

Registry No.—Carapanaubine, 1355-16-4; pteropodine, 1366-32-1; isopteropodine, 1351-28-6; rauniticine-*allo*-oxindole-A, 11019-89-9; rauniticine-*epiallo*-oxindole-A, 11019-90-2; rauniticine-*epiallo*-oxindole-B, 11019-91-3; rauvoxine, 11019-92-4; rauvoxinine, 1352-85-8; mitraphylline, 1415-26-5; isomitraphylline, 1415-10-7; formosanine, 1414-95-5; isoformosanine, 11019-77-5.

A Convenient Synthesis of *cis,cis*-1,5-Cyclononadiene

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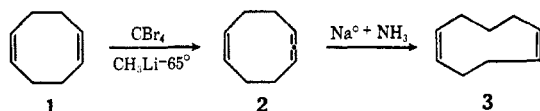
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Our varied interest in the chemistry of medium-ring diene, *cis,cis*-1,5-cyclononadiene (**3**), prompted the search for a convenient synthesis, the results of which are the subject of this report.

1,2,6-Cyclononatriene (**2**) was prepared starting from the easily available *cis,cis*-1,5-cyclooctadiene (**1**) in one step by the method of Untch and co-workers.¹ The treatment of a fourfold excess of *cis,cis*-1,5-cyclooctadiene (**1**) with 1 equiv of carbon tetrabromide and 2 equiv of methyllithium in diethyl ether at *ca.* -65° gave 1,2,6-cyclononatriene (**2**) in 62% yield based on carbon tetrabromide. Its properties corresponded well with those reported.²

We³ had demonstrated earlier that sodium in liquid ammonia reduces allenes to olefins in about 80% yields. Reduction of 1,2,6-cyclononatriene (**2**) using sodium-ammonia provided 84% of the *cis,cis*-1,5-cyclononadiene (**3**). The assignment of the configurations of the double bonds and the structure of diene **3** were established by physical and chemical data.



Gas chromatographic analysis of diene **3** indicated it to be a single substance. The infrared spectrum showed a weak band at 6.04 (C=C stretching) and a strong band in the 13.4–14.2- μ (out-of-plane hydrogen bending) region characteristic of a *cis* double bond and no absorption in the 10.25- μ (out-of-plane hydrogen bending) region which is reported to be characteristic of a *trans* double bond.⁴ Thus the configurations of the two double bonds in diene **3** were established to be *cis,cis*. The ultraviolet spectrum showed only end absorption. Nuclear magnetic resonance showed a multiplet at τ 4.65 corresponding to four olefinic protons.

The amount of unsaturation in diene **3** was estimated by hydrogenation. The hydrogenation value was found to be 2.02. The hydrogenated product was

shown to be cyclononane. The positions of the double bonds were established by ozonolysis followed by oxidation and esterification which gave only dimethyl succinate and dimethyl glutarate as products.

The molecular model construction of both *cis-cis* and *cis-trans* isomers suggests that the latter is more strained than the former. Probably this may be one of the reasons for the stereochemical course of the sodium-ammonia reduction of allene **2** to diene **3**.

Experimental Section

1,2,6-Cyclononatriene (2).—From 54 g (0.50 mole) of *cis,cis*-1,5-cyclooctadiene (**1**), 41.5 g (0.125 mole) of carbon tetrabromide, and 154.5 ml (0.260 mole) of methyllithium in diethyl ether, 9.3 g (62%) of 1,2,6-cyclononatriene (**2**), bp 61° (13 mm), n_D^{25} 1.5212 (lit.² bp 61° at 13 mm, n_D^{25} 1.5216), was prepared by the procedure described by Untch and co-workers.¹ The identity was established by comparison of vapor phase chromatographic retention times and infrared spectra with those of an authentic sample.

***cis,cis*-1,5-Cyclononadiene.**—A 1-l. three-necked flask was fitted with an inlet tube for ammonia gas and a large Dry Ice reflux condenser leading to a mercury bubbler. About 250 ml of commercial anhydrous ammonia was distilled directly into the flask from the tank without purification. Sodium (9.2 g, 0.40 atom) was added in the form of small pieces and the mixture was stirred for 15 min. A solution of 12 g of 1,2,6-cyclononatriene (**2**) (0.10 mole) in 100 ml of anhydrous ether was added dropwise with stirring. After stirring for *ca.* 2 hr following the completion of addition, the excess of sodium was decomposed by adding ammonium chloride in small quantities. The product was isolated by adding water to the residue remaining after the evaporation of ammonia and extraction of the product with ether. The combined extracts were washed twice with water and dried over anhydrous magnesium sulfate. Distillation of the residue remaining after the removal of the solvent through an efficient column gave 10 g (84%) of *cis,cis*-1,5-cyclononadiene (**3**): bp 56° (17 mm); n_D^{25} 1.4927.

Anal. Calcd for C₉H₁₄: C, 88.45; H, 11.54. Found: C, 88.54; H, 11.60.

Analysis by vapor phase chromatography (Aerograph A-90-P3) on 0.25 in. \times 5 ft silver nitrate-Carbowax and 0.25 in. \times 8 ft Ucon columns indicated **3** to be a single substance. The infrared spectrum (Perkin-Elmer Infracord 137 spectrophotometer) of the neat sample gave the expected strong band in the 13.4–14.2- μ region (*cis* double band) and an nmr spectrum (Varian A-60 spectrometer on 20% solution in carbon tetrachloride, using tetramethylsilane as internal standard) gave resonance signal, a multiplet at τ 4.65 (4 H) for olefinic protons.

Hydrogenation.—A solution of 200 mg (1.64 mmoles) of *cis,cis*-1,5-cyclononadiene (**3**) in methanol was reduced with 100 mg of Pd-C catalyst in a microhydrogenator. The uptake of hydrogen ceased after 2.02 mole equiv had been absorbed. The usual work-up procedure afforded 120 mg of cyclononane. Authenticity was established by comparison of vapor phase chromatographic retention times and superimposable infrared spectra using an authentic sample of cyclononane.

Ozonation.—A solution of 3 g (0.04 mole) of *cis,cis*-1,5-cyclononadiene (**3**) in 35 ml of carbon tetrachloride was ozonized at -30° by the general method. To this mixture was added 25 ml of 10% sodium hydroxide. The flask was fitted with a reflux condenser and gently warmed until a vigorous reaction set in (*Caution!*). After the spontaneous reaction had ceased (20–30 min), the reaction mixture was heated under reflux for 6 hr. The aqueous layer was acidified and was subjected to continuous hot ether extraction for 48 hr. The ether solution was dried and the solvent distilled to give 3.7 g (60%) of acid residue. This was esterified using diazomethane in ether and worked up in the usual manner to obtain 4.1 g (91%) of mixture of esters. Vapor phase chromatographic examination of the mixture on a 0.25 in. \times 5 ft polyethylene glycol succinate column revealed the presence of only two components in about equal amounts. These were separated and identified as dimethyl succinate and dimethyl glutarate using authentic samples by vapor phase chromatography and infrared spectroscopy.

Registry No.—**3**, 14255-64-2.

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