In Table III the Mg etio II–methanol complex is compared to free methanol. Closs, *et al.*,[8] recently reported a similar but smaller effect in methanol chlorophyl b complexes. The methanol being less tightly bound than the pyridine exhibits a smaller shift to high field.

TABLE III
P.M.R. SHIFTS OF
Mg ETIO II–METHANOL COMPLEX

	CH_3	Shift	OH	Shift
CH_3OH[a]	6.72		5.73	
Mg etio II–CH_3OH	11.00	4.28	10.82	5.09

[a] *Ca.* 0.4 *M* in benzene.

In Table IV the positions of the porphyrin complex chemical shifts are compared to the resonance positions in the free bases. Caughey and Koski[9] have noted that the introduction of a metal ion normally results in a general shift to higher field for those protons affected by the ring current. The effect of the magnesium and the various ligands is slight and in no case is any nonequivalence of any of the porphyrin protons induced.

TABLE IV
P.M.R. SHIFTS OF
ETIO II, TPP, AND MAGNESIUM COMPLEXES

	CH_3	CH_2CH_3	CH_2CH_3	Methine
Etio II[a]	6.38	8.13	5.90	−0.13
Mg etio II·$2C_5H_5N$	6.35	8.13	5.88	−0.15
Mg etio II·$1C_5H_5N$	6.37	8.14	5.88	−0.11
Mg etio II·$1CH_3OH$	6.40	8.17	5.94	−0.03

	Phenyl hydrogens		
	β-H	o-H	m- and p-H
TPP	1.05	1.70	2.20
Mg TPP·$2C_5H_5N$	1.05	1.70	2.20
Mg TPP·$1C_5H_5N$	1.05	1.70	2.23

Experimental

The spectra were recorded on a Varian A-60 n.m.r. spectrometer in $CDCl_3$ solution at *ca.* 0.05 *M* concentrations. Neither the etio II nor TPP nor their magnesium derivatives show concentration dependence of their chemical shifts such as have been reported for porphyrins containing polar functional groups.[8,10] The τ-values were determined from the calibrated paper relative to tetramethylsilane internal standard, τ 10. All spectra were recorded at 35°.

The magnesium diiodide hexapyridinate, magnesium porphyrin mono- and dipyridinates, and Mg etio II monomethanolate were prepared by the method of Wei, Corwin, and Arellano.[11] The electronic spectra of the magnesium porphyrins corresponded to those reported in the literature.[11,12] The number of ligands attached to the magnesium porphyrin were determined by proton integration.

The N-alkylpyrroles were synthesized from potassium pyrrole and the alkyl diiodide[13,14] and distilled, and the p.m.r. spectra were taken in $CDCl_3$.

(8) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3809 (1963).
(9) W. S. Caughey and W. S. Koski, *Biochemistry*, **1**, 923 (1962).
(10) R. J. Abraham, P. A. Burbidge, A. H. Jackson, and G. W. Kenner, *Proc. Chem. Soc.*, 134 (1963).
(11) P. E. Wei, A. H. Corwin, and R. Arellano, *J. Org. Chem.*, **27**, 3344 (1962).
(12) J. R. Miller and G. D. Dorough, *J. Am. Chem. Soc.*, **74**, 3977 (1952).
(13) N. Lubivan, *Ber.*, **2**, 101 (1868).
(14) C. A. Bell, *ibid.*, **11**, 1810 (1878).

The Structure of Acetonepyrrole[1]

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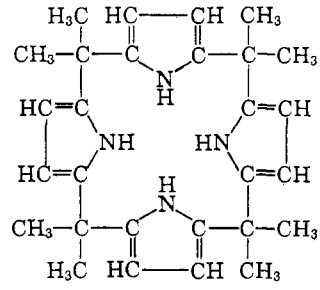
Acetonepyrrole (**1**), the acid-catalyzed condensation product of acetone and pyrrole, was first reported by A. Baeyer[3] in 1886. A structure was proposed by Chelintzev and Tronov[4] and named α,β,γ,δ-octamethylporphinogen by H. Fisher.[5] Rothemund and Gage[6] recently investigated the structure by hydrogenolysis and pyrolytic degradation. Their conclusion was that at least three of the four bridge carbons were linked to the α-positions of the pyrrole nuclei but that the nature



1
acetonepyrrole

of the linkage of the fourth bridge carbon remained in doubt. Examination of Stuart–Breiglieb molecular models reveals that either the α- or β-linkage is sterically feasible.

The proton magnetic resonance (p.m.r.) spectrum of a molecule is sensitive to both the electronic environment of the proton, as shown by the chemical shift, and the symmetry of the molecule, as shown by spin–spin interactions. The p.m.r. spectrum of acetonepyrrole shows only three peaks. A sharp singlet at δ 1.53 is assigned to the eight bridge methyl groups. A doublet at 6.00 (J = 2.80 c.p.s.) is assigned to the eight protons at the β-positions on the pyrrole rings. Abraham and Bernstein[7] have observed coupling between the protons at the 1- and 3-positions in β-free pyrroles. In the cases they investigated the coupling constant was 2.43 c.p.s. The slightly larger coupling constant in the case of acetonepyrrole may be due to the lack of intermolecular hydrogen bonding in this molecule. In alkyl-substituted pyrroles the chemical shifts of the α- and β-protons are separated by *ca.* 0.5 p.p.m. with the β-protons falling in the region of δ 6.[8] If any β-linkages were present the α-proton would then be observed in the region of δ 6.5. A broad peak at δ 7.1 is assigned to the

(1) Porphyrin studies XXXIV. Paper XXXIII: C. B. Storm and A. H. Corwin, *J. Org. Chem.*, **28**, 3700 (1964).
(2) National Institutes of Health Predoctoral Fellow, 1962–1964.
(3) A. Baeyer, *Ber.*, **19**, 2184 (1886).
(4) V. V. Chelintzev and B. V. Tronov, *J. Russ. Phys. Chem. Soc.*, **48**, 105, 127 (1916).
(5) H. Fisher and H. Orth, "Die Chemie des Pyrroles," Vol. I, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1934, pp. 20, 394.
(6) P. Rothemund and C. L. Gage, *J. Am. Chem. Soc.*, **77**, 3340 (1955); and references contained therein.
(7) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 905 (1961).
(8) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

four N–H protons. This peak is broadened by the quadrupole moment of the nitrogens to which the protons are attached.[9] The ratios of the integrated peak areas are 6:2:1 in agreement with the empirical formula. None of the chemical shifts are concentration dependent over a range of 0.07 to 0.20 M indicating that no intermolecular association is occurring.

The infrared spectrum of acetonepyrrole shows a band at 3440 cm.$^{-1}$ (N–H stretch) in both $CHCl_3$ solution and KBr pellet. This band is characteristic of a free N–H stretching frequency. No band was observed in the region of 3300 cm.$^{-1}$ characteristic of a hydrogen bonded N–H.[10] Examination of molecular models shows that if any β-bridge linkages were present the pyrrole ring would be twisted considerably out of the general plane of the molecule and intermolecular hydrogen bonding could take place. If all α-bridge linkages exist the N–H groups will be buried in the center of the molecule and no hydrogen bonding could take place.

For a molecule of this size to have only three peaks in its p.m.r. spectrum it must be very symmetrical. The spectral data, in conjunction with the earlier work of Rothemund and Gage then demonstrate the proposed $\alpha,\beta,\gamma,\delta$-octamethylporphinogen structure to be correct.

Experimental

The p.m.r. spectra were run on a Varian Associates A-60 spectrometer in $CDCl_3$. The chemical shifts and coupling constants were determined from the calibrated paper relative to tetramethylsilane internal standard at 0 p.p.m.

The infrared spectra were recorded on a Perkin-Elmer 337 grating Infracord in KBr pellets and $CHCl_3$ solutions.

The acetonepyrrole was synthesized by the method followed by Rothemund and Gage[8] except that p-toluenesulfonic acid was used as a catalyst.

Anal. Calcd. for $C_{28}H_{36}N_4$: C, 78.46; H, 8.47. Found: C, 78.01; H, 8.73.

The molecular weight as determined by vapor phase osmometry in o-dichlorobenzene at 100° was found to be 428 ± 20.

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(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 72.

(10) L. P. Kuhn and G. C. Kleinspehn, *J. Org. Chem.*, **28**, 721 (1963).

A Test for Hydrogen Rearrangement in the Deamination of Cyclopropylamine to Allyl Alcohol

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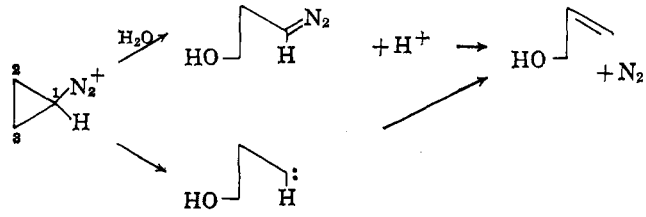
The reaction of cyclopropylamine with nitrous acid in aqueous solution has been reported to give allyl alcohol as the principal neutral product.[2] Fission of the three-membered ring and formation of allylic alcohols has also been observed with other cyclopropylamine derivatives in the deamination reaction, *e.g.*, spiropentylamine[3] and 7-aminobicyclo[4.1.0]heptane.[4] Although ring opening of a cyclopropyl cation to a planar, charge-delocalized allylic cation is undoubtedly thermodynamically favorable, it must be recognized that rather drastic changes in molecular geometry are required; the C-2–C-3 bond must be stretched and broken, and simultaneously there must be rotation about C-1–C-2 and C-1–C-3 bonds to place the hydrogens and carbons in one plane. This complex but direct process is clearly not unreasonable in view of the great instability of cyclopropyl cations and cyclopropyl diazonium ions.[5] However, it seemed worthwhile to consider the possibility of a less direct route for the cyclopropyl → allyl conversion in which the stereoelectronic demands are not so severe. Such an alternative mechanism can be derived by supposing that C-1–C-2 fission can occur instead of C-2–C-3 fission; this leads to variants such as shown in Scheme I.

SCHEME I



A consequence of such schemes is that C-1 of cyclopropylamine becomes one of the terminal carbons of allyl alcohol, whereas by the direct route C-1 of cyclopropylamine becomes C-2 of allyl alcohol. Thus, the direct and indirect mechanisms can be distinguished by a labeling experiment.

To this end cyclopropylamine-1-*d* was synthesized from cyclopropane–carboxylic acid-1-*d* and subjected to deamination with nitrous acid in water at 0°. Allyl alcohol was obtained as the *p*-phenylazobenzoate derivative in 44% yield and it was shown by n.m.r. analysis that essentially all the deuterium was located at C-2. Thus the indirect mechanism shown in Scheme I can be excluded and a measure of support is provided for the direct mechanism.

It should be noted that in certain special cases cyclopropylamines yield cyclopropanol derivatives by deamination.[6,7]

Experimental

Preparation of Cyclopropylamine-1-*d*.—1,1-Cyclopropanedicarboxylic acid[8] (9.0 g., 0.0692 mole) was dissolved in 15 ml. of deuterium oxide; the solution was then frozen and dried *in vacuo*, and the process was repeated with an additional 15 ml. of deuterium oxide. The diacid was then heated at 165–170° at a pressure of 38 mm. for 5 hr.[9] The products of decarboxylation distilled out as formed. A solution of the crude product in ether was cooled in ice and saturated with anhydrous ammonia. The

(1) National Science Foundation Predoctoral Fellow, 1962–1963.

(2) (a) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **37**, 316 (1905); (b) P. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, **499**, 1 (1932).

(3) D. E. Applequist and G. F. Fanta, *J. Am. Chem. Soc.*, **82**, 6393 (1960).

(4) J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, **28**, 3356 (1963).

(5) The formation of allenes from cyclopropylidene derivatives appears to proceed by this type of direct process: see W. M. Jones, J. W. Wilson, Jr., and Frank B. Tutwiler, *J. Am. Chem. Soc.*, **85**, 3309 (1963).

(6) P. Lipp and C. Padberg, *Ber.*, **54B**, 1316 (1921).

(7) H. Hart and R. A. Martin, *J. Am. Chem. Soc.*, **82**, 6362 (1960).

(8) A. W. Dox and L. Yoder, *ibid.*, **43**, 2097 (1921).

(9) L. W. Jones and A. W. Scott, *ibid.*, **44**, 413 (1922).