The Mechanism of the Perkow Reaction: Triethyl Phosphite and Trichloroacetylthiourea

J. S. AYRES and G. O. OSBORNE*

(*Lincoln College, University of Canterbury, P.O Box 40, Canterbury, New Zealand*)

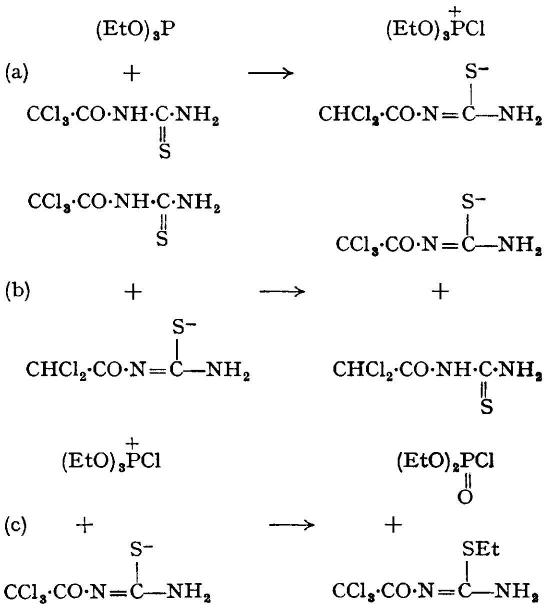
TRIALKYL PHOSPHITES react with α-halogenocarbonyl compounds to yield vinyl phosphates (Perkow reaction) and/or ketophosphonates (Arbusow reaction). A number of schemes for the Perkow reaction have been suggested.[1]

We have now investigated the reaction between triethyl phosphite and trichloroacetylthiourea, in which the halogen atoms are relatively positive and attack on the carbonyl group is hindered sterically so that initial attack by P at halogen is likely to be favoured. Moreover, the carbanion generated in such an attack can be converted into an isothiouronium ion which could function preferentially as a dealkylating agent.[2] Reaction with chlorotriethoxyphosphonium cations (Scheme I) would then give a P–Cl compound and an *N*-acyl-*S*-alkylisothiourea. The isolation of these products would provide clear evidence for initial attack by phosphorus at the halogen.

Equimolar proportions of triethyl phosphite and trichloracetylthiourea[3] reacted rapidly in benzene at 25° for 30 min., on cooling to ice temperature a crystalline deposit formed which was identified by infrared spectrum and elemental analysis as dichloroacetylthiourea (20%, m.p. 120°). Analysis of the reaction mixture by g.l.c. ('Aerograph' model 200) using a 5% silicone oil–Chromosorb column indicated the presence of diethyl phosphorochloridate (45%, subsequently converted into diethyl-*N*-phenylphosphoramidate), unchanged triethyl phosphite (10%), and triethyl phosphate (20%).

Removal of solvent by distillation at room temperature gave a residual gum. This partially crystallised on cooling at ice temperature for two days to give *S*-ethyl-*N*-trichloroacetylisothiourea (15%, m.p. 125°).

The isolation of these products is consistent with the following reaction scheme:

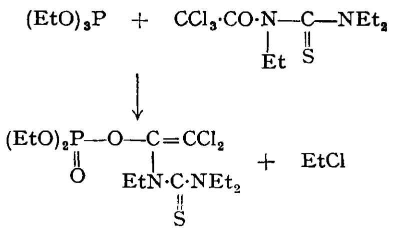


SCHEME I

An alternative interpretation involving initial dealkylation of triethyl phosphite by trichloroacetylthiourea followed by attack of diethyl phosphite at chlorine is not supported by the pattern of products obtained. Moreover, thiourea does not dealkylate triethyl phosphite under the conditions employed.

Trialkyl phosphate present in the reaction mixture may arise from the action of adventitious moisture on the ions produced in the first step of the reaction [Scheme I (a)].

The comparable reaction between triethyl phosphite and 1,1,3-triethyl-3-trichloroacetylthiourea has also been examined. The principal reaction product was now a colourless oil which decomposed on standing at room temperature for several days. It has been characterised as diethyl 2,2-dichloro-1-(1,3,3-triethylthioureido)vinyl phosphate.



$$(\mathrm{EtO})_3\mathrm{P} + \mathrm{CCl_3{\cdot}CO{\cdot}}\underset{\mathrm{Et}}{\mathrm{N}}-\underset{\mathrm{S}}{\mathrm{C}}-\mathrm{NEt_2}$$

$$\downarrow$$

$$(\mathrm{EtO})_2\underset{\mathrm{O}}{\mathrm{P}}-\mathrm{O}-\underset{\mathrm{EtN{\cdot}}\underset{\mathrm{S}}{\mathrm{C}}\mathrm{{\cdot}NEt_2}}{\mathrm{C}}=\mathrm{CCl_2} + \mathrm{EtCl}$$

The carbanion formed in attack by phosphorus at halogen cannot isomerise and the normal product of the Perkow reaction is now obtained.

(*Received, December 11th*, 1967; *Com.*1327.)

---

[1] R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry", Academic Press, 1965, p. 153.

[2] G. Hilgetag, G. Lehmann, A. Martini, G. Schramm, and H. Teichmann, *J. prakt. Chem.*, 1959, **8**, 207.

[3] W. Ger. Pat., 940,554.