

In another run using benzene as a solvent, the fraction boiling at 220–260° (0.5 mm.) solidified to a crystalline mass which gave colorless needles from ethanol. The elementary composition of these crystals corresponds to 1,4-dicyano-1,4-dibenzylidenebutane.

Anal. Calcd. for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.37; H, 5.43; N, 9.99.

β -Phenyl- α -formylacrylonitrile (Independent Preparation of Compound D).—A mixture of β -hydroxy- α -benzylidene-propionitrile (0.20 g.), freshly precipitated manganese dioxide (2.0 g.) and carbon tetrachloride (12 ml.) was stirred at room temperature for two hours. The mixture was filtered to remove the excess manganese dioxide and the latter washed with a mixture of carbon tetrachloride and chloroform. The combined filtrates on evaporation *in vacuo* gave a lustrous white residue (0.16 g., 80% yield) which crystallized from benzene-petroleum ether in colorless needles, m.p. 97–99°, and was found to be identical with compound D (VI) by mixture melting point and infrared spectra.

Formation of β -Hydroxy- α -benzylidenepropionitrile (IV) from Compound A (I).—A mixture of benzaldehyde (21.2 g.), compound A (12.4 g.), *t*-butyl alcohol (35 ml.) and a solution (3 ml., 30%) of potassium hydroxide in methanol was stirred at 40–50° for 5 hours and allowed to stand overnight. It was then neutralized with dilute hydrochloric

acid (10%) and extracted with ether. The ether layer was washed repeatedly with water and dried over anhydrous sodium sulfate. The oil obtained after removal of ether was distilled *in vacuo* to yield recovered benzaldehyde (14 g.) and an oil (2 g.), b.p. 150° (0.3 mm.). The infrared spectrum of the latter shows characteristic absorption of hydroxyl and conjugated nitrile groups and corresponds exactly to the spectrum of β -hydroxy- α -benzylidenepropionitrile (IV). The alcohol IV was also obtained when the above reaction was carried out in the presence of sodium ethoxide or sodium hydride in dioxane.

Conversion of Compound C (IV) to β,β' -Dicyano- α -benzylidenediethyl Ether (I).—Acrylonitrile (0.53 g.) was added dropwise to a stirred mixture of β -hydroxy- α -benzylidenepropionitrile (1.59 g.) and one drop of 20% potassium hydroxide solution, at 40°. The temperature was maintained at 40–42° for one hour longer and the stirring was continued at room temperature for 24 hours. The mixture was neutralized with dilute hydrochloric acid, and the product isolated by ether extraction. The yellow oil thus obtained was distilled *in vacuo* and the fraction b.p. 155–175° (0.5 mm.) (0.55 g.) was collected. Redistillation of this fraction yielded a pure sample, b.p. 175–180° (0.5 mm.), which was shown to be identical (infrared spectra) with compound A.

NEW HAVEN, CONNECTICUT

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

Cyclic Polyolefins. XL. *cis-cis*- and *cis-trans*-1,3-Cyclooctadiene from Cycloocten-3-yldimethylamine¹

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Application of the Hofmann exhaustive methylation procedure to cycloocten-3-yldimethylamine has been shown to yield a mixture of 1,3-cyclooctadienes. The mixture was separated by extraction with 20% aqueous silver nitrate into the *cis-trans* isomer (15%), soluble in the silver nitrate solution, and the *cis-cis* isomer (41%), which was insoluble. Cycloocten-3-yldimethylamine oxide on heating formed *cis-cis*-1,3-cyclooctadiene (50%) by elimination of N,N-dimethylhydroxylamine. O-Cycloocten-3-yl-N,N-dimethylhydroxylamine also was formed to the extent of approximately 19% by rearrangement of the cyclooctenyl group from the nitrogen to the oxygen atom.

1,3-Cyclooctadiene has been prepared by dehydrobromination of 3-bromocyclooctene with quinoline and also by application of the Hofmann exhaustive methylation procedure to cycloocten-3-yldimethylamine. Since the properties of the 1,3-cyclooctadiene from the two methods of preparation were different, it was suggested that the product of the exhaustive methylation reaction contained the less stable *cis-trans* isomer in addition to the *cis-cis* isomer.³ Evidence supporting this view has been reported recently. The mixture was treated with phenyl azide and with hexachlorocyclopentadiene; derivatives of the more reactive (presumably *cis-trans*) isomer were formed in amounts corresponding to the presence of 10% in one experiment and 30% in another.⁴

In the present work, the method previously used for the separation of *cis*- and *trans*-cyclooctene⁵ has been applied successfully to the separation of the mixture of 1,3-cyclooctadienes prepared by

the Hofmann exhaustive methylation route. The thermal decomposition of cycloocten-3-yldimethylamine oxide also has been investigated.

Cycloocten-3-yltrimethylammonium hydroxide was prepared by a method described previously³ and decomposed by distillation under reduced pressure. The distillate was extracted with 20% (by weight) aqueous silver nitrate, and the fraction that was insoluble in this reagent was distilled. In this way *cis-cis*-1,3-cyclooctadiene, with an infrared spectrum essentially identical with a sample prepared by dehydrobromination of 3-bromocyclooctene, was isolated in 41% yield. Addition of ammonium hydroxide to the silver nitrate extract formed an unstable hydrocarbon, C_8H_{12} (I), in 15% yield. This hydrocarbon had a characteristic unpleasant odor resembling that of cyclopentadiene. It was found necessary to protect the hydrocarbon I from atmospheric oxygen and to determine physical properties and carry out reactions immediately with freshly prepared material, because of the rapidity with which it polymerized. The hydrocarbon could not be stored at –80° without change in its index of refraction, but it formed a more stable crystalline 1:1 adduct with silver nitrate from which it could be regenerated by addition of ammonium hydroxide.

The structure of the hydrocarbon I was de-

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(2) United States Rubber Co. Fellow, 1954–1955.

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

(4) K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kühlhorn and J. Schneider, *Ann.*, **589**, 122 (1954).

(5) A. C. Cope, R. A. Pike and C. F. Spencer, *THIS JOURNAL*, **78**, 3212 (1953).

terminated by quantitative hydrogenation to cyclooctane and by oxidation with aqueous potassium permanganate to adipic acid. The ultraviolet spectrum showed a broad maximum at 230.5 $m\mu$, $\log \epsilon$ 3.42 (in cyclohexane). This spectrum is very similar to the spectrum of *cis-cis*-1,3-cyclooctadiene (λ_{max} 228 $m\mu$, $\log \epsilon$ 3.75 in cyclohexane) and is consistent with a conjugated diene structure in which the double bonds are forced into a non-planar conformation by strain.⁶ The infrared spectrum of I showed strong absorption in the 10.0–10.5 μ region which is characteristic of *trans* double bonds.⁷ *cis-cis*-1,3-Cyclooctadiene has bands at 11.0 and 8.65 μ in the infrared that are not present in the spectrum of the hydrocarbon I, while I has bands at 10.5, 10.3 and 8.4 μ that are absent in the spectrum of *cis-cis*-1,3-cyclooctadiene. It is concluded that the hydrocarbon I is *cis-trans*-1,3-cyclooctadiene and that the Hofmann exhaustive methylation route leads to a mixture of *cis-cis*- and *cis-trans*-1,3-cyclooctadienes. With the infrared spectra of the pure isomers available, it was possible to estimate the composition of the mixture formed by the exhaustive methylation procedure. Due to rapid polymerization of the unstable *cis-trans* isomer, fractional distillation of the mixture enriches the distillate in the *cis-cis* isomer, and analyses of redistilled material show less of the *cis-trans* isomer to be present than was originally formed. Calculations based on the percentage transmission at 10.5 and 11.0 μ of a redistilled sample of a mixture of 1,3-cyclooctadienes prepared by exhaustive methylation (n_D^{25} 1.4919) indicated a ratio of *cis-trans* to *cis-cis* isomers of 3:7.

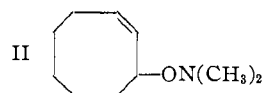
cis-trans-1,3-Cyclooctadiene is of interest as the cyclic diene of smallest ring size with conjugated *cis* and *trans* double bonds that has been isolated to date. The next higher ring homolog that is known is *cis-trans*-1,3-cyclodecadiene, which was prepared by a route analogous to that used in this work and which also appears to be sterically strained.⁸

cis-trans-1,3-Cyclooctadiene was isomerized at room temperature in carbon tetrachloride containing a trace of iodine to the more stable *cis-cis* isomer. No evidence of isomerization of the *cis-trans* form by silver nitrate was obtained; addition of ammonium hydroxide to a sample of the solid *cis-trans*-1,3-cyclooctadiene-silver nitrate adduct that had been stored at room temperature for 2 days and at 10° for 4 days resulted in recovery of the *cis-trans* isomer.

The formation of a mixture of *cis-cis*- and *cis-trans*-1,3-cyclooctadienes by the exhaustive methylation route containing approximately 30% of the unstable *cis-trans* isomer may be compared with the formation of a mixture of *cis*- and *trans*-cyclooctenes (from cyclooctyltrimethylammonium hydroxide) which contained 60% of the less stable *trans* isomer.⁵ Only *trans*-cyclononene and *trans*-cyclodecene were obtained from cyclononyldi-

methylamine and cyclodecyldimethylamine by the Hofmann exhaustive methylation route.^{9,10} The related amine oxide pyrolysis route to olefins from cycloalkyldimethylamines led to *cis*-cyclooctene,⁵ but resulted in formation of *trans*-cyclononene and *trans*-cyclodecene.¹¹ It was of interest to continue comparison of the Hofmann *vs.* the amine oxide route to olefins by study of the thermal decomposition of cycloocten-3-yldimethylamine oxide.

The oxidation of cycloocten-3-yldimethylamine to the amine oxide with 30% aqueous hydrogen peroxide in methanol was shown to be essentially quantitative by isolation of the amine oxide picrate in 97% yield. The amine oxide decomposed on heating at 105–165° and 7–3 mm., yielding *cis-cis*-1,3-cyclooctadiene (50%), identified by its infrared spectrum, and O-cycloocten-3-yl-N,N-dimethylhydroxylamine (II, 19%). It was difficult to purify II completely by removal of the small amount of



of cycloocten-3-yldimethylamine that it contained. Analytical and infrared data indicated 90% purity for II from this source, and the presence of 10% of the tertiary amine formed by loss of oxygen from the amine oxide.¹² It proved to be possible to purify the hydroxylamine derivative II by extraction with sufficient acid to remove the more basic tertiary amine. The formation of II is explained by the thermal rearrangement of the amine oxide, with migration of the cyclooctenyl group from the nitrogen to the oxygen atom, a type of reaction previously shown to be general for allyldialkylamine oxides.¹³ The structure of II was confirmed by synthesis (in very poor yield) from 3-bromocyclooctene and the sodium derivative of N,N-dimethylhydroxylamine, prepared from N,N-dimethylhydroxylamine hydrochloride and sodium amide. The infrared spectrum of the product indicated that it was a mixture of II and cycloocten-3-yldimethylamine, which could have been formed by N-alkylation of the sodium derivative of N,N-dimethylhydroxylamine followed by loss of oxygen from the resulting amine oxide. The infrared spectrum of II has bands at 12.3 and 10.65 μ that are not present in the spectrum of cycloocten-3-yldimethylamine, while the amine has bands at 11.4, 9.1 and 7.9 μ which are absent in the spectrum of II. Cycloocten-3-yldimethylamine was isolated in one preparation by distillation and identified by its infrared spectrum and preparation of the picrate. In another preparation, sufficient acid was added to the mixture to remove the amine, and the hydroxylamine derivative II that re-

(9) A. T. Blomquist, L. H. Liu and J. C. Bohrer, *ibid.*, **74**, 3643 (1952).

(10) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *ibid.*, **74**, 3636 (1952).

(11) A. C. Cope, D. C. McLean and N. A. Nelson, *ibid.*, **77**, 1628 (1955).

(12) Amine oxides are known to form amines by loss of oxygen on heating. See C. C. J. Culvenor, *Revs. Pure Appl. Chem. (Australia)*, **3**, 94 (1953); Sidgwick, "The Organic Chemistry of Nitrogen," revised by Taylor and Baker, University Press, Oxford, 1942, p. 167.

(13) A. C. Cope and P. H. Towle, *THIS JOURNAL*, **71**, 3423 (1949).

(6) E. A. Braude, *Chemistry and Industry*, 1557 (1954).

(7) D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard and G. B. E. M. Sutherland, *J. Chem. Soc.*, 915 (1950).

(8) A. T. Blomquist and A. Goldstein, *THIS JOURNAL*, **77**, 998 (1955).

mained was converted to the picrate, which showed no depression in a mixed melting point with the picrate of II formed by rearrangement of cycloocten-3-yltrimethylamine oxide.

Experimental¹⁴

cis-trans-1,3-Cyclooctadiene (I).—A solution of 61.4 g. of cycloocten-3-yltrimethylammonium iodide⁹ in 200 ml. of water was stirred overnight at room temperature with the freshly precipitated alkali-free silver oxide prepared from 71.6 g. of silver nitrate. The mixture was filtered, and the filtrate was concentrated under reduced pressure. The residual quaternary base was decomposed by heating in a nitrogen atmosphere at 28–10 mm. with a bath temperature of 70–185°. The distillate was collected in three traps in series, the first and second cooled with Dry Ice and the third cooled with liquid nitrogen. Nitrogen was introduced into the system after completion of the decomposition, which required 1 hour. A residue of 4.3 g. remained in the flask. The distillate was added to 200 ml. of pentane and the resulting mixture was washed successively with 120 ml. of cold 10% hydrochloric acid solution, 125 ml. of 5% sodium bicarbonate solution and 125 ml. of water. The pentane solution was then shaken for 5 minutes with 200 g. of 20% (by weight) aqueous silver nitrate solution. The silver nitrate solution was washed with 50 ml. of pentane, and the combined pentane solutions (containing the *cis-trans* isomer) were dried over magnesium sulfate. To the silver nitrate solution, cooled in an ice-bath, was added 50 ml. of concentrated ammonium hydroxide. The hydrocarbon that separated was extracted with two 25-ml. portions of pentane and the combined pentane extracts were dried over magnesium sulfate for 40 minutes. The pentane solution was concentrated under reduced pressure, and the residue was distilled under nitrogen through a semi-micro column. Nitrogen was introduced into the system after completion of the distillation, which yielded 1.63 g. (7.2%) of *cis-trans*-1,3-cyclooctadiene, b.p. 37.5° (11 mm.), n_D^{25} 1.4975. The infrared spectrum of this compound is shown in Fig. 1.

Anal. Calcd. for C_8H_{12} : C, 88.82; H, 11.18. Found: C, 88.91; H, 11.03.

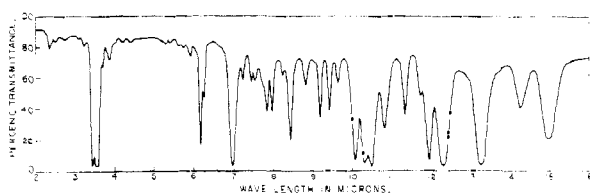


Fig. 1.—Infrared absorption spectrum of *cis-trans*-1,3-cyclooctadiene, determined on the pure liquid in a 0.032-mm. cell.

A residue of 1.05 g. remained in the distillation flask. Similar experiments showed that the ratio of distillate to residue depended on the rate of distillation. The yield of the *cis-trans* diene I could be raised to 15% by distilling rapidly under reduced pressure into receivers cooled in a Dry Ice-acetone-bath.

The pentane solutions containing the *cis-cis* isomer were distilled through a 38 × 1.5-cm. Vigreux column and yielded 8.35 g. (37%) of *cis-cis*-1,3-cyclooctadiene, b.p. 50.5–51° (30 mm.), n_D^{25} 1.4905. A residue of 2.53 g. (presumably polymer) remained in the distillation flask. In another preparation of *cis-cis*-1,3-cyclooctadiene by this procedure, the yield was 41%. The infrared spectrum was the same as that of an authentic sample prepared by dehydrobromination of 3-bromocyclooctene.³

Hydrogenation of I.—On quantitative reduction of a 142-mg. sample of freshly prepared I in 10 ml. of 95% ethanol in the presence of 300 mg. of prerduced platinum oxide, 95% of two molar equivalents of hydrogen was absorbed in 135 minutes and 31 mg. of cyclooctane (21%), b.p. 63° (45

(14) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Infrared spectra were determined with a Baird double beam recording spectrometer, model B, with a sodium chloride prism. Ultraviolet spectra were determined with a Cary ultraviolet recording spectrophotometer, model 11 MS.

mm.), n_D^{25} 1.4550, m.p. 9.5–12.5° (indicating 98% purity¹⁵) was isolated by the following procedure. The catalyst was separated and the filtrate was added to 200 ml. of water. The mixture was extracted with one 20-ml. portion and three 10-ml. portions of pentane. The combined pentane solutions were washed with 50 ml. of 10% calcium chloride solution, then with 50 ml. of water and dried over magnesium sulfate. Careful distillation of the pentane solution through a semi-micro column yielded cyclooctane with the properties given above. Due to the tendency of I to polymerize, especially in contact with acid, the hydrogenation was carried out in 95% ethanol, using a large ratio of catalyst to compound in order to accelerate the reduction. The extractions required to remove ethanol and the small scale of the reduction account for the low yield of cyclooctane isolated.

Oxidation of I.—To a mixture of 6.60 g. of freshly prepared I in 200 ml. of water was added with stirring a total of 136 g. of potassium permanganate over a period of 7.5 hr., while the temperature was kept below 35° by cooling with an ice-bath. The mixture was then stirred overnight at room temperature. To the mixture, acidified by addition of 50 ml. of concentrated sulfuric acid, was added a total of 140 g. of sodium bisulfite. Insoluble inorganic salts were removed by filtration, and the filtrate was continuously extracted with ether for 54 hr. The ether solution was concentrated and yielded 1.76 g. (20%) of adipic acid, m.p. 145.5–152°; mixed m.p. of a sample crystallized from water with an authentic sample of adipic acid was 150.6–152.4°.

Silver Nitrate Adduct of I.—A mixture of 0.08 g. of freshly prepared I, 0.5 ml. of 20% silver nitrate solution and 0.5 ml. of pentane was stored at approximately –10° for 2 days. The mixture was then filtered, and yielded 159 mg. (77%) of a white crystalline solid, m.p. (sealed capillary) 122–124° dec. An analytical sample that was recrystallized from absolute ethanol had m.p. (sealed capillary) 126–127.5° dec. when placed in a bath at 115° rising at 2° per minute.

Anal. Calcd. for $C_8H_{12} \cdot AgNO_3$: C, 34.55; H, 4.35; Ag, 38.79. Found: C, 34.65; H, 4.45; Ag, 38.90.

Regeneration of I from its Silver Nitrate Adduct.—A 3.08-g. sample of the silver nitrate adduct of I had a brown appearance after storage for 2 days at room temperature and 4 days at 10°. The adduct was decomposed by addition of 50 ml. of concentrated ammonium hydroxide. The resulting mixture was washed with two 50-ml. portions of pentane. The combined pentane solutions were washed with 50 ml. of 20% (by weight) aqueous silver nitrate for 5 minutes and dried over magnesium sulfate. *cis-trans*-1,3-Cyclooctadiene was isolated from the silver nitrate extract as described above for the preparation of I. The yield was 0.29 g. (24%). A residue of 0.08 g. remained in the distillation flask. The infrared spectrum of I regenerated from its silver nitrate adduct was essentially unchanged. Careful distillation of the pentane solution containing any material insoluble in 20% silver nitrate yielded only solvent and 0.16 g. of a polymeric residue. The poor recovery of I in this experiment is attributed to mechanical losses and to some decomposition of the silver nitrate adduct on storage.

Reaction of *cis-trans*-1,3-Cyclooctadiene with Maleic Anhydride.—A mixture of 0.19 g. of freshly prepared I, 0.17 g. of maleic anhydride and 3 ml. of benzene was allowed to stand at room temperature for 3 days. The mixture was filtered and yielded 117 mg. of a fine, white powder which melted with decomposition from 143 to 250°, with blackening above 250°. Addition of 2 ml. of absolute ethanol to a solution of the white powder in 5 ml. of dimethylformamide yielded a resinous material which was analyzed after digestion with 10 ml. of hot benzene.

Anal. Calcd. for the 1:1 copolymer, $C_{10}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 67.53; H, 7.10.

Conversion of I to *cis-cis*-1,3-Cyclooctadiene.—A solution of 1.3 g. of freshly prepared I in 15 ml. of carbon tetrachloride containing 13 mg. of iodine was stored in the dark at room temperature for 92 hr. The infrared spectrum of an aliquot taken after this time showed no band at 10.5 μ (characteristic of I) and showed a strong band at 11.0 μ (characteristic of the *cis-cis* isomer). The solution was

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

distilled through a semi-micro column and yielded 0.90 g. (69%) of *cis-cis*-1,3-cyclooctadiene with an infrared spectrum essentially identical to the spectrum of an authentic sample.³

A mixture of *cis-cis*- and *cis-trans*-1,3-cyclooctadiene for infrared analysis was obtained by decomposing the quaternary base prepared from 12.0 g. of cycloocten-3-yltrimethylammonium iodide as described above. The distillate was acidified with 10% hydrochloric acid solution and the organic layer (2.74 g.) was removed with a capillary pipet and dried by cooling with Dry Ice and decanting from the ice that formed. A sample distilled through a semi-micro column for infrared analysis had b.p. 48° (22 mm.), n_D^{20} 1.4919. As noted in the introductory part, this sample contained approximately 30% of the *cis-trans* isomer I and 70% of *cis-cis*-1,3-cyclooctadiene.

Neutralization of the aqueous acid solution remaining after removal of the organic layer from the exhaustive methylation reaction produced an oil which was extracted with ether. Distillation of the dried ether extract yielded 0.52 g. (8.4%) of cycloocten-3-yldimethylamine, with an infrared spectrum essentially the same as that of an authentic sample.³

Cycloocten-3-yldimethylamine Oxide.—Cycloocten-3-yldimethylamine³ was oxidized with 30% hydrogen peroxide according to the procedure described for the oxidation of cyclooctyldimethylamine.⁵

An aqueous methanolic solution of cycloocten-3-yldimethylamine oxide prepared from 1.00 g. of cycloocten-3-yldimethylamine on treatment with an aqueous solution of 1.50 g. of picric acid yielded 2.53 g. (97%) of the amine oxide picrate, m.p. 186–189° dec. An analytical sample recrystallized once from ethanol and three times from methanol had a constant melting point of 199.3–200° dec.

Anal. Calcd. for $C_{11}H_{22}N_4O_3$: C, 48.24; H, 5.57; N, 14.06. Found: C, 48.16; H, 5.50; N, 13.73.

cis-cis-1,3-Cyclooctadiene.—Cycloocten-3-yldimethylamine oxide prepared from 5.66 g. of the amine was decomposed in a nitrogen atmosphere at 7–3 mm. with a bath temperature of 105–165° according to the procedure described for the decomposition of cyclooctyldimethylamine oxide.⁵ *cis-cis*-1,3-Cyclooctadiene was isolated in the same manner as *cis-cis*-cyclooctene.⁵ The yield of *cis-cis*-1,3-cyclooctadiene was 2.00 g. (50%), b.p. 54–54.5° (35 mm.), n_D^{20} 1.4911. The average yield of three preparations was 48%. The infrared spectrum of the product was the same as that of an authentic sample of *cis-cis*-1,3-cyclooctadiene.³

O-Cycloocten-3-yl-N,N-dimethylhydroxylamine (II). (a).—The amine oxide prepared from 8.49 g. of cycloocten-3-yldimethylamine was decomposed and *cis-cis*-1,3-cyclooctadiene was removed as described above. The remaining aqueous hydrochloric acid solution was made alkaline by addition of 5% sodium hydroxide solution, and the resulting oil was extracted with three 100-ml. portions of ether. The combined ether solutions, after drying over magnesium sulfate, were distilled through a semi-micro column and yielded 3.26 g. of a colorless oil, b.p. 86–88° (9.5 mm.), n_D^{20} 1.4741–1.4708. Analyses of the higher boiling fractions (2.02 g.), n_D^{20} 1.4711–1.4708, were consistent with values calculated for a mixture containing approximately 90% of II and 10% of cycloocten-3-yldimethylamine. The infrared spectrum had weak bands at 7.9 and 9.1 μ (where bands are present in the spectrum of the amine but absent in the spectrum of II), but in other respects the spectrum was

essentially the same as that of pure II (described below). Assuming the higher boiling material to be 90% II, the yield of II was 19%. An analytical sample of II was obtained in a similar experiment by the following procedure. The higher boiling fractions from two distillations of crude II through a semi-micro column were combined to give a 0.90-g. sample (n_D^{20} 1.4685) which was dissolved in 10 ml. of ether. The ether solution was shaken for 5 minutes with 1.1 ml. of 10% hydrochloric acid solution, washed with 5 ml. of water and dried over magnesium sulfate. Distillation through a semi-micro column yielded 0.17 g. of II, b.p. 75.5° (5 mm.), n_D^{20} 1.4680.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.95; H, 11.32; N, 8.28. Found: C, 71.10; H, 11.46; N, 8.49.

A 0.23-g. sample of II, purified as described above, on treatment with an alcoholic solution of 0.31 g. of picric acid, yielded yellow needles of the picrate of II, m.p. 113.2–113.8°, unchanged on recrystallization from 95% ethanol.

Anal. Calcd. for $C_{16}H_{22}N_4O_3$: C, 48.24; H, 5.57; N, 14.06. Found: C, 48.11; H, 5.86; N, 14.31.

(b).—A liquid ammonia solution of sodium amide was prepared by adding 6.1 g. of sodium to 250 ml. of liquid ammonia containing a trace of ferric nitrate. To the sodium amide solution was added during 5 minutes 12.9 g. of N,N-dimethylhydroxylamine hydrochloride.¹⁶ The mixture was stirred for 3 hr., and then 200 ml. of anhydrous ether was added over a period of 30 minutes. After allowing the ammonia to evaporate, a solution of 25.0 g. of 3-bromocyclooctene³ in 150 ml. of anhydrous ether was added (10 minutes). The mixture was stirred vigorously under reflux for 13 hr. The mixture was filtered and the filtrate was washed with two 100-ml. portions of 10% hydrochloric acid solution. The acid solution was made alkaline by addition of 10% sodium hydroxide solution, and the oil was extracted with two 100-ml. and one 50-ml. portion of ether. The combined ether solutions were dried over magnesium sulfate. The ether was removed by distillation through a 38 × 1.5-cm. Vigreux column and the residue was distilled through a semi-micro column yielding 0.55 g. of a colorless oil, b.p. 76° (6 mm.), n_D^{20} 1.4768–1.4788. The infrared spectrum of an intermediate fraction (n_D^{20} 1.4771) showed bands at 12.25 and 10.6 μ (where bands are present in the spectrum of II and absent in the spectrum of cycloocten-3-yldimethylamine) and at 11.4 and 7.9 μ (where bands are present in the spectrum of the amine and absent in that of II). A 0.10-g. sample (made up of fractions having n_D^{20} 1.4768–1.4772) was shaken for 5 minutes with 0.17 g. of 10% hydrochloric acid solution. The mixture was washed with 0.5 ml. of ether and the ether solution was added to alcoholic picric acid. The yellow needles that were obtained were identical, according to melting point and mixed melting point, to the picrate of II described above. From another experiment, cycloocten-3-yldimethylamine was isolated by washing the reaction mixture with acid, neutralizing the acid extract, extracting the amine with ether and distilling. The amine had the same infrared spectrum as an authentic sample,³ and formed an identical picrate, m.p. 210.6–211.4° dec. (lit.³ 208.6–209° dec.).

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(16) Prepared from dodecyldimethylamine oxide by a procedure similar to the one described by A. C. Cope, T. T. Foster and P. H. Towle, *THIS JOURNAL*, **71**, 3929 (1949).