Cyclic Polyolefins. XXVII. cis- and trans-Cyclooctene from N,N-Dimethylcyclooctylamine[1]

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RECEIVED FEBRUARY 5, 1953

Thermal decomposition of N,N-dimethylcyclooctylamine oxide yielded cis-cyclooctene (90%), indicating that this reaction occurs by an intramolecular cyclic mechanism, with elimination of the cis-β-hydrogen, forming N,N-dimethylhydroxylamine. Decomposition of N,N,N-trimethylcyclooctylammonium hydroxide formed a mixture of cis- and trans-cyclooctenes in 89% yield, which contained 60% of the trans and 40% of the cis isomer according to infrared analysis. The mixture was separated by extraction of the trans isomer with aqueous silver nitrate. Reaction of cis-cyclooctene with osmium tetroxide followed by hydrolysis of the osmic ester formed cis-1,2-cyclooctanediol, while trans-cyclooctene formed trans-1,2-cyclooctanediol. Only the cis isomers of cycloheptene and cyclohexene were formed by the amine oxide elimination and Hofmann exhaustive methylation procedures, the yields of cycloheptene being 92 and 87% and of cyclohexene 83 and 62%, respectively, by the two methods.

Investigation of the thermal decomposition of several N,N-dimethylalkylamine oxides with α- and β-substituents has shown that the reaction proceeds with elimination of a β-hydrogen atom and the amine oxide group, forming an olefin and N,N-dimethylhydroxylamine.[2] An intramolecular cyclic mechanism was proposed for the reaction. If this mechanism is correct, formation of a cis rather than a trans cyclic olefin would be predicted from decomposition of an N,N-dimethylalicyclicamine oxide, because the atoms eliminated could be in a (preferred) planar structure in the transition state[3] only if the hydrogen that is eliminated is cis to the amine oxide group. Study of the preparation of cyclooctene from N,N-dimethylcyclooctylamine oxide accordingly was undertaken, since both cis- and trans-cyclooctene are known, the trans isomer being formed by the Hofmann exhaustive methylation route (thermal decomposition of N,N,N-trimethylcyclooctylammonium hydroxide).[4]

N,N-Dimethylcyclooctylamine oxide was prepared by oxidation of the amine with 35% aqueous hydrogen peroxide in methanol solution, and the excess hydrogen peroxide was decomposed catalytically by addition of platinum black. It was convenient to follow the conversion of this and other amines to the oxide by spot tests with phenolphthalein;

Fig. 1.—Infrared absorption spectra: curve 1, cis-cyclooctene; curve 2, trans-cyclooctene, both as pure liquids in a 0.025 mm. cell.

the amine oxides are not sufficiently basic to give a color test with the indicator. The decomposition of the hydrogen peroxide, which must be complete to avoid danger of explosion in concentration of the solution, was followed by periodic tests with lead sulfide paper, which is whitened immediately by hydrogen peroxide in low concentration but not by solutions of amine oxides.[5] Decomposition of the amine oxide occurred at 100–120° at 10 mm. and yielded pure cis-cyclooctene (90%) with an infrared spectrum identical with the spectrum of an authentic sample (Fig. 1, curve 1). In the isolation of cis-cyclooctene (and other olefins of low molecular weight) high and reproducible yields could be obtained by acidifying the crude distillate with dilute hydrochloric acid, freezing the aqueous layer and separating the hydrocarbon. This procedure avoids extraction with an organic solvent, which in small scale preparations can be separated from the product by fractionation only with some loss. Concentration of the hydrochloric acid solution yielded N,N-dimethylhydroxylamine hydrochloride (95%).

In order to compare the spectra of cis- and trans-cyclooctene, and the yields obtainable by the amine oxide and Hofmann exhaustive methylation procedures, the preparation of trans-cyclooctene from N,N,N-trimethylcyclooctylammonium hydroxide was repeated. The infrared spectrum of the cyclooctene obtained by this method (in 89% yield) indicated that it was a mixture of the cis and trans isomers, rather than the pure trans form, as previously supposed.[4] It proved possible to separate the mixture by extraction with 20% aqueous silver nitrate, which dissolved the trans (but not the cis) form. Regeneration of the hydrocarbon from the silver nitrate solution with ammonium hydroxide yielded pure trans-cyclooctene (56%), while the fraction insoluble in silver nitrate was cis-cyclooctene (31%) containing not more than 1.5% of the trans isomer. With the infrared spectra of pure cis- and trans-cyclooctene available (Fig. 1), it was possible to analyze the mixture formed by the Hofmann exhaustive methylation procedure, comparing infrared spectra of known mixtures of the isomers and estimating the composition from the per cent. transmission at 11.2 and 13.3 μ (bands present in cis- but not in trans-cyclooctene; trans-cyclooctene has bands at 11.8 and

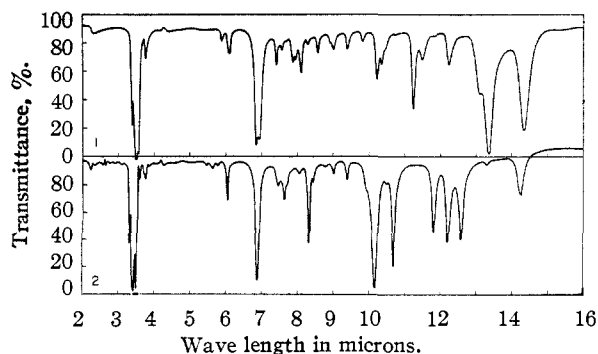(1) Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-356-096.

(2) A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, 71, 3929 (1949).

(3) D. H. R. Barton and E. Miller, ibid., 72, 1066 (1950); D. H. R. Barton and W. J. Rosenfelder, J. Chem. Soc., 1048 (1951).

(4) K. Ziegler and H. Wilms, Ann., 567, 1 (1950).

(5) We are indebted to Theodore T. Foster for determining the applicability of these tests.

12.6 μ not present in the spectrum of *cis-*cyclooc-tene).[6] This analysis showed that the mixture obtained by the Hofmann route was 60% *trans-* and 40% *cis-*cyclooctene, in reasonable agreement with the yields of the two forms obtained after separation with silver nitrate (56 and 31%, respectively). Tests showed that *trans-*cyclooctene is isomerized very slowly if at all to *cis-*cyclooctene by 20% silver nitrate at room temperature. The amount of *cis-*cyclooctene present in a sample of *trans-*cyclooctene that had stood in 20% aqueous silver nitrate for 26 hours at room temperature was approximately 1.5% (estimated by partial separation and infrared analysis), or near the limit of the amount that could have been present in the original sample and escaped detection by infrared under the conditions used.

*cis-*Cyclooctene reacted with osmium tetroxide in pyridine to form an osmic ester (93%), which on hydrolysis in the presence of sodium sulfite formed *cis-*1,2-cyclooctanediol (38%), m.p. 76.5–78°, m.p. of the bis-phenylurethan and mixed m.p. with an authentic sample, 172–174°.[7] Under similar conditions *trans-*cyclooctene formed an osmic ester (93%) that on hydrolysis yielded liquid *trans-*1,2-cyclooctanediol, m.p. and mixed m.p. of the bis-phenylurethan with an authentic sample,[7] 176–177°. Accordingly these *cis–trans* isomers can be distinguished by hydroxylation through the osmic esters, *cis-*cyclooctene forming the *cis-* and *trans-*cyclooctene the *trans-*1,2-glycol. Similar results were reported recently by Prelog, Schenker and Günthard[8] for the hydroxylation of *cis-* and *trans-*cyclodecene through the osmic esters.

An attempt to convert *cis-* to *trans-*cyclooctene by a procedure similar to one reported by Hoff, Greenlee and Boord[9] for interconversion of acyclic *cis* and *trans* olefins was unsuccessful. *trans-*1,2-Dibromocyclooctane (from *cis-*cyclooctene and bromine) was dehydrobrominated with dimethylamine to 1-bromocyclooctene,[10] which on treatment with sodium in liquid ammonia yielded *cis-*cyclooctene. Acyclic *cis* olefins (through 1,2-dichlorides) in the first step of this sequence form *trans* structures, which are retained in the second; in this case the greater stability of *cis-* compared to *trans-*cyclooctene must have either prevented formation of *trans-*1-bromocyclooctene or resulted in rearrangement of a *trans* to a *cis* structure in the dehalogenation with sodium.

Cycloheptene[11] and cyclohexene[12] have been prepared by the Hofmann exhaustive methylation procedure as *cis* isomers, presumably formed because of the large amount of strain that would be present in the unknown *trans* forms, in spite of the tendency of the Hofmann procedure to yield *trans* isomers by *trans* elimination. These preparations

were repeated to determine whether the presence of small amounts of *trans* isomers could be detected in the products by their infrared spectra and to compare yields obtained by the Hofmann and amine oxide procedures. Both methods led to pure *cis* isomers of each olefin, the yield of cycloheptene being 92% by the amine oxide and 87% by the Hofmann route, while the yields of cyclohexene were 93% from the amine oxide and 62% from the quaternary base.

From the present work, which is being continued, it appears that two stereoisomeric olefins (*cis* and *trans*) should be obtainable in a number of cases from the same N,N-dimethylalkylamine, one by the amine oxide elimination and the other by the Hofmann exhaustive methylation procedure.

Experimental[13,14]

N,N-Dimethylcyclooctylamine Oxide.—A solution of 47.5 g. of 1-dimethylamino-3-cyclooctene[15] in 200 ml. of glacial acetic acid was hydrogenated at room temperature and atmospheric pressure in the presence of 0.5 g. of prereduced platinum oxide. After separation of the catalyst the solution was added to 700 ml. of 20% sodium hydroxide with cooling, and the N,N-dimethylcyclooctylamine was extracted with ether, dried over magnesium sulfate and distilled; the yield was 44.8 g. (93%), b.p. 69–70° (4 mm.), n^{25}D 1.4710.

A solution of 5.0 g. (0.032 mole) of N,N-dimethylcyclooctylamine in 10 ml. of methanol was cooled with ice and 10.0 g. (0.094 mole) of 35% hydrogen peroxide was added slowly (30 minutes). The solution was allowed to come to room temperature and stand for 26 hours, at which time it gave a negative spot test for the amine with phenolphthalein.[16] The excess hydrogen peroxide was decomposed by stirring the solution with 0.25 g. of platinum black[17] for 5 hours, at which time a drop failed to whiten lead sulfide paper (negative hydrogen peroxide test[16]). The platinum black was separated and the filtrate was concentrated at 10–12 mm. with a bath temperature of 30–40°, leaving the amine oxide as a colorless, viscous sirup.

An aliquot of an aqueous methanol solution of N,N-dimethylcyclooctylamine oxide prepared by the method described above, corresponding to 0.005 mole of the amine, was added to an aqueous solution of 1.08 g. of picric acid (after decomposition of the excess hydrogen peroxide with platinum). The picrate that separated was washed with cold water and air dried; the yield was 1.84 g. (98%), m.p. 150–152.5° (dec.). Several crystallizations from absolute ethanol gave an analytical sample with a constant melting point of 158–159.5° (dec.).

Anal. Calcd. for $C_{16}H_{24}N_4O_8$: C, 47.99; H, 6.04; N, 13.99. Found: C, 48.06; H, 5.91; N, 13.80.

*cis-***Cyclooctene.** (a).—The N,N-dimethylcyclooctylamine oxide described above was heated in a nitrogen atmosphere at 10 mm. in a 100-ml. round-bottomed flask connected through a short Vigreux column to two traps in series, the first cooled with Dry Ice and the second with liquid nitrogen. The flask was placed in an oil-bath and the temperature was raised 1–2° per minute; decomposition of the amine oxide began at 100° and was complete at 120° after 25 minutes, at which time practically no material remained in the flask. The distillate was acidified with dilute hydrochloric acid and the aqueous layer was frozen by

(6) We are indebted to Dr. R. C. Lord for discussions of the infrared spectra.

(7) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

(8) V. Prelog, K. Schenker and H. H. Günthard, *Helv. Chim. Acta*, **35**, 1598 (1952).

(9) M. C. Hoff, K. W. Greenlee and C. E. Boord, THIS JOURNAL, **73**, 3329 (1951).

(10) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *ibid.*, **61**, 1057 (1939).

(11) R. Willstätter, *Ann.*, **317**, 204 (1901).

(12) A. Skita and H. Rolfes, *Ber.*, **53**, 1242 (1920).

(13) Melting points are corrected and boiling points are uncorrected.

(14) We are indebted to Dr. S. M. Nagy and his associates for analyses and for the infrared spectra, which were determined with a Baird Double Beam Infrared Recording Spectrometer, Model B, fitted with a sodium chloride prism.

(15) A. C. Cope and L. L. Estes, Jr., THIS JOURNAL, **72**, 1128 (1950).

(16) The phenolphthalein test will detect 0.1% of an alkyldimethylamine in the presence of 10% of the amine oxide and 1% hydrogen peroxide, and the lead sulfide paper test will detect 0.1% of hydrogen peroxide in the presence of 10% of the amine oxide and 1% of the amine.

(17) Prepared by the procedure of R. Feulgen, *Ber.*, **54**, 360 (1921) and added as an aqueous suspension.

cooling with Dry Ice. The layer of cis-cyclooctene was removed with a pipet and distilled through a semimicro column.[18] The yield was 3.22 g. (90%), b.p. 65° (59 mm.), $n^{25}D$ 1.4684, and the infrared spectrum of the product was identical with the spectrum of an authentic sample of cis-cyclooctene described below.

After removal of the cis-cyclooctene, the aqueous hydrochloric acid solution was concentrated under reduced pressure, and the residual N,N-dimethylhydroxylamine hydrochloride was dried by adding absolute ethanol and removing it under reduced pressure. After further drying in a vacuum desiccator over potassium hydroxide the N,N-dimethylhydroxylamine hydrochloride weighed 2.91 g. (95%), m.p. 100–103° (sealed capillary), raised to 104.5–106° (sealed capillary) by two crystallizations from ethanol–ether.

(b).—An authentic sample of cis-cyclooctene was obtained from cis-cyclooctene prepared by partial hydrogenation of cyclooctatetraene.[16,19] Addition of 71.5 g. of bromine to 49.2 g. of cyclooctene in 300 ml. of carbon tetrachloride yielded 98.2 g. (81%) of trans-1,2-dibromocyclooctane[10,20,21] b.p. 89–91° (0.5 mm.), $n^{25}D$ 1.5522.

Anal.[22] Calcd. for $C_8H_{14}Br_2$: C, 35.58; H, 5.23. Found: C, 35.78; H, 5.30.

Treatment of 1,2-dibromocyclooctane with an excess of zinc dust in refluxing methanol for 1 hour yielded authentic cis-cyclooctene, b.p. 42° (18 mm.), $n^{25}D$ 1.4682, m.p. −15.5 to −14.5°, d^{25}_4 0.8448. Microhydrogenation in glacial acetic acid in the presence of prereduced platinum oxide resulted in the absorption of 98.7% of one molar equivalent of hydrogen and yielded cyclooctane melting at 8–9.5° (indicating 97% purity[23]).

trans-Cyclooctene.—A solution of 29.2 g. of N,N,N-trimethylcyclooctylammonium iodide[4,21] in 150 ml. of water was stirred for 4 hours at room temperature with the moist, neutral silver oxide freshly precipitated from 34 g. of silver nitrate. The mixture was filtered, the solid was washed with 75 ml. of water, and the filtrate was concentrated at 30 mm. with a bath temperature of 65°. The residual quaternary base was decomposed by heating in a nitrogen atmosphere at 11 mm. with a bath temperature of 105–120°. The distillate was collected in a trap cooled with liquid nitrogen, and subsequently was acidified with dilute sulfuric acid. The product was isolated in the same manner as cis-cyclooctene from N,N-dimethylcyclooctylamine oxide (described above). The yield of cyclooctene was 9.73 g. (89%). Analysis of this sample by comparison of the strength of infrared bands at 11.2 and 13.3 μ (cis-cyclooctene bands) with the spectra of known mixtures of cis- and trans-cyclooctene indicated that it was composed of 60% trans- and 40% cis-cyclooctene.

A 9.50-g. sample of the mixture of cyclooctenes described above was dissolved in 100 ml. of pentane and extracted with five 75-ml. portions of 20% (by weight) silver nitrate solution. The extracts were washed twice with 20-ml. portions of pentane, and the combined pentane solutions (containing cis-cyclooctene) were dried over sodium sulfate. The silver nitrate solutions were added slowly to 150 ml. of concentrated ammonium hydroxide containing cracked ice. The hydrocarbon that separated was extracted with three 75-ml. portions of pentane, and the combined extracts were dried over sodium sulfate and concentrated. Distillation of the residue through a semimicro column yielded 5.37 g. (56%) of trans-cyclooctene, b.p. 75° (78 mm.), $n^{25}D$ 1.4741, d^{25}_4 0.8456. The infrared spectrum of trans-cyclooctene (Fig. 1, curve 2) purified in this way showed no appreciable contamination with the cis isomer (compare Fig. 1, curve 1). Quantitative reduction of a 220-mg. sample of trans-cyclooctene in 10 ml. of acetic acid in the presence of 200 mg. of prereduced platinum oxide resulted in the absorption of 97% of one molar equivalent of hydrogen and yielded 131 mg. of cyclooctane, $n^{25}D$ 1.4561, m.p. 11–12.5° (indicating 99% purity[23]).

The pentane solutions containing cis-cyclooctene were concentrated and distilled and yielded 2.92 g. (31%) of cis-cyclooctene, b.p. 75° (80 mm.), $n^{25}D$ 1.4690. The infrared spectrum of this sample showed that trans-cyclooctene was present in a quantity not greater than 1.5%.

Stability of trans-Cyclooctene in Silver Nitrate.—trans-Cyclooctene (0.30 g., $n^{25}D$ 1.4741, with an infrared spectrum identical to curve 1, Fig. 1) was dissolved in 15 ml. of 20% (by weight) silver nitrate, and the solution was extracted with 30 ml. of pentane. Distillation of the pentane through a packed column left no residue. The silver nitrate solution was allowed to stand for 26 hours, during which time there was no evidence of separation of a hydrocarbon. The solution was extracted with two 15-ml. portions of pentane, which were distilled through a packed column, leaving a residue that was distilled through a micro column and yielded 13 mg. of a mixture of cis- and trans-cyclooctene (principally trans, but containing the cis isomer since the infrared spectrum showed bands at 11.2 and 13.3 μ). The trans-cyclooctene was isolated from the silver nitrate solution by the procedure described above under trans-cyclooctene in a yield of 0.19 g., $n^{25}D$ 1.4740, and had an infrared spectrum identical with curve 1, Fig. 1.

Conversion of Isomeric Cyclooctenes to Cyclooctanediols. cis-1,2-Cyclooctanediol from cis-Cyclooctene.—A solution of 1.0 g. of osmium tetroxide in 30 ml. of ether was added to a solution of 0.432 g. of cis-cyclooctene in 30 ml. of ether and 1.5 ml. of pyridine. The brown osmic ester that precipitated immediately was separated after 24 hours and air-dried; the yield was 1.91 g. (93%). A solution of 8.1 g. of sodium sulfite in 40 ml. of water was added to a solution of the osmic ester in 50 ml. of ethanol, and the mixture was heated under reflux on a steam-bath for 1 hour. The solid that formed was separated, and the filtrate was concentrated under reduced pressure and poured into 500 ml. of water. The solution was extracted with three 75-ml. portions of chloroform, and the extracts were dried over sodium sulfate and concentrated. The solid residue was sublimed at 0.6 mm. with a heating block temperature of 55°, and yielded 0.199 g. (38%) of cis-1,2-cyclooctanediol, m.p. 76.5–78°; m.p. of the bis-phenylurethan and mixed m.p. with an authentic sample,[7] 172–174°. ·

trans-1,2-Cyclooctanediol from trans-Cyclooctene.—By a procedure similar to the one described above, 0.432 g. of trans-cyclooctene and 1.0 g. of osmium tetroxide yielded 1.91 g. (93%) of the osmic ester of trans-1,2-cyclooctanediol. The ester on treatment with sodium sulfite yielded 0.19 g. (36%) of trans-1,2-cyclooctanediol, b.p. 95° (0.5 mm.), $n^{25}D$ 1.4970, which was converted to the bis-phenylurethan, m.p. and mixed m.p. with an authentic sample,[7] 176–177°; mixed m.p. with cis-1,2-cyclooctanediol bis-phenylurethan, 156–166°.

Attempted Conversion of cis- to trans-Cyclooctene.—trans-1,2-Dibromocyclooctane (prepared from cis-cyclooctene and bromine) was converted to 1-bromocyclooctene by treatment with dimethylamine.[10] A 4.99-g. sample of 1-bromocyclooctene was added to 75 ml. of anhydrous liquid ammonia in a 200-ml. three-necked flask fitted with a stirrer and a condenser cooled with Dry Ice. Small pieces of sodium were added with stirring until a permanent blue color was produced (1.2 g.). The solution was stirred for an additional period of 0.5 hour, after which ammonium chloride was added to neutralize the sodium and sodamide. The ammonia was allowed to evaporate, and the residue was dissolved in 150 ml. of water and extracted with three 50-ml. portions of ether. The extracts were dried over sodium sulfate, and the ether was distilled through a glass helix-packed column. Distillation of the residue through a semimicro column yielded 1.65 g. (57%) of cis-cyclooctene, m.p. −15.1 to −14.2°, $n^{25}D$ 1.4682.

N,N-Dimethylcycloheptylamine Oxide and Cycloheptene. —Cycloheptylamine was prepared in 79% yield by hydrogenation of cycloheptanone oxime in ethanol saturated with ammonia, in the presence of Raney nickel at 140° and 1200 p.s.i. Methylation with formaldehyde and formic acid[24] yielded N,N-dimethylcycloheptylamine (67%). N,N-Dimethylcycloheptylamine oxide was prepared by the procedure described for N,N-dimethylcyclooctylamine oxide; a sample prepared from 0.308 g. of the amine, on treatment with an aqueous solution of 0.50 g. of picric acid, yielded

(18) C. W. Gould, Jr., G. Holzman and C. Niemann, Anal. Chem., 20, 361 (1948).

(19) W. Reppe, O. Schlichting, K. Klager and T. Toepel, Ann., 560, 1 (1948).

(20) M. W. Lister, THIS JOURNAL, 63, 143 (1941).

(21) R. Willstätter and E. Waser, Ber., 43, 1176 (1910).

(22) Analysis of this compound apparently was not reported in earlier references.

(23) A. C. Cope and F. A. Hochstein, THIS JOURNAL, 72, 2515 (1950).

(24) H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, ibid., 55, 4571 (1933).

0.79 g. (94%) of the amine oxide picrate, m.p. 150–151°. An analytical sample that was recrystallized from ethanol had the same melting point.

Anal. Calcd. for $C_{15}H_{22}N_4O_8$: C, 46.63; H, 5.74; N, 14.50. Found: C, 46.34; H, 5.77; N, 14.46.

A sample of N,N-dimethylcycloheptylamine oxide prepared from 8.0 g. of the amine was decomposed in a nitrogen atmosphere at 13 mm., with a bath temperature of 125–135°. The cycloheptene was isolated in the same manner as *cis*-cyclooctene (described above) in a yield of 5.07 g. (92%), b.p. 72° (300 mm.), $n^{25}D$ 1.4569. N,N-Dimethylhydroxylamine hydrochloride was isolated from the aqueous layer as before in a yield of 4.2 g. (76%).

Decomposition of the quaternary base prepared from 15 g. of N,N,N-trimethylcycloheptylammonium iodide[11] under the conditions described above for the amine oxide decomposition and isolation of the product in the same manner, yielded 4.35 g. (87%) of cycloheptene, b.p. 72° (300 mm.), $n^{25}D$ 1.4570. Cycloheptene also was prepared in 85% yield from 10 g. of cycloheptanol and 5.5 g. of boric acid, heated in a bath at 175 to 275°[25]; b.p. 72° (300 mm.), $n^{25}D$ 1.4570. The cycloheptene samples prepared by these three methods had essentially identical infrared spectra.

(25) W. Brandenberg and A. Galot, This Journal, **72**, 3275 (1950).

N,N-Dimethylcyclohexylamine Oxide and Cyclohexene.— N,N-Dimethylcyclohexylamine oxide was prepared by the method described for N,N-dimethylcyclooctylamine oxide. A sample prepared from 0.277 g. of the amine was treated with an aqueous solution of 0.5 g. of picric acid, and yielded 0.75 g. (93%) of the amine oxide picrate, m.p. 153–154°. An analytical sample that was recrystallized from ethanol had the same melting point.

Anal. Calcd. for $C_{14}H_{20}N_4O_8$: C, 45.16; H, 5.42; N, 15.05. Found: C, 45.35; H, 5.55; N, 14.88.

A sample of N,N-dimethylcyclohexylamine oxide that was prepared from 9.50 g. of the amine was decomposed by heating in a nitrogen atmosphere at 11 mm. with a bath temperature of 145–160°. The cyclohexene formed was condensed in a trap cooled with liquid nitrogen and purified in the manner described above for *cis*-cyclooctene. The yield of cyclohexene was 5.11 g. (83%), and the yield of N,N-dimethylhydroxylamine hydrochloride was 6.8 g. (93%). Decomposition of the quaternary base prepared from 8.0 g. of N,N,N-trimethylcyclohexylammonium iodide[12] by the procedure described above yielded 1.5 g. (62%) of cyclohexene and 0.56 g. (15%) of N,N-dimethylcyclohexylamine. The infrared spectra of the two samples of cyclohexene and a purified commercial sample were identical.

Cambridge 39, Mass.

Cyclic Polyolefins. XXVIII. Functionally Substituted Cyclooctatetraenes from Acetylenic Alcohols[1]

By Arthur C. Cope and Donald F. Rugen

Cyclooctatetraenylmethyl alcohol (I) and β-cyclooctatetraenylethyl alcohol (III) have been prepared by copolymerization of acetylene with propargyl alcohol and 3-butyn-1-ol, respectively. N,N-Dimethyl-β-cyclooctatetraenylethylamine (V) also has been prepared by copolymerization. The *p*-toluenesulfonate of the alcohol III has proved to be a useful intermediate for the synthesis (by displacement reactions) of other cyclooctatetraene derivatives, including the N,N-dimethylamino compound V, the cyanide VII and the bromide X. Reduction of the cyanide VII with lithium aluminum hydride yielded the primary amine VIII without reduction of nuclear double bonds, and basic hydrolysis of the cyanide yielded β-cyclooctatetraenylpropionic acid (IX). The acid IX formed a crystalline salt with quinine, but could not be resolved through the salt under conditions that were examined. Absorption bands present in the infrared spectra of a number of cyclooctatetraene derivatives have been noted that appear to be characteristic of the nucleus and are useful for the identification of such compounds.

This paper reports an extension of the preparation of substituted cyclooctatetraenes by copolymerization of substituted acetylenes with acetylene[2] to the synthesis of cyclooctatetraene derivatives containing an alcoholic hydroxyl or dimethylamino group attached to an alkyl side chain. These compounds were prepared by copolymerization of acetylenic alcohols and an acetylenic amine with acetylene. Other cyclooctatetraene derivatives were prepared by utilizing β-cyclooctatetraenylethyl alcohol as an intermediate.

Copolymerizations of the functionally substituted acetylenes with acetylene were conducted in dry tetrahydrofuran in the presence of nickel acetylacetonate catalyst and calcium carbide as a drying agent in a stirred autoclave at 85–95° with acetylene pressures of 300–150 p.s.i. The volatile products formed from such copolymerizations with propargyl alcohol and 3-butyn-1-ol were separated by steam distillation, and the crude alcohols (cyclooctatetraenylmethyl alcohol, I, and β-cyclooctatetraenylethyl alcohol, III) were isolated by frac-

(1) Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR356-096.

(2) A. C. Cope and H. C. Campbell, This Journal, **73**, 3536 (1951); **74**, 179 (1952).

tionation of the organic portions of the distillates. The alcohols could not be separated completely from hydrocarbon impurities by distillation, but it was possible to purify them by chromatography on silica gel, from which they were eluted with pentane containing 1 to 10% of ether, after elution of the hydrocarbons with pentane. The pure alcohols I and III were obtained in 17 and 24% yields, respectively. Both were yellow liquids which formed crystalline 3,5-dinitrobenzoates. Quantitative hydrogenations of the two alcohols in the presence of platinum resulted in the absorption of 98.5% of four molar equivalents of hydrogen and formed the colorless, saturated alcohols, cyclooctylmethyl alcohol (II), and β-cyclooctylethyl alcohol (IV). Both II and IV were characterized by preparation of crystalline 3,5-dinitrobenzoates. The structures of these compounds were proved by independent synthesis of authentic samples of the saturated alcohols II and IV by treating cyclooctylmagnesium bromide with formaldehyde and ethylene oxide, respectively.

N,N - Dimethyl - β - cyclooctatetraenylethylamine (V) also was prepared by copolymerization, from acetylene and N,N-dimethyl-3-butynylamine.