10.2; adenine:pentose:total P:labile P = 1:1:2:1. Found: C, 46.0, 45.7; H, 4.32, 4.20; N, 13.7; P, 9.30, 9.56; adenine:pentose:total P:labile P = 1:0.97:1.98:0.93), which is indistinguishable from an authentic sample by mixture m.p., comparison of infrared and ultraviolet spectra, and mobility in paper chromatographic and electrophoretic systems, and which is enzymatically active (pyruvate kinase coupled with lactic dehydrogenase).[14]

Solutions of AMP-I, prepared from AMP monohydrate and excess CDI, react with phosphoric acid to produce a mixture of compounds, the nature of which will be described in a future communication.

(14) T. Bücher and G. Pfleiderer, "Pyruvate Kinase from Muscle," in S. P. Colowick and N. O. Kaplan, eds., "Methods in Enzymology," Vol. I, Academic Press, Inc., New York, N. Y., 1955, pp. 435–440.

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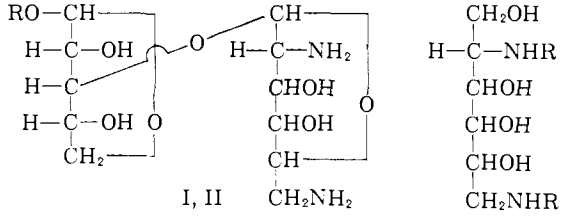
RECEIVED APRIL 28, 1960

CHEMISTRY OF THE NEOMYCINS. VI. STRUCTURE OF NEOBIOSAMINE B[1]

Sir:

Neobiosamine B[1,2] has been shown to be a disaccharide composed of a diaminohexose, neosamine B,[1,3] linked glycosidically[2] to D-ribose.[1,4] In this report neobiosamine B is shown to have the structure and partial stereochemistry of I.



I, II

D-Ribose — Neosamine B — IIIa,b,c

I, R = H (Neobiosamine B)
II, R = CH_3 (Methyl neobiosaminide B)

IIIa, R = H
IIIb, R = 2,4-$(O_2N)_2$-C_6H_3
IIIc, R = $COCH_3$

N,N′-Bis-(2,4-dinitrophenyl)-neosaminol B (IIIb), obtained by sodium borohydride reduction of neosamine B to neosaminol B (IIIa) and subsequent dinitrophenylation,[1] consumed 1.91 mole of sodium metaperiodate with formation of only 0.03 mole of formaldehyde (chromotropic acid method). Periodate–permanganate oxidation[5,6] of the same compound (IIIb) gave glycine DNP, R_f 0.384 (BEW 415),[7] 0.260 (AA)[7] [authentic sample: R_f 0.381 (BEW 415), 0.267 (AA)] and L-serine DNP, $[\alpha]^{27}D$ +68° (*c* 0.25, 4% aq. $NaHCO_3$), R_f 0.365 (BEW 415), 0.240 (AA) [authentic sample: R_f 0.365 (BEW 415), 0.240 (AA)]. Identical oxidation of N-2,4-dinitrophenyl-D-glucosaminol, m.p. 163–164° [*Anal.* Found: C, 41.46; H, 4.94; N, 11.74.], also gave L-serine DNP, $[\alpha]^{25}D$ +66° (*c* 0.325, 4% $NaHCO_3$), R_f 0.365 (BEW 415). Similar, confirmatory, results were obtained with the N,N′-diacetyl derivative (IIIc)[8] and will be reported in the full paper. The structure and partial stereochemistry of neosaminol B are thus as shown in (IIIa).

Neosamine B consumed 2.56 mole of periodate in 35 min. with formation of only 0.02 mole of formaldehyde; this result establishes the compound as an aldohexose rather than a ketohexose (which would have given formaldehyde). Further, it exists in the pyranose form in methyl neobiosaminide B (II) since the latter compound[2] consumed 1.98 mole of periodate in 40 min. with formation of only 0.05 mole of formaldehyde. Ribose was recovered from hydrolysis of the oxidized methyl neobiosaminide B. Its protection from periodate oxidation establishes (1) that neobiosamine B must be a neosaminidoribose, rather than a ribosido-neosamine (a conclusion reached earlier from the relative ease of hydrolysis of methyl neobiosaminide B and neobiosamine B),[2] and (2) that neosamine B is *not* linked at the C-4 or C-5 position of ribose (which would have necessitated a three-mole periodate uptake with no recovered ribose).

The position of the ribose linkage was determined ultimately by periodate oxidation of neobiosaminol B, obtained by borohydride reduction of neobiosamine B.[1] The reduced disaccharide consumed 4.2 mole of periodate during one hour with formation of 1.6 mole of formaldehyde; this establishes the linkage at ribose C-3 (rather than C-2).

This position was confirmed by methylation studies. Methyl neobiosaminide B was N-acetylated with acetic anhydride and silver acetate,[9] then O-methylated with methyl iodide and barium oxide.[10] The product was hydrolyzed in dilute hydrochloric acid to 2,4-O,O-dimethyl-D-ribose, $[\alpha]^{26}D$ −30.5° (*c* 2.6, H_2O), R_f 0.61, R_{ribose} 2.18 (BAW 415)[7] [lit.[11] values for 2,5 (and 3,5-)-O,O-dimethyl-D-ribose: R_f 0.69, R_{ribose} 2.30 (BAW 415)]. On paper electrophoresis in borate buffer the isolated dimethylribose did not migrate,[11] and it consumed only 0.04 mole of periodate in 52 hr.; these observations establish the C-2 O-methyl group. The C-4 O-methyl group was demonstrated by reducing the dimethylribose with sodium borohydride to 2,4-O,O-dimethylribitol. In the reduced compound the methyl groups were located by its lack of reactivity with sodium metaperiodate (0.00 mol. uptake in 79 hr.) and with periodate–permanganate spray reagent and by its optical inactivity within experi-

(1) Paper V, K. L. Rinehart, Jr., A. D. Argoudelis, W. A. Goss, A. Sohler and C. P. Schaffner, THIS JOURNAL, **82**, in press (1960).

(2) K. L. Rinehart, Jr., P. W. K. Woo, A. D. Argoudelis and A. M. Giesbrecht, *ibid.*, **79**, 4567 (1957).

(3) K. L. Rinehart, Jr., P. W. K. Woo and A. D. Argoudelis, *ibid.*, **80**, 6461 (1958).

(4) K. L. Rinehart, Jr., P. W. K. Woo and A. D. Argoudelis, *ibid.*, **79**, 4568 (1957).

(5) R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

(6) R. U. Lemieux and H. F. Bauer, *Anal. Chem.*, **26**, 920 (1954).

(7) BEW 415: *n*-butyl alcohol:ethyl alcohol:water, 4:1:5, by volume. AA: isoamyl alcohol containing 1% acetic acid. BAW 415: *n* butyl alcohol:acetic acid:water, 4:1:5, by volume.

(8) A. D. Argoudelis, Ph.D. Thesis, University of Illinois, August, 1959.

(9) T. White, *J. Chem. Soc.*, 428 (1940).

(10) R. Kuhn, H. H. Baer and A. Seeliger, *Ann.*, **611**, 236 (1957).

(11) D. M. Brown, D. I. Magrath and A. R. Todd, *J. Chem. Soc.*, 1442 (1954).

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 paramobiosamine, a degradation product of the antibiotic paramomycin [T. H. Haskell, J. C. French and Q. R. Bartz, THIS JOURNAL, **81**, 3481 (1959)].

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RECEIVED APRIL 8, 1960

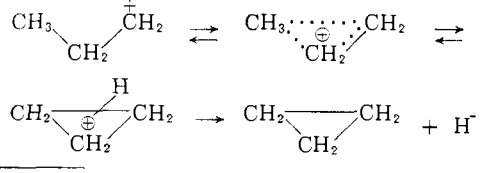
CYCLIZATION OF CARBONIUM TO CYCLOPROPANES[1]

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 alcohol[2] *n*-propyl carbonium ion being the postulated intermediate, that cyclopropane and propylene were reaction products. The resulting C_3H_6 is 90% propylene and 10% cyclopropane. Nitrous acid deamination of *n*-propylamine in aqueous solution also yields C_3H_6 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_nH_{2n} products, %
i-Propyl	None
n-Propyl	10
n-Butyl	2
i-Butyl	4
s-Butyl	<0.5
t-Butyl	None
Neopentyl	None
t-Amyl	None
Amine[b]	
n-Propyl	10
Neopentyl	None
4,4-Dimethyl-1-pentyl	No cyclopropane

[a] At reflux, $HCBr_3$ 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.

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RECEIVED APRIL 2, 1960

FORMATION OF 1,2-DIMETHYLCYCLOPROPANE IN THE DEAMINATION OF SATURATED ALIPHATIC AMINES[1]

Sir:

The hydrocarbon fraction from the deamination of 3-methyl-2-aminobutane[2] at 56° in acetic acid has been found to contain the expected[3] 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 oxi-

(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.