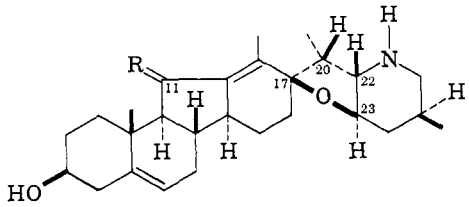
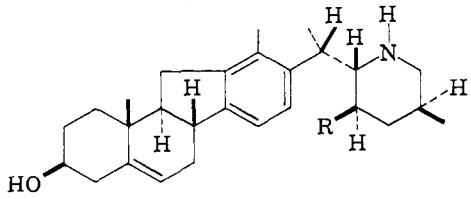


I, R = O
II, R = 
III, R = H_2



IV, R = OH
V, R = H

comparison of a sample of jervin-11β-ol, prepared by reduction of jervine,[8] with an authentic sample of veratrobasine[9] (by mixture melting point, mixture tlc, optical rotation, high-resolution ir, nmr, and mass spectral comparisons[10]); the respective materials were, indeed, found to be identical.

The interrelation of veratrobasine (II) with jervine (I) establishes: (1) the β orientation of the 17-oxide in jervine (and, hence, in 11-deoxojervine (III)[11]); (2) the α orientation of the 20-methyl group in jervine (and, hence, in 11-deoxojervine (III),[11] veratramine (IV),[12] and verarine (V)[13]), as suggested earlier by biogenetic analogy;[3] (3) the C-22α and C-23β configurations for the substituents at the respective positions in jervine and related alkaloids, in confirmation of the recently revised assignments on the basis of elegant chemical studies by Johnson, *et al.*;[14] and (4) the absolute configuration of veratrobasine (II) as that which occurs in normal steroids, for the absolute confirmation of jervine (I) has been established earlier by interrelation with hecogenin.[15,16]

(9) We thank Dr. D. Stauffacher, Sandoz Ltd., Basel, for the authentic sample of veratrobasine.

(10) We thank Dr. G. Van Lear and Dr. F. W. McLafferty of the Purdue Mass Spectrometry Center, supported under U. S. Public Health Service Grant FR-00354, for the mass spectral data.

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(17) National Institutes of Health Predoctoral Fellow, 1966–1968.

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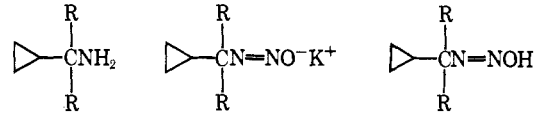
Fate of the Cyclopropylcarbinyl Cation in Aqueous Base[1,2]

Sir:

Recently we contrasted nitrous acid deamination of 2-aminooctane with hydrolysis of octane-2-diazotate and showed that free carbonium ions were largely bypassed in the latter process.[3] Some years ago, discussing the methylene group scrambling observed in the deamination of cyclopropylcarbinylamine (I), Roberts remarked: "Matters would be greatly helped by study of these interconversion reactions in bonafide carbonium processes in much more nucleophilic solvents so that the intermediates . . . could be trapped before they become so extensively interconverted."[4] Therefore, we extended our studies[3] to a comparison of the nitrous acid deamination of I (pH 2) and the hydrolysis of the related diazotate, II (pH 14).[2] In both cases, the products included cyclopropylcarbinol, cyclobutanol, and allylcarbinol. Over several experiments,[2] typical values for the ratio of cyclopropylcarbinol to cyclobutanol ("product ratio") were 1.16 for the deamination of I



I, R = H; I-*d*, R = D
II, R = H; II-*d*, R = D
III, R = H; III-*d*, R = D

and 1.28 for the hydrolysis of II, suggesting that SN2 displacement on the diazotic acid III was not the major pathway to cyclopropylcarbinol at high [OH^-] and that "the diazotate hydrolysis occurs *via* cationic intermediates *similar* to those involved . . . in the deamination of cyclopropylcarbinylamine."[2] We now report a closer examination of these reactions.

II was hydrolyzed with water containing 22.6% ^{18}O. The product alcohols were isolated by vpc, converted to benzoates with benzoyl chloride–pyridine, and analyzed by mass spectroscopy. The cyclopropylmethyl benzoate contained 19.9% ^{18}O and the cyclobutyl benzoate contained 19.3% ^{18}O, indicating that the alcohols had been formed with *ca.* 11.9 and 14.7% return (respectively) of the ^{16}OH originally present in the diazotic acid III derived from II.[5] A parallel experiment with the deuterated diazotate, II-*d*, afforded cyclopropylmethyl benzoate containing 19.7% ^{18}O, corresponding to 12.9% ^{16}OH return.

These experiments should be compared to the hydrolysis of octane-2-diazotate in $H_2{}^{18}O$ in which 2-octanol is formed with 40% return of the diazotate's ^{16}OH.[3] Assuming the main course of diazotate hydrolysis to be that outlined in eq 1, the observed greater

$$\underset{\text{III}}{RN{=}NOH} \longrightarrow [R\cdots\overset{\delta+}{N}{=}N\cdots\overset{\delta-}{O}H] \longrightarrow \underset{\text{IV}}{[R^+OH^-]} \longrightarrow ROH \qquad (1)$$

loss of original hydroxide from III could be attributed to a greater stability and hence longer lifetime of the cyclopropylcarbinyl cation *vis-à-vis* the 2-octyl cation, leading to more complete hydroxide exchange with solvent water at the ion-pair stage, IV.[6]

(1) The Solvolysis of Alkyl Diazotates. IV.

(2) Part III: R. A. Moss and F. C. Shulman, *Tetrahedron*, **24**, 2881 (1968).

(3) R. A. Moss and S. M. Lane, *J. Am. Chem. Soc.*, **89**, 5655 (1967).

(4) E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961).

(5) Dilution of the ^{18}O pool by ^{16}O from II was negligible.

(6) (a) The possibility that ^{18}O incorporation occurs at a prior stage, *via* an equilibrium such as a, must be considered. Although hydrox-

$$RN{=}NOH \rightleftharpoons RN{\equiv}N^+\,OH^- \qquad (a)$$

ide exchange from a diazonium hydroxide ion pair would be likely if R was an *ordinary primary* alkyl group, it is unlikely in the present case where R is cyclopropylcarbinyl. Thus Whiting[6b] has shown that nitrogen loss from RN=NX involves essentially *synchronous* cleavage of

Amine I-*d* was prepared by reduction of cyclopropyl cyanide with $LiAlD_4$. Nmr spectra revealed no carbinyl protons. I-*d* was deaminated (pH 2, 0°) with aqueous nitrous acid,[4] and the vpc-isolated cyclopropylcarbinol was examined by nmr.[7] Integrals of the proper signals[8] allowed calculation of the ratio of cyclopropylcarbinol-α,α-d_2 to cyclopropylcarbinol-γ,γ-d_2, the "label ratio," as 0.85. This value can be compared with 0.50 expected for statistical scrambling of the methylene groups (in the absence of isotope effects) and 1.10 found by Roberts[9] in deamination of cyclopropylcarbinylamine-α-^{14}C.[10] The product ratio observed in deamination of I-*d* was 1.09 (vpc).

I-*d* was converted to diazotate II-*d*,[2,3,11] which was hydrolyzed as a dry salt at 0°. Nmr examination[8] of the isolated cyclopropylcarbinol[7] gave the label ratio as 1.15; the product ratio was 1.24. A second experiment gave the label ratio as 1.60 and the product ratio as 1.37.[12]

In terms of (1), the similar and nearly complete loss of original hydroxide ion in the formation of cyclopropylcarbinol and cyclobutanol from II and III rules out a *large* incursion of SNi processes or internal return in IV as sources of cyclopropylcarbinol. This alcohol arises *mainly via* carbonium ion intermediates, though the higher product ratios found for hydrolysis of II, as opposed to deamination of I, do suggest small contributions of other pathways from III to cyclopropylcarbinol in aqueous base.

Considering the disparate nature of the deaminative processes here applied to the cyclopropylcarbinyl derivatives, the key cationic intermediates in each process exhibit a remarkable similarity. (This contrasts greatly with results for the 2-octyl system.[3]) Although the slightly higher label ratios observed in the diazotate hydrolyses might suggest a shorter lifetime for the cyclopropylcarbinyl cation under the more nucleophilic conditions of this reaction, the principal result of these experiments is that this extraordinary cation is capable of methylene scrambling almost as efficiently in strong aqueous base as in strong aqueous acid. In terms of (1), the lifetime of IV is sufficient not only for essentially complete gegenion exchange but also for methylene scrambling in the cationic component essentially equivalent to that observed for the free cyclopropylcarbinyl cation in aqueous acid.

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R–N and N–X bonds if R affords a reasonably stable carbonium ion (secondary or better). On this basis, the decomposition of RN=NOH (R = cyclopropylcarbinyl) should certainly follow Whiting's synchronous mechanism, precluding equilibrium a. (b) M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966); H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965). (c) Reviews which discuss the stability of the cyclopropylcarbinyl cation: N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129, (1964); R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963; A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(7) The benzoate derived from this alcohol was greater than 97% d_2 (mass spectroscopy).

(8) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 3773 (1964).

(9) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(10) The differing label ratios may be due to differing isotope effects on methylene group scrambling for the ^{14}C and d_2 labels.

(11) R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966).

(12) All reactions were carried out under conditions where cyclopropylcarbinol does not rearrange to cyclobutanol and the methylene groups of the former do not scramble.[9]

Additions and Corrections

Benzvalene, the Tricyclic Valence Isomer of Benzene [*J. Am. Chem. Soc.*, **89**, 1031 (1967)]. By K. E. WILZBACH, JAMES S. RITSCHER, and LOUIS KAPLAN, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

In footnote 11, 1-*endo*- should read 6-*endo*. In footnote 12, 4-*endo*-(?)-, 1-*endo*-, and 1-*exo*- should read 4-*exo*-, 6-*endo*-, and 6-*exo*-.

Pyracylene. A Pentalenoid System? [*J. Am. Chem. Soc.*, **89**, 4244 (1967)]. By BARRY M. TROST and G. MIKE BRIGHT, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

The ultraviolet spectrum of pyracylene showed maxima (mμ) at 427, 408, 405, 385, 358, 341, 332, 326, and 218 with extensive tailing to 650 mμ.

Dielectric Measurements on Triethylamine–Iodine Complex [*J. Am. Chem. Soc.*, **90**, 517 (1968)]. By PIERRE BOULE, Laboratoire de Chimie Théorique, Université de Nancy, Nancy, France.

In Table I, the entry for run 1 in cyclohexane at 25° should read 5.9 instead of 5.0.

Rate Constants for the Self-Reactions of *n*- and *sec*-Butylperoxy Radicals and Cyclohexylperoxy Radicals. The Deuterium Isotope Effect in the Termination of Secondary Peroxy Radicals [*J. Am. Chem. Soc.*, **90**, 1058 (1968)]. By J. A. HOWARD and K. U. INGOLD, Division of Applied Chemistry, National Research Council, Ottawa, Canada.

In Table II, the heading for the third column should be $(k_5)_H/(k_5)_D$.