REACTION OF CHLOROPYRIDO[2,3-d]PYRIMIDINES WITH DMSO*

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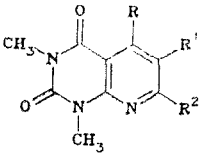
We have observed an unusual reaction involving replacement of the chlorine atoms by a hydroxy group in pyrido[2,3-d]pyrimidines Ia-h by refluxing in DMSO for 0.5-2 h and subsequent dilution of the reaction mixture with water. Compounds IIa-f are formed as a result of this reaction. With respect to their physicochemical and spectral characteristics, pyridopyrimidines IIa-c were identical to previously described samples [2].

The reaction of 5,6,7-trichloropyridopyrimidine Ie with DMSO leads to 5-hydroxy-6,7-dichloro derivative IIe. Only the previously described pyridopyrimidine IIf [3] is isolated from 6-nitro derivatives If-h; in addition to replacement of the halogen atom by a hydroxy group, hydrolysis of the methoxy group attached to the $C_{(7)}$ atom occurs in the case of Ig. The reaction with DMSO proceeds only when there is an electron-acceptor substituent attached to the $C_{(6)}$ atom; the character of the products depends on the nature of this substituent.



Ia-h IIa-f

I a R=Cl, $R^1=NO_2$, R^2=H; b R=Cl, R^1=Br, R^2=H; c R=R^1=Cl, R^2=H; d R=NHC_4H_9, $R^1=NO_2$, R^2=Cl; e R=$R^1=R^2$=Cl; f R=R^2=Cl; $R^1=NO_2$; g R=Cl, $R^1=NO_2$, $R^2=OCH_3$; h R=OH, $R^1=NO_2$, R^2=Cl; II a R=OH, $R^1=NO_2$, R^2=H; b R=OH, R^1=Br, R^2=H; c R=OH, R^1=Cl, R^2=H; d R=NHC_4H_9, $R^1=NO_2$, R^2=OH; e R=OH, $R^1=R^2$=Cl; f R=R^2=OH, $R^1=NO_2$

5-Butylamino-7-hydroxy-1,3-dimethyl-6-nitro-1,2,3,4-tetrahydropyrido[2,3-d]pyrimidine-2,4-dione (IId, $C_{13}H_{17}N_5O_5$). This compound had mp 264°C (from acetone). IR spectrum: 3109 (NH); 1667, 1725 (CO); 1345, 1509 cm^{-1} (NO_2). PMR spectrum ($CDCl_3$): 3.24 (3H, s), 3.47 (3H, s), 0.87 (3H, t, J = 5 Hz), 1.15-1.66 (4H, m), 2.85-3.05 (2H, m), 9.33 ppm (1H, t, J = 5 Hz).

5-Hydroxy-1,3-dimethyl-6,7-dichloro-1,2,3,4-tetrahydropyrido[2,3-d]pyrimidine-2,4-dione (IIe, $C_9H_7Cl_2N_3O_3$). This compound had mp 175-176.5°C (from benzene). IR spectrum: 1667, 1727 cm^{-1} (CO). PMR spectrum (in $CDCl_3$): 3.42 (3H, s), 3.60 (3H, s), 12.94 ppm (1H, s). Mass spectrum, m/z: M^+ 277, [M + 2] 279, [M + 4] 281.

TABLE 1. Compounds IIa-f

Compound	t_{react}, h	Yield, %	Compound	t_{react}, h	Yield, %	Compound	t_{react}, h	Yield, %
IIa	0,5	92	IId	2	95	IIe (from Ig)	1	75
IIb	1	93	IIe	2	93			
IIc	1	93	IIf (from If)	0,5	~100	IIf (from Ih)	1	~100

*Communication 5 from the series "Pyrido[2,3-d]pyrimidines." See [1] for communication 4.

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2. I. D. Bystryakova, O. A. Burova, G. M. Chelysheva, N. M. Smirnova, and T. S. Safonova, Khim.-farm. Zh. (in press).
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SYNTHESIS OF NEW DEUTEROPORPHYRIN-IX DERIVATIVES BY THE REACTION OF HEMATOPORPHYRIN-IX DIESTER DIETHERS WITH ACETYLACETONE IN THE PRESENCE OF ZINC ACETATE

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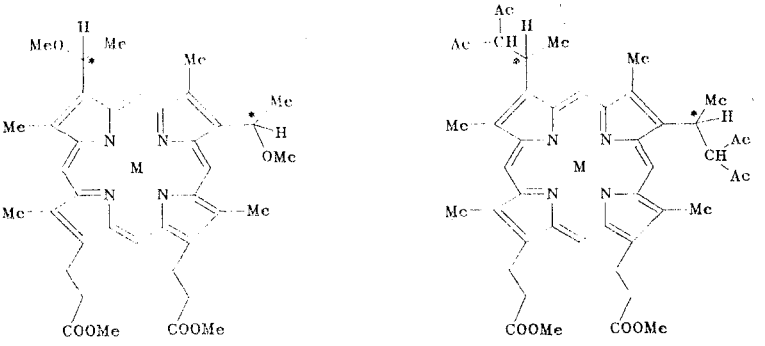
meso-Aminomethylporphyrins react with CH acids in the presence of zinc acetate owing to the development of an intermediate zinc complex of the carbonium ion of meso-methyleneporphyrin [1].

We have established that hematoporphyrin-IX and its alkyl diester diethers [2] also react readily with CH acids under similar conditions.

Thus, for example, heating (for 20-30 min at 110°C) hematoporphyrin-IX dimethyl ester dimethyl ether (I) in acetylacetone in the presence of a tenfold excess (by mass) of zinc acetate leads, through the intermediate Zn complex (II) of porphyrin-I, to Zn complex III, after demetallation of which with HCl porphyrin IV was obtained in quantitative yield based on starting porphyrin I.



I, II I, IV M=2H; II, III M=Zn III, IV

The IR spectrum of porphyrin IV contains two intense bands at 1734 and 1700 cm^{-1} ($\nu_{C=O}$ for COOMe and COMe groups). An M^+ peak, which is the most intense peak in the spectrum, and peaks of $[M^+ - CHAc_2]$ and $[M^+ - 2CHAc_2]$ ions are present in the mass spectrum. In the PMR spectrum of porphyrin IV (in $CDCl_3$) the signals of the protons of the $-CH(CH_3)CH(COCH_3)COCH_3$ group are very broad. The spectrum of a solution in CF_3COOD is more informative. Since starting diester diether I is a mixture of diastereomers [the substituents in the 2 and 4 positions have (R) and (S) configurations], doubling of most of the signals in the PMR spectrum (δ, ppm) is also characteristic for porphyrin IV: 11.28, 11.27, 11.25, 11.24, 11.20, 11.19 (3H each, meso-H); 11.01 (1H,

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