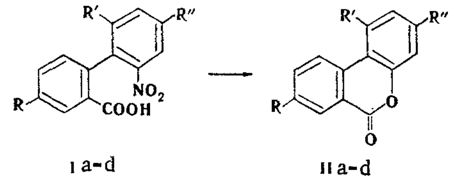

I,IIa,d $R=R''=NO_2$; b $R=NO_2$; c $R=R''=H$; a,c $R'=COOH$; b,d $R'=H$

30 min, 97%, 238-238.5° (dec., from 5% hydrochloric acid); IIb, 6 h, 42%, 246-247° (dec., from benzene); IIc, 6 h, 34%, 218.5-219° (dec., from benzene); IId, 1 h, 85%, 210-211° (from acetone). Compound IId was isolated from the reaction mixture by pouring into hydrochloric acid. The results of elementary analysis of IIa-d were in agreement with the calculated values. The individuality of the compounds was evaluated by thin-layer chromatography on Silufol (the spots had blue fluorescence in UV light). The band of the stretching vibrations of the lactone C=O group in the IR spectra of II lies at 1750-1760 cm^{-1} and the carboxyl group C=O band is observed at 1695-1715 cm^{-1}.

SYNTHESIS OF 4H-1,3-OXAZIN-4-ONIUM SALTS

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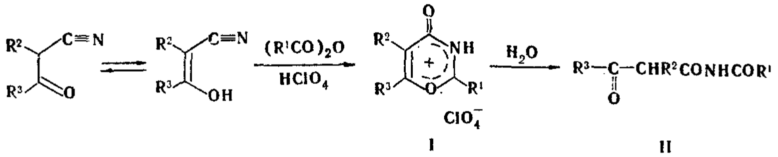
We have obtained the previously unknown 4H-1,3-oxazin-4-onium perchlorates (I) by acylation of β-ketonitriles with aliphatic acid anhydrides in the presence of equimolar amounts of 70% perchloric acid:



The IR spectra of I contain the following bands: an intense band at 1750 cm^{-1} (C=O) and a band of medium intensity at 1520 cm^{-1} $O{=}\overset{+}{C}{=}N$ fragment), which are characteristic for 4H-1,3-benzoxazin-4-onium salts, and a strong band at 1650 cm^{-1} (probably the stretching vibrations of a carbon-carbon double bond).

The action of water on perchlorates I gives β-keto acid N-acylamides: IIa, mp 103-104° (from benzene; in agreement with the literature value); IIb, mp 119-120° (from benzene); IIc,

TABLE 1

Compound	R¹	R²	R³	mp, °C	Yield, %
Ia	CH_3	H	C_6H_5	165	70
Ib	C_2H_5	H	C_6H_5	142—144	50
Ic	C_3H_7	H	C_6H_5	157—159	55
Id*	CH_3	C_6H_5	CH_3	131	66

*PMR spectrum (CF_3COOH, 20°C, hexamethyldisiloxane): 2.30 (s, 6-CH_3), 2.55 (s, 2-CH_3), and 7.15-7.18 ppm (m, phenyl protons).

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mp 90-91.5° (from aqueous alcohol). An intense violet coloration is produced when II is treated with an alcohol solution of ferric chloride.

The compositions of I and II were confirmed by the results of elementary analysis.

CONVERSION OF 1-ALKOXY(ARYLOXY)-5-METHYL-1,2,3,6-TETRAHYDRO-1,2,6-PHOSPHADIAZINE-1,3-DIONES TO 4-HYDROXY-6-METHYLPYRIMIDINE

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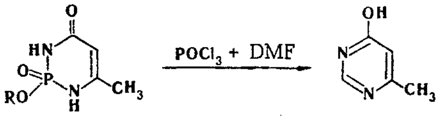
UDC 547.854:543.422.25.4.6

We have observed that treatment of 1-ethoxy- (I) and 1-phenoxy-5-methyl-1,2,3,6-tetrahydro-1,2,6-phosphadiazine-1,3-dione (II) with a twofold excess of the $POCl_3$–dimethylformamide (DMF) complex gives, instead of 4-formyl derivatives, 4-hydroxy-6-methylpyrimidine (III), which, according to the results of elementary analysis and the IR, UV, and PMR spectroscopic data, is identical to the substance obtained by desulfuration of 2-thio-6-methyluracil with Raney nickel.



I, II   III

I $R=C_2H_5$; II $R=C_6H_5$

Thus a solution of 2.7 mmole of I in 7.5 ml of DMF was mixed with a solution of 0.25 ml of $POCl_3$ in 0.83 ml of DMF at 0°, after which the mixture was stirred at 20° for 6 h. It was then poured into two volumes of ice water, and the aqueous mixture was neutralized to pH 7 with Dowex-50 (1 × 8) (OH^-) and evaporated. The residue was subjected to preparative chromatography on silica gel plates [chloroform–methanol (4:3)], and the product was crystallized from benzene to give pyrimidine III, with mp 146-148°, in 36% yield. PMR spectrum (in $CDCl_3$), ppm: 8.16 (1H, s, 2-H), 6.34 (1H, s, 5-H), and 2.34 (3H, s, CH_3).

A precipitate formed after 4 h in the reaction of II with $POCl_3$–DMF under the same conditions. It was removed by filtration, washed with DMF, and vacuum dried. This intermediate (evidently a noncyclic compound) did not contain a PhOPO group. It was dissolved in alcohol, and the solution was refluxed for 10 min. It was then evaporated, and the residue was chromatographed with a column filled with silica gel [chloroform–methanol (3:1)] to give III in 64% yield.

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