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# TRIETHOXYDI-IODOPHOSPHORANE

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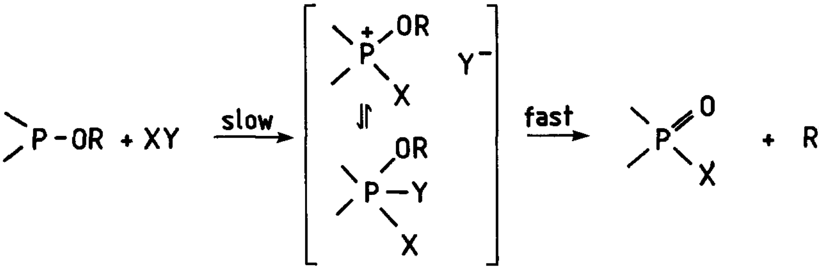
Summary. Triethyl phosphite and iodine in solution give triethoxydi-iodophosphorane. This has a half life in solution of several days and can be used as a dehydrating or condensing agent.

The Arbuzov reaction (equation 1), in its many variations, occupies a central position in organophosphorus chemistry[1]. Only in exceptional cases have the intermediate phosphonium salts or phosphoranes been isolated. However, since the advent of FT $^{31}P$ n.m.r. spectroscopy, an increasing number of such transients have been detected, usually at low temperatures[2]. This communication describes a surprisingly stable Arbuzov intermediate.



(1)

When triethyl phosphite in $CH_3CN$, $CH_2Cl_2$, or ether, is treated at 0°C with one mole equivalent of iodine, the iodine colouration is immediately discharged and the $^{31}P$ n.m.r. spectrum of the resulting solution shows only one absorption at -42.5 ppm (ether; to high field of 85% $H_3PO_4$). Experiments with different ratios of phosphite and iodine show that this is due to a 1:1-complex which we formulate as triethoxydi-iodophosphorane (1). No analogous species is observed in the corresponding reaction with bromine even at -78°C. Over a period of days at room temperature the absorption at -42.5 ppm is slowly replaced by a major absorption at -13.0 ppm, due to polymer (2), and minor absorptions at -13.9 and -1.0 ppm. Previous accounts[3] of the reaction between phosphites and iodine have described rapid reactions at low temperatures leading to alky. iodides and polymers anologous to (2).

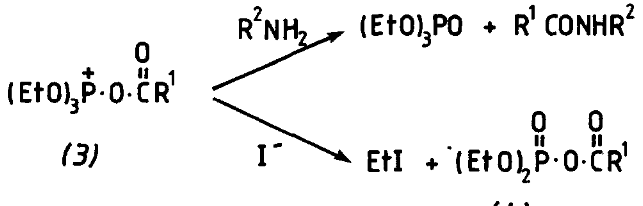
$$\underset{(1)}{(EtO)_3PI_2} \dashrightarrow \underset{(2)}{[EtOPO_2]_n} + 2nEtI$$

The stability of (1) allows it to be used as a dehydrating or condensing agent in the presence of tertiary amine (equation 2) in a manner analogous to the use of $Ph_3PCl_2$ or $Ph_3P$-$CCl_4$[4].

$$(EtO)_3PI_2 + \begin{bmatrix} XH + YOH \\ \text{or } H_2O \end{bmatrix} \xrightarrow{2 \times R_3N} (EtO)_3PO + 2R_3\overset{+}{N}H\,I^- + (X-Y) \qquad (2)$$

In general a solution of iodine in $CH_3CN$ or $CH_2Cl_2$ is added at 0°C to a solution of equivalent amounts of the reactant(s), and phosphite plus two equivalents of $Et_3N$ in the same solvent and the mixture stirred at room temperature for 2 hours. Work-up is aided by the water solubility of the by-products. In this way benzoic acid and benzylamine gave the amide (89%), benzamide gave benzonitrile (64%), and benzaldoxime gave benzonitrile (61% isolated; 89% by glc). *N*-Benzoyl-L-leucine and ethyl glycinate (Young test[5]) gave racemic *N*-benzoylleucylglycine ethyl ester but in the presence of 1-hydroxybenzotriazole[6] an 83% yield of peptide having a 39% excess of the L-enantiomer was obtained. Monitoring of the reactions by $^{31}P$ n.m.r showed that in all cases triethyl phosphate was formed in high yield.

The intermediate in amide formation is the phosphonium ion (3) which is attacked at carbonyl carbon by the amine. In the absence of amine, a slower Arbuzov reaction gives the mixed anhydrides (4).



*(3)* *(4)*

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