

Cyclic Polyolefins. XLV. *cis,trans*-1,5-Cyclooctadiene¹Arthur C. Cope, Charles F. Howell,² John Bowers, R. C. Lord, and George M. Whitesides*Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received April 14, 1967*

Abstract: Hofmann degradation of N,N-dimethyl-*cis*-4-cyclooctenylamine afforded *cis,cis*-1,3-cyclooctadiene and *cis,trans*-1,5-cyclooctadiene in a ratio of 1:9. Chemical and spectral evidence for the structure of the latter olefin is discussed.

The labile cyclooctadiene prepared by Willstätter and Veraguth³ from N,N-dimethyl-4-cyclooctenylamine ("desdimethylgranatanine") was shown by ozonolysis to be a 1,5-diene.^{4,5}

In later work this diene, prepared by Hofmann degradation of N-methylgranatanine, was found to differ from the stable *cis,cis*-1,5-cyclooctadiene obtained by the dimerization of butadiene⁵ or by reduction of 1,6-dichloro-1,5-cyclooctadiene (chloroprene dimer) with sodium in liquid ammonia.⁶

The compound had been partially hydrogenated to *cis*-cyclooctene and was shown to add only 1 mole of phenyl azide.^{5,7} Although this chemical evidence favored *cis,trans*-1,5-cyclooctadiene as the structure, the difficulty encountered in constructing molecular models and an interpretation of the Raman spectrum⁸ of the diene were considered as evidence in favor of the *trans,trans*-1,5-cyclooctadiene structure.^{5,7} Reexamination of the previous evidence in light of the work reported here demonstrates that the diene is *cis,trans*-1,5-cyclooctadiene.

N,N-Dimethyl-*cis*-4-cyclooctenylamine (2), the precursor of *cis,trans*-1,5-cyclooctadiene, was prepared by three different procedures (Figure 1) in order to remove any doubt that the initial double bond had the *cis* configuration. Hofmann degradation of N-methylgranatinine (1) yielded *cis*-4-cyclooctenylamine (2; 87%) which was separated from unchanged 1 by treatment of the mixture with methyl iodide followed by fractional crystallization of the methiodides.⁹ The N,N,N-trimethyl-*cis*-4-cyclooctenylammonium iodide (3) purified in this manner was reduced with lithium aluminum hydride to the desired tertiary amine.¹⁰

In a second synthesis of amine 2, *cis,cis*-1,5-cyclooctadiene (4) was treated with hydrogen bromide followed by dimethylamine.⁵ The mixture of amines, obtained in 25% over-all yield, was shown to contain 75% of N,N-dimethyl-*cis*-4-cyclooctenylamine by vapor phase chromatography (vpc).

Amine 2 was also obtained in 22% yield by reaction of *cis*-4-cyclooctenyl *p*-bromobenzenesulfonate¹¹ (5) with dimethylamine in dioxane at 80°. The samples of amine 2 prepared by this method and by Hofmann degradation of N-methylgranatanine had identical infrared spectra and refractive indices and were chromatographically homogeneous. In addition, the mixture melting point of their picrates was not depressed.

Pyrolysis of N,N,N-trimethyl-*cis*-4-cyclooctenylammonium hydroxide gave a mixture of olefins which was shown by vpc to consist of *cis,trans*-1,5-cyclooctadiene (90%) and *cis,cis*-1,3-cyclooctadiene (10%);¹² the latter presumably is formed by base-catalyzed isomerization of 1,4-cyclooctadiene initially formed in the Hofmann elimination. Within the limit of detection (0.5%) no other olefins were formed, and there was no evidence for the formation of any bicyclic products as had previously been suggested.^{3,5}

The *cis,trans*-1,5-cyclooctadiene was quantitatively removed from *cis,cis*-1,3-cyclooctadiene by extraction with aqueous silver nitrate¹³ and was recovered in 58% yield by treatment of the silver nitrate complex with concentrated ammonium hydroxide. Isomerization of the diene with iodine afforded *cis,cis*-1,5-cyclooctadiene (65% yield).

Pyrolysis of *cis*-4-cyclooctenyldimethylamine oxide gave *cis,cis*-1,4-cyclooctadiene as a major product (91%) in addition to *cis,cis*-1,5-cyclooctadiene (6%) and two unidentified hydrocarbons (3%).

The 1,5-cyclooctadiene structure for the olefin obtained by two successive Hofmann degradations of N-methylgranatanine has been clearly established since ozonolysis followed by oxidation gave only succinic acid.³⁻⁵ The facile isomerization of the diene to *cis,cis*-1,5-cyclooctadiene supports this assignment of the positions of the double bonds and also shows that the material is not *cis,cis*-1,5-cyclooctadiene. Thus the difference must be in the stereochemistry about the double bonds and the molecule must have either the *cis,trans* or the *trans,trans* structure.

Chemical evidence strongly supports the *cis,trans* structure. Partial hydrogenation of the material yielded *cis*-cyclooctene under conditions which do not cause isomerization of *trans*-cyclooctene to *cis*-cyclooctene.⁵ The molecule readily added 1 mole of

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

(2) James Flack Norris Fellow, 1956-1957.

(3) R. Willstätter and H. Veraguth, *Ber.*, **38**, 1975 (1905); **40**, 957 (1907).

(4) C. Harries, *ibid.*, **41**, 671 (1908).

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

(6) A. C. Cope, C. L. Stevens, and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2510 (1950).

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

(8) J. Goubeau, *ibid.*, **567**, 214 (1950).

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

(10) (a) G. W. Kenner and M. A. Murray, *J. Chem. Soc.*, 406 (1950); (b) A. C. Cope, E. Ciganek, L. J. Fleckenstein, and M. A. P. Meisinger, *J. Am. Chem. Soc.*, **82**, 4651 (1960).

(11) A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

(12) Harries⁴ had previously suggested 1,3-cyclooctadiene as the unidentified impurity (20%) in his mixture since it formed an unsaturated monoozonide; this behavior had been observed with other conjugated dienes.

(13) A. C. Cope and C. L. Bumgardner, *J. Am. Chem. Soc.*, **78**, 2812 (1956).

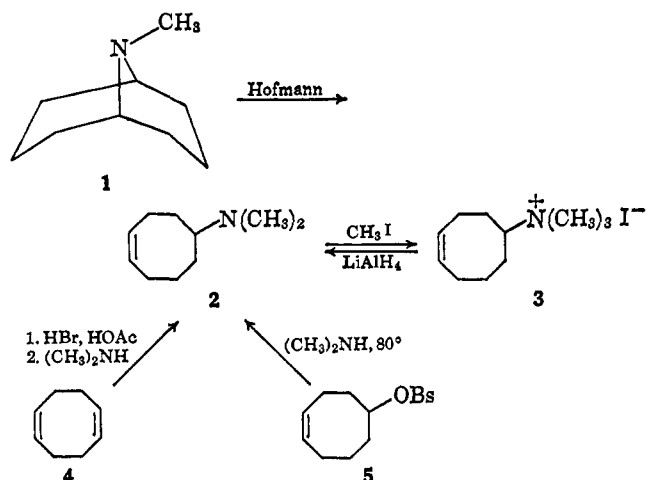


Figure 1. Syntheses of N,N-dimethyl-*cis*-4-cyclooctenylamine.

phenyl azide,⁷ as does *trans*-cyclooctene; the *trans,trans* structure would be expected to react with 2 moles of phenyl azide. The formation of a silver nitrate complex is also indicative of a (cyclic) *trans*-olefinic bond. The starting amine has been shown to be N,N-dimethyl-*cis*-4-cyclooctenylamine (2) and there is no evidence to indicate that this is isomerized to the thermodynamically less stable *trans* olefin during the Hofmann degradation.

Since the only substantial evidence in favor of the *trans,trans* structure was the interpretation of the Raman spectrum of the unstable diene by Goubeau,⁸ we have redetermined this spectrum as well as the Raman spectra of *cis,cis*-1,5-cyclooctadiene and *cis,cis*-1,3-cyclooctadiene. The spectra were recorded on a Cary Model 81 photoelectric Raman spectrometer and agreed very well with those reported earlier⁸ with the following exceptions. (1) There were minor differences in frequency and intensity, as would be expected in comparing photoelectric with photographic intensity measurements. (2) In the spectrum of the unstable diene, we were unable to verify five lines of weak but significant intensity (mostly of level 1) reported in the earlier work. While these lines are presumably due to a small amount of one or more impurities, they do not appear to arise from contamination by other cyclooctadienes and we do not wish to speculate further on the nature of the impurities. (3) Most importantly, the line in the spectrum of the unstable diene reported earlier as a singlet at 1622 cm^{-1} has been resolved into two lines at 1622 and 1635 cm^{-1} of equal peak intensity and half-width. When the spectral slit width of the spectrometer was approximately 3 cm^{-1} , the intensity minimum between the two peaks at 1628 cm^{-1} was less than 40% of the peak intensity. In the spectrum of *cis,cis*-1,5-cyclooctadiene a scan with the same spectral slit width produced no evidence of doublet structure at 1662 cm^{-1} . If this line is double, the separation of the components must be 3 cm^{-1} or less in view of the spectral slit width and the observed half-width of 7 cm^{-1} . The double-bond line in the 1,3-cyclooctadiene spectrum also appears to be single, but its larger half-width of about 14 cm^{-1} suggests the possibility of an overlapping doublet; its frequency of 1630 cm^{-1} is consistent with the conjugated double-bond structure.

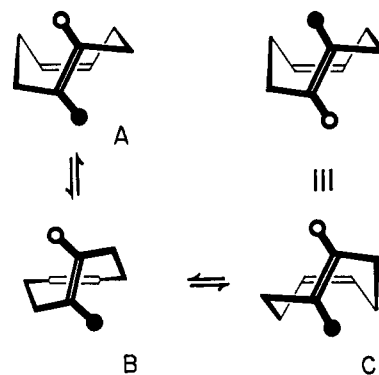


Figure 2. Possible conformations of *cis,trans*-1,5-cyclooctadiene.

The existence of two C=C stretching frequencies in the spectrum of the unstable diene separated by 13 cm^{-1} suggests strongly¹⁴ that there are two olefinic double bonds in the molecule, one *cis* and one *trans*. Thus the new Raman data also strongly support the *cis,trans* structure.

There is one feature of the Raman spectrum of special interest, namely that the center of gravity of the two double-bond frequencies, 1628 cm^{-1} , is much lower than the expected range of the mean of isolated *cis* and *trans* double bonds in open-chain olefinic compounds, namely 1655–1665 cm^{-1} . The explanation of this discrepancy of about 30 cm^{-1} is not obvious. It might be the result of ring strain as suggested earlier,⁸ but the evidence is available mainly from the spectra of molecules in which the four atoms around the double bond are coplanar. It seems reasonable to suppose that strained *cis* and *trans* double bonds in which the four carbon atoms are not coplanar should show lowered C=C frequencies both because of weakening of the double bond and because the contribution of the force constants of the C-C single bonds to the double-bond frequency should be less. As can be inferred from Figure 2, the *cis* double bond in *cis,trans*-1,5-cyclooctadiene is distorted very little, but the *trans* double bond is strained considerably by having one C-C bond rotated out of the plane formed by the double bond and the other C-C bond. We therefore suggest that the one Raman line at 1635 cm^{-1} arises from a slightly strained *cis* double bond displaced by 10–15 cm^{-1} from its expected position at 1645–1650 cm^{-1} . The other at 1622 cm^{-1} is then attributed to the *trans* double bond whose frequency is much farther displaced from an expected value of about 1660–1665 cm^{-1} . This point could be readily checked by selective isotopic substitution.

The infrared spectrum of pure *cis,trans*-1,5-cyclooctadiene had strong bands at 980 and 710 cm^{-1} ¹⁵ which were also present in *cis,trans*-1,3-cyclooctadiene.¹³ Our spectrum of *cis,trans*-1,5-cyclooctadiene is in agreement with the published one⁷ except for a strong band at about 675 cm^{-1} and weaker ones at about 765, 815, and 915 cm^{-1} in the latter spectrum; these bands may be attributed to the presence of *cis,cis*-1,3-cyclooctadiene.

(14) See ref 8; also see J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, N. Y., 1939, Chapter 11.

(15) These absorption bands are within the ranges 990–965 and 728–675 cm^{-1} ascribed to *trans* and *cis* —HC=CH—, respectively: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 45–49.

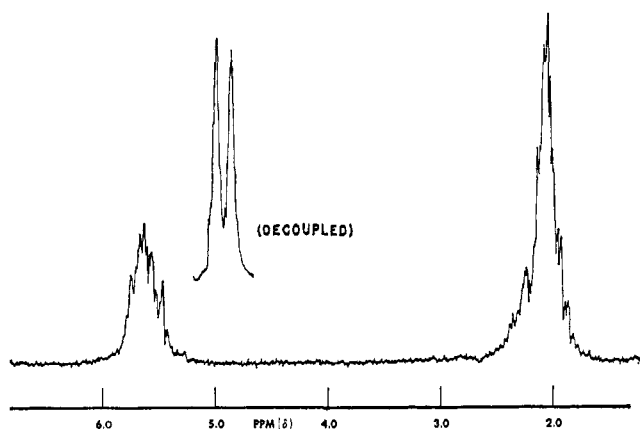


Figure 3. Frequency-sweep nmr spectra of *cis,trans*-1,5-cyclooctadiene at 60 MHz. The two peaks in the decoupled spectrum of the olefinic protons are separated by 9.0 Hz.

The nmr spectrum of *cis,trans*-1,5-cyclooctadiene is entirely consistent with its assigned structure. In particular, the undecoupled frequency-sweep spectrum of the olefinic protons consists of a complex pattern, due in part to spin-spin coupling between the olefinic and aliphatic protons (Figure 3). When the effects of these spin-spin couplings are removed by strong irradiation at the frequency of the aliphatic absorption, the olefinic resonance is simplified to two sharp lines. Examination of Courtauld or Fieser models suggests that the most favorable conformation of *cis,trans*-1,5-cyclooctadiene can be represented by structure A of Figure 2. The olefinic protons of both the *cis* and *trans* double bonds in this conformer are geometrically nonequivalent; consequently, the decoupled nmr spectrum of the olefinic protons might be expected to consist of two superimposed AB spectra. However, *cis,trans*-1,5-cyclooctadiene has available a low-energy flipping process (represented by $A \rightleftharpoons C$) which averages the magnetic environments of the protons on each type of double bond. Although these data do not permit a decision as to whether a rapid conformational equilibration between these conformers is responsible for the observed spectrum or whether this compound actually exists in solution in the symmetrical conformation B, the observation of two distinct types of uncoupled olefinic protons clearly supports the assignment of the *cis,trans* structure.¹⁶ Because of the rigidity of the molecule, the *trans* double bond is unable to rotate with respect to the rest of the ring and the molecule should exist as two optically active enantiomers.⁶ This has been confirmed by stereoselective synthesis of the diene from optically active (+ or -) N,N-dimethyl-*cis*-4-cyclooctenylamine¹⁷ and by resolution of *cis,trans*-1,5-cyclooctadiene *via* a platinum complex containing an optically active amine.¹⁸

Experimental Section¹⁹

N,N-Dimethyl-*cis*-4-cyclooctenylamine (2). A. By Hofmann Degradation of N-Methylgranatanine. Pseudopelletierine²⁰ was

(16) The undecoupled spectrum showed no important change with temperature between +30 and -90°. Hence, if an equilibrium between A and C is involved in averaging the olefinic chemical shifts, the rate of this equilibration must be very rapid.

(17) A. C. Cope, C. F. Howell, and A. Knowles, *J. Am. Chem. Soc.*, **84**, 3190 (1962).

(18) A. C. Cope, J. K. Hecht, H. W. Johnson, Jr., H. Keller, and H. J. S. Winkler, *ibid.*, **88**, 761 (1966).

converted to N-methylgranatanine in 77% yield by Wolff-Kishner reduction.²¹ N-Methylgranatanine methiodide²² (28.1 g) was stirred overnight with 2 equiv of silver oxide in 500 ml of water, and the suspension was filtered. The solid quaternary hydroxide obtained on concentration of the aqueous solution was decomposed at 3-5 mm⁵ to a mixture of amines. A solution of the mixture in 50 ml of methanol was heated under reflux for 2 hr with 7.8 ml of methyl iodide. After cooling at 5° overnight, 2.4 g (7.6%) of N-methylgranatanine methiodide, mp 379-380° dec, was obtained.⁹ The filtrate was evaporated to dryness and redissolved in 25 ml of absolute ethanol. After gradual addition of 600 ml of anhydrous ether, 25.6 g (87%) of N,N,N-trimethyl-*cis*-4-cyclooctenylammonium iodide (3) was obtained, mp 264.4-264.8° dec (lit.³ 264° dec), and recrystallized from dioxane-1-butanol (2:1). A solution of iodide 3 (19.4 g) in dioxane (400 ml) was stirred and heated under reflux for 24 hr with 9.6 g of lithium aluminum hydride.¹⁰ After addition of 25 ml of ethyl acetate, the dioxane was removed by adding water and distilling with steam. Sodium hydroxide (40 g) was added, and distillation was continued until the distillate was neutral. The distillate was acidified and the acid-insoluble material was extracted with ether. The aqueous solution was then made alkaline and extracted with ether; the ether extracts were dried (sodium sulfate) and distilled through a semimicro column, giving 9.06 g (90%) of N,N-dimethyl-*cis*-4-cyclooctenylamine (2), bp 69-70° (4 mm), *n*^{25D} 1.4801-1.4805 [lit.³ bp 89.5-92° (14.5 mm)]. The picrate had mp 172.4-173.0° (lit.⁵ mp 171.0-171.5°). Vapor phase chromatography on silicone oil and bis-2-ethylhexyl sebacate showed the presence of only one component.

Hydrogenation of the amine afforded N,N-dimethylcyclooctylamine,²³ the picrate of which had mp 197.6-198.0° (lit.²³ mp 197.4-198.2°).

B. From *cis*-4-Cyclooctenyl Bromide. Treatment of *cis,cis*-1,5-cyclooctadiene (4) with hydrogen bromide in glacial acetic acid afforded impure *cis*-4-cyclooctenyl bromide, which when heated with dimethylamine for 72 hr was converted to impure amine 2 in 25% yield [bp 63.0-65.5° (3.6 mm), *n*^{25D} 1.4750-1.4809].⁵ Vapor phase chromatography (silicone oil) showed in addition to 2 (75%) the presence of five minor components. Three of the latter, on the basis of their retention times on a 4-methyl-4-nitropimelonitrile (NMPN) column at 100°, were identified as 1,3-, 1,4-, and 1,5-cyclooctadiene.¹¹ The remaining components were two unidentified bicyclic hydrocarbons.

C. From *cis*-4-Cyclooctenyl *p*-Bromobenzenesulfonate (5). A mixture of 2.84 g of brosylate 5,¹¹ 1.5 g of dimethylamine, and 11 ml of dioxane was agitated in a 50-ml autoclave at 80° for 24 hr. After cooling, the mixture in the autoclave was extracted with ether. The ether layer was washed with water and extracted with two 50-ml portions of 1 N hydrochloric acid. The acid extract was treated with 5 ml of 10% sodium hydroxide and extracted with ether. The dried ether extract was evaporated, and the residue was distilled, giving 0.276 g (22%) of N,N-dimethyl-*cis*-4-cyclooctenylamine, *n*^{25D} 1.4803. This material and amine 2 prepared from N-methylgranatanine (method A) had identical infrared spectra.

The picrate of amine 2 prepared from the brosylate 5 had mp 171.8-172.4° and on admixture with the picrate of the amine prepared from N-methylgranatanine had mp 171.2-172.4°.

***cis,trans*-1,5-Cyclooctadiene.** *cis,trans*-1,5-Cyclooctadiene was prepared from N,N,N-trimethyl-*cis*-4-cyclooctenylammonium iodide (7.37 g) according to the procedure described for *cis,trans*-1,3-cyclooctadiene,¹³ except that the decomposition was carried out at 3 mm. Gas chromatographic analysis (NMPN, 98°) of the crude product showed the presence of 90% *cis,trans*-1,5-cyclooctadiene and 10% *cis,cis*-1,3-cyclooctadiene and the absence of any other cyclooctadienes (within the limit of detection, 0.5%). The product was dissolved in 25 ml of cold pentane and washed

(19) Melting points are corrected and boiling points are uncorrected. Analyses were performed by Dr. S. M. Nagy. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer by Mrs. Nancy Alvord, Mrs. L. Taylor, and Mrs. M. G. Howell. Gas chromatographic analyses were carried out using 180 × 0.8 cm Pyrex tubes packed with 48-100 mesh Firebrick coated with the appropriate stationary phase.

(20) A. C. Cope, H. L. Dryden, and C. F. Howell, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 816.

(21) D. Todd, *Org. Reactions*, **4**, 378 (1948).

(22) A. C. Cope and C. G. Overberger, *J. Am. Chem. Soc.*, **70**, 1433 (1948).

(23) A. C. Cope and L. L. Estes, *ibid.*, **72**, 1128 (1950).

rapidly in succession with cold 25-ml portions of 10% hydrochloric acid, 5% sodium bicarbonate, and water. The pentane solution was extracted successively with 24 g of 20% silver nitrate diluted with 75 ml of water, 25 ml of water, 24 g of 20% silver nitrate, and again with 25 ml of water.

The remaining pentane solution, containing only *cis,cis*-1,3-cyclooctadiene according to vpc, was dried over magnesium sulfate, concentrated, and distilled giving 110 mg (41%) of *cis,cis*-1,3-cyclooctadiene, n_D^{25} 1.4874 (lit.¹³ n_D^{25} 1.4911). The infrared spectrum of a sample collected by vpc was identical with that of authentic material.¹³

Treatment of the hydrochloric acid extract with base afforded 77 mg (2.0%) of amine 2, n_D^{25} 1.4792.

The silver nitrate extracts were treated with excess cold concentrated ammonium hydroxide.¹³ Distillation²⁴ at 42.0–43.5° (20 mm) gave 1.58 g (58.5%) of *cis,trans*-1,5-cyclooctadiene, n_D^{25} 1.4891 (lit.⁵ n_D^{25} 1.4894).²⁵ The infrared spectrum of this material, unchanged after collection by gas chromatography, was nearly identical with the published spectrum⁷ (see Discussion). Its ultraviolet spectrum showed only end absorption.

Silver Nitrate Adduct of *cis,trans*-1,5-Cyclooctadiene. A mixture of 625 mg of *cis,trans*-1,5-cyclooctadiene, 980 mg of silver nitrate, and 2 ml of water was stirred for 30 min with cooling and filtered, giving 523 mg (35%) of the adduct, mp 174–178° dec. An analytical sample, recrystallized from methanol–ether, melted at 180–181° dec after drying at 25° (0.1 mm) for 1.5 hr.

Anal. Calcd for $C_8H_{12} \cdot AgNO_3$: C, 34.55; H, 4.35; Ag, 38.79. Found: C, 34.60; H, 4.30; Ag, 38.75.

cis,trans-1,5-Cyclooctadiene, regenerated by treatment with concentrated ammonium hydroxide of a sample of the silver nitrate adduct which had been stored at –10° for 5 weeks, had an infrared spectrum identical with that of the freshly prepared diene.

(24) Distillation must be carried out carefully since the labile diene polymerized explosively upon warming to 135–150° and rapidly formed a crystalline dimer at room temperature.^{3,4}

(25) Ziegler and Wilms⁵ reported the following physical properties for *cis,trans*-1,5-cyclooctadiene: mp –62°; d_4^{20} , 0.8735, n_D^{20} 1.4933; and for *cis,cis*-1,5-cyclooctadiene: mp –70.1°; d_4^{20} , 0.8811, n_D^{20} 1.4936. These compounds had different Raman⁸ and infrared spectra.⁷

Isomerization of *cis,trans*-1,5-Cyclooctadiene to *cis,cis*-1,5-Cyclooctadiene. A solution of 650 mg of *cis,trans*-1,5-cyclooctadiene in 8.5 ml of carbon tetrachloride containing 8 mg of iodine was stored in the dark at room temperature for 48 hr.¹³ Short-path distillation yielded 421 mg (65%) of *cis,cis*-1,5-cyclooctadiene, n_D^{25} 1.4910 (lit.⁵ n_D^{25} 1.4936). It was shown to be 95% pure by vpc and had an infrared spectrum identical with that of an authentic sample.

***cis,cis*-1,4-Cyclooctadiene.** Amine 2 (3.76 g) was oxidized with 30% hydrogen peroxide according to a procedure described previously.¹⁴ An aliquot of the solution containing 0.49 mmole of amine oxide was added to 115 mg of picric acid in water. The amine oxide picrate (184 mg, 95%) had mp 162.4–163.8°; after recrystallization from ethyl acetate, mp 163.4–164.4°.

Anal. Calcd for $C_{16}H_{22}N_4O_8$: C, 48.24; H, 5.57; N, 14.07. Found: C, 48.15; H, 5.62; N, 14.10.

Decomposition of the remaining amide oxide at 90–105° gave a mixture which was shown by vpc (NMPN, 98°) to consist of *cis,cis*-1,4-cyclooctadiene (91%), *cis,cis*-1,5-cyclooctadiene (6%), and two unknown compounds (2.4 and 0.6%). The mixture was dissolved in 25 ml of pentane, rapidly washed successively with hydrochloric acid, sodium bicarbonate, and water, dried, and distilled through a semimicro column. Preparative vpc (NMPN, 98°) of the distillate (2.173 g, 84%) yielded 610 mg of *cis,cis*-1,4-cyclooctadiene, n_D^{25} 1.4862 (lit.⁵ n_D^{25} 1.4859), 32 mg of *cis,cis*-1,5-cyclooctadiene, and 13 mg of an unidentified compound. The infrared spectrum of *cis,cis*-1,4-cyclooctadiene prepared in this manner was identical with that of the diene prepared by the reaction of *cis*-4-cyclooctenyl bromide⁷ with dimethylamine and purified by gas chromatography.¹¹

Acknowledgment. We thank Mr. G. J. Thomas, Jr., and Mr. C. C. Milionis for obtaining the Raman spectra, Mr. G. L. Goe for preparation of the samples used in determining the nmr spectra, and Mr. R. Bach for a helpful discussion concerning the conformation of the diene. We are grateful to the National Science Foundation for a grant used to purchase the Cary Model 81 Raman instrument.