242. *Esters Containing Phosphorus. Part III. Dialkyl Iodophosphonates.*

By H. McCombie, B. C. Saunders, and G. J. Stacey.

Dialkyl iodophosphonates, although very unstable, can be obtained in ethereal solution by the action of iodine on trialkyl phosphites. The iodophosphonates are converted practically quantitatively into the corresponding aminophosphonates on treatment with the appropriate amine. Iodine has no marked action on dialkyl hydrogen phosphites, and therefore a trialkyl phosphite can be detected in the presence of a dialkyl hydrogen phosphite by this means.

In Parts I and II (this vol., pp. 380, 873) it was shown that dialkyl chlorophosphonates could be readily prepared by the action of chlorine on the corresponding dialkyl hydrogen phosphites :

$$(RO)_2POH + Cl_2 = (RO)_2\underset{\underset{O}{\|}}{P} - Cl + HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Atherton, Openshaw, and Todd (this vol., p. 382) carried out a similar reaction with dibenzyl hydrogen phosphite and obtained the unstable chlorophosphonate in ethereal solution. With a view to the preparation of the hitherto undescribed diethyl iodophosphonate, we investigated the action of iodine on diethyl hydrogen phosphite and found that practically no change took place, due presumably to the fact that the hydrogen iodide formed immediately reduced any iodophosphonate to the original hydrogen phosphite :

$$(EtO)_2IP{:}O + HI \rightleftharpoons (EtO)_2POH + I_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Evidence for this reaction has been obtained by passing gaseous hydrogen iodide into an ethereal solution of diethyl iodophosphonate (prepared as described below) and finding that iodine was liberated in accordance with equation (*b*). Attempts, however, to isolate the hydrogen phosphite have so far not been successful owing to difficulties in removing the iodine completely and to decomposition during the final distillation. It is also probable that the reaction is more complex than indicated by equation (*b*).

Attempts were then made to prepare the dialkyl iodophosphonate from the trialkyl phosphite by the action of iodine in a suitable solvent. By analogy with the corresponding reaction between chlorine and a trialkyl phosphite (Part I, *loc. cit.*; Gerrard, *J.*, 1940, 1464), it was to be expected that no hydrogen iodide would be evolved and so the reaction should proceed to completion. This was shown to be the case.

$$(EtO)_3P + I_2 = (EtO)_2IP{:}O + C_2H_5I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

When an ethereal solution of iodine was added to triethyl phosphite a rapid reaction ensued, the iodine being taken up quantitatively in accordance with equation (*c*). This ethereal solution proved to be fairly stable but, in removing the ether at room temperature, some separation of solid took place. The iodophosphonate could not be purified by distillation as decomposition set in with the formation of the iodides of phosphorus. Although it could not be isolated, further evidence for the quantitative production of the iodophosphonate in ethereal solution was obtained by its conversion, in almost theoretical yield, into the stable crystalline diethyl anilinophosphonate and aniline hydriodide by means of aniline.

$$(EtO)_2IP{:}O + 2PhNH_2 = (EtO)_2(PhNH)P{:}O + PhNH_2{,}HI$$

An account is given below of the preparation in ethereal solution of dimethyl, diethyl, and di-*iso*propyl iodophosphonates and of the preparation from the appropriate solution of *dimethyl anilinophosphonate*, diethyl anilinophosphonate, *diethyl methylaminophosphonate*, and di-*iso*propyl anilinophosphonate.

In view of the fact that iodine reacts quantitatively with a trialkyl phosphite, but not to any detectable extent with a dialkyl hydrogen phosphite, it was thought that a method of estimating a trialkyl phosphite in the presence of a dialkyl hydrogen phosphite might be devised (such an estimation is of importance in that the hydrogen phosphite is often a by-product in the preparation of a trialkyl phosphite and *vice versa*). Experiments with this object in view were carried out with known mixtures of triethyl phosphite and diethyl hydrogen phosphite. A sharp end-point (appearance of a permanent yellow coloration) was obtained by running a benzene solution of iodine into a benzene solution of the phosphites. The reaction was rapid, but low results were always obtained for the percentage of trialkyl phosphite in the mixture. The error in the result increased as the percentage of hydrogen phosphite increased. The correct titration value was, however, obtained for triethyl phosphite in the absence of hydrogen phosphite.

Thus, while it is not possible at present to employ the method on a strictly quantitative basis, it is of some use in detecting the existence of mixtures of trialkyl phosphites and dialkyl hydrogen phosphites, and of obtaining a very rough estimate of the proportions present. The method has been found particularly useful in detecting the presence of di-*n*-butyl hydrogen phosphite in samples of tri-*n*-butyl phosphite, which have similar b. p.'s.

EXPERIMENTAL.

Ethereal Solution of Dimethyl Iodophosphonate.—To a solution of trimethyl phosphite (5·0 g., 0·04 mol.) in ether (20 c.c.), cooled in ice-water, was slowly added a solution of iodine (10·2 g., 0·04 mol.) in ether (80 c.c.). The end of the reaction was indicated sharply by the appearance of a permanent yellow coloration. This ethereal solution was used immediately for the preparation of the anilinophosphonate.

Dimethyl Anilinophosphonate.—To the ethereal solution of the iodophosphonate, aniline (7·4 g., 0·08 mol.) in ether (50 c.c.) was added slowly with shaking and cooling. The precipitated aniline hydriodide (8·5 g.) was separated and the ether removed from the filtrate leaving *dimethyl anilinophosphonate* as a white crystalline solid in theoretical yield (8·2 g.). The product was recrystallised from a fairly large volume of water. It tended to separate as an oil, but this was usually prevented by the addition of a few drops of methanol. It had m. p. 88—88·5° (Found : C, 48·0; H, 6·33; N, 7·22. $C_8H_{12}O_3NP$ requires C, 47·8; H, 6·02; N, 6·97%).

Ethereal Solution of Diethyl Iodophosphonate.—To a solution of triethyl phosphite (3·3 g., 0·02 mol.) in dry ether (10 c.c.) cooled in ice-water, iodine (5·1 g., 0·02 mol.) dissolved in dry ether (40 c.c.) was slowly added. Each portion of the iodine was immediately decolorised and the appearance of a permanent yellow coloration coincided almost exactly with the end of the addition. The yellow coloration was discharged by the further addition of a few drops of triethyl phosphite. (If the ether was distilled away under reduced pressure at room temperature, the residual liquid quickly developed a brown coloration, and a brown powder, containing iodides of phosphorus, soon separated. The ethereal solution was therefore used for subsequent experiments.)

Diethyl Anilinophosphonate.—To the ice-cold ethereal solution of iodophosphonate, was added slowly aniline (3·7 g., 0·04 mol.) dissolved in ether (20 c.c.). The white precipitate of aniline hydriodide was separated and the filtrate evaporated to dryness leaving the anilinophosphonate (41 g., 90%) which was recrystallised from water. It had m. p. 95·5—96·5° and was identified as diethyl anilinophosphonate (cf. Part I, *loc. cit.*).

Diethyl Methylaminophosphonate.—To a solution of methylamine (3·1 g., 0·1 mol.) in ether (50 c.c.) cooled to 0° was added slowly a solution of diethyl iodophosphonate [prepared from triethyl phosphite (6·6 g., 0·04 mol.) in ether (20 c.c.) and iodine (10·2 g., 0·04 mol.) in ether (80 c.c.)]. A small quantity of a sticky solid separated from the mixture. The ether was evaporated and benzene (50 c.c.) added to bring about the separation of the methylamine hydriodide in a crystalline form. After separating the hydriodide, the benzene was distilled from the filtrate and the residue distilled at 135°/17 mm.; some fuming occurring during the distillation. The yield was 1·7 g., 26% (Found: C, 35·9; H, 8·44; N, 8·55. $C_5H_{14}O_3NP$ requires C, 35·9; H, 8·44; N, 8·38%).

*Ethereal Solution of Di-*iso*propyl Iodophosphonate.*—The procedure was similar to that for the corresponding ethyl compound. As before, decomposition occurred when the ether was distilled from the reaction mixture and the ethereal solution was therefore used directly for the preparation of di-*iso*propyl anilinophosphonate; it was obtained in almost theoretical yield, and recrystallised from a rather large volume of aqueous methanol. It had m. p. 121—121·5° which was unchanged on admixture with an authentic specimen of di-*iso*propylanilinophosphonate (cf. Part I, *loc. cit.*).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

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