Pentacovalent Intermediate in the Arbuzov Reaction

By ALEKSANDRA SKOWROŃSKA,* JERZY MIKOŁAJCZAK, and JAN MICHALSKI*
(*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90–362 Łódź, Boczna 5, Poland*)

Summary Direct evidence by ^{31}P-n.m.r. spectroscopy is presented for the formation of a five-co-ordinate intermediate in the Arbuzov reaction of tervalent phosphorus esters with elemental chlorine or elemental bromine and benzenesulphenyl chloride.

IN his classic work Arbuzov formulated the five-co-ordinate compound (**1**) as an intermediate in the reaction of trialkyl phosphites with alkyl halides and elemental halogens.[1,2] Phosphonium salts were generally assumed to be Arbuzov intermediates[2] and recently, in the case of sterically hindered phosphites, they have been isolated and characterized by ^{31}P-n.m.r. spectroscopy.[3,4] A phosphonium intermediate was also detected in the bromination of $P(OCH_2)_3CMe$.[5] Recent results on the reaction of diastereoisomeric cyclic phosphites with alkyl halides revealed a lack of stereospecificity at phosphorus which was explained by the intermediacy of a pentacovalent intermediate[6]. To our knowledge there is no reported direct evidence for a five-co-ordinate intermediate in the Arbuzov reaction.

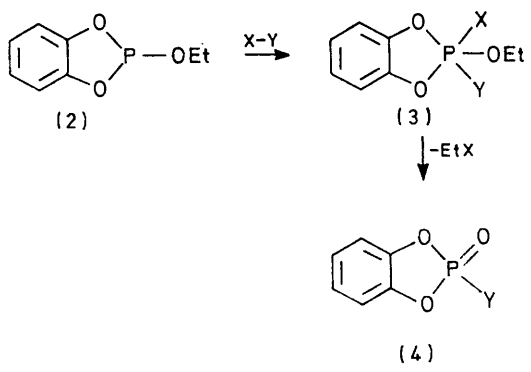
$$(R^1O)_3P \xrightarrow{R^2X} (R^1O)_2\underset{\displaystyle R^2}{\overset{\displaystyle X}{P}}\!-\!O\!-\!R^1 \xrightarrow{-R^1X} (R^1O)_2P(O)R^2$$

(**1**)

Equimolar quantities of the phosphite (**2**) and Cl_2 in EtCl solution were allowed to react in a sealed n.m.r. tube at −85 °C. The n.m.r. spectrum showed only the presence of the five-co-ordinate intermediate (**3a**) with a characteristic high-field chemical shift [δ (^{31}P + 35 p.p.m.] relative to 85% H_3PO_4. At −40 °C a new peak appeared [δ (^{31}P) −19 p.p.m.] corresponding to the phosphorochloridate (**4a**).

In the reaction of (**2**) with elemental bromine under the same conditions, the phosphorane intermediate (**3b**) [δ (^{31}P)

+195 p.p.m. and the phosphorobromidate (**4b**) [δ (^{31}P) −3·5 p.p.m.] were the only observed components of the systems.



(2) (3) (4)

a; X=Y=Cl
b; X=Y=Br
c; X=Cl, Y=Ph

The reaction of (**2**) with PhSCl is somewhat more complex owing to the side reaction (1), which is similar to that

$$(\mathbf{3c}) + \mathrm{PhSCl} \rightarrow (\mathbf{4a}) + (\mathrm{PhS})_2 \quad (1)$$

observed by Chang and Denney in the reaction between the methyl analogue of (**2**) with ethyl benzenesulphenate.[7] The proportions of the components of the system discussed, estimated by integration of the ^{31}P-n.m.r. spectra, are as follows. At −80 °C two peaks were observed corresponding to (**3c**) [δ (^{31}P) +19·3 p.p.m.] (85%) and (**3a**) [δ (^{31}P +35 p.p.m.] (15%). At 0 °C (**3c**) and (**3a**) had disappeared and two new peaks corresponding to (**4c**) [δ (^{31}P) −40·7 p.p.m.] and (**4a**) [δ (^{31}P) −19 p.p.m.] (15%) were observed. Diphenyl disulphide was isolated and characterised independently. These results constitute the first characterisation of a five-co-ordinate intermediate in the Arbuzov reaction. A sequence of five co-ordinate, phosphonium, and dealkylation steps provide a plausible mechanistic interpretation of the Arbuzov reaction consistent with known experimental facts.

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[1] A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 395, 549.
[2] R. G. Harvey and E. R. Sombre, 'Topics in Phosphorus Chemistry,' Vol. 1, eds. M. Grayson and E. J. Griffith, Wiley, New York, 1964, p. 57; B. Miller, *ibid.*, Vol. 2, 1965, p. 133.
[3] A. J. Razumov, B. G. Liorbov, T. V. Zhykova, and J. Ya. Bambushek, *Zhur. obshchei Khim.*, 1970, **40**, 2009.
[4] H. R. Hudson, R. G. Rees, and J. E. Weeks, *Chem. Comm.*, 1971, 1297; *J.C.S. Perkin I*, 1974, 982.
[5] G. K. McEwen and J. G. Verkade, *Chem. Comm.*, 1971, 668.
[6] C. L. Bodkin and P. Simpson, *Chem. Comm.*, 1970, 1579; *J.C.S. Perkin II*, 1972, 2049.
[7] L. L. Chang and D. B. Denney, *J.C.S. Chem. Comm.*, 1974, 84.