[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Unsaturated Amines. I. Determination of the Proximity of Nitrogen to a Double Bond by Infrared Absorption Spectra[1,2]

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The infrared absorption spectra have been determined for a series of α,β- and β,γ-unsaturated tertiary amines and their salts. The absorption maximum in the double bond stretching region does not shift appreciably in going from a β,γ-unsaturated amine to its salt. By contrast, a decided shift (*ca.* 20–50 cm.$^{-1}$) toward higher frequency is observed in going from an α,β-unsaturated amine (enamine) to its salt, corresponding to the structural transformation: $\gt C{=}\underset{|}{C}{-}N\lt \longrightarrow \gt CH{-}\underset{|}{C}{=}\overset{+}{N}\lt$. A method is thus provided for differentiating between an α,β-unsaturated tertiary amine and one in which the double bond is further removed from the nitrogen.

An important problem frequently encountered in the determination of the structure of alkaloids is the location of unsaturation. Of greatest interest is the fixing of the position of a double bond with reference to a basic nitrogen. The same problem exists in synthetic work with certain nitrogen-containing organic compounds. It would therefore be useful to devise a method whereby one could distinguish at least between α,β-unsaturated amines (tertiary) and those in which the double bond is further removed from the nitrogen. Aside from the usual chemical methods which can be applied to any structural situation, the only well-tested method is that of Adams and Mahan,[3] which relies upon the fact that vinyl tertiary amines are more basic than the corresponding saturated compounds. One limitation of the method lies in the necessity of determining the basicity of both the unsaturated and the saturated amine in order to reach a safe conclusion as to whether or not the double bond in the unsaturated molecule is α,β to the nitrogen.

It is possible to detect the same structural feature by means of comparative ultraviolet absorption spectra, but this method has not been applied extensively: Braude[4] reported the wave length of the ultraviolet maximum of 1-butenylpiperidine as 228 mμ, and Herr and Heyl[5] have used maxima in this region of the ultraviolet to characterize the α,β-unsaturated amines obtained on condensation of certain steroidal aldehydes and ketones with piperidine and pyrrolidine. In the second paper[6] in our series will be found ultraviolet absorption data for several groups of α,β-unsaturated, β,γ-unsaturated, and saturated amines, and a delineation the scope of the ultraviolet spectral method of differentiation. The present paper is devoted to the infrared method.

The determination of the infrared absorption spectra of an unsaturated amine and its salt generally provides a decision as to the proximity of nitrogen and the double bond, as indicated by the data in Table I. Thus, the representative substituted Δ^2-tetrahydropyridines have an absorption maximum at about 1650 cm.$^{-1}$, whereas their perchlorate salts absorb at about 1685 cm.$^{-1}$. A definite shift to higher frequency is also observed in going from the representative substituted Δ^2-pyrrolines to the corresponding salts. By contrast, the β,γ-unsaturated amines listed in Table I: 1-ethyl-Δ^3-tetrahydropyridine, 1-ethyl-2,5-dimethyl-Δ^3-pyrroline, 1-allylpiperidine and 1-allylpyrrolidine, if they absorb radiation in the 6 μ region, have maxima at approximately the same frequency as do their salts. The shift toward higher frequency exhibited by the salts of the α,β-unsaturated amines is accompanied by an intensification of the absorption maximum. The salts of the β,γ-unsaturated amines exhibit very weak absorption. The same behavior has been noted[7] for unsaturated tertiary amines of more complicated structure, *i.e.*, bicyclic and tetracyclic types.

TABLE I

INFRARED ABSORPTION MAXIMA, CM.$^{-1}$

Tetrahydropyridines	Base[a]	Perchlorate[b]
1-Ethyl-Δ^3-tetrahydro	1662	1664
1,2-Dimethyl-Δ^2-tetrahydro	1650	1686
1-*n*-Butyl-2-methyl-Δ^2-tetrahydro	1649	1684
N-Allyl compounds		Hydrobromide
1-Allylpiperidine	1644	1646
1-Allylpyrrolidine	1644	1637
Pyrrolines		Hydriodide
1-Ethyl-2,5-dimethyl-Δ^3	..[c]	..[c]
		Perchlorate
1,2-Dimethyl-Δ^2	[d]	1699
1-*n*-Butyl-2-methyl-Δ^2	1639	1685
1-Methyl-2-*n*-propyl-Δ^2	1665(1701)	1685
1-Methyl-2-*n*-butyl-Δ^2	1665(1700)	1686

[a] Obtained on a thin film (0.013 or 0.02 mm.) of the analytically pure liquid unless otherwise stated. [b] Obtained on a Nujol mull. [c] No appreciable absorption in the 1500–1800 cm.$^{-1}$ region. [d] Not determined.

The infrared maxima of the unsaturated amines (Table I) are in the frequency range characteristic

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[1] This investigation was supported in part by a grant from the Research Board of the University of Illinois.

[2] Presented at the 5th Summer Seminar in the Chemistry of Natural Products at the University of New Brunswick, Fredericton, N. B., Canada, August 19, 1953.

[3] R. Adams and J. E. Mahan, THIS JOURNAL, **64**, 2588 (1942).

[4] E. A. Braude, *Ann. Reps. Chem. Soc.*, **42**, 105 (1945); see also K. Bowden, E. A. Braude, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 45 (1946); K. Bowden, E. A. Braude and E. R. H. Jones, *ibid.*, 948 (1946).

[5] M. E. Herr and F. W. Heyl, THIS JOURNAL, **74**, 3627 (1952); F. W. Heyl and M. E. Herr, *ibid.*, **75**, 1918 (1953).

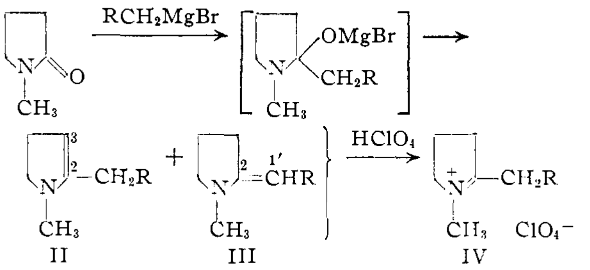
[6] N. J. Leonard and D. M. Locke, *ibid.*, in press.

[7] V. W. Gash, Ph.D. Thesis, University of Illinois, 1952.

of C=C stretching,[8] and are more dependent upon substitution, ring size and symmetry considerations than upon position relative to the tertiary nitrogen. The intense maxima observed for the salts[9] of the α,β-unsaturated amines lie in a frequency range which has been associated with C=N stretching. Thus, acetoxime[10a] absorbs at 1683 cm.$^{-1}$ and phenaceturiminomethyl ether hydrochloride, at 1694 cm.$^{-1}$.[10b] Moreover, Goulden[11] has shown that the presence of a positive charge on the nitrogen atom gives rise to a higher C=N frequency value, for example, by 13 cm.$^{-1}$ in the case of 2-phenyl-N-piperonylidene-ethylamine and its methiodide. Also, Edwards, Clarke and Douglas,[12] in a current investigation, have assigned the band at 1682 cm.$^{-1}$ observed for the anhydronium perchlorate of 17-hydroxylupanine to the $\rangle C=\overset{+}{N}\langle$ grouping.[13]

It appears from infrared assignments that the shift toward higher frequency observed in going from an α,β-unsaturated amine to its salt is best explained by the structural transformation: $\rangle C=\underset{|}{C}-N\langle \longrightarrow \rangle CH-\underset{|}{C}=\overset{+}{N}\langle$ (I),[14] which has been postulated by Adams and Mahan[3] to account for the strong basicity of vinyl tertiary amines, Such a quaternary salt would be capable of resonance stabilization, $\rangle C=\overset{+}{N}\langle \longleftrightarrow \rangle\overset{+}{C}-N\langle$, and might be expected to undergo nucleophilic reactions at carbon, similar to those at the carbon of a carbonyl group. Transformation to the quaternary salt type would not be possible for those unsaturated amines wherein the double bond is further removed than the $\Delta^{\alpha,\beta}$-location to nitrogen.

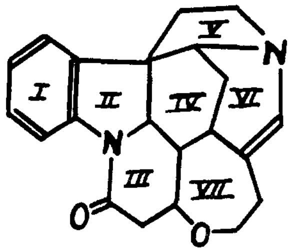
Evidence in support of the quaternary salt form I is also to be found in the infrared data for the Δ^2-pyrrolines having an alkyl group other than methyl at the 2-position and the salts of these pyrrolines (Table I). 1-Methyl-2-*n*-propyl-Δ^2-pyrroline exhibits infrared peaks at 1665 and 1701 cm.$^{-1}$, whereas the perchlorate salt has a sole maximum (in this region) at 1685 cm.$^{-1}$. Similarly, 1-methyl-2-*n*-butyl-Δ^2-pyrroline has maxima at 1665 and 1701 cm.$^{-1}$; the perchlorate, a single maximum at 1686 cm.$^{-1}$. The double absorption observed for the free bases can be explained by the concept that they are not pure Δ^2-pyrrolines, as originally supposed.[3,15,16] The method of synthesis employed for IIa and IIb: addition of a Grignard reagent to 1-methyl-2-pyrrolidone followed by acid hydrolysis, basification, steam distillation and extraction, would be expected to produce some of the isomeric 1-methyl-2-alkenylpyrrolidine in each case (IIIa, IIIb), so that the products can be mixtures of the $\Delta^{2,3}$- and $\Delta^{2,1'}$-compounds.



(a, R = C_2H_5; b, R = *n*-C_3H_7)

The single absorption of the perchlorate is taken as evidence that this is a unique salt (therefore, IV) formed from the mixture of isomeric α,β-unsaturated bases (II and III).[17] The amine which is recovered from the salt by basification and extraction shows the two absorption maxima observed originally.

An ideal test of the hypothesis that formation of a quaternary salt type (I) is responsible for the shift toward higher-frequency infrared absorption (Table I) would be to observe the behavior of an α,β-unsaturated tertiary amine–salt combination, wherein structure I is sterically incapable of existence and the salt must be of the normal type (Ia). Such a test is provided by neostrychnine (V), an



V

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[8] P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch and G. W. Wood, *J. Chem. Soc.*, 2402 (1951); N. Sheppard and D. M. Simpson, *Quart. Rev.*, **6**, 1 (1952); *e.g.*, see also American Petroleum Institute, "Catalog of Infra-Red Spectrograms," National Bureau of Standards, curve no. 697.

[9] The perchlorate salts were used wherever possible because they are easily prepared, they are usually not hygroscopic, in contrast to the hydrochlorides and hydrobromides, and the anion does not absorb above 1200 cm.$^{-1}$ (H. Cohn, *J. Chem. Soc.*, 4282 (1952)).

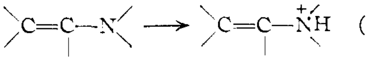
[10] (a) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 182; (b) p. 184. See also pp. 5, 20.

[11] J. D. S. Goulden, *J. Chem. Soc.*, 997 (1953).

[12] D. E. Edwards, F. H. Clarke and B. Douglas, *Can. J. Chem.* **32**, 235 (1953). The author wishes to thank Dr. Léo Marion of the Canadian National Research Council for making this article available in manuscript form.

[13] B. Witkop and J. B. Patrick, THIS JOURNAL, **75**, 4474 (1953); B. Witkop, J. B. Patrick and H. M. Kissman, *Ber.*, **85**, 949 (1952).

[14] The alternative possibility, that normal salt formation


(Ia)

$$\rangle C=\underset{|}{C}-N\langle \longrightarrow \rangle C=\underset{|}{C}-\overset{+}{N}H\langle \quad \text{(Ia)}$$

involving a change in polarity of the C=C bond, accounts for the shift in frequency and increase in intensity of absorption, is less attractive for a number of reasons, including chemical evidence which will be presented in later publications. The intensity of the band for the salt is much greater than that normally observed for C=C, but commensurate with that associated with C=O stretching. The shift toward *higher* frequency is the reverse of that to be expected as a result of increased polarization of a (C=C) double bond. Thus A. D. Walsh (*Trans. Farday Soc.*, **43**, 158 (1947)) has shown that as the polarity of a bond increases, so the bond is weakened. In particular, as the polarity of the carbonyl bond increases, so its stretching force constant and bond energy decrease. Interpreted in terms of infrared absorption, this corresponds to a lower frequency for the C=O stretching band (R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2828 (1952)), and presumably also for the C=C stretching band, although the latter case has not yet been investigated thoroughly in a series which excludes conjugative influences.

[15] L. C. Craig, *ibid.*, **55**, 295 (1933).

[16] L. C. Craig, *ibid.*, **55**, 2543 (1933).

[17] It would be expected that synthesis directed toward a 2-methyl-substituted pyrroline[3] would lead to a product in which the Δ^2-pyrroline predominates over the isomer with an exocyclic methylene (*cf.* the single maximum for 1-*n*-butyl-2-methyl-Δ^2-pyrroline).

α,β-unsaturated amine whose weak basicity[18] has been ascribed to steric resistance to double bond $\left(\gt C{=}\overset{+}{N}\lt\right)$ formation at the bridgehead of the tricyclic moiety comprising rings IV, V and VI. A comparison of the infrared spectra of neostrychnine and its perchlorate, as determined in the mull (Fig. 1), reveals that the salt does *not* absorb at appreciably higher frequency than the free base, in marked contrast to the behavior of the other α,β-unsaturated amines considered in this study.

Acknowledgment.—We wish to thank Mr. Allan S. Hay, Mr. Richard W. Fulmer and Dr. Stefano Chiavarelli for their kind assistance. The author is indebted to Dr. R. B. Woodward, Harvard University, for a sample of neostrychnine.

Experimental[19]

Absorption Spectra.—The infrared absorption spectra were obtained with Perkin–Elmer automatic recording infrared spectrometers, Models 12B and 21. The estimated error of the data in Table I is ±3 cm.$^{-1}$.

Amines and their Salts.—The preparation and properties of the perchlorate (and in one case, hydriodide) salts are described in Table II. Those amines for which references are indicated were prepared by methods previously described. Samples of the amines submitted for spectral analysis were microanalytically pure as obtained by a final vacuum distillation under nitrogen. 1-Allylpiperidine[3] and 1-allylpyrrolidine[23,24] failed to form crystalline perchlorates, so that the crystalline but hygroscopic hydrobromides were used for spectral analysis of the salt form (Table I).

TABLE II

PERCHLORATE SALTS

Amine	Solvent for Formation[a]	Solvent for Recrystal.	Crystal form[b]	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1-Ethyl-Δ^3-tetrahydropyridine	*i*-PrOH	EtOH–pet. ether	Prisms	66–68	$C_7H_{14}ClNO_4$	39.72	39.62	6.67	6.80	6.62	6.36
1,2-Dimethyl-Δ^2-tetrahydropyridine[3]	EtOH	EtOH–Et$_2$O	Needles	227[c]	$C_7H_{14}ClNO_4$	39.72	39.48	6.67	6.81	6.62	6.81
1-*n*-Butyl-2-methyl-Δ^2-tetrahydropyridine[3,20]	*i*-PrOH	EtOAc	Needles	136–137	$C_{10}H_{20}ClNO_4$	47.33	47.62	7.94	8.10	5.52	5.57
1-Ethyl-2,5-dimethyl-Δ^3-pyrroline[21]	EtOH–Et$_2$O	EtOH–Et$_2$O	Prisms[d]	246.5–247.5	$C_8H_{16}IN$	37.96	38.17	6.37	6.38	5.53	5.43
1,2-Dimethyl-Δ^2-pyrroline[22]	EtOH	EtOH	Plates	235.5–236.5	$C_6H_{12}ClNO_4$	36.46	36.52	6.12	5.82	7.09	6.92
1-*n*-Butyl-2-methyl-Δ^2-pyrroline[3]	MeOH–Et$_2$O	*i*-PrOH–Et$_2$O	Needles	99.5–101	$C_9H_{18}ClNO_4$	45.09	44.83	7.57	7.61	5.84	5.90
1-Methyl-2-*n*-propyl-Δ^2-pyrroline[15]	*i*-PrOH–Et$_2$O	EtOAc–MeOH	Needles	97–98	$C_8H_{16}ClNO_4$	42.57	42.71	7.15	7.22	6.21	6.21
1-Methyl-2-*n*-butyl-Δ^2-pyrroline[3,15]	MeOH	EtOH–Et$_2$O	Needles	117–118	$C_9H_{18}ClNO_4$	45.09	45.12	7.57	7.78	5.84	6.10

[a] The amine was dissolved in this solvent and 65% perchloric acid was added until the mixture was acidic to congo red. [b] Colorless. [c] With decomposition. [d] This is the hydrogen iodide salt.

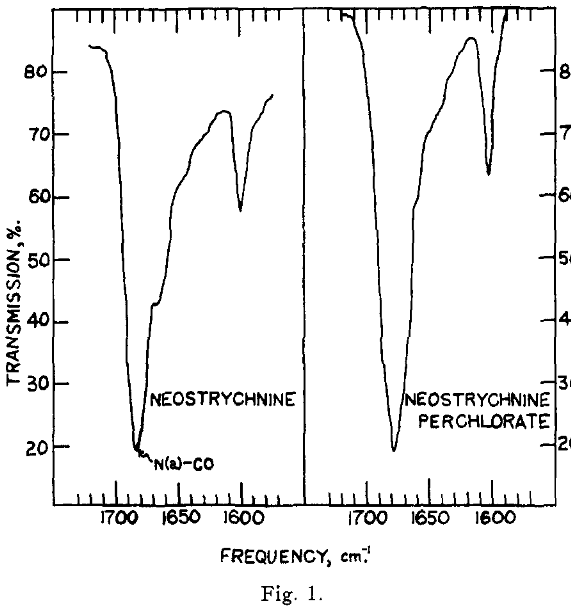


Fig. 1.

1-Ethyl-4-piperidinol.—The reduction method used by Craig and Tarbell[25] for the 1-methyl compound was most satisfactory. A solution of 16.4 g. (0.127 mole) of 1-ethyl-4-piperidone[26–28] in 200 ml. of ethanol absorbed the theoretical amount of hydrogen within 1 hour upon reduction in the presence of platinum oxide catalyst. The catalyst was removed by filtration and the filtrate was evaporated *in vacuo*. The product was distilled at 108–109° (15 mm.); n^{20}_D 1.4800 (reported[27] b.p. 102–103° (15 mm.), $n^{19.8}_D$ 1.4796), d^{20}_4 0.969, MR_D calcd. 37.56, found 37.88; yield 15.3 g. (92%). The **hydrochloride** crystallized from ethanol–ether as colorless prisms, m.p. 168–170° dec.

Anal. Calcd. for $C_7H_{16}ClNO$: C, 50.75; H, 9.74; N, 8.46. Found: C, 50.57; H, 9.59; N, 8.56.

A sample of 1-ethyl-4-piperidinol treated consecutively with thionyl chloride, then methanolic sodium methoxide, gave a low yield of 1-ethyl-Δ^3-tetrahydropyridine, isolated as the perchlorate, m.p. 66–68° (see below and Table II).

Treatment of the molten 1-ethyl-4-piperidinol hydrochloride with dry hydrogen chloride, bubbled through the melt, gave a very low yield of **1-ethyl-4-chloropiperidine**, isolated as the **picrate**, prisms from ethanol, m.p. 164–166°.

Anal. Calcd. for $C_{13}H_{17}ClN_4O_7$: C, 41.44; H, 4.55; N, 14.87. Found: C, 41.88; H, 4.43; N, 14.62.

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[18] V. Prelog and O. Häfliger, *Helv. Chim. Acta*, **32**, 1851 (1949).

[19] All melting points are corrected. We are indebted to Miss Emily Davis, Mrs. Katherine Pih, Mrs. Esther Fett and Mr. Joseph Nemeth for microanalyses, and to Miss Elizabeth M. Petersen, Miss Helen Miklas and Mrs. Rosemary F. Hill for determination of the absorption spectra.

[20] E. Ochiai, K. Tsuda and J. Yokayama, *Ber.*, **68**, 2291 (1935).

[21] See N. J. Leonard, J. W. Curry and J. J. Sagura, THIS JOURNAL, **75**, 6249 (1953), for preparation of 1-ethyl-2,5-dimethylpyrrole and -pyrrolidine.

[22] A sample of 1,2-dimethyl-Δ^2-pyrroline perchlorate was kindly provided by R. Adams and J. E. Mahan.

[23] Yu. K. Yur'ev, L. E. Aleksandrov, A. V. Arbatskiĭ, V. M. Karataev, I. K. Korobitsyna and M. A. Pryanishnikova, *Zhur. Obshchei Khim.*, **19**, 1730 (1949).

[24] J. Braun and E. Miller, *Ber.*, **50**, 292 (1917).

[25] L. E. Craig and D. S. Tarbell, THIS JOURNAL, **71**, 465 (1949).

[26] S. M. McElvain, *ibid.*, **46**, 1721 (1924).

[27] N. W. Bolyard and S. M. McElvain, *ibid.*, **51**, 922 (1929).

[28] R. C. Fuson, W. E. Parham and L. J. Reed, *ibid.*, **68**, 1239 (1946).

1-Ethyl-4-acetoxypiperidine.—To a stirred solution of 15 g. (0.116 mole) of 1-ethyl-4-piperidinol in 100 ml. of dry benzene was added 15 g. (0.147 mole) of acetic anhydride. The solution was heated under reflux for 1 hour, then poured over crushed ice. Sodium carbonate was added in excess, and the product was isolated by ether extraction. The solvents were removed, and the residue was distilled at 105–109° (26 mm.); $n^{20}\text{D}$ 1.4545, d^{20}_4 0.979, yield 15.8 g. (80%).

Anal. Calcd. for $C_9H_{17}NO_2$: C, 63.13; H, 10.01; MR_D, 47.33. Found: C, 63.17; H, 10.20; MR_D, 47.69.

Pyrolysis of 1-ethyl-4-acetoxypiperidine was carried out in an apparatus[29–32] consisting of a Pyrex tube, 50 × 2 cm., packed with glass beads for a height of 26 cm., heated with an electric furnace for a height of 30 cm. at 485 ± 10°. The system was initially flushed with nitrogen, and a slow stream of nitrogen was passed during the pyrolysis. The acetoxy compound (15 g., 0.088 mole) containing a small amount of *p*-*t*-butylcatechol was dropped at the rate of 1 drop per second into the pyrolysis tube. The dark red condensate was poured into concentrated aqueous sodium carbonate, and the product, 1-ethyl-Δ^3-tetrahydropyridine, was extracted with ether, isolated and distilled, b.p. 57–59° (43 mm.); conversion 3.59 g. (37%), $n^{20}\text{D}$ 1.4620, d^{20}_4 0.8525, MR_D calcd. 35.97, found 35.85.

The **picrate** of 1-ethyl-Δ^3-tetrahydropyridine, formed in 95% ethanol, was crystallized from the same solvent as yellow needles, m.p. 169–171° dec.

Anal. Calcd. for $C_{13}H_{16}N_4O_7$: N, 16.47. Found: N, 16.47.

1-Ethyl-2,5-dimethyl-Δ^3-pyrroline.—The procedure of Andrews and McElvain[33] and Treibs and Dinelli[34] was followed for the partial reduction of 1-ethyl-2,5-dimethylpyrrole[21] to 1-ethyl-2,5-dimethyl-Δ^3-pyrroline,[35] b.p. 131–132°, $n^{22}\text{D}$ 1.4467.

The **picrate** was recrystallized from methanol–ether as yellow needles, m.p. 167.5–169° dec.

Anal. Calcd. for $C_{14}H_{18}N_4O_7$: N, 15.81. Found: N, 15.57.

The **methiodide**, prepared in the usual manner, separated as colorless crystals from ethanol–ether, m.p. 276.5° dec. The compound was light-sensitive.

Anal. Calcd. for $C_9H_{18}IN$: C, 40.46; H, 6.79; N, 5.24. Found: C, 40.96; H, 6.86; N, 5.17.

δ-Ethylaminovaleronitrile.—To a solution of 40 g. (0.88 mole) of ethylamine in 360 ml. of absolute ethanol was added 81 g. (0.5 mole) of δ-bromovaleronitrile. The resulting solution was stirred at 65–70° for 24 hours and then evaporated *in vacuo*. Ether extraction followed by distillation gave 22.1 g. (35%) of the mono-condensation product, b.p. 60–61° (1 mm.), $n^{19}\text{D}$ 1.4409, d^{20}_4 0.8574, and a larger amount of high-boiling material.

Anal. Calcd. for $C_7H_{14}N_2$: C, 66.62; H, 11.18; N, 22.20. Found: C, 66.44; H, 11.07; N, 22.24.

δ-(N-Ethylbenzamido)-valeronitrile.—Excess benzoyl chloride was added to a solution of 19 g. (0.15 mole) of δ-ethylaminovaleronitrile in 150 ml. of benzene. When the exothermic reaction had ceased, 20% aqueous sodium hydroxide solution was added, and the organic layer was separated and distilled as a pale yellow viscous oil, b.p. 162–166° (0.02 mm.); $n^{24.7}\text{D}$ 1.5263, d^{20}_4 1.0663, yield 29.4 g. (85%).

Anal. Calcd. for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88; N, 12.17. Found: C, 72.88; H, 7.62; N, 11.87.

1,3,3-Trimethylsuccinimide.—Aqueous methylamine solution (35%) was added in excess to 15.2 g. (0.104 mole) of α,α-dimethylsuccinic acid, and the resulting solution was evaporated to dryness. The viscous residue crystallized slowly after standing several hours, m.p. 92–98°. The crude material, which consisted mainly of the bismethylammonium salt of the acid, was heated at 140° for 1 hour, then at 180–190° for 30 minutes. The product was distilled as a colorless oil at 108–109° (17 mm.); $n^{20}\text{D}$ 1.4680; d^{20}_4 1.0760, yield 12.1 g. (83%).

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.55; H, 7.85; N, 9.92; MR_D, 36.17. Found: C, 59.30; H, 7.73; N, 10.17; MR_D, 36.47.

1,3,3-Trimethylpyrrolidine.—The usual conditions were employed for the lithium aluminum hydride reduction of 1,3,3-trimethylsuccinimide to 1,3,3-trimethylpyrrolidine,[36] b.p. 77–79°, $n^{20.6}\text{D}$ 1.3842; yield 61%. The **picrate** was prepared in and recrystallized from ethanol as yellow needles, m.p. 226–227° dec.

Anal. Calcd. for $C_{13}H_{18}N_4O_7$: C, 45.61; H, 5.30; N, 16.37. Found: C, 45.86; H, 5.23; N, 16.37.

Neostrychnine Perchlorate.—Addition of 65% perchloric acid to a chloroform solution of neostrychnine[37] gave the salt, which crystallized as prisms from 95% ethanol (containing a drop of perchloric acid); decomposition point >350°.

Anal. Calcd. for $C_{21}H_{23}ClN_2O_6$: C, 58.00; H, 5.33; Cl, 8.15; N, 6.44. Found: C, 57.14; H, 5.29; Cl, 7.96; N, 6.36.

In Nujol mull, the following infrared maxima and inflection points were observed (cm.$^{-1}$):

	N(a)–CO	C=C		Phenyl
Strychnine	1669	~1652	~1642(?)	1602
Neostrychnine	1684	~1666	~1642(?)	1600
Neostrychnine perchlorate	1679	~1665	~1642(?)	1603

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(29) E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1810 (1950).

(30) C. D. Hurd and F. H. Blunck, *ibid.*, **60**, 2421 (1938).

(31) C. S. Marvel, R. L. Meyers and J. H. Saunders, *ibid.*, **70**, 1694 (1948).

(32) C. S. Marvel and J. L. R. Williams, *ibid.*, **70**, 3842 (1948).

(33) L. H. Andrews and S. M. McElvain, *ibid.*, **51**, 887 (1929).

(34) A. Treibs and D. Dinelli, *Ann.*, **517**, 170 (1935).

(35) See also G. C. Evans, THIS JOURNAL, **73**, 5230 (1951).

(36) *E.g.*, see R. B. Moffett, *Org. Syn.*, **33**, 32 (1953), for the conversion of 5,5-dimethyl-2-pyrrolidone to 2,2-dimethylpyrrolidine.

(37) R. N. Chakravarti and Sir Robert Robinson, *J. Chem. Soc.*, 78 (1947).