

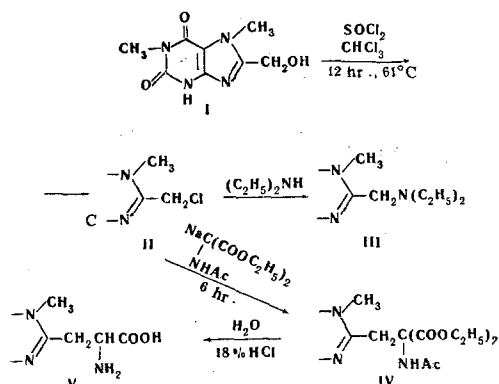
## THE SYNTHESIS OF SOME NEW DERIVATIVES OF 1,7-DIMETHYLXANTHINE

I. M. Ovcharova, E. S. Chaman, and E. S. Golovchinskaya

Kimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 6, p. 1129, 1967

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We have synthesized a group of new 8-substituted 1,7-dimethylxanthines which are of interest for biological investigation as very close structural analogs of some 8-substituted theobromine derivatives obtained previously. In particular, we have carried out the conversion of 8-hydroxymethyl-1,7-dimethylxanthine (I) [1] into 8-chloromethyl-1,7-dimethylxanthine (II) and from this, by heating it for 6 hours with an excess of diethylamine or by condensing it with sodioacetylaminomalonic ester in ethanol we have obtained 8-diethylaminomethyl-1,7-dimethylxanthine (III) and its hydrochloride (compare [2]) or 8-( $\beta$ -acetyl-amino- $\beta$ , $\beta$ -diethoxycarbonyl-ethyl)-1,7-dimethylxanthine (IV). The hydrolytic cleavage of the latter, accompanied by partial decarboxylation, led to 1,7-dimethyl-8-xanthinylalanine (V) (cf. [3]).



II: mp 250°–251° C (decomp., from a mixture of ethanol and dimethylformamide.) Found, %: Cl 15.47; N 24.63. Calculated for  $C_8H_9ClN_4O_2$ , %: Cl 15.53; N 24.57.

III: mp 192°–194° C (from 30% ethanol). Found, %: N 25.77. Calculated for  $C_{12}H_{19}N_5O_2$ , %: N 26.41. Hydrochloride: mp 260°–262° C (decomp.). Found, %: Cl 11.57; N 23.00. Calculated for  $C_{12}H_{19}N_5O_2 \cdot HCl$ , %: Cl 11.77; N 23.22.

IV: mp 229°–230° C (from ethanol). Found, %: C 50.17; H 5.79; N 17.29. Calculated for  $C_{17}H_{23}N_5O_7$ , %: C 49.87; H 5.62; N 17.11.

V: mp 265° C (from water). Found, %: C 42.40; H 5.13; N 24.56;  $H_2O$  6.0. Calculated for  $C_{10}H_{13}N_5O_4 \cdot H_2O$ , %: C 42.10; H 5.20; N 24.55;  $H_2O$  6.3.

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Ordzhonikidze All-Union Chemical and Pharmaceutical Scientific Research Institute

## SOME REACTIONS OF PHOSPHORUS-CONTAINING HETEROCYCLES

B. A. Arbuzov, A. O. Vizel, and K. M. Ivanovskaya

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It has been reported previously that derivatives of dioxaphospholene [1] and oxaphospholene [2] react readily with water. The reaction, which is a saponification of a cyclic ester, ends with the formation of the corresponding acid, which contains a keto group in the organic

part of the molecule. The reaction of the cyclic compounds mentioned with alcohols has not been studied.

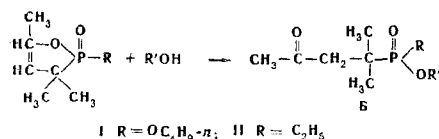
We have found [3] that derivatives of oxaphospholene readily react with alcohols on being heated, forming the corresponding esters of

Esters of Ketophosphonic and Ketophosphinic Acids

Compound	R	R'	Bp, °C (pressure, mm)	$n_D^{20}$	$d_4^{20}$	Empirical formula	Found				Calculated				Yield, %
							C, %	H, %	P, %	MR <sub>D</sub>	C, %	H, %	P, %	MR <sub>D</sub>	
I	OCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	73–74 (0.04)	1.4467	1.0896	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub> P	48.67	8.43	13.81	54.45	48.64	8.62	13.94	54.64	65.8
II	OC <sub>2</sub> H <sub>5</sub> -n	C <sub>2</sub> H <sub>5</sub>	76–78 (0.02)	1.4429	1.0235	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> P	54.46	10.03	11.68	68.46	54.53	9.53	11.72	68.49	41.6
III	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	71–72 (0.1)	1.4540	1.0638	C <sub>9</sub> H <sub>11</sub> O <sub>4</sub> P	52.02	9.39	15.38	53.48	52.42	9.29	15.02	53.52	71.6
IV	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	78–80 (0.07)	1.4595	1.0362	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> P	54.48	9.67	13.91	58.15	54.53	9.61	14.06	58.14	30.8
V	C <sub>2</sub> H <sub>5</sub>	H	MP, 112–113	—	—	C <sub>8</sub> H <sub>17</sub> O <sub>4</sub> P	49.52	8.64	15.78	192.10*	50.00	8.92	16.11	192.18*	89.0

\*Equivalent weight, found 192.10, calculated 192.18.

ketophosphonic and ketophosphinic acids. The reaction takes place in accordance with the following equation.



The products and their constants are given in the table. The initial cyclic ester I was obtained by the reaction of butanol with 2-chloro-3,3,5-trimethyl-2-oxo-1,2-oxaphosphol-4-ene [4] in the presence of triethylamine with a yield of 38%. Bp 127°–129° C (9 mm);  $d_4^{20}$  1.0390;  $n_D^{20}$  1.4535. Found, %: P 14.27; MR<sub>D</sub> 56.81. Calculated for C<sub>10</sub>H<sub>19</sub>O<sub>3</sub>P, %: P 14.19; MR<sub>D</sub> 56.58. The cyclic compound II was obtained from ethyldichlorophosphine, mesityl oxide, and acetic anhydride in a manner similar to that described by Bergesen [2] with a yield of 48%. Bp 69°–71° C (0.1 mm);  $d_4^{20}$  1.0565;  $n_D^{20}$  1.4757. Found, %: C 55.54; H 8.55; P 17.45; MR<sub>D</sub> 46.34. Calculated for

C<sub>8</sub>H<sub>15</sub>O<sub>2</sub>P, %: C 55.16; H 8.68; P 17.78; MR<sub>D</sub> 46.22. The structure of the products was confirmed by their spectra and chemical reactions.

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Arbuzov Institute of Organic and Physical Chemistry, AS USSR, Kazan

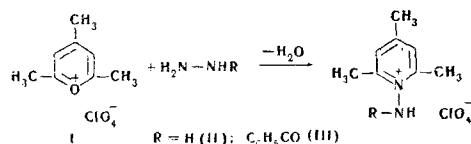
## CONVERSION OF PYRYLIUM SALTS INTO 1-AMINOPYRIDINIUM AND PYRAZOLE DERIVATIVES

G. N. Dorofenko, A. N. Narkevich, and Yu. A. Zhdanov

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It is known that the reaction of pyrylium salts with arylhydrazines gives 1-arylamino-pyridinium salts, which are converted by the action of bases into pyridinium betaines [1]. In order to obtain 1-aminopyridinium compounds, we have studied the reaction of pyrylium salts with hydrazine. We have found that the reaction of 2,4,6-trimethylpyrylium perchlorate (I) with an equimolecular amount of hydrazine hydrate takes place in ethanolic solution with cooling to form 1-aminocollidinium perchlorate (II) with a yield of 24–25%.

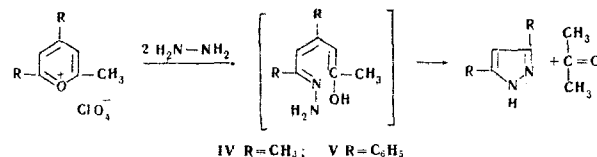


Compound II forms colorless needles soluble in water and ethanol with mp 185° C (from ethanol). Found, %: C 40.83; H 5.48; Cl 15.32. Calculated for C<sub>8</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>4</sub>, %: C 40.60; H 5.53; Cl 14.98. 1-Benzoylamino-collidinium perchlorate (III) was obtained by boiling benzoylhydrazine with I in glacial acetic acid with a yield of 73%. Colorless crystals readily soluble in ethanol, sparingly soluble in water, mp 147° C (from water). Found, %: C 52.38; H 5.08; Cl 10.23. Calculated for C<sub>15</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>5</sub>, %: C 52.87; H 5.02; Cl 10.40.

The reaction of I with a twofold amount of hydrazine hydrate yielded a crystalline product IV containing no halogen to which the structure of 3,5-dimethylpyrazole has been assigned on the basis of its analysis and IR spectrum. Colorless plates soluble in benzene, ethyl acetate, and water, with mp 106°–107° C (from ethyl acetate). Found, %: C 62.57; H 8.44. Calculated for C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>, %: C 62.46; H 8.38. The IR spectrum of IV and that of an authentic sample of 3,5-dimethyl-

pyrazole were completely identical, and the mixture gave no depression of the melting point.

Obviously, in this case the intermediate 1,5-diketone hydrazone undergoes cleavage with subsequent cyclization to form a pyrazole compound.



6-Methyl-2,4-diphenylpyrylium perchlorate and hydrazine hydrate (1:2) yielded 3,5-diphenylpyrazole (V). Crystalline product, soluble in ethanol and benzene. Mp 200° C (from benzene). Found, %: C 82.39; H 5.48. Calculated for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>, %: C 81.81; H 5.49. The structure of the product was shown in a manner similar to that of IV.

The investigation of the reactions of pyrylium salts with hydrazine is continuing.

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Rostov-on-Don State University