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 S$_N$i 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 $(k_5)_H/(k_5)_D$.