

mental accuracy. Since the C-2 and C-4 hydroxyl groups were methylated (hence, free), the C-3 hydroxyl must have been bound in the glycoside linkage and the C-5 hydroxyl in a pyranose ring, as shown in I and II.¹² This result does not however, establish definitely the ring form of ribose in intact neomycin B; this point and others dealing with the stereochemistry of neosamine B and the glycosidic link in neobiosamine B will be the subjects of future reports.

Acknowledgment.—This investigation was supported in part by a research grant, No. E-1278, from the National Institute of Allergy and Infectious Diseases, Public Health Service. We wish to express our thanks to the Upjohn Company for a gift of neomycin and also for assistance with paper electrophoreses.

(12) A structure similar to I recently has been assigned to paramo-biosamine, a degradation product of the antibiotic paramomycin [T. H. Haskell, J. C. French and Q. R. Bartz, *THIS JOURNAL*, **81**, 3481 (1959)].

KENNETH L. RINEHART, JR.
DEPARTMENT OF CHEMISTRY ALEXANDER D. ARGOUEDELIS
AND CHEMICAL ENGINEERING TOWNLEY P. CULBERTSON
UNIVERSITY OF ILLINOIS W. SCOTT CHILTON
URBANA, ILLINOIS KLAUS STREIGLER

RECEIVED APRIL 8, 1960

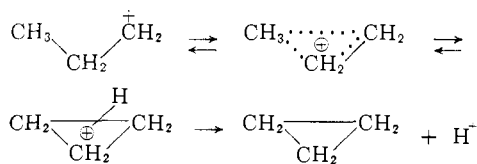
CYCLIZATION OF CARBONIUM TO CYCLOPROPANES¹

Sir:

A primitive mechanistic explanation of rearrangements invoked cyclic intermediates such as cyclopropanes, epoxides, etc. Although these intermediates were discarded in the early part of this century, they have returned to the current literature in various forms as bridged ions. Experiments cited below emphasize the importance of some bridged intermediates.

It was noted in the de-oxidation of *n*-propyl alcohol² *n*-propyl carbonium ion being the postulated intermediate, that cyclopropane and propylene were reaction products. The resulting C₃H₆ is 90% propylene and 10% cyclopropane. Nitrous acid deamination of *n*-propylamine in aqueous solution also yields C₃H₆ which is 90% propylene and 10% cyclopropane. Also, cyclopropanes have been detected in other systems involving carbonium ion.^{3,4}

These results can be rationalized by assuming that a protonated cyclopropane is a short-lived intermediate in this reaction.



(1) We wish to express our appreciation to Dr. M. S. Silver of Amherst College for communicating his results and for delaying publication of his work to permit simultaneous publication of these complementary results.

(2) P. S. Skell and I. Starer, *THIS JOURNAL*, **81**, 4117 (1959).

(3) M. S. Silver, *ibid.*, **82**, 2971 (1960).

(4) Probably related are the cationoid type reactions of diazo compounds in proton-donating solvents: L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959).

CYCLOPROPANE FORMATION FROM DE-OXIDATION AND DIAZOTIZATION REACTIONS

Alcohol ^a	Cyclopropane in C _n H _{2n} products, %
<i>i</i> -Propyl	None
<i>n</i> -Propyl	10
<i>n</i> -Butyl	2
<i>i</i> -Butyl	4
<i>s</i> -Butyl	<0.5
<i>t</i> -Butyl	None
Neopentyl	None
<i>t</i> -Amyl	None
Amine ^b	
<i>n</i> -Propyl	10
Neopentyl	None
4,4-Dimethyl-1-pentyl	No cyclopropane

^a At reflux, HCB₃ and RO⁻ in ROH. ^b Aqueous solution at 100°.

It is attractive to think of the possibility that protonated cyclopropanes are not only intermediates in the route to cyclopropanes, but may also be the intermediates in the major pathways leading to rearranged carbonium ions. Thus, the opening of the three-membered ring may be the preferred route for alkyl substituted derivatives which can proceed to the more stable secondary and tertiary carbonium ions.⁵ Labeling experiments suggested by these considerations are being examined. These suggestions, if valid, differ from the earlier ones in proposing that reaction of the protonated cyclopropane to yield cyclopropane and rearranged carbonium ions is rapid compared to protonation of the cyclopropane.

(5) The interconversion of *s*-butyl and *i*-butyl benzenes, etc., studied by R. M. Roberts, *et al.*, may involve a protonated cyclopropane lying perpendicular to the plane of the benzene ring, one edge of the cyclopropane closely associated with the aromatic π -electron system: *THIS JOURNAL*, **81**, 640 (1959), and earlier papers.

(6) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Office of Ordnance Research, Contract No. DA-36-061-ODR-607.

THE DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

P. S. SKELL⁶

I. STARER

RECEIVED APRIL 2, 1960

FORMATION OF 1,2-DIMETHYLCYCLOPROPANE IN THE DEAMINATION OF SATURATED ALIPHATIC AMINES¹

Sir:

The hydrocarbon fraction from the deamination of 3-methyl-2-aminobutane² at 56° in acetic acid has been found to contain the expected³ 3-methyl-1-butene, 2-methyl-1-butene and 2-methyl-2-butene and two additional compounds. These compounds have been identified as *cis*- and *trans*-1,2-dimethylcyclopropane on the basis of gas chromatographic retention times, resistance to permanganate ox-

(1) This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society, and grateful acknowledgment is hereby made to the donors.

(2) Prepared according to J. S. Buck and A. M. Hjort, *THIS JOURNAL*, **59**, 2567 (1937), the amine had b.p. 85–87°. D. Trasciatti, *Gazz. chim. ital.*, **29**, II, 92 (1899) [*Chem. Zentr.*, **70**, II, 801 (1899)] gives b.p. 84–87°.

(3) S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958), have studied the acetolysis of 3-methyl-2-butyl *p*-toluenesulfonate.