The results are summarized in Table I and compared with the quantities of free purines and pyrimidines found in acid hydrolysates of nucleic acids (*Procedure 3*).[4] It will be seen that the nucleotide analyses presented here contribute to a more complete understanding of ribonucleic acid composition, mainly with respect to uridylic acid which has proved relatively resistant to formic acid hydrolysis.[4] They also reveal remarkable differences between ribonucleic acids from different sources.

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REARRANGEMENT OF 2-BROMOBICYCLO[2,2,2]OCTANE WITH SILVER BROMIDE

Sir:

We have found that the brominative decarboxylation[1] of a suspension of the silver salt of bicyclo[2,2,2]octane-2-carboxylic acid[2] (I) affords 2-bromobicyclo[1,2,3]octane (II), m. p. 39–41°. The structure of II is tentatively assigned on the grounds (a) that reduction with sodium and alcohol gives bicyclo[1,2,3]octane (III) [*Anal.* Calcd. for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 86.88; H, 13.14], m. p. 139.5–141°, reported 133°[3,4] and 141°[5] and (b) that aqueous alcoholic alkali gives an alcohol, m. p. 183–184°, which is apparently identical with the bicyclo[1,2,3]octane-2-ol, m. p. 183°, of Alder and Windemuth[5] by virtue of the similarity of the phenylurethan [*Anal.* Calcd. for $C_{15}H_{19}O_2N$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.62; H, 7.74; N, 5.64], m. p. 128–129.5°, reported[5] 130° and the hydrogen phthalate [*Anal.* Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.11; H, 6.74], m. p. 118–119°, reported[5] 116–117°.

This rearrangement, the first example of the conversion of the bicyclo[2,2,2]octane system to the bicyclo[1,2,3]octane system,[6] has prompted examination of the effect of silver bromide on the potentially initial product, 2-bromobicyclo[2,2,2]-octane (IV). Unrearranged IV [*Anal.* Calcd. for $C_8H_{13}Br$: C, 50.81; H, 6.93; Br, 42.26. Found: C, 50.90; H, 6.89; Br, 42.13], m. p. 64–65.5°, is prepared from bicyclo[2,2,2]octene[2] by the addition of hydrogen bromide in ether,[7] and can be reduced to bicyclo[2,2,2]octane (V), m. p. 169.5–170.5°. On treatment in carbon tetrachloride either with silver bromide or with silver acetate and bromine but not with bromine alone, IV is converted in good yield to II (identified by reduction to III).

The silver bromide-catalyzed rearrangement affords strong experimental support to the hypothesis that silver bromide is a Lewis acid of sufficient strength to weaken *observably* the carbon–bromine bond of an alkyl bromide. Limiting the establishment of a mechanism for the brominative decarboxylation is the corollary hypothesis that the alkyl bromide actually *isolated*, having been subject to alteration by silver bromide, is not necessarily identical with the bromide produced initially in the decarboxylation. Consequently, the rearrangement observed in the decarboxylation of I may not, in the absence of further experimentation, form the basis for a mechanistic hypothesis. Similarly no mechanistic significance is attributable to the optical inactivity of the 3-bromoheptane isolated from the brominative decarboxylation of optically active silver heptane-3-carboxylate,[8] in the absence of observations on the optical stability of 3-bromoheptane in the presence of silver bromide.

[1] *Cf.* Kleinberg, *Chem. Rev.*, **40**, 381 (1947).

[2] Seka and Tramposch. *Ber.*, **75**, 1379 (1942).

[3] Komppa, *et al.*, *Ann.*, **521**, 242 (1936).

[4] Barrett and Linstead, *J. Chem. Soc.*, 611 (1936).

[5] Alder and Windemuth, *Ber.*, **71**, 2404 (1938).

[6] The driving force is plausibly derived from the relief of Pitzer strain [Beckett, Pitzer and Spitzer, THIS JOURNAL, **69**, 2488 (1947)].

[7] Following Meerwein and von Emster, *Ber.*, **55**, 2500 (1922).

[8] Arnold and Morgan, THIS JOURNAL, **70**, 4248 (1948).

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VITAMIN B_{12}. V. IDENTIFICATION OF CRYSTALLINE VITAMIN B_{12a}

Sir:

Catalytic reaction of vitamin B_{12} with hydrogen has yielded a crystalline product which shows high hematopoietic activity in pernicious anemia, although it is somewhat less active than vitamin B_{12}.

To a solution of 26.3 mg. of vitamin B_{12} in 15 ml. of water, 78 mg. of platinum oxide catalyst was added and the mixture was shaken with hydrogen at atmospheric pressure for twenty hours. During reaction, the red color changed to dark brown, but on contact with air the red color returned indicating changes in the cobalt ion. The filtrate from the catalyst was evaporated *in vacuo* at 25°. The residue was dissolved in 1 ml. of water and 6 ml. of acetone was added. After several hours, 1–2 mg. of precipitate formed and was removed. Acetone (2 ml.) was added again and, after standing, 4–5 mg. of precipitate was removed. Acetone (2 ml.) was added, and dark-red crystals formed during twenty-four hours; yield, 12 mg. Further addition of acetone yielded more crystalline material.

After two recrystallizations from water by the addition of acetone, the red crystals showed refractive indices[1a] of α, 1.580; β, 1.640; and γ, 1.654. The cobalt (4.58%) and phosphorus (2.43%) content reveal that the B_{12} molecule is not grossly altered.

[1] Courtesy of (a) Dr. Charles Rosenblum; (b) Mr. David Hendlin; (c) Dr. Gladys Emerson; (d) Dr. Walther Ott.