complex multiplet entered at approximately τ 7.85. The olefinic and methine chemical shifts and splittings were unique for all of the compounds encountered in this study and were very useful for both qualitative and quantitative analysis. The ratio of methylene–olefin–methine protons found was 6.1:2.0:1.0 (theory, 6:2:1).

1-Cyanocyclohexene was synthesized according to a literature procedure.[9] The olefinic proton appeared as a multiplet (at least seven lines) in the nmr spectrum centered at τ 3.42. The methylene protons appeared as two distinct, equal-intensity multiplets centered at τ 7.85 and 8.32.

Dehydrochlorination and Disproportionation of 4-Chloro-4-cyanocyclohexene (in *t*-Butyl Alcohol).—To a nitrogen-blanketed, stirred solution of 0.63 mole of sodium *t*-butoxide, prepared from 14.5 g (0.63 g-atom) of sodium and 1250 ml of *t*-butyl alcohol, was slowly added a solution of 89.1 g (0.63 mole) of 4-chloro-4-cyanocyclohexene in 300 ml of *t*-butyl alcohol at a rate sufficient to maintain the temperature of the reaction mixture at 20–30° (the reaction was exothermic). After addition was complete, the reaction mixture was heated under reflux for 3 hr and then allowed to cool to room temperature. The sodium chloride formed was collected by filtration, washed with ether, and then dried (36.8 g, 100%). Evaporation of the ether afforded a small amount of crystalline residue identified as benzamide *via* infrared and mixture melting point (undepressed) with an authentic sample. The filtrate from the sodium chloride isolation step was treated with water. The resulting mixture was extracted with methylene chloride. This solution was then washed with water and dried over anhydrous sodium sulfate. Fractional distillation of the residue, after evaporation of methylene chloride *in vacuo*, afforded only one fraction (27 g, 40.8%), bp 43–44° (2 mm); no attempt was made to maximize this.

The infrared absorption of this product showed two nitrile bands at 2210 and 2230 cm^{-1}, as well as typical absorptions for monosubstituted aromatic compounds. Analysis of the products *via* glpc on columns A, B, and C showed three peaks which were identified as benzonitrile (25.7%), a mixture of 1- and 4-cyanocyclohexene (24.7%) (these compounds did not separate on any of the glpc columns investigated), and 2-cyano-1,3-cyclohexadiene (41.8%). The identity of benzonitrile and the isomeric cyanocyclohexenes *via* glpc was based on comparisons of retention times with those of authentic samples and analysis of synthetic mixtures of these compounds. The identity of 2-cyano-1,3-cyclohexadiene was based on nmr and isolation of the tetracyanoethylene Diels–Alder adduct (see below). The spectrum of the reaction mixture clearly showed benzonitrile (multiplet at τ 2.41). The olefin region was complex. Rudiments of both the 1- and 4-cyanocyclohexene olefinic proton resonances were recognizable but both were broadened and contained lines not present in the pure compounds. A relatively intense multiplet not contained in either and centered at 3.95 was present. Since 2-cyano-1,3-cyclohexadiene would be expected to have three distinct olefinic resonances, this is taken as strong evidence that the strong glpc peak was attributable to this compound. As further evidence of this, the dehydrochlorination reaction was repeated exactly as described above except at room temperature throughout. Under these conditions sodium chloride is readily formed. Analysis of the reaction mixture (after 25 hr) *via* glpc showed only starting 4-chloro-4-cyanocyclohexene and the peak attributed to 1-cyano-1,3-cyclohexadiene (32.5%). No benzonitrile or cyanocyclohexene peaks were detectable. Interestingly, however, if the room-temperature reaction was allowed to proceed for prolonged periods (*e.g.*, 1 week), ample evidence (glpc) of disproportionation was detectable. Hence, the cyanocyclohexadiene disproportionation not only occurred in *t*-butyl alcohol but does so, albeit slowly, at nominal temperatures.

Preparation of the Tetracyanoethylene Adduct of 2-Cyano-1,3-cyclohexadiene.—A 5.4-g portion of the reaction mixture obtained from treatment of 4-chloro-4-cyanocyclohexene with sodium *t*-butoxide in *t*-butyl alcohol (bp 43–44° (2 mm)) was mixed with 3.8 g (0.03 mole) of tetracyanoethylene and 0.1 g of hydroquinone. This combination was heated in a sealed tube at 105–110° for 3 hr. The dark reaction mixture was allowed to cool to room temperature slowly (over a period of 2 hr) and the solid precipitate which formed was collected *via* filtration. The precipitate was washed with cold toluene and cold carbon tetrachloride and then dried *in vacuo* (2.7 g, pale yellow crystals). Recrystallization from benzene gave a white crystalline solid, mp 214–215° (sealed tube). Bicyclo[2.2.2]oct-5-ene-2,2,3,3,5-pentacarbonitrile was reported[4] to melt at 214–215°.

Anal. Calcd for $C_{13}H_7N_5$: C, 66.94; H, 3.03; N, 30.03. Found: C, 66.52; H, 2.95; N, 30.48.

Only one peak was obtained on glpc analysis (Carbowax 20M (20%) on Chromosorb W at 160° (retention time, 19.8 min). The nmr spectrum in hexadeuteriodimethyl sulfoxide showed only one olefinic hydrogen (multiplet, at least three lines, at 3.08). The presence of 1-cyano-1,3-cyclohexadiene was not established; however, small amounts would not have been detected by the above procedure.

Disproportionation of 2-Cyano-1,3-cyclohexadiene.—A portion of the reaction product isolated above (containing 2-cyano-1,3-cyclohexadiene, benzonitrile, and the isomeric cyanocyclohexenes) was treated an additional 6 hr with sodium *t*-butoxide (equimolar, based on the cyclohexadiene derivative) in refluxing *t*-butyl alcohol. At the end of this period, the only products detectable by glpc were benzonitrile and 1- and 4-cyanocyclohexene (41 and 59%, respectively, as determined from nmr). All peaks attributable to the cyclohexadiene completely disappeared in the nmr spectrum as well and only olefinic proton resonances attributable to the two isomeric monoenes described above were found (these were superimposable in every detail with those of the known reference compounds).

Dehydrochlorination and Disproportionation in Pyridine.—A solution of 4-chloro-4-cyanocyclohexene (7.08 g, 0.05 mole) in 3.96 g (0.05 mole) of pyridine (dried over barium oxide) was protected from atmospheric moisture and allowed to reflux for 20 hr. The crude reaction mixture was directly analyzed *via* glpc. All of the original chloro compound had disappeared and the products derived from it were benzonitrile (38.9%), 2-cyano-1,3-cyclohexadiene (24.5%), and a mixture of 1- and 4-cyanocyclohexene (36.6%).

Registry No.—**1**, 14210-94-7; **2**, 100-47-0; **3**, 100-45-8; **4**, 1855-63-6; CCC, 14210-93-6; bicyclo[2.2.2]oct-5-ene-2,2,3,3,5-pentacarbonitrile, 7149-13-5.

Acknowledgment.—We are indebted to Professor William Huntsman, Department of Chemistry, Ohio University, for obtaining all of the nmr spectra discussed in this paper.

(9) S. M. McElvain and R. E. Starr, Jr., *J. Am. Chem. Soc.*, **77**, 4571 (1955).

Mass Spectrometry and the Stereochemistry of the Pentacyclic Oxindole Alkaloids

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Following the elucidation of the stereochemistry of the pentacyclic oxindole alkaloids by a combination of spectral, chemical, and kinetic methods,[1] it was decided to carry out a comparative study of the mass spectra of these compounds in the hope that some correlations could be established between stereochemistry and intensity of fragment ions.

The mass spectral fragmentation patterns for some of the pentacyclic oxindoles have previously been reported and the mechanism of formation of the principal ions has been supported by deuterium labeling. It has been shown that the three most intense ions in the mass spectra of the pentacyclic oxindoles arise from the cleavages seen in Scheme I.[2]

(1) M. Shamma, R. J. Shine, I. Kompis, T. Sticzay, F. Morsingh, J. Poisson, and J. L. Pousset, *J. Am. Chem. Soc.*, **89**, 1739 (1967).

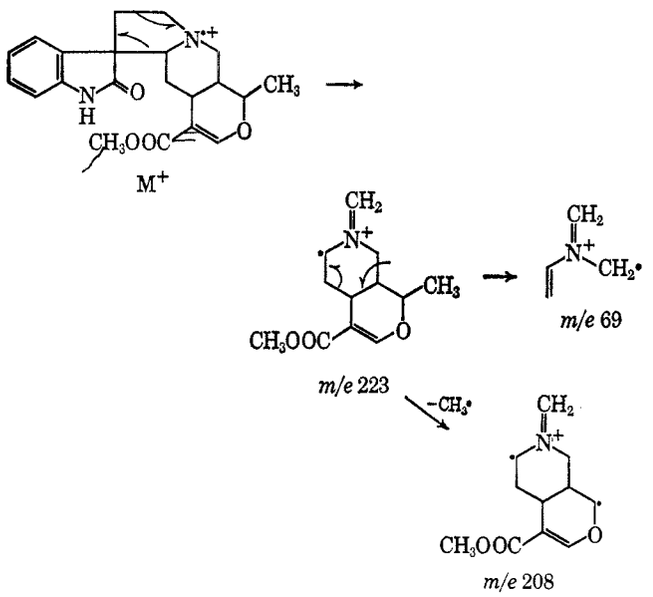
(2) B. Gilbert, J. A. Brissolese, N. Finch, W. I. Taylor, H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *ibid.*, **85**, 1523 (1963).

TABLE I

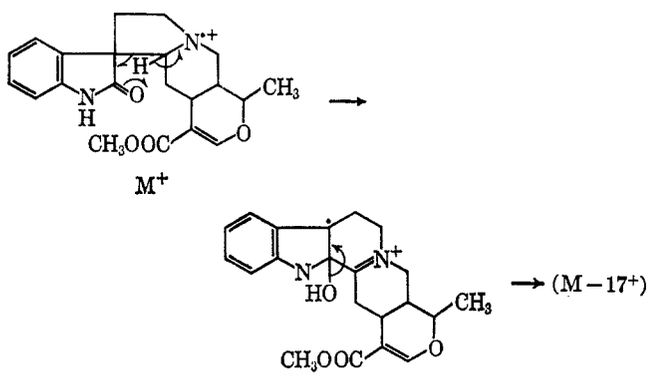
MASS SPECTRAL PATTERNS OF PENTACYCLIC OXINDOLES AT 70 EV

	% $\Sigma_{50} \times 10^3$					
m/e	M	223	69	208	M − 17	180
allo-α-C-19-Methyl						
Carapanaubine	40	60	38	27	3.1	20
Pteropodine	53	66	98	20	4.4	22
Isopteropodine	45	76	91	19	5.2	21
allo-β-C-19-Methyl						
Rauniticine-*allo*-oxindole-A	49	124	27	32	4.0	7.1
epiallo-β-C-19-Methyl						
Rauniticine-*epiallo*-oxindole-A	42	63	85	12	2.6	2.2
Rauniticine-*epiallo*-oxindole-B	41	80	70	18	3.7	4.3
epiallo-α-C-19-Methyl						
Rauvoxine	31	42	41	32	1.9	20
Rauvoxinine	114	34	40	39	7.7	26
Normal α-C-19-methyl						
Mitraphylline	57	139	72	18	5.6	3.9
Isomitraphylline	51	95	75	15	3.9	2.6
Normal β-C-19-methyl						
Formosanine	40	111	73	14	3.6	8.8
Isoformosanine	39	39	55	11	3.8	7.5

SCHEME I

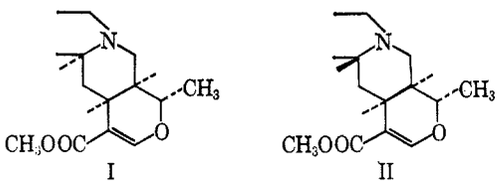


Another fragmentation is the loss of 17 mass units from the molecular ion in the following process.

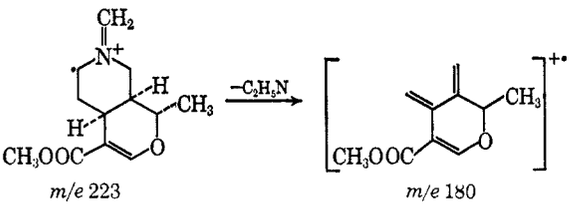


To compare the intensities of a given ion in the spectra of a series of stereoisomeric compounds, it is preferable to express an intensity value as a percentage of the total ion intensity for any one spectrum. The ion intensities in the present work were, therefore, expressed as per cent of Σ_{50}, signifying the value for the intensity of a given peak relative to the sum of the intensities for all peaks from *m/e* 50 up to the molecular ion.

As can be seen from Table I, no reliable assignment of stereochemistry can be made on the basis of the intensities of the peaks for the molecular ion and for $(M - 17)^+$, or for those at *m/e* 223, 69, and 208. On the other hand, the peak at *m/e* 180 does have stereochemical import. Oxindole alkaloids with *allo* or *epiallo* configurations and α-C-19-methyl groups (*e.g.*, I or II) show a $\%\Sigma_{50} \times 10^3$ between 20 and 26 at *m/e* 180. This same peak is much less intense in all of the other stereochemical groups, the corresponding values lying between 2 and 9.



The nature of the *m/e* 180 peak is indicated by the fact that it is not shifted to higher masses when methoxyl substituents are present in ring A, so that it must originate from rings D and E. Additionally, the presence of a metastable peak at *m/e* 145 only in the pentacyclic oxindoles of types I and II indicates that the *m/e* 180 peak may arise from fragmentation of the *m/e* 223 ion since $180^2/223 = 145$.



In conclusion, therefore, the *m/e* 180 peak can be used to recognize pentacyclic oxindole alkaloids of types I and II, such as carapanaubine, pteropodine, isopteropodine, rauvoxine, and rauvoxinine.[3,4]

(3) The values quoted in Table I were obtained at 70 ev. The spectra at 20 ev were not substantially different from those at 70 ev.

(4) This research was supported by Grant GP-6394 from the National Science Foundation.

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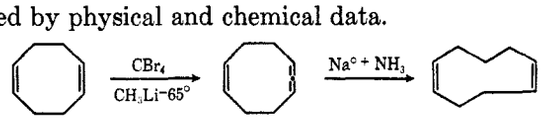
Our varied interest in the chemistry of medium-ring diene, *cis,cis*-1,5-cyclononadiene (**3**), prompted the search for a convenient synthesis, the results of which are the subject of this report.

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]

We[3] 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.



1 **2** **3**

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**.

(1) K. G. Untch, D. J. Martin, and N. T. Castellucci, *J. Org. Chem.*, **30**, 3572 (1965).
(2) L. R. Skattebøl, *Acta. Chem. Scad.*, **17**, 1683 (1963).
(3) D. Devaprabhakara and P. D. Gardner, *J. Am. Chem. Soc.*, **85**, 648 (1963).
(4) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, **74**, 3643 (1952).

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^{25}D 1.5212 (lit.[2] bp 61° at 13 mm, n^{24}D 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^{22}D 1.4927.

Anal. Calcd for C_9H_{14}: 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. × 5 ft silver nitrate–Carbowax and 0.25 in. × 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. × 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.