

THE ARBUZOV REACTION OF TRIETHYL PHOSPHITE
 WITH ELEMENTAL IODINE

A. Skowrońska*, M. Pakulski and J. Michalski*

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies,
 Boczna 5, 90-362 Łódź, Poland

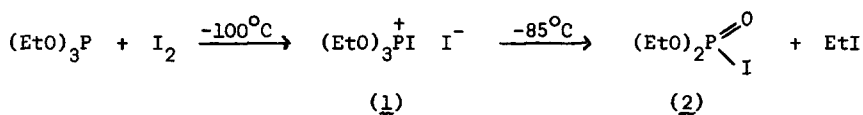
D. Cooper and S. Trippett*

Department of Chemistry, The University, Leicester LE1 7RH, England

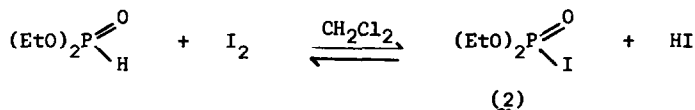
Summary: Triethyl phosphite and elemental iodine in solution give transient iodotriethylphosphonium iodide which eliminates ethyl iodide to form diethyl phosphoriodidate. An examination of the ^{31}P NMR and IR spectra over the temperature range $-100^\circ - 0^\circ\text{C}$ fails to disclose any evidence for triethoxydi-iodophosphorane, contrary to a previous claim.

Two of us recently described¹ the reaction of triethyl phosphite and elemental iodine in solution at 0°C and the use of the resulting reagent in dehydration and condensation reactions. Because of the ^{31}P chemical shift (42.5 ppm, in ether, to high field of 85% H_3PO_4) and the formation of large amounts of triethyl phosphate following use of the reagent, we gave it the structure of triethoxydi-iodophosphorane. This assignment is wrong; the Arbuzov reaction is rapid above -85°C and the species having ^{31}P -42.5 ppm (ether) is diethyl phosphoriodidate (2).²

When the reaction of triethyl phosphite and iodine is carried out at -100°C in ethyl chloride solution, the phosphonium salt (1; ^{31}P +15 ppm) is formed in quantitative yield almost instantaneously.³ Above -85°C this is rapidly transformed into (2) with the simultaneous appearance of phosphoryl absorption at 1270 cm^{-1} . ^1H nmr shows the immediate quantitative formation of ethyl iodide when the reaction is carried out in CD_2Cl_2 at 0°C .



The phosphoriodidate (2; -41.0 ppm in CH_2Cl_2) is also observed by ^{31}P nmr as a major component when diethyl phosphite and iodine react in CH_2Cl_2 solution at room temperature.⁴



When triethyl phosphite-iodine is used as a dehydrating or condensing agent, and the iodine added as the last component, then large amounts of triethyl phosphate are formed. Under these conditions the intermediate (1) can be intercepted by other nucleophiles. If the phosphite and iodine are allowed to react before the other components are added then no triethyl phosphate is produced and (2) presumably functions as a dehydrating agent in a manner analogous to the bromide $(\text{EtO})_2\text{P}(\text{O})\text{Br}$.⁵

References and Footnotes

1. D. Cooper and S. Trippett, Tetrahedron Letters, 1979, 1725.
2. Relatively high field ^{31}P nmr shifts are characteristic of $\text{P}(\text{X})\text{I}$ compounds e.g. K. B. Dillon, M. G. Craveirinha Dillon, and T. C. Waddington, Inorg. Nucl. Chem. Letters, 1977, 13, 349.
3. The chemical shifts of $(\text{EtO})_3\text{P}^+\text{Cl}^-$ and $(\text{EtO})_3\text{P}^+\text{Br}^-$ are +16.2 and +11.5 ppm respectively in ethyl chloride; see A. Skowronska, J. Michalski, and J. Mikolajczak, J.C.S. Chem. Comm., 1975, 791, J. Michalski, J. Mikolajczak, and A. Skowronska, J. Amer. Chem. Soc., 1978, 100, 5386, J. Michalski, M. Pakulski, and A. Skowronska, J.C.S. Perkin I, in Press.
4. H. McCombie, B. C. Saunders, and G. J. Stacey, J. Chem. Soc., 1945, 921.
5. A. Gorecka, M. Leplawy, J. Zabrocki, and A. Zwierzak, Synthesis, 1978, 474.

(Received in UK 6 November 1979)