suction filtration and crystallized once with 25 cc. of 2:1 benzene-alcohol; 1.4 g. of faintly yellow crystals melting 174–176°, 52% of the theoretical.

Anal. Calcd. for $C_{20}H_{12}O_6Cl_2N_2$: Cl, 15.8; mol. wt., 447.2. Found: Cl, 15.4; mol. wt., 425, 487.

When the carbinol and 3,5-dinitrobenzoyl chloride were allowed to react without pyridine as a solvent, di-(*p,p'*-dichlorobenzohydryl) ether, m. p. 120–123°, was obtained.[2] Determination of the molecular weight of the 3,5-dinitrobenzoate ebullioscopically in benzene consistently gave values ranging from 1.5–2 times the theoretical, indicating that association probably had occurred. The reported values were obtained with acetone as the solvent.

SHERWIN-WILLIAMS LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO
OLIVER GRUMMITT
ALLEN BUCK
RUTH JOSEPH

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[2] Grummitt and Buck, THIS JOURNAL, **67**, 693 (1945).

COMMUNICATIONS TO THE EDITOR

FURAN AND TETRAHYDROFURAN DERIVATIVES. IV. THE SYNTHESIS OF HEXAHYDRO-2-OXO-1-FURO[3,4]IMIDAZOLE DERIVATIVES

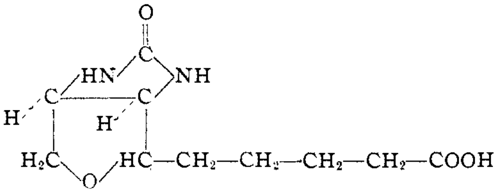
Sir:

In a search for convenient methods to synthesize biotin-like compounds, a number of 3,4-diaminocarbethoxyfurans have recently been prepared.[1] It has now been observed that low pressure hydrogenation converts these substances into the corresponding tetrahydro derivatives. Thus, catalytic hydrogenation of 3,4-diaminocarbethoxy-2-methylfuran under conditions which favor *cis* addition of hydrogen gave a *cis* 3,4-diaminocarbethoxy-2-methyltetrahydrofuran isomer,[2] m. p. 95–96°. (*Anal.* Calcd. for $C_{11}H_{20}O_5N_2$: C, 50.75; H, 7.74; N, 10.75; OC_2H_5, 34.62. Found: C, 50.80; H, 7.79; N, 10.68; OC_2H_5, 34.87.) Mild hydrolysis of this substance with dilute barium hydroxide resulted in a ring closure and a hexahydro-2-oxo-4-methyl-1-furo[3,4]imidazole isomer, m. p. 234–236°, was obtained. (*Anal.* Calcd. for $C_6H_{10}O_2N_2$: C, 50.71; H, 7.09; N, 19.70. Found: C, 51.11; H, 7.26; N, 19.38.)

The structure of this compound was established by drastic hydrolysis with barium hydroxide at 130–140° for twenty hours, which opened the urea ring with the formation of the corresponding *cis*-3,4-diamino-2-methyltetrahydrofuran, isolated as the crystalline sulfate, m. p. 270–275°. (*Anal.* Calcd. for $C_5H_{14}O_5N_2S$: C, 28.03; H, 6.59; N, 13.07; S, 14.97. Found: C, 27.82; H, 6.38; N, 12.89; S, 15.35.) Treatment of the above diamine sulfate with phosgene in sodium bicarbonate solution gave a hexahydro-2-oxo-4-methyl-1-furo[3,4]imidazole, m. p. 234–236°. (*Anal.* Calcd. for $C_6H_{10}O_2N_2$: N, 19.70. Found: N, 20.03), which by mixed melting point was found to be identical with the starting material.

The above described reactions demonstrate that *cis*-3,4-diaminocarbethoxy-2 substituted tetrahydrofurans on treatment with dilute barium hydroxide undergo ring closure to form hexahydro-2-oxo-1-furo[3,4]imidazoles. This novel procedure represents a convenient way to prepare derivatives of this new class of compounds.

Hydrogenation of 3,4-diaminocarbethoxy-2-furanpentanol[1] followed by mild alkaline treatment gave a hexahydro-2-oxo-1-furo[3,4]-imidazole-4-pentanol isomer, m. p. 152–153°. (*Anal.* Calcd. for $C_{10}H_{18}O_3N_2$: C, 56.07; H, 8.47; N, 13.07. Found: C, 56.06; H, 8.18; N, 12.90), which on oxidation was converted into the corresponding hexahydro-2-oxo-1-furo[3,4]imidazole-4-valeric acid (I), m. p. 208–210°. (*Anal.* Calcd. for $C_{10}H_{16}O_4N_2$: C, 52.63; H, 7.07; N, 12.27. Found: C, 52.67; H, 7.43; N, 12.12.) Compound (I) represents one of the oxygen analogs of biotin. Further work which is at present under way will demonstrate the stereochemical relationships between this new compound and biotin.



(I)

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA
KLAUS HOFMANN

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[1] Hofmann and Bridgwater, THIS JOURNAL, in press.

[2] The designation *cis* indicates the position of the amino groups. The steric position of the side chain is not established.

STUDIES IN THE TERPENE SERIES. II.[1] HYDROGEN DISPROPORTIONATION OF LIMONENE

Sir:

During the study of bromination of terpenic hydrocarbons it was noticed that the unreacted terpenes contained a large amount of aromatic hydrocarbons. On further investigation it was found that a small amount of organic bromides admixed with *d*-limonene caused hydrogen transfer to occur during the process of distillation,

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[1] For Paper I of this series, see V. N. Ipatieff and H. Pines, THIS JOURNAL, **66**, 1120 (1944).