

## Organophosphorus Compounds. II\*

### Ethyl Phenylphosphinate

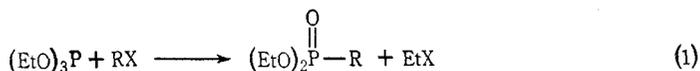
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#### Abstract

Ethyl phenylphosphinate,  $\text{PhPH}(=\text{O})\text{OEt}$ , is conveniently prepared in one step by the reaction of phosphinic acid with ethyl chloroformate in the presence of pyridine.

Because of their considerable nucleophilicity, esters of phosphinic, phosphonous and phosphorous acids are of great use in the synthesis of organophosphorus compounds. One of the most widely used reactions in the area is exemplified by the interaction of triethyl phosphite with an alkyl halide [equation (1)] to form a diethyl alkylphosphonate (the Arbusov reaction):<sup>1a</sup>



On some occasions it is more convenient to use monoesters of phosphinic acids. These compounds are powerfully nucleophilic in their own right, and may be made even more so by conversion into the corresponding sodium or potassium salt. The monoesters have been prepared in several ways in the past: (i) direct esterification of the phosphinic acid by refluxing alcohol in the presence of mineral acid;<sup>1b</sup> (ii) partial hydrolysis of a phosphonous diester or ester amide;<sup>1c</sup> or (iii) reaction of a dichlorophosphine with an alcohol in the presence of more than one mole of tertiary base.<sup>1d</sup>

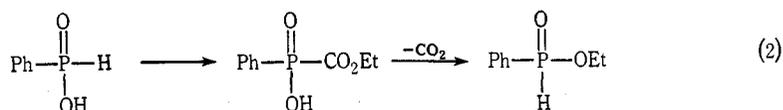
I have now found a new method which may find use where the earlier methods are unsatisfactory or unsuccessful. Phenylphosphinic acid is simply suspended in chloroform or dichloromethane containing an equimolar amount of ethyl chloroformate. One mole of a tertiary base (pyridine or triethylamine) is then added dropwise. Vigorous effervescence of carbon dioxide is observed, the phosphinic acid dissolves, and the solution becomes warm. The solution need then only be washed with water, and the dried solvent evaporated to leave pure ethyl phenylphosphinate. The product is pure by g.l.c., n.m.r. and i.r., and may be used immediately for subsequent reactions.

\* Part I, *Aust. J. Chem.*, 1977, 30, 579.

<sup>1</sup> Kosolapoff, G. M., and Maier, L., (Eds) 'Organophosphorus Compounds' (a) Vol 5, p. 70 *et seq.*; (b) Vol. 4, p. 272; (c) Vol. 4, pp. 272, 275; (d) Vol. 4, p. 268 (John Wiley: New York 1976).

We have not investigated in detail the scope or mechanism of the reaction. However, a different course is followed with phosphinic acids lacking a P-H. In these cases, an unstable intermediate showing strong carbonyl absorption at about  $1780\text{ cm}^{-1}$  is formed. In general, this intermediate decomposes spontaneously within 24 h, reverting to the starting phosphinic acid. In one case, that of diphenylphosphinic acid, a small amount of ethyl diphenylphosphinate could be isolated.

These limited observations suggest the involvement of the P-H bond in the case of the reaction with phenylphosphinic acid [equation (2)]. Reaction of carbonyl compounds on phosphorus has been observed in the past.<sup>2</sup>



## Experimental

General details were described earlier.<sup>3</sup>

### Ethyl Phenylphosphinate

Pyridine (0.8 g) was added slowly to a solution of phenylphosphinic acid (1.4 g) and ethyl chloroformate (1.1 g) in chloroform (50 ml). The solution became warm and effervesced. After 10 min it was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to leave pure ethyl phenylphosphinate (1.65 g). The infrared and n.m.r. spectra were identical with those of an authentic sample.<sup>4</sup> No impurities were detected by g.l.c.

### Reaction of Ethyl Chloroformate with Diphenylphosphinic Acid

A procedure identical with the above gave a colourless oil. P.m.r.  $\delta$  4.13, quartet, 2H ( $\text{CH}_3\text{CH}_2\text{OCO}_2$ ),  $J$  7.3 Hz; 1.18, triplet, 3H ( $\text{CH}_3\text{CH}_2$ ),  $J$  7.3 Hz; 7.3-8.0, multiplet, 10H (ArH).  $\nu_{\text{max}}$  (film)  $1775\text{ cm}^{-1}$  (OCOO).

After heating for 10 min at  $150\text{--}200^\circ$  (effervescence) the n.m.r. spectrum had changed significantly. The quartet at  $\delta$  4.13 had been replaced by a quintet at 4.07 ( $\text{CH}_3\text{CH}_2\text{OP}$ ) with  $J$  6.65 Hz. Preparative thin-layer chromatography permitted the isolation of a low yield of ethyl diphenylphosphinate, with infrared and n.m.r. spectra identical with those of an authentic sample.<sup>5</sup>

The same decomposition occurred spontaneously on a film of the material in the beam of an infrared spectrophotometer. A band at  $2350\text{ cm}^{-1}$  indicated the formation of carbon dioxide.

## Acknowledgment

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<sup>2</sup> E.g., Pudovik, A. N., Gur'yanova, I. V., and Romanov, G. V., *Zh. Obshch. Khim.*, 1969, **39**, 2418 (*Chem. Abstr.*, 1970, **72**, 79164z).

<sup>3</sup> Hewitt, D. G., and Newland, G. L., *Aust. J. Chem.*, 1977, **30**, 579.

<sup>4</sup> Kosolapoff, G. M., *J. Am. Chem. Soc.*, 1950, **72**, 4292.

<sup>5</sup> Cadogan, J. I. G., Sears, D. J., and Smith, D. M., *J. Chem. Soc. C*, 1969, 1314.