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

Cyclic Polyolefins. IV. 1,3-Cycloöctadiene[1]

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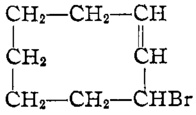
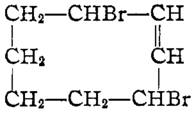
Several possible routes to functional derivatives of cycloöctatetraene involve the progressive introduction of double bonds into a substituted cycloöctene. Accordingly we have investigated the introduction of additional double bonds into cycloöctene itself as a model case.

Cycloöctatetraene was prepared by the catalytic polymerization of acetylene, and converted to cycloöctene[2] by partial hydrogenation in the presence of 1% palladium-on-calcium carbonate.[3] The reaction of one molar equivalent of N-bromosuccinimide with cycloöctene in carbon tetrachloride in the presence of a small amount of benzoyl peroxide gave 3-bromocycloöctene (I) in 55–65% yield and 15% of a dibromide which is presumed to be 3,8-dibromocycloöctene (II). The reaction of two molar equivalents of N-bromosuccinimide with cycloöctene gave I in 19% yield and 43% of the dibromide.



I



II

The reaction of I with dimethylamine in benzene at room temperature gave 1-dimethylamino-3-cycloöctene (III) in 78% yield, which was characterized by quantitative hydrogenation to dimethylaminocycloöctane (identified as the picrate and methiodide by m. p. and mixed m. p.[4]). The reaction of III with methyl iodide gave a 91–95% yield of a methiodide (IV) which was converted to the quaternary base by treatment with silver oxide. Decomposition of the quaternary base by distillation gave 1,3-cycloöctadiene (V) in 82% yield as a colorless, mobile liquid which on redistillation polymerized partially and gave V in 55% yield. V prepared in this way was moderately stable, and could be stored under nitrogen at 0–5° and redistilled without much polymerization. It had a disagreeable, penetrating odor resembling that of cyclopentadiene, which was detectable in very small concentration. The structure of V was established by quantitative hydrogenation to cycloöctane, by its ultraviolet absorption spectrum, which indicated conjugation of the double bonds, and by ozonization followed by reaction of the ozonide with hydrogen peroxide, which gave adipic acid.

After this phase of the work was completed Ziegler and Wilms[2] reported the isolation of isomeric forms (probably *cis* and *trans*) of cyclooctene and 1,5-cycloöctadiene. Since in both cases the less stable (probably *trans*) forms were obtained by the Hofmann exhaustive methylation route, it was of interest to prepare V by dehydrohalogenation. This was accomplished by heating I with quinoline, which gave 1,3-cycloöctadiene (Vb) in 93.5% yield with a somewhat different index of refraction ($n^{25}\text{D}$ 1.4908 compared to 1.4940) from 1,3-cycloöctadiene prepared by the Hofmann route (Va) and which did not have the characteristic odor of Va. The ultraviolet absorption spectra of the two samples were identical. Their infrared absorption spectra showed the same major bands (Fig. 2), but the product of the Hofmann exhaustive methylation reaction showed bands which were not present in V prepared by dehydrohalogenation. The melting point of Vb was -51 to $-49°$, compared to -57.5 to $-55°$ for Va, and a mixed m. p. of the two was intermediate.

The reaction of Va with aqueous silver nitrate gave an unstable crystalline adduct, from which 1,3-cycloöctadiene could be regenerated by the addition of water or sodium chloride solution. 1,3-Cycloöctadiene purified in this way had the same index of refraction and infrared absorption spectrum as the sample (Vb) prepared by dehydrohalogenation. It is concluded from these data that the 1,3-cycloöctadiene samples prepared by the two routes were identical after purification, but that the product of the Hofmann exhaustive methylation reaction initially contained an undetermined amount of a less stable isomer. The stable form Vb is probable the *cis–cis* isomer, while Va may contain some of the *cis–trans* isomer, which would be expected to be less stable.

Attempts to establish the structure of the dibromo compound prepared from cycloöctene and N-bromosuccinimide by oxidative degradation were unsuccessful, but structure II is the one expected from the method of preparation. The dibromide absorbed 98% of three molar equivalents of hydrogen is a quantitative hydrogenation, so the only uncertainty concerning its structure lies in the position of the bromine atoms, which could reach the 3,4-positions by an allylic rearrangement. Unlike 3-bromocycloöctene, the dibromide reacted relatively slowly and incompletely with dimethylamine in benzene. Products which were isolated from the reaction mixture were an impure bromocycloöctadiene and a mixture of a bromodimethylaminocycloöctene and a bis-(dimethylamino)-cycloöctene. This mixture was not separated, but evidence for its

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(1) Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96.

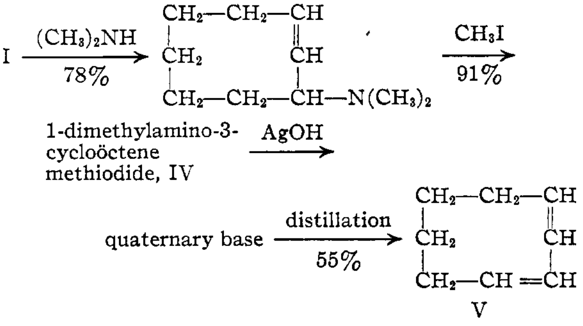
(2) Ziegler and Wilms, *Naturwissenschaften*, **35**, 157 (1948), state that cycloöctene prepared in this way is probably the *cis* form.

(3) Reppe, Schlichting, Klager and Toepel, *Ann.*, **560**, 1 (1948).

(4) Dimethylaminocycloöctane prepared by hydrogenation of α-des-dimethylgranatenine was converted to the picrate by Calvin L. Stevens and to the methiodide by C. G. Overberger; Cope and Overberger, THIS JOURNAL, **70**, 1433 (1948).

composition was obtained by hydrogenation, which yielded dimethylaminocycloöctane (identified by known derivatives) and a bis-(dimethylamino)-cycloöctane which was different from the isomer obtained by hydrogenation of 1,6-bis-(dimethylamino)-2,4-cycloöctadiene.[4]

The failure of II to give a bis-(dimethylamino)-cycloöctene in fair yield is in contrast to the behavior of 3,7-dibromocycloheptene, which Willstätter[5] was able to convert to a bis-(dimethylamino)-cycloheptene and subsequently to cycloheptatriene by the Hofmann exhaustive methylation procedure. In preliminary experiments the reaction of 1,3-cycloöctadiene with N-bromosuccinimide led to polymerization rather than bromination, and this route also does not at present seem promising for the introduction of a third double bond into the eight-membered ring.



Experimental[6]

Cycloöctatetraene—Cycloöctatetraene was prepared[7] by the catalytic polymerization of acetylene in a 1-l. stainless steel stirred autoclave manufactured by Autoclave Engineers, Inc. The procedure used was similar to the one described by Reppe, Schlichting, Klager and Toepel.[3] In a typical preparation 200 g. of dry tetrahydrofuran, 10 g. of nickel acetylacetonate and 20 g. of powdered calcium carbide were placed in the autoclave and the air was displaced with acetylene, which was then introduced at a pressure of 200–300 p. s. i., and the mixture was stirred and heated at 90°. Acetylene was introduced periodically to keep the pressure in the range of 300–150 p. s. i., and sufficient was absorbed in a period of ten to twelve hours to amount to an increase in weight of 300–400 g. Steam distillation after addition of hydroquinone as a polymerization inhibitor separated the product from a large amount of polymer. The steam distillate was washed well with water, dried over magnesium sulfate and distilled under nitrogen through an 18 × 1.8 cm. helix-packed column, after addition of a small amount of hydroquinone. The distillation separated 70–100 g. of benzene (plus some tetrahydrofuran) from 75–125 g. of cycloöctatetraene, b. p. 73.5–74° (90 mm.), $n^{25}_{\rm D}$ 1.5342. The cycloöctatetraene contained less than 0.5–1.0% of styrene, according to its infrared spectrum. Higher polymers were separated in the still residue, which amounted to 5–15 g.

Cycloöctene.—The procedure for partial reduction of cycloöctatetraene[8] was modified with respect to temperature and amount of catalyst. A suspension of 30 g. of 1.5% palladium hydroxide on calcium carbonate[8] in 50 ml. of dry methanol was shaken with hydrogen, and 96.5 g. of freshly distilled cycloöctatetraene in 100 ml. of dry methanol was added. The mixture was cooled to 3–5° in an ice-bath and shaken with hydrogen at 30–15 p. s. i. After about 60% of three molar equivalents of hydrogen had been absorbed the cooling bath was removed and the reduction was continued while the mixture warmed to room temperature. After 2.7 hours 99% of three molar equivalents of hydrogen had been absorbed and the rate of hydrogenation decreased sharply. The mixture was filtered, the filtrate was diluted with 400 ml. of water, and the colorless layer of cycloöctene was extracted with 200 ml. of ether. The extract was washed with seven 150-ml. portions of water to remove methanol, dried over magnesium sulfate, and distilled through an 18 × 1.8 cm. helix-packed column. The yield of cycloöctene was 87.3 g. (85.5%), b. p. 58–59° (50 mm.), $n^{25}_{\rm D}$ 1.4684, m. p. approximately −15°. The product contained no cycloöctatetraene detectable in a colorimeter (which would detect a concentration of 0.1%), and presumably contained a small amount of cycloöctane from over-reduction.

3-Bromocycloöctene (I).—A mixture of 34 g. of cycloöctene, 200 ml. of carbon tetrachloride, 54.8 g. of recrystallized N-bromosuccinimide and 0.2 g. of benzoyl peroxide was heated to boiling on a steam-bath under reflux in a nitrogen atmosphere. The reaction became exothermic within three to five minutes, and was complete after forty-five minutes. Succinimide was removed by filtration and the filtrate was washed with 100 ml. of 5% sodium bicarbonate solution and two 100-ml. portions of water and dried over magnesium sulfate. The product was distilled rapidly without fractionation at 1 mm. and then fractionated through a 30 × 1.2 cm. Vigreux column equipped with a total condensation head. The yield of 3-bromocycloöctene was 31.2 g. (54%), b. p. 77–79° (5 mm.). Cycloöctene (1.1 g.) was separated as a forerun, and dibromocycloöctene (7.5 g.) as a high boiling fraction. The average yield of 3-bromocycloöctene in four preparations was 55%. A redistilled analytical sample had b. p. 79° (5 mm.), $n^{25}_{\rm D}$ 1.5230, d^{25}_{4} 1.3308.

Anal. Calcd. for $C_8H_{13}Br$: C, 50.81; H, 6.93; Br, 42.26. Found: C, 50.86; H, 6.95; Br, 42.36.

3,8-Dibromocycloöctene (II).—Dry carbon tetrachloride (400 ml.), 50.9 g. of cycloöctene, 164.2 g. of recrystallized N-bromosuccinimide and 1 g. of benzoyl peroxide were placed in a 1-l. three-necked flask equipped with a mechanical stirrer and a reflux condenser. The air in the flask was displaced with nitrogen, and the reaction mixture was stirred and heated in a bath at 90–95°. After ten to fifteen minutes the solvent refluxed vigorously, and after an additional thirty to forty minutes the reaction was complete, as determined by a negative test for N-bromosuccinimide with acidified potassium iodide. The mixture was cooled, succinimide was separated by filtration, and the filtrate was washed with three 250-ml. portions of water and dried over magnesium sulfate. The product was distilled as rapidly as possible without fractionation at 0.4 mm. to separate a tarry residue. The colorless distillate was washed with two 50-ml. portions of 5% sodium carbonate to remove benzoic acid, then with two 100-ml. portions of water, and dried over magnesium sulfate. The product was distilled through a 23 × 1.0 cm. Vigreux column with a total condensation head; some decomposition occurred with the formation of hydrogen bromide. The distillation separated 16.4 g. (19%) of 3-bromocycloöctene and 53.7 g. (43%) of 3,8-dibromocycloöctene, b. p. 106–110° (2.5 mm.), $n^{25}_{\rm D}$ 1.5644–1.5665. A sample redistilled from a simple flask at 0.1 mm. (to minimize loss of hydrogen bromide) was colorless,

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(5) Willstätter, *Ann.*, **317**, 258 (1901).

(6) Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy and Mrs. Louise W. Spencer for analyses.

(7) By a group composed of the authors and Alfred A. D'Addieco, Theodore T. Foster, Edward C. Hermann, Elbert C. Herrick, F. A. Hochstein, Mark W. Kinter and William R. Schmitz, to whom we are indebted for the cycloöctatetraene used. Precautions recommended because of the danger of explosive decomposition of acetylene are described by Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 310.

(8) Busch and Stove, *Ber.*, **49**, 1063 (1916).

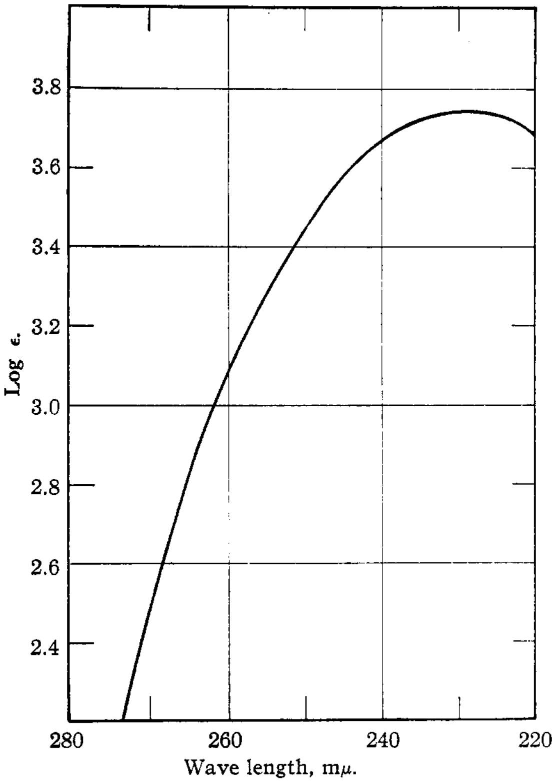

Fig. 1.—Ultraviolet absorption spectrum of 1,3-cyclooctadiene (V).

had a sweet odor and no lachrymatory properties; $n^{25}D$ 1.5680, d^{25}_4 1.6552.

Anal. Calcd. for $C_8H_{12}Br_2$: C, 35.85; H, 4.52. Found: C, 36.44; H, 4.55.

In a quantitative hydrogenation in the presence of Adams platinum catalyst a sample of II in glacial acetic acid containing sodium acetate absorbed 98% of three molar equivalents of hydrogen.

1-Dimethylamino-3-cycloöctene (III).—A solution of 45.7 g. of 3-bromocycloöctene in 25 ml. of benzene was added to a cold solution of 27 g. of dimethylamine in 200 ml. of dry benzene. The mixture was allowed to warm to room temperature, and dimethylamine hydrobromide began to separate in ten to twenty minutes. The mixture was stoppered and allowed to stand overnight. After filtering to remove 25.7 g. of dimethylamine hydrobromide, the solution was extracted with 150 and 50 ml. portions of 10% hydrochloric acid, which were combined and warmed on a steam-bath at 55–60° for three to five minutes to hydrolyze any vinylamine types present. The solution was cooled and extracted with two 100-ml. portions of ether, which were discarded. The aqueous solution was made basic by addition of 100 ml. of 20% sodium hydroxide, with cooling, and extracted with three 100-ml. portions of ether. The extracts were dried over sodium hydroxide, concentrated, and the residue was fractionated under nitrogen through a 23 × 1.0 cm. Vigreux column. The yield of III was 29 g. (78%), b. p. 70–72° (6 mm.). An analytical sample had b. p. 80° (10.5 mm.), $n^{25}D$ 1.4812, d^{25}_4 0.8827.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.49; N, 9.14. Found: C, 78.52; H, 12.52; N, 9.08.

The picrate of III was prepared in ethanol and recrystallized from a mixture of methanol and acetone; m. p. 208.6–209° (dec.).

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.25; H, 5.80; N, 14.65. Found: C, 50.14; H, 5.91; N, 14.71.

Hydrogenation of 0.24 g. of III in 5 ml. of glacial acetic acid in the presence of 0.106 g. of prereduced Adams platinum oxide catalyst was complete in thirty-five minutes and required 101% of one molar equivalent of hydrogen. The dimethylaminocycloöctane formed was isolated as the picrate and recrystallized from 9:1 ethanol–acetone; m. p. 197.4–198.2°, which was not depressed in a mixed m. p. with a sample derived from α-des-dimethylgranatenine by hydrogenation and conversion to the picrate.[4]

The product of a similar hydrogenation was converted to the methiodide, which was recrystallized from a mixture of acetone and hexane; m. p. 274–275° (ref. 4 reports m. p. 274–275°).

1-Dimethylamino-3-cycloöctene Methiodide (IV).—A solution of 29 g. of III and 34 g. of methyl iodide in 250 ml. of cyclohexane was heated under reflux for twenty minutes. The solid was collected on a suction filter and washed with 200 ml. of cyclohexane, and the filtrate was heated under reflux with an additional 20 g. of methyl iodide for two hours. The solid which separated was combined with the main portion; the total yield was 50.8 g. (91%), m. p. 185–186° (dec.).[9] The average yield of four preparations was 94.5%. An analytical sample recrystallized from 2:1 benzene–acetone had m. p. 184.2–185° (dec.).[9]

Anal. Calcd. for $C_{11}H_{22}IN$: C, 44.75; H, 7.51; N, 4.75. Found: C, 44.86; H, 7.41; N, 4.75.

1,3-Cycloöctadiene (V). (a) Preparation of V from IV.—A solution of 50.8 g. of IV in 300 ml. of water was stirred for one hour at 25° with the freshly precipitated alkali-free silver oxide prepared from 58.5 g. of silver nitrate. The mixture was filtered and the filter cake was stirred with 100 ml. of water. After refiltering, the combined filtrates were concentrated under reduced pressure and the concentrate was distilled to dryness in a 250 ml. Claisen flask (attached to a receiver cooled with Dry Ice) at 15 mm. and a bath temperature of 100–110°. The upper portions of the flask were rinsed with 10 ml. of water and the solution again was distilled to dryness. The distillate was neutralized with dilute sulfuric acid, and the colorless product (14.2 g., 82%) was taken up in 100 ml. of ether. The aqueous layer was extracted with 50 ml. of ether and the combined extracts were dried over magnesium sulfate. The solution was filtered, a small amount of hydroquinone was added as a polymerization inhibitor, and the ether was distilled through a Widmer column. Distillation of the residue from a modified Claisen flask yielded 10.28 g. (55%) of V as a colorless, mobile liquid, b. p. 42–43° (20 mm.). An orange polymeric residue (3.9 g.) remained in the distilling flask. An analytical sample of V distilled through a semi-micro column[10] had b. p. 48° (25 mm.), m. p. −57.5 to −55°, $n^{25}D$ 1.4940, d^{25}_4 0.8699.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.53; H, 10.94.

V prepared in this manner had a strong, characteristic disagreeable odor resembling the odor of cyclopentadiene, which was detectable in very low concentrations and appeared to cause headache on prolonged exposure.[11]

Hydrogenation of a 0.100-g. sample of V in the presence of 0.063 g. of prereduced Adams platinum oxide catalyst was complete in twenty-two minutes and required 98.5% of two molar equivalents of hydrogen. Purification of the product by distillation through a micro column[12] followed

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(9) The sample was introduced into the melting point bath 10° below the m. p. and the temperature was increased at a rate of 2° per minute.

(10) Gould, Holzman and Niemann, *Anal. Chem.*, **20**, 361 (1948).

(11) Other reports of the preparation of V do not contain data which permit a comparison of properties; Ziegler, Spaeth, Schaaf, Schumann and Winkelmann, *Ann.*, **551**, 101 (1942); Mousseron, Granger, Winternitz and Combes, *Bull. soc. chim. France*, 616 (1946); Domnin, *Vestnik Leningrad Univ.*, **1**, No. 3, 103 (1946) [*C. A.*, **42**, 3337 (1948)].

(12) Gettler, Niederl and Benedetti-Pichler, *Microchem.*, **11**, 174 (1932).

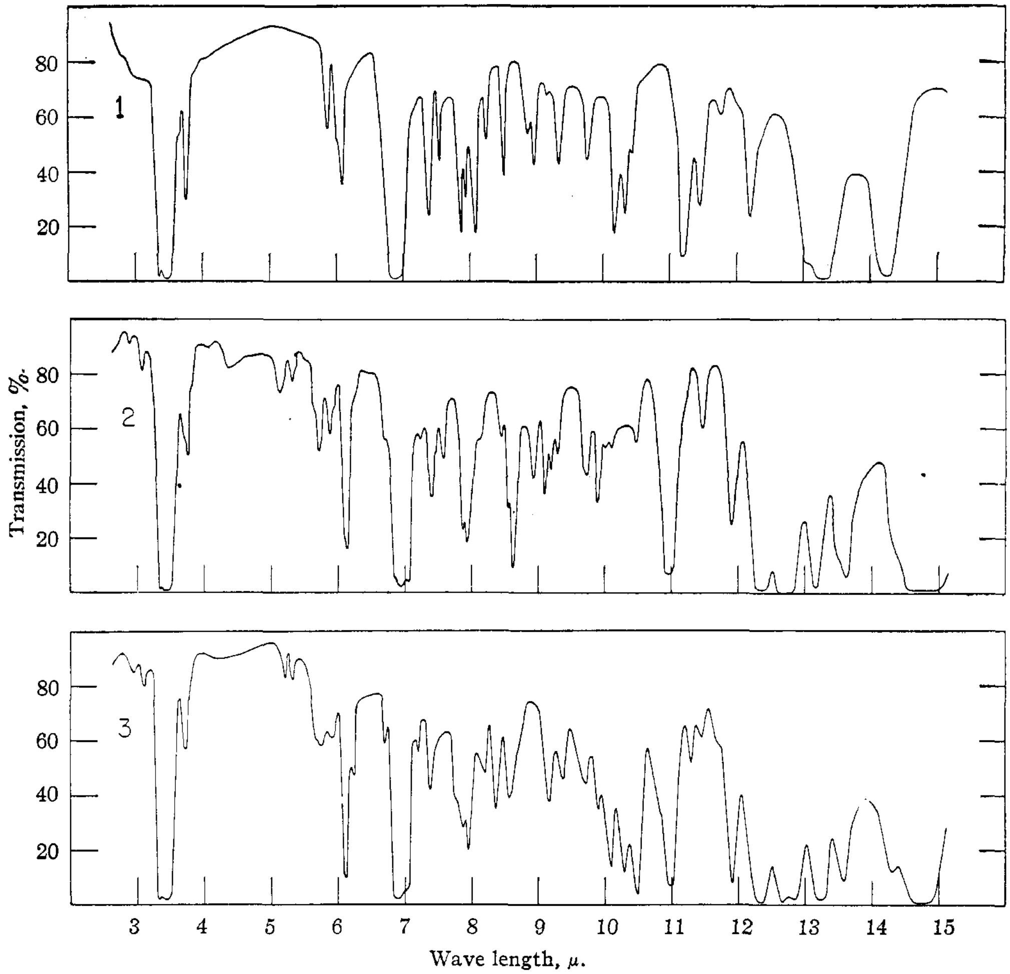

Fig. 2.—Infrared absorption spectra: Curve 1, cycloöctene prepared by partial hydrogenation of cycloöctatetraene; curve 2, 1,3-cycloöctadiene (V), $n^{25}\text{D}$ 1.4908, prepared by dehydrohalogenation of I; curve 3, 1,3-cycloöctadiene (V), $n^{25}\text{D}$ 1.4940, prepared from IV.

by passage through activated silica gel gave cycloöctane, m. p. 9.6–10°.

A 0.636-g. sample of V in 20 ml. of ethyl acetate was ozonized at −30°. The solvent was removed under reduced pressure, and the ozonide was decomposed by heating with 15 ml. of glacial acetic acid and 10 ml. of 35% hydrogen peroxide for two hours on a steam-bath. The mixture was concentrated under reduced pressure, and the residue was dissolved in 10 ml. of sodium bicarbonate solution. The solution was extracted with ether to remove any neutral material, acidified with hydrochloric acid, and extracted with ether in a continuous extractor for twenty-four hours. The extract was concentrated, and the solid residue was recrystallized from concentrated nitric acid and from water, yielding 0.317 g. (37%) of adipic acid, m. p. 150–151°, mixed m. p. with an authentic sample 151–152°.

A solution of 0.481 g. of V and 0.436 g. of freshly distilled maleic anhydride in 5 ml. of dry benzene was allowed to stand overnight at room temperature. A white, polymeric product separated which appeared to be non-crystalline under a polarizing microscope, and was insoluble in common organic solvents with the exception of dimethylformamide. A sample was purified for analysis by digestion with hot, dry benzene. It melted to a clear orange resin at 275–290°.

Anal. Calcd. for the 1:1 copolymer, $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 68.29; H, 6.72.

A 1-g. sample of V, 3.2 g. of N-bromosuccinimide and 0.01 g. of benzoyl peroxide in 25 ml. of carbon tetrachloride showed no evidence of reaction after boiling under reflux for three hours. After twenty hours the mixture had become brown and a dark resin had formed on the sides of the flask. No succinimide had separated, and the odor of V was still evident.

Addition of one molar equivalent of bromine in chloroform to V at −5° gave 78% of a dibromide, b. p. 73–76° (0.3 mm.), $n^{25}\text{D}$ 1.5648–1.5687, with the same properties as II prepared from cycloöctene and two molar equivalents of N-bromosuccinimide, but no solid derivatives of the dibromide were obtained through which the identity of the two samples could be established.

A 1.48-g. sample of freshly distilled V, $n^{25}\text{D}$ 1.4940, was stirred with a solution of 10 g. of silver nitrate in 6 ml. of water. The heavy, white crystalline precipitate which formed in one to two minutes was separated by centrifugation in a Craig tube.[13] The adduct lost V rapidly on exposure to air. A sample which was heated in a capillary softened at 120–130° and melted at the m. p. of silver nitrate. The adduct was dried by pressing it on filter paper briefly, then was added to water and decomposed by the addition of an excess of sodium chloride. The hydrocarbon layer was taken up in 20 ml. of ether, combined with

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[13] Craig and Post, *Ind. Eng. Chem., Anal. Ed.*, **16**, 413 (1944).

an ether extract of the aqueous layer, and dried over magnesium sulfate. The ether was distilled after addition of a few crystals of hydroquinone, and the residue was distilled through a semi-micro fractionating column,[10] yielding 0.50 g. of V, b. p. 46.5° (25 mm.), $n^{25}\text{D}$ 1.4909. The infrared absorption spectrum of V purified in this manner was identical with the spectrum of V obtained from I and quinoline, described below.

(b) **Preparation of V from I.**—3-Bromocycloöctene (9.0 g.) was added to 12.3 g. of quinoline with cooling, and the mixture was heated to 210° in a short-necked distilling flask attached to a cooled receiver. The product distilled at 145°; yield 4.81 g. (93.5%). It was dissolved in 25 ml. of ether, washed with two 10-ml. portions of 5% hydrochloric acid, dried over magnesium sulfate and redistilled through a semi-micro column[10]; b. p. 55° (34 mm.); m. p. −51 to −49°; $n^{25}\text{D}$ 1.4908.

Anal. Calcd. for C_8H_{12}: C, 88.89; H, 11.11. Found: C, 88.91; H, 11.38.

V prepared in this manner had an odor similar to cyclohexene rather than the penetrating odor which characterized V prepared by route (a). It gave a mixed m. p. with V prepared by route (a) of −58 to −51°. Catalytic hydrogenation of a 0.109 g. sample in the presence of 0.047 g. of prereduced Adams platinum oxide catalyst in acetic acid was complete in forty-six minutes and required 100.5% of two molar equivalents of hydrogen. Like V prepared by route (a), V prepared by route (b) gave a crystalline silver nitrate adduct which lost V on exposure to air, and had the same m. p. behavior (softened at 120–130° and melted at the m. p. of silver nitrate).

Reaction of II with Dimethylamine.—A solution of 23.9 g. of II in 25 ml. of absolute ethanol was added to a cold solution of 26 g. of dimethylamine in 150 ml. of absolute ethanol. The solution was allowed to warm to room temperature, diluted to 250 ml. with absolute ethanol, stoppered, and 1-ml. aliquots were titrated for bromide ion at intervals. The per cent. reaction according to the titration was as follows: after twenty hours, 50%; sixty-six hours, 62.5%. The reaction was continued at 50–55°: total per cent. reaction after seventeen hours at that temperature, 72%; after sixty-three hours, 75%.

The black reaction mixture was acidified with hydrochloric acid and neutral material was extracted with ether and distilled. An impure bromocycloöctadiene was obtained (1.5 g., b. p. 52–55° at 1.5 mm., $n^{25}\text{D}$ 1.5333. Calcd. for $C_8H_{11}Br$: C, 51.35; H, 5.93. Found: C, 53.13; H, 6.68). This compound decomposed partially on fractional distillation and was not obtained pure. It gave a precipitate with hot but not with cold alcoholic silver nitrate. A sample absorbed 96.5% of three molar equivalents of hydrogen in the presence of Adams platinum catalyst in acetic acid containing sodium acetate. The ultraviolet absorption spectrum showed a maximum consistent with a conjugated diene structure; $\lambda_{\text{max.}}$ 220 mμ (log ϵ 3.92).

The hydrochloric acid solution containing basic products was heated to 50–60° to hydrolyze vinylamine types, concentrated to remove alcohol, made alkaline with sodium hydroxide and extracted with ether. A black polymeric oil (5 g.) was insoluble in both the water and ether phases. Distillation of the extracts separated an additional 4.9 g. of a polymer (as a residue) from 4.9 g. of a mixture of a bromodimethylaminocycloöctene and a bis-(dimethylamino)-cycloöctene, b. p. 59–74° (0.7 mm.), which could not be separated by distillation of the quantity which was available. Analysis of one of the fractions indicated the composition of the mixture; b. p. 72–74° (0.7 mm.), $n^{25}\text{D}$ 1.5080. Calcd. for $C_{10}H_{18}BrN$: C, 51.73; H, 7.81; Br, 34.42. Calcd. for $C_{12}H_{24}N_2$: C, 73.41; H, 12.32. Found: C, 56.41; H, 8.85; Br, 24.73. None of the fractions gave a precipitate with hot 2% alcoholic silver nitrate. The combined fractions (2.61 g.) were hydrogenated in the presence of 0.3 g. of prereduced Adams platinum catalyst in 25 ml. of glacial acetic acid containing 2 g. of sodium acetate in a period of two hours. The basic products were separated by addition of sodium hydroxide, extraction with ether, and fractionation through a semi-micro column.[10] This distillation separated two components: (1) dimethylaminocycloöctane, 1.27 g., b. p. 79–80° (6 mm.), $n^{25}\text{D}$ 1.4706; m. p. of the picrate and mixed m. p. with a known sample 197.2–197.8°. (2) A bis-(dimethylamino)-cycloöctane, 0.52 g., b. p. 98–104° (3 mm.), $n^{25}\text{D}$ 1.4808.

Anal. Calcd. for $C_{12}H_{26}N_2$: C, 72.66; H, 13.21; N, 14.13. Found: C, 72.54; H, 13.14; N, 13.81.

The picrate of this bis-(dimethylamino)-cycloöctane was prepared in ethanol and recrystallized to constant m. p. from 1:1 ethanol–water; m. p. 214.8–215.6° (dec.).

Anal. Calcd. for $C_{24}H_{32}N_8O_{14}$: C, 43.90; H, 4.90. Found: C, 44.25; H, 5.11.

Another sample of the bis-(dimethylamino)-cycloöctane in methanol was neutralized to congo red with perchloric acid. The monoperchlorate began to crystallize while the solution was still basic, and was crystallized to constant m. p. from absolute ethanol; m. p. 246.6–247° (dec.).

Anal. Calcd. for $C_{12}H_{27}ClN_2O_4$: C, 48.23; H, 9.12; N, 9.38. Found: C, 48.29; H, 9.28; N, 9.08.

Absorption Spectra.—The ultraviolet absorption spectra of V prepared from IV (before purification through the silver nitrate adduct, $n^{25}\text{D}$ 1.4940) and of V prepared from I ($n^{25}\text{D}$ 1.4908) were identical. The absorption curve is shown in Fig. 1, as determined with a Beckman model DU quartz ultraviolet spectrophotometer for V in purified cyclohexane as a solvent ($\lambda_{\text{max.}}$ 228 mμ, log ϵ = 3.75).

We are indebted to Dr. R. C. Lord, Mr. R. S. McDonald and Miss B. J. Fax for determining the infrared spectra of cycloöctene and 1,3-cyclooctadiene (Fig. 2).

Summary

Cycloöctene, prepared by the partial hydrogenation of cycloöctatetraene, has been converted to 3-bromocycloöctene and a dibromide (probably 3,8-dibromocycloöctene) by bromination with N-bromosuccinimide. 1,3-Cycloöctadiene has been prepared from 3-bromocycloöctene by conversion to 1-dimethylamino-3-cycloöctene followed by application of the Hofmann exhaustive methylation procedure, and also by direct dehydrobromination with quinoline.

CAMBRIDGE, MASSACHUSETTS
RECEIVED SEPTEMBER 30, 1949