to be of the same order of activity as the authentic material.

LABORATORY OF ORGANIC CHEMISTRY
UNIVERSITY OF WISCONSIN WILLIAM S. JOHNSON
MADISON, WISCONSIN ROBERT P. GRABER

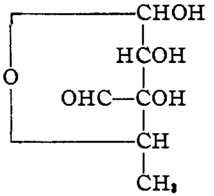
RECEIVED JUNE 14, 1948

STREPTOMYCES ANTIBIOTICS. XIX. DIHYDROSTREPTOSONIC ACID LACTONE AND CONFIGURATION OF STREPTOSE AND STREPTOBIOSAMINE

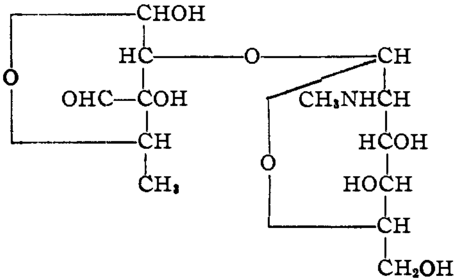
Sir:

2-Methyl pentaacetyldihydrostreptobiosaminide[1] was allowed to react stepwise with ethyl mercaptan–hydrogen chloride, acetic anhydride, and mercuric chloride for the preparation of amorphous pentaacetyldihydrostreptobiosamine.[2] Acetylation of this compound gave hexaacetyldihydrostreptobiosamine.[2] Oxidation by bromine and hydrolysis by hydrochloric acid of pentaacetyldihydrostreptobiosamine gave the known N-methyl-L-glucosamine and the new dihydrostreptosonic acid lactone, m. p. 143–144°, $[\alpha]_D$ −32° (*c*, 0.40 in water). Reaction of the lactone with hydrazine gave dihydrostreptosonic acid hydrazide, m. p. 137–139°, $[\alpha]_D$ +23° (*c*, 0.9 in water).

Application of Hudson's rules of rotation to streptosonic acid diamide[3] and dihydrostreptosonic acid hydrazide shows that the hydroxyl group at C_2 of streptose lies on the right. Since it has already been shown[4] that the hydroxyl groups at C_2 and C_3 of streptose are *cis*, and that the configuration about C_4 is *levo*,[5] the configuration of L-streptose is represented by structure I. On the basis of these data, and the calculations of the glycosidic linkage between streptose and N-methyl-L-glucosamine to be α-L,[6] the configuration of streptobiosamine is represented by structure II. The levorotations of streptosonic acid lactone[3] and dihydrostreptosonic acid lactone support the applicability of Hudson's rules to these streptose derivatives, since it is established conclusively that the configuration about C_4 of these lactones is L. That the lactone of dihydrostreptosonic acid lactone involves the secondary hydroxyl group at C_4 is shown by the liberation of formaldehyde when the lactone reacts with two equivalents of periodic acid.



I



II

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[1] Brink, Kuehl, Flynn and Folkers, THIS JOURNAL, **68**, 2557 (1946).

[2] Stavely, Wintersteiner, Fried, White and Moore, *ibid.*, **69**, 2742 (1947).

[3] Kuehl, Flynn, Brink and Folkers, *ibid.*, **68**, 2679 (1946).

[4] Brink, Kuehl, Flynn and Folkers, *ibid.*, **68**, 2405 (1945).

[5] Fried, Walz, and Wintersteiner, *ibid.*, **68**, 2746 (1946).

[6] Lemieux, DeWalt and Wolfrom, *ibid.*, **69**, 1838 (1947).

FREDERICK A. KUEHL, JR.
RESEARCH DEPARTMENT MARY NEALE BISHOP
MERCK AND CO., INC. EDWIN H. FLYNN
RAHWAY, N. J. KARL FOLKERS

RECEIVED MAY 27, 1948

CHARACTERISTICS OF THE DROPPING MERCU ELECTRODE IN FUSED SALTS

Sir:

In a preliminary investigation of the applicability of polarographic techniques to fused salt media we have obtained typical polarographic reduction waves for the cations of a number of salts dissolved in a fused salt solvent. The results indicate that the Ilkovic equation[1,2] is applicable to the melt employed, a ternary eutectic consisting of 66.65 mole % ammonium nitrate, 25.76% lithium nitrate, and 7.59% ammonium chloride (m. p. 86.2°).[3]

Mercury was used for the dropping electrode and the stationary unpolarized anode pool in a cell maintained at 125 ± 0.5° in an oil-bath. Drops were collected in a Pyrex spoon, washed, dried, and weighed for tests of the Ilkovic equation.

Characteristic reduction waves were obtained with nickel(II), copper(II), and bismuth(III), the latter two exhibiting maxima. A trace of potassium iodide eliminated the maximum in the case of copper. Varying degrees of success have been had with other solute salts, prime difficulties being limited solubility in or reaction with the solvent electrolyte.

TABLE I

TEST OF THE ILKOVIC EQUATION

No.	C, mmol./l.	i_d, μ amp.	m mg./sec.	$t_{max.}$, sec.	$\frac{i_d}{Cm^{2/3}t^{1/6}_{max}}$
1	1.95	3.74	1.41	4.0	1.21
2	4.98	10.0	1.45	4.5	1.22
3	6.77	12.8	1.37	3.9	1.22
4	9.97	17.2	1.45	3.4	1.10
5	12.8	21.6	1.40	3.5	1.09
6	12.8	16.6	0.658	7.6	1.22

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[1] D. Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **6**, 498 (1934).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 38.

[3] E. P. Perman and R. H. Wilson, *J. Chem. Soc.*, **125**, 1709 (1924).

The results obtained by varying the concentration of nickelous nitrate in the ternary solvent are presented in Table I.

Test no. 6 was made on same solution as no. 5 but with a different capillary. With a value of 13.29 g./cc. for the density of mercury at 125°, the Ilkovic equation becomes

$$i_d = 614nD^{1/2}Cm^{2/3}t_{\max}^{1/6}$$

with the symbols having the usual meaning given by Kolthoff and Lingane.[2] The agreement of the experimental data with the Ilkovic equation can be seen from the essential constancy of the ratio $i_d/Cm^{2/3}t_{\max}^{1/6}$ in the last column of the table. The average deviation in the ratio is ±4.3%. Substitution of the average ratio, 1.18, into the Ilkovic equation gives a diffusion coefficient equal to 9.2×10^{-7} cm.²/sec. for the nickel bearing ion.

Work is in progress to eliminate the solubility and solvent instability difficulties by employing more stable solvent electrolytes, *e. g.*, alkali halides, at higher temperatures. This will also allow investigation of a number of metals for the dropping electrode.

INSTITUTE FOR THE STUDY OF METALS
UNIVERSITY OF CHICAGO N. H. NACHTRIEB
CHICAGO, ILL. M. STEINBERG

RECEIVED MAY 7, 1948

EXCHANGE REACTIONS BETWEEN IODINE ATOMS AND ORGANIC IODIDES

Sir:

Several workers have reported exchange reactions between organic iodine compounds and inorganic iodides, but there are very few known examples of exchanges with neutral iodine atoms or molecules. Methyl iodide[1] and several diiodophenols[2] have been shown to exchange with elementary iodine in polar solvents, but the mechanisms of these reactions were not elucidated. Noyes, Dickinson and Schomaker[3] demonstrated that neutral atoms were involved in the exchange of 1,2-diiodoethylene with elementary iodine in saturated hydrocarbon solvents.

We have now observed atomic exchange reactions with some other representative organic iodides. The experiments were conducted with iodine-131 supplied by the Oak Ridge National Laboratory and obtained on allocation from the United States Atomic Energy Commission. Hexane solutions 0.002 molar (0.004 normal) in radioactive iodine and 0.04 molar in organically combined iodine were illuminated with a tungsten lamp at about 30°. The iodine in each solution was then extracted by shaking it with an acidic aqueous solution of sodium sulfite, and the activities in one or both of the separated solutions were measured with a jacketed counter. Comparative approximate rate constants based on *trans*-diiodoethylene as unity were as follows:

Allyl iodide	much greater than	200
Trans-diiodoethylene		1.0
Iodobenzene		0.002
Ethyl iodide	less than	0.001

The rate constant for allyl iodide could not be obtained with any precision, for exchange was 60% complete in twenty seconds under the normal illumination of the laboratory desk. This amount of exchange corresponds to a rate approximately 200 times as fast as the rate of exchange of *trans*-diiodoethylene under the much more intense illumination employed in the other experiments. When the laboratory was darkened to an extent such that the necessary operations could barely be carried out, exchange of allyl iodide was 25% complete in twenty seconds. Therefore, at least a large fraction of the exchange appears to involve free atoms, but the possibility of an accompanying dark reaction is not excluded. Studies of the separation procedure demonstrated that allyl iodide underwent no more than 1% of exchange with iodide ion under the conditions employed in the reduction of the iodine.

A solution of ethyl iodide which was illuminated for one week underwent a significant amount of exchange, but the data did not permit the calculation of a reliable rate constant.

That exchange in the last three compounds in the table requires free atoms is indicated by the fact that duplicate solutions stored in the dark for as much as one week underwent no more than 1% of exchange.

We are undertaking a more thorough investigation of the kinetics of these reactions.

CONTRIBUTION FROM THE CHEMICAL LABORATORIES
OF COLUMBIA UNIVERSITY
NEW YORK 27, N. Y. RICHARD M. NOYES

RECEIVED JUNE 7, 1948

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(1) H. A. C. McKay, *Nature*, **139**, 283 (1937).

(2) W. H. Miller, G. W. Anderson, R. K. Madison and D. J. Salley, *Science*, **100**, 340 (1944).

(3) R. M. Noyes, R. G. Dickinson and V. Schomaker, THIS JOURNAL, **67**, 1319 (1945).

AN INTERRELATIONSHIP OF THYMIDINE AND VITAMIN B$_{12}$

Sir:

In a series of studies on factors functionally related to folic acid and *p*-aminobenzoic acid, thymidine was isolated from liver as a factor preventing the toxicity of a competitive antagonist of folic acid.[1] The recently reported isolation of vitamin B$_{12}$ as a growth factor for *Lactobacillus lactis* Dorner[2,3] necessitated a study of the function of the vitamin to determine whether or not it is identical with a factor found in this Laboratory to be concerned with the biosynthesis of thymidine. As vitamin B$_{12}$ has been isolated using an assay with *Lactobacillus lactis* Dorner, this organism was utilized in the present investigation.

A medium suitable for assay techniques has not

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(1) Shive, *et al.*, THIS JOURNAL, in press.

(2) Rickes, *et al.*, *Science*, **107**, 396 (1948).

(3) Shorb, *ibid.*, **107**, 397 (1948).