated at a temperature which maintained a slow reflux. The temperature of the liquid rose from 61 to 80° during sixty hours and was kept at 80–84° for an additional seventy hours by regulating the bath temperature. Hydrogen chloride escaped through the pop-valve during the heating period. The mixture was transferred to a 2-liter round-bottomed flask connected to a water-cooled condenser, receiver, Dry Ice trap and a water pump, and distilled as rapidly as possible under reduced pressure without fractionation. After separation of recovered chloroprene, which collected in the Dry Ice trap, the distillation was continued at 20–30 mm. and completed at a pressure of about 1 mm. with an oil pump protected from hydrogen chloride with soda-lime towers. This operation separated polymer and phenothiazine from the distillate containing dimers. The distillate was fractionated fairly rapidly under nitrogen at 3 mm. pressure through a total condensation, variable take-off column with a 30 × 2 cm. section packed with glass helices. This distillation separated an additional portion of recovered chloroprene, xylene, and crude six-membered ring dimers (b. p. up to 76° (3 mm.)) from the highest boiling fraction, b. p. 76–90° (3 mm.), containing the eight-membered ring dimer (and some six-membered ring dimers). The last fraction was heated for twenty-four hours at 60° with a solution equivalent to 90 g. of sodium hydroxide in 1400 ml. of absolute alcohol (prepared by adding sodium and water to absolute alcohol). The alcoholic solution was added to 2 l. of water and the product was extracted with four-400 ml. portions of benzene. The extracts were dried over anhydrous magnesium sulfate and concentrated. The residue was fractionated carefully through the 30 × 2 cm. helix-packed column in an atmosphere of nitrogen. Several such

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[9] We are indebted to Dr. R. C. Lord, Jr., and Mr. R. S. McDonald for the infrared data.

[10] Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy, Mr. Philip H. Towle and Mrs. Louise W. Spencer for analyses.

[11] Obtained from the Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.

preparations yielded the following data: xylene present in the chloroprene dimerized, 10–12%; chloroprene recovered, 13–16%. The following percentages are based on the weight of chloroprene actually consumed in the reaction (subtracting the amount recovered): polymer formed, 9–23%; yield of crude six-membered ring dimers, 40–46%; yield of the fraction containing the eight-membered ring dimer from the first fractionation, 23–25%; yield of dichloro-1,5-cycloöctadiene (I) after alkali treatment and refractionation, 10–13%; b. p. 88–89° (3.3 mm.); 92–94° (3.8 mm.); $n^{25}D$ 1.5300–1.5310.

Anal. Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.11; H, 5.74; Cl, 39.9.

Preliminary fractionation to remove most of the six-membered ring dimers should precede alkali treatment of the product, as in the procedure described. Otherwise a compound which corresponded closely in analysis to $C_8H_{10}(OC_2H_5)Cl$ was formed in an amount corresponding to about half of the yield of I. This compound, evidently derived from a 6-membered ring dimer containing a reactive chlorine atom, boiled approximately 3° higher than I and its presence complicated the fractionation.[12]

A sample (10.00 g.) of the dichloro-1,5-cycloöctadiene in 60 ml. of glacial acetic acid was hydrogenated in the presence of 14.5 g. of anhydrous sodium acetate and 1.1 g. of pre-reduced Adams platinum oxide catalyst; 101% of four molar equivalents of hydrogen was absorbed. The solution was made basic with sodium carbonate and extracted with ether. Fractionation through a 15 × 1.2 cm. helix-packed column yielded 3.74 g. (59%) of cycloöctane, b. p. 148–149°; $n^{25}D$ 1.4557; m. p. 12.0°.

1,5-Cycloöctadiene (II).—Sodium (39.3 g., 1.7 moles) was dissolved in 2.5 l. of liquid ammonia in a 3-liter three-necked flask equipped with a stirrer, dropping funnel and thermometer. The ammonia solution was cooled to −75° in a Dry Ice-trichloroethylene-bath and a solution of 75 g. (0.42 mole) of dichloro-1,5-cycloöctadiene in 100 ml. of dry ether (also cooled with Dry Ice) was added with stirring during three-quarters of one minute. The mixture was stirred for two minutes, during which time the temperature of the liquid rose to −55 to −45°. Powdered ammonium nitrate (80 g.) was then added rapidly (one-half minute) and the ammonia was allowed to evaporate through a water-cooled reflux condenser while the reaction mixture stood overnight. Water was added to the residue and the product was extracted with ether, dried over magnesium sulfate and distilled. The yield of 1,5-cycloöctadiene was 25.4 g. (56%); b. p. 148–149°; $n^{25}D$ 1.4905; d^{25}_4 0.8818.[13]

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 89.13; H, 11.22.

A polymeric residue of 13.2 g. remained after distillation of the product. Titration of an aliquot portion of the aqueous solution after separation of the product showed the presence of 90% of the theoretical 0.84 equivalent of chloride ion.

Hydrogenation of a 1.21-g. sample of 1,5-cycloöctadiene in 20 ml. of glacial acetic acid in the presence of 0.1 g. of reduced platinum oxide required 101% of two molar equivalents of hydrogen. The product was identified as cycloöctane by its physical properties after purification by extraction from alkaline solution and distillation through a Craig micro column[14]; $n^{25}D$ 1.4555; m. p. 11.2°.

A 1.00-g. sample of 1,5-cycloöctadiene in 25 ml. of ethyl acetate was ozonized at −30°. The ethyl acetate was removed under reduced pressure and the ozonide was decomposed by heating on the steam-bath for three hours with 12 ml. of 30% hydrogen peroxide in 20 ml. of glacial acetic acid. After concentration under reduced pressure, the residue was dissolved in a sodium bicarbonate solution, which was extracted with ether to remove any neutral material. The alkaline solution was acidified and extracted with ether in a continuous extractor for two days. The ether extract was distilled and the residue recrystallized from water. Succinic acid was isolated in a yield of 1.62 g. (74%), m. p. and mixed m. p. with a known sample 186–187°.

Reaction of 1,5-Cycloöctadiene with N-Bromosuccinimide.—1,5-Cycloöctadiene (16.4 g.) in 50 ml. of dry carbon tetrachloride was stirred under reflux (80°) for one hour with 9.0 g. of N-bromosuccinimide and 0.25 g. of benzoyl peroxide. The succinimide formed was removed by filtration and the solution was fractionated through a 15 × 1.2 cm. helix-packed column. The recovery of 1,5-cycloöctadiene was 10.7 g. (determined by the weight of carbon tetrachloride–1,5-cycloöctadiene mixture recovered, and comparison of its refractive index with a linear plot of the refractive indices of known mixtures), and 5.4 g. (57% based on the N-bromosuccinimide) of bromocycloöctadiene (III) was obtained, b. p. 64° (1.9 mm.); $n^{25}D$ 1.5410; d^{25}_4 1.3420.

Anal. Calcd. for $C_8H_{11}Br$: C, 51.35; H, 5.93; Br, 42.72. Found: C, 51.27; H, 6.07; Br, 42.84.

Dibromocycloöctadiene was isolated in one instance from the reaction of 10.8 g. of 1,5-cycloöctadiene and 36 g. of N-bromosuccinimide in 100 ml. of dry carbon tetrachloride, which were heated under reflux with stirring in the presence of 0.5 g. of benzoyl peroxide for one hour. The succinimide formed was removed by filtration and the filtrate was washed with water, dried over Drierite and distilled under nitrogen. The dibromocycloöctadiene (14.2 g., b. p. 110–116° (2 mm.)) turned black after standing at room temperature for a few minutes, and in subsequent preparations was not isolated, but was treated directly with dimethylamine as outlined under the preparation of VII.

Dimethylaminocycloöctadiene (IV).—Bromocycloöctadiene (12.6 g.) and 250 ml. of a 20% solution of dimethylamine in benzene were allowed to stand for three days at room temperature. The mixture was extracted with 15% hydrochloric acid solution, which was then made basic with 20% sodium hydroxide and extracted with ether. The extracts were dried over magnesium sulfate, concentrated, and the residue was distilled under nitrogen through a 15 × 1.2 cm. helix-packed column. The yield of dimethylaminocycloöctadiene was 6.2 g. (61%); b. p. 58–60° (1.2 mm.); $n^{25}D$ 1.4972.

Anal. Calcd. for $C_{10}H_{17}N$: C, 79.40; H, 11.33; N, 9.26. Found: C, 79.39; H, 11.45; N, 9.17.

Dimethylaminocycloöctadiene was also prepared in about the same over-all yield from 1,5-cycloöctadiene in a similar preparation in which the intermediate bromo compound was not isolated, and was obtained as a by-product in the preparation of 1,6-bis-(dimethylamino)-2,4-cycloöctadiene (see below).

Dimethylaminocycloöctadiene methiodide (V) was prepared from 12.8 g. of dimethylaminocycloöctadiene and 30 g. of methyl iodide in 70 ml. of absolute alcohol. The solution was allowed to stand for thirty minutes and heated under reflux for one hour. The crystalline methiodide (V) separated on cooling in a yield of 22.6 g. (91%), m. p. 163–166° (dec.). An analytical sample which was recrystallized twice from absolute alcohol melted at 168–169° (dec.).

Anal. Calcd for $C_{11}H_{10}NI$: C, 45.05; H, 6.88; N, 4.77; I, 43.28. Found: C, 44.76; H, 6.95; N, 4.66; I, 43.14.

Although this methiodide had a relatively sharp melting point (with decomposition) it is believed to be a mixture of isomers (Va and Vb), for further recrystallization raised the m. p. to 174–175°; moreover, a mixed m. p. of V with the isomeric α-des-dimethylgranatenine methiodide[4] was not depressed but intermediate between the two decomposition points (174–176° dec.), proving that

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[12] We are indebted to Dr. Calvin L. Stevens for these data.

[13] Impure 1,5-cycloöctadiene containing about 20% of a bicyclo-öctene has been prepared by the Hofmann exhaustive methylation procedure from des-dimethylgranatanine; Willstätter and Veraguth, *Ber.*, **38**, 1979 (1905); *ibid.*, **40**, 960 (1907); Willstätter and Kametka, *ibid.*, **41**, 1482 (1908); Harries, *ibid.*, **41**, 672 (1908).

[14] Craig, *Ind. Eng. Chem., Anal. Ed.*, **9**, 441 (1937).

the decomposition points of mixtures of such isomeric methiodides can be sharp and not markedly lowered.[12]

A 2.24-g. sample of dimethylaminocycloöctadiene in 70 ml. of absolute alcohol was hydrogenated in the presence of 0.4 g. of prereduced platinum oxide catalyst. Hydrogen absorption was 99.5% of two molar equivalents. The dimethylaminocycloöctane produced was isolated by distillation in a Craig micro column; n^{25}_{D} 1.4717 (ref. 4, n^{25}_{D} 1.4707).

Anal. Calcd. for $C_{10}H_{21}N$: C, 77.34; H, 13.63; N, 9.02. Found: C, 77.36; H, 13.46; N, 9.15.

Dimethylaminocycloöctane methiodide was prepared as a derivative and recrystallized from absolute alcohol; m. p. 273–274° (dec.) (ref. 4, m. p. 274–275° dec.).

Anal. Calcd. for $C_{11}H_{24}NI$: C, 44.44; H, 8.13; N, 4.71; I, 42.70. Found: C, 44.16; H, 8.09; N, 4.63; I, 42.46.

Cycloöctatriene (VI).—Dimethylaminocycloöctadiene methiodide (21.4 g.) in 300 ml. of water and the silver hydroxide prepared from 37.5 g. of silver nitrate and 8.8 g. of sodium hydroxide were stirred at room temperature for one and one-half hours. The mixture was filtered and the filtrate was concentrated under reduced pressure. The quaternary base was decomposed by continuing the distillation at a pressure of 20 mm. and a bath temperature of 90°. The distillate, which was collected in a receiver cooled with Dry Ice, was extracted with ether, and the extracts (to which 1% of *t*-butylcatechol was added as a polymerization inhibitor) were dried over magnesium sulfate. Distillation through a 15 × 1.2 cm. helix-packed column under nitrogen yielded 6.1 g. (78%) of cyclooctatriene, b. p. 76° (90 mm.); n^{25}_{D} 1.5187; d^{25}_{4} 0.8971.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.28; H, 9.47.

1,6-bis-(Dimethylamino)-2,4-cycloöctadiene (VII).—1,5-Cycloöctadiene (21.6 g., 0.2 mole) in 300 ml. of dry carbon tetrachloride, 72.g. (0.4 mole) of N-bromosuccinimide and 1 g. of benzoyl peroxide were stirred vigorously and heated under reflux (80°) for one hour. Succinimide was separated by filtration and most of the carbon tetrachloride was removed from the filtrate by distillation under reduced pressure. To the residue was added 500 ml. of a 22.5% solution of dimethylamine in benzene, and the mixture was allowed to stand for ten days at room temperature. Fifteen per cent. hydrochloric acid was added until the mixture was acid (*p*H 2), and the amine salts were extracted with two portions of 0.01 *N* hydrochloric acid. The acid extracts were made basic with 20% sodium hydroxide and the amines were extracted three times with ether. The ether was distilled and the residue was heated at 60° for three minutes with 400 ml. of 2 *N* hydrochloric acid to hydrolyze substituted vinyl amine types. The solution was cooled, extracted with ether to remove any neutral material, and made basic with 20% sodium hydroxide. The product was extracted with ether and the extracts were dried over magnesium sulfate. The ether was distilled and the residue fractionated under nitrogen through a 15 × 1.2 cm. helix-packed column. Dimethylaminocycloöctadiene (IV) (5.1 g., 17%) was obtained as a low boiling fraction, followed by 13.3 g. (34%) of 1,6-bis-(dimethylamino)-1,4-cyclooctadiene (VII), b. p. 90° (1 mm.); n^{25}_{D} 1.4995; d^{25}_{4} 0.932 (ref. 4, n^{25}_{D} 1.4990; d^{25}_{4} 0.9317).

Anal. Calcd. for $C_{12}H_{22}N_2$: C, 74.16; H, 11.41. Found: C, 73.94; H, 11.06.

1,6-bis-(Dimethylamino)-2,4-cycloöctadiene dipicrate was prepared as a derivative and recrystallized from 95% alcohol; m. p. 194–195° (dec.) (ref. 4, m. p. 194.6–195.2°, dec.).

Anal. Calcd. for $C_{24}H_{28}N_8O_{14}$: C, 44.17; H, 4.33; N, 17.17. Found: C, 44.01; H, 4.52; N, 17.26.

1,6-bis-(Dimethylamino)-2,4-cycloöctadiene dimethiodide was prepared from 6.2 g. of 1,6-bis-(dimethylamino)-2,4-cycloöctadiene and 15 g. of methyl iodide in 50 ml. of absolute alcohol by refluxing for one hour. The salt which separated on cooling solidified on standing and was crystallized from a mixture of 90% alcohol and petroleum ether; yield 13.4 g. (87%), m. p. 172–173° (dec.); m. p. after recrystallization from absolute alcohol 172–173° (dec.)[12] (ref. 4, m. p. 173–174°, dec.).

Anal. Calcd. for $C_{14}H_{28}N_2I_2$: C, 35.16; H, 5.90; N, 5.86; I, 53.08. Found: C, 35.06; H, 5.91; N, 5.78; I, 53.28.

The above methiodide was separated from a much smaller amount (2–5%) of an isomeric dimethiodide which was relatively insoluble in alcohol. After two recrystallizations from alcohol and benzene the isomer (which may be a stereo or position isomer) darkened at 237–239° but did not liquefy or decompose with gas evolution below 285°.[12]

Anal. Calcd. for $C_{14}H_{28}N_2I_2$: C, 35.16; H, 5.90; N, 5.86; I, 53.08. Found: C, 35.25; H, 6.09; N, 6.01; I, 52.94.

A 2.30-g. sample of 1,6-bis-(dimethylamino)-2,4-cycloöctadiene in 30 ml. of absolute alcohol absorbed 110% of two molar equivalents of hydrogen slowly (during thirteen hours) in the presence of 0.5 g. of pre-reduced platinum oxide. The 1,4-bis-(dimethylamino)-cyclooctane formed was distilled through a Craig micro column: n^{25}_{D} 1.4820; d^{25}_{4} 0.9155 (ref. 4, n^{25}_{D} 1.4823, d^{25}_{4} 0.9166).

Anal. Calcd. for $C_{12}H_{26}N_2$: C, 72.66; H, 13.21; N, 14.13. Found: C, 72.62; H, 12.99; N, 14.07.

1,4-bis-(Dimethylamino)-cycloöctane dipicrate was prepared as a derivative and recrystallized from 95% alcohol; m. p. 173–174° (dec.) (ref. 4, m. p. 171.5–172.2°, dec.).

Anal. Calcd. for $C_{24}H_{32}N_8O_{14}$: C, 43.90; H, 4.90; N, 17.07. Found: C, 43.98; H, 5.04; N, 16.95.

1,4-bis-(Dimethylamino)-cycloöctane dimethiodide was prepared as a second derivative and recrystallized from 90% alcohol and petroleum ether; m. p. 255–256° (dec.) (ref. 4, m. p. 258–259°, dec.).

Anal. Calcd. for $C_{14}H_{32}N_2I_2$: C, 34.86; H, 6.69. Found: C, 34.81; H, 7.04.

Cycloöctatetraene.—1,6-bis-(Dimethylamino)-2,4-cycloöctadiene dimethiodide (22 g.), 100 ml. of water and the silver hydroxide prepared from 25.5 g. of silver nitrate and 6.0 g. of sodium hydroxide were stirred for one hour at room temperature and one hour at 50°. The mixture was filtered and the filtrate was concentrated under reduced pressure. The final stages of concentration and decomposition of the quaternary base were conducted at a pressure of 0.15–1 mm. and a bath temperature of 50° during four hours. The flask was heated at 100° for twenty minutes after the decomposition appeared to be complete. The distillate, which was collected in a receiver cooled with Dry Ice, was extracted with ether. The extracts were dried over magnesium sulfate, concentrated, and the residue distilled through a Craig micro column. The yield of cycloöctatetraene was 0.74 g. (15.5%); n^{25}_{D} 1.5342 (ref. 4, n^{25}_{D} 1.5342).

Anal. Calcd. for C_8H_8: C, 92.26; H, 7.74. Found: C, 91.92; H, 7.88.

The cycloöctatetraene obtained melted at −8.7 to −7.9°, and gave a mixed melting point with a sample of cycloöctatetraene prepared from acetylene (m. p. −5.9 to −5.3°) of −7.6 to −6.5°.

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra of compounds VI, VII and the cycloöctatetraene prepared in this way were determined in purified cyclohexane solution with a Beckmann quartz ultraviolet spectrophotometer. Absorption curves are shown in Figs. 1–3, in which curves for VII prepared from pseudopelletierine and cycloöctatetraene prepared from acetylene[4] are included for comparison.

Summary

Cycloöctatetraene has been prepared by a seven-step synthesis from chloroprene.

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