

an order of magnitude faster than the ultrafast reaction of $\text{NH}_4^+:\text{NH}_3$ hydrogen exchange (II).⁷ We infer that the chemical mobility of the electrons in these solutions matches their physical mobility (e.g., electrical conductivity), and that this may be correlated with the physical models being proposed⁸ to describe metal-ammonia solutions. In these solutions, the electron attack on an electron-attracting entity appears to be *via* a mechanism quite different from that of ordinary ionic transport.

(7) Because the reactant ratio of $\text{Li}:\text{NH}_4^+$ is high, there is the possibility that only the ammonia associated with one equivalent of lithium should be considered as exchanging with the ammonia associated with ammonium ion. This seems improbable, since it would involve the mixing of all the NH_4Br solution with only a part of the Li solution. It is more straight-forward to assume that the mixing involves approximately equal amounts of both solutions at all times, that both solutions mix fairly uniformly in order for all the NH_4^+ to react, that both reactions I and II are diffusion controlled, and that the rate of attack of NH_4^+ ions by electrons competes effectively with the rate of attack (exchange) of NH_4^+ ions by NH_3 molecules.

(8) G. Lepoutre and J. F. Dewald, *THIS JOURNAL*, **78**, 2953 (1956); E. Becker, R. H. Lindquist and B. J. Alder, *J. Chem. Phys.*, **25**, 971 (1956); M. C. R. Symons, *ibid.*, **30**, 1628 (1959).

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THE SYNTHESIS OF 2-DEOXY-D-RIBOFURANOSE 1-PHOSPHATE

Sir:

Cleavage of a ribonucleoside with a nucleoside phosphorylase was reported by Kalckar¹ to give a ribose 1-phosphate. Subsequently, this product was shown to be α -D-ribofuranose 1-phosphate on the basis of certain chemical tests, as well as by chemical synthesis of both anomers.² In a presumably similar fashion, the action of the appropriate nucleoside phosphorylases on deoxyribonucleosides leads to the formation of an extremely acid-labile 2-deoxy-D-ribofuranose 1-phosphate,³⁻⁵ which has been isolated as a crystalline di-(cyclohexylammonium) salt.^{4,5} The optical rotation of this material, $[\alpha]_D +38.8^\circ$,⁵ and the manner in which it is enzymatically synthesized, suggest⁵ that, like its D-ribose analog, it possesses the α -configuration. This conclusion is supported by the present work, in which we describe the chemical synthesis of a 2-deoxy-D-ribofuranose 1-phosphate of high biological activity.

Crystalline 3,5-di-*O-p*-toluoyl-2-deoxy-D-ribofuranosyl chloride⁶ was condensed in benzene solution with disilver phosphate⁷ (previous workers who have used this material for the synthesis of phosphates⁸ have termed it "monosilver phosphate"). The product of the condensation was saponified in aqueous alcohol with lithium hydroxide, the lithium replaced by cyclohexylamine using an ion exchange

(1) H. M. Kalckar, *J. Biol. Chem.*, **167**, 477 (1947).

(2) R. S. Wright and H. G. Khorana, *THIS JOURNAL*, **78**, 811 (1956); G. M. Tener, R. S. Wright and H. G. Khorana, *ibid.*, **79**, 441 (1957).

(3) M. Friedkin and H. M. Kalckar, *J. Biol. Chem.*, **184**, 437 (1950).

(4) M. Friedkin, *ibid.*, **184**, 449 (1950); M. Friedkin and D. Roberts, *ibid.*, **207**, 257 (1954).

(5) H. L. A. Tarr, *Can. J. Biochem. and Physiol.*, **36**, 517 (1958).

(6) M. Hoffer, R. Duschinsky, J. J. Fox and N. Yung, *THIS JOURNAL*, **81**, 4112 (1959).

(7) R. Flatt and G. Brunisholz, *Helv. Chim. Acta*, **34**, 692 (1951).

(8) F. Lipmann and L. C. Tuttle, *J. Biol. Chem.*, **153**, 571 (1944).

resin and the crude dry salts extracted with *n*-propyl alcohol to remove cyclohexylammonium *p*-toluolate. Inorganic phosphate then was removed as magnesium ammonium phosphate and the resulting material crystallized as the di-(cyclohexylammonium) salt from methanol-ether or from aqueous acetone. The product, which was obtained in a yield of *ca.* 30%, based on the chloride, showed $[\alpha]_D^{20}$ of about $+22^\circ$ in water. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{37}\text{N}_2\text{O}_7\text{P}$ (412.47): C, 49.49; H, 9.04; N, 6.79; P, 7.51. Found: C, 49.33; H, 9.32; N, 6.63; P, 7.53.

In *n*-propyl alcohol-ammonia-water and in isopropyl alcohol-ammonia-water the material is chromatographically homogeneous, and possesses the same R_f as authentic, enzymatically prepared 2-deoxy-D-ribofuranose 1-phosphate. Fractional crystallization of the synthetic salt has not been entirely successful; however, using methanol-ether, fractions were obtained with $[\alpha]_D^{20}$ as high as $+30^\circ$ (C, 49.44; H, 8.76; N, 6.87; P, 7.48). One of these fractions, when assayed enzymatically using fish nucleoside phosphorylase,⁵ had about 80% of the activity of natural 2-deoxy-D-ribofuranose 1-phosphate.

Since crystalline acylated 2-deoxy-D-ribofuranosyl halides have been shown⁶ to give rise to anomeric mixtures of 2-deoxy-D-ribofuranosides, it seems probable that the phosphate obtained here is a mixture of anomers. A comparison of our product and the natural material on the basis of optical rotation and biological activity supports the assumption⁵ that the natural substance of $[\alpha]_D +38.8^\circ$ is the α -anomer and, furthermore, one may calculate that the β -anomer would have an $[\alpha]_D$ of approximately -10° .

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THE PHOTOREDUCTION OF PORPHYRINS AND THE OXIDATION OF AMINES BY PHOTO-EXCITED DYES

Sir:

Two distinct series of hydro-porphyrins are known. The hydrogens may be located on the peripheral "pyrrole" ring carbons (chlorophyll and bacteriochlorophyll), or they may be on the methine carbons (porphomethenes,¹ I and II, and porphyrinogens). The photoreduction of uroporphyrin produces, in addition to a transitory compound absorbing at 440 and 735 $\mu\mu$, a more stable substance absorbing at 500 $\mu\mu$ which is related to the second series of hydro-porphyrins, the porphomethenes.

Porphyrins may be photoreduced by a wide variety of compounds, e.g., ascorbic acid, glutathione and tertiary amines. The reduction of uroporphyrin with ethylenediaminetetraacetic acid

(1) D. Mauzerall and S. Granick, *J. Biol. Chem.*, **232**, 1141 (1958).