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.

Acknowledgment.—The authors wish to thank the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

(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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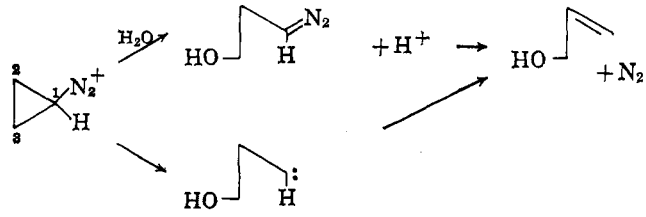
The reaction of cyclopropylamine with nitrous acid in aqueous solution has been reported to give allyl alcohol as the principal neutral product.[2] Fission of the three-membered ring and formation of allylic alcohols has also been observed with other cyclopropylamine derivatives in the deamination reaction, *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).

white ammonium salt[9] was collected, washed with ether, and dried *in vacuo*, yielding 4.59 g. of the crude product.

A modification of the procedure of Weinstock[10] was used for the conversion of cyclopropanecarboxylic acid-1-*d* to cyclopropylamine-1-*d*. The unpurified ammonium cyclopropanecarboxylate-1-*d* prepared above was dissolved in 12.5 ml. of water, and 0.4 g. of triethylamine in 30 ml. of dioxane was added. This was cooled in ice, and a solution of 6.3 g. (0.058 mole) of ethyl chloroformate in 23 ml. of dioxane was added slowly. After stirring for 70 min. with ice cooling, 4.3 g. (0.066 mole) of sodium azide in 12.5 ml. of water was added dropwise with stirring. After 30 min., the two layers were separated and the aqueous layer was extracted with 60 ml. of toluene. Addition of toluene to the other layer caused water to separate; it was removed and the organic phase was washed with saturated sodium chloride solution. The combined organic layers were dried with anhydrous magnesium sulfate and molecular sieve. Ethanol (4.0 g., 0.087 mole) and triethylamine (0.1 g.) were mixed with the dried solution. This was then added dropwise with stirring to a flask heated to 105–110° equipped with a condenser cooled with ice–salt. Heating was continued for 4 hr. Removal of the solvent yielded 4.84 g. of a yellow oil (cyclopropylethylurethan).

The urethane was hydrolyzed by heating for 5 hr. with 6 g. of potassium hydroxide in 6 ml. of water and 8 ml. of ethylene glycol. This was carried out under nitrogen with stirring, and the amine distilled out as formed. The crude product was purified by reaction with oxalic acid in ether followed by two recrystallizations from absolute alcohol, giving a 13% yield (1.359 g.) of cyclopropylamine-1-*d* hydrogen oxalate, m.p. 123.5–124.5°. An additional 0.124 g., melting at 120–124°, was obtained by concentrating the mother liquors. Analysis of the product by n.m.r. (D_2O, 60°) shows two singlets at δ 0.62 and 4.78; the integration shows 94.4 ± 2.8% deuterium substitution on C-1.

Deamination of Cyclopropylamine-1-*d*.—A portion (0.440 g., 2.97 mmoles) of the cyclopropylamine-1-*d* hydrogen oxalate prepared above was dissolved in 3.6 ml. of water and chilled in an ice-bath. Sodium nitrite (0.32 g., 4.6 mmoles) dissolved in 0.45 ml. of water was added over 1 hr. The system was kept in ice for an additional 3 hr. until gas evolution had nearly ceased. The reaction mixture was then saturated with potassium carbonate, filtered, and extracted with eight 10-ml. portions of benzene. The benzene solution was dried with anhydrous magnesium sulfate, and 0.63 g. (2.57 mmoles) of *p*-phenylazobenzoyl chloride and 0.41 g. (5.14 mmoles) of pyridine were added. The mixture was allowed to stand for 5.5 hr., then refluxed for 12 hr. After cooling in ice, 0.18 g. (10 mmoles) of water in a few milliliters of acetone was added and the mixture was stirred for 1 hr. The solvent was then removed, and the product was twice recrystallized from ethanol. A 44% yield (0.346 g.) was obtained of allyl-2-*d* *p*-phenylazobenzoate: m.p. 67.5–68.5°; $\lambda_{max}^{CHCl_3}$ 5.81 μ; n.m.r. ($CDCl_3$), δ = 4.13 (singlet, two methylene protons), 4.65 (multiplet, two vinyl protons), and 6.7–7.6 p.p.m. (aromatic protons). Integration of the n.m.r. spectrum showed 89.7 ± 5.1% deuterium substitution. Mixture melting point with an authentic sample prepared from allyl alcohol and *p*-phenylazobenzoyl chloride[11] showed no depression. An analysis was obtained for the undeuterated derivative.

Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.08; H, 5.33; N, 10.51.

A second deamination similarly yielded allyl-2-*d* *p*-phenylazobenzoate with 90 ± 7% deuterium substitution.

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Cleavage of 2,2-Dialkyl-1,3-diols[1]

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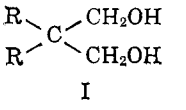
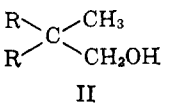
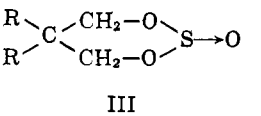
It has been reported that 2,2-dialkyl-1,3-propanediols (I) react with sodium sulfite, sodium hydroxide, and water at 140° to yield 2,2-dialkylpropanols (II).[4] It was further reported that the corresponding cyclic sulfites (III) react with sodium hydroxide and water at 140° to yield the same 2,2-dialkylpropanols (II).



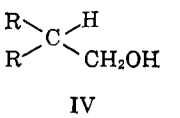
I



II



III



IV

We were interested in this reaction as a synthetic method for 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5). Accordingly, 2,2-diethyl-1,3-propanediol (I, R = C_2H_5) was added to sodium sulfite, sodium hydroxide, and water at 140° as described by Crowdle, *et al.*[4] Distillation of the reaction product gave a 63% yield of 2-ethyl-1-butanol (IV, R = C_2H_5) instead of the expected 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5). The corresponding cyclic sulfite (III, R = C_2H_5) also reacted with sodium hydroxide and water at 140° to yield 2-ethyl-1-butanol (IV, R = C_2H_5). 2-Ethyl-2-methyl-1-butanol (II, R = C_2H_5) was not obtained under any of the reaction conditions that were tried.

Identification of the distilled reaction product was made by boiling point, refractive index, 3,5-dinitrobenzoate derivative, and infrared and n.m.r. spectra. The infrared spectrum of the alcohol obtained from the diol reaction was identical with the infrared spectrum of commercially available 2-ethyl-1-butanol (IV, R = C_2H_5) but was substantially different from the infrared spectrum of 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5) prepared in this laboratory by another method.

The integrated n.m.r. spectrum of the alcohol product with a trace of added acid showed one hydroxyl proton as a singlet at τ 5.2, two hydroxymethylene protons as a doublet at 6.6, and eleven protons as a multiplet at higher field. This multiplet consisted mainly of an A_3B_2 spectrum which would be expected for two ethyl groups. The fact that the hydroxymethylene protons appeared as a doublet indicated the presence of a proton on an α-carbon. 2-Ethyl-1-butanol (IV, R = C_2H_5) has such a proton, whereas 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5) does not.

For comparison, the n.m.r. spectra of several derivatives of 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5) prepared in this laboratory showed the two hydroxymethylene protons as a singlet (*i.e.*, no protons of an α-carbon) and 13 protons as a multiplet at higher field. The multiplet at higher field consisted of the sharp singlet expected for the unsplit methyl group superimposed on the A_3B_2 spectrum expected for two ethyl groups.

The cleavage of 2,2-dialkyl-1,3-propanediols (I) at elevated temperatures and under strongly basic conditions to 2,2-dialkylethanols (IV) has been previously reported.[5] Specifically, 2,2-diethyl-1,3-propanediol (I,

(1) This work was supported by the Army Research Office (Durham).

(2) Du Pont Teaching Fellow, 1962–1963.

(3) Sloan Foundation Fellow.

(4) J. H. Crowdle, J. E. Knipper, J. E. Schmidt, and R. T. Conley, *J. Org. Chem.*, **25**, 1687 (1960).

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