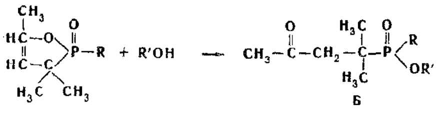
ketophosphonic and ketophosphinic acids. The reaction takes place in accordance with the following equation.



I $R = OC_4H_9$-*n*; II $R = C_2H_5$

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_D 56.81. Calculated for $C_{10}H_{19}O_3P$, %: P 14.19; MR_D 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_D 46.34. Calculated for $C_8H_{15}O_2P$, %: C 55.16; H 8.68; P 17.78; MR_D 46.22. The structure of the products was confirmed by their spectra and chemical reactions.

REFERENCES

1. F. Ramirez, O. P. Madan and C. P. Smith, J. Am. Chem. Soc., **87**, 670, 1965.
2. K. Bergesen, Acta Chem. Scand., **19**, 1784, 1965.
3. B. A, Arbuzov and A. O. Vizel, USSR Authors' Certificate, 185903, 1965; Byull. izobr., No. 18, 1966.
4. L. Anschutz, E. Klein and G. Cermak, Ber., **77**, 726, 1944.

4 October 1966

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

---

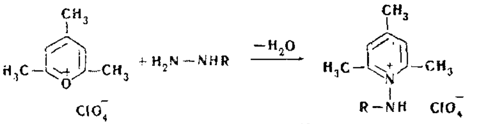
CONVERSION OF PYRYLIUM SALTS INTO 1-AMINOPYRIDINIUM AND PYRAZOLE DERIVATIVES

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

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 6, pp. 1130—1131, 1967

UDC 547.813+547.821+547.772

It is known that the reaction of pyrylium salts with arylhydrazines gives 1-arylaminopyridinium 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%.

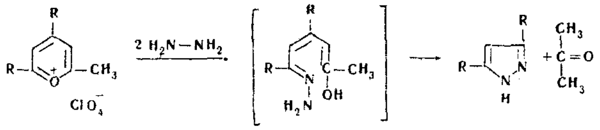


I $R = H$ (II); C_6H_5CO (III)

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 $C_8H_{13}ClN_2O_4$, %: C 40.60; H 5.53; Cl 14.98. 1-Benzoylaminocollidinium 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 $C_{15}H_{17}ClN_2O_5$, %: 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 $C_5H_8N_2$, %: C 62.46; H 8.38. The IR spectrum of IV and that of an authentic sample of 3, 5-dimethylpyrazole 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.



IV $R = CH_3$; V $R = C_6H_5$

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 $C_{15}H_{12}N_2$, %: 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.

REFERENCE

1. A. T. Balaban, P. T. Frangopol, G. Mateescuet, and C. D. Nenitzescu, Bull. Soc. chim. France, 288, 1962.

28 February 1967

Rostov-on-Don State University