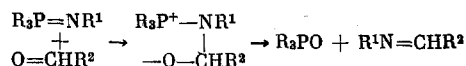


REACTION OF ALKOXYIMIDOPHOSPHORUS COMPOUNDS
WITH ALDEHYDES

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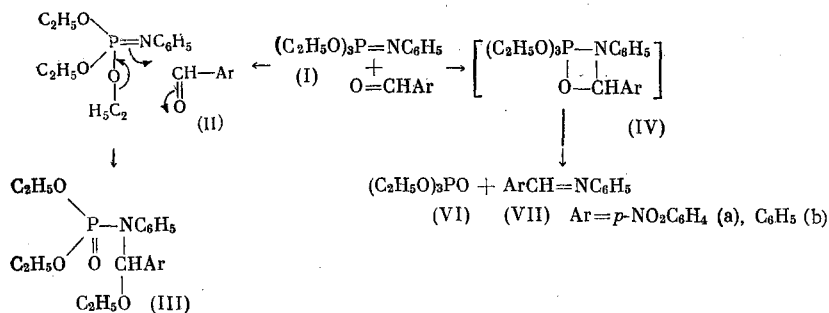
UDC 542.91:547.1'118

One of the properties of alkoxyimidophosphorus compounds is the ability to undergo imide–amide rearrangement [1], which occurs on heating or when treated with electrophilic reagents. As is known, phosphine imines when treated with aldehydes are converted to phosphine oxides and anils [2], and evidently this reaction proceeds via the zwitter-ion step [3]



While studying the kinetics of the reaction of phosphine imines with aldehydes and the Wittig reaction it was concluded that a synchronous mechanism prevails, with a four-membered transition state containing pentavalent phosphorus [4].

The reaction of alkoxyimidophosphorus compounds with aldehydes has not been studied.* This reaction was examined by us on the example of triethyl N-phenylimidophosphate (I). In the case of a synchronous mechanism a six-membered transition state (II) can be formed, which in type is close to that in the imide–amide rearrangement, with the formation of amide (III). In the case of a four-membered transition state (IV)† the reaction of imidophosphate (I) with aldehydes will not differ from the reaction of phosphine imines with aldehydes, i.e., the formation of triethyl phosphate and anils could be expected



As it proved, the amidophosphate reacts with benzaldehydes in the same manner as phosphine imines. The reaction of (I) with p-nitrobenzaldehyde and benzaldehyde proceeds under mild conditions without a solvent. The constants and IR spectrum of triethyl phosphate (VI) coincided with the literature data. The structure of anils (VIIa, b) was proved by comparing with the authentic compounds [6, 7]. When the reaction of imidophosphate (I) with p-nitrobenzaldehyde was run in solvents that differed sharply in polarity (benzene and dimethylformamide) the direction of the reaction did not change.

*While this paper was being prepared for publication a communication appeared [5] on the reaction of O,O-diethyl-O-p-hydroxyphenyl-N-phenylimidophosphate with benzaldehyde, which led to the formation of O,O-diethyl-N-p-hydroxyphenylphosphate and benzalaniline.

†The formation of the betaine $(C_2H_5O)_3P^{\ddagger}-NC_6H_5$ as an intermediate product is not excluded.



Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 10, pp. 2374–2375, October, 1973. Original article submitted April 4, 1973.

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It should be mentioned that a high electrophilicity of the carbonyl group is necessary if imidophosphate (I) is to react with carbonyl compounds. Thus, acetone does not react with imidophosphate (I), either when refluxed (6 h) or when heated in an autoclave at 100°C (10 h).

EXPERIMENTAL METHOD

Reaction of Triethyl-N-phenylimidophosphate (I) with p-Nitrobenzaldehyde. Without a Solvent. To 2.55 g of (I) was added 1.51 g of p-nitrobenzaldehyde. Heat was evolved and a light brown homogeneous solution was formed. Then the mixture was heated at 70–80° for 2 h. The crystals obtained on cooling were separated and washed with hexane. We obtained 2.00 g (90%) of p-nitrobenzalaniline (VIIa), mp 85–87°. After recrystallization from benzene–hexane mixture, mp 92–93°; see [6]. The mixed melting point with an authentic sample was 92–93°.

The filtrate was evaporated and the residue was distilled to give 1.6 g (90%) of triethyl phosphate [8–10], bp 91–92° (10 mm); n_D^{20} 1.4070; d_4^{20} 1.0693.

In Benzene. A solution of 2.55 g of (I) and 1.51 g of p-nitrobenzaldehyde in 10 ml of absolute benzene was refluxed for 2 h, after which the benzene was vacuum-distilled, 5 ml of heptane was added to the residue, and the crystals were separated. We obtained 1.92 g (86%) of (VIIa), mp 92–93°. Distillation of the filtrate gave 1.52 g (85%) of triethyl phosphate.

In Dimethylformamide. A solution of 2.55 g of (I) and 1.51 g of p-nitrobenzaldehyde in 10 ml of DMF was heated at 70–80° for 2 h, the solvent was vacuum-distilled, 5 ml of heptane was added to the residue, and the crystals were separated. We obtained 1.87 g (84%) anil (VIIa), mp 92–93°. Distillations of the filtrate gave 1.50 g (85%) of triethylphosphate.

Reaction of Triethyl-N-phenylimidophosphate (I) with Benzaldehyde. A mixture of 1.05 g of benzaldehyde and 2.55 g of (I) was heated at 70–80° for 2 h. Distillation gave 1.40 g (80%) of triethyl phosphate and 1.40 g (80%) of benzalaniline (VIIb), bp 153–154° (10 mm), mp 51–52°; see [7]. The mixed melting point with an authentic sample was 51–52°.

CONCLUSIONS

The reaction of triethyl-N-phenylimidophosphate with aldehydes proceeds with the formation of triethyl phosphate and anils.

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