

840. The Reactivity of Organophosphorus Compounds. Part XVIII.¹ The Reaction of Triethyl Phosphite with Chloroform.

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Triethyl phosphite and chloroform react at 130° to give diethyl ethylphosphonate in high yield. Chloroform is not consumed to a great extent and diethyl dichloromethylphosphonate is not a final product of the reaction, although its intermediate formation is invoked in a rationalisation of the reaction, which is accelerated by the presence of a free-radical initiator (di-*t*-butyl peroxide). In the presence of ethanol and triethyl phosphite, chloroform is reduced to methylene dichloride, a reaction also assisted by di-*t*-butyl peroxide. Mechanisms are proposed.

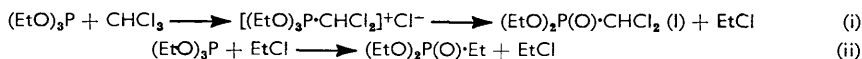
It was originally stated by Kamai² that identifiable products could not be obtained from the reaction of triethyl phosphite and chloroform. Crofts and Kosolapoff³ later stated that the compounds did not react, even under drastic conditions (160°), to give the expected Arbusov product, diethyl dichloromethylphosphonate, (EtO)₂P(O)·CHCl₂ (I). They noted without comment, however, that 12% of the phosphite was converted into the isomeric diethyl ethylphosphonate, (EtO)₂P(O)·Et. The later statement by Griffin⁴ that reaction between triethyl phosphite and chloroform to give diethyl dichloromethylphosphonate could be induced by the addition of dibenzoyl peroxide acting as a free-radical initiator [reaction (i)] was subsequently disproved by Burn, Cadogan, and Bunyan,⁵ who demonstrated (a) that dibenzoyl peroxide decomposed in a heterolytic manner in the presence of triethyl phosphite and chloroform and (b) that chloroform did not participate in the latter reaction at all.

It has now been shown that carefully purified triethyl phosphite (1 mol.) in chloroform (2 mol.) under nitrogen at 130° is slowly consumed, 6% of the phosphite being left after 4 days, to give a mixture of diethyl ethylphosphonate (86%) and a high-boiling mixture of products which did not contain chlorine. Neither diethyl dichloromethylphosphonate (I) nor diethyl trichloromethylphosphonate, (EtO)₂P(O)·CCl₃ (II), were present among the products of the reaction [$<0.1\%$ would have been detected by gas-liquid chromatography (g.l.c.)].

It has also been shown that triethyl phosphite alone does not undergo isomerisation to diethyl ethylphosphonate and that the latter does not react with triethyl phosphite under the conditions used for the above reaction. On the other hand, diethyl dichloromethylphosphonate and triethyl phosphite gave diethyl ethylphosphonate (90%) and the same unknown high-boiling products; most of the dichloromethylphosphonate being recovered.

Similar results were obtained in the presence of added di-*t*-butyl peroxide (0.025 mol.), but the reaction was complete in less than 23 hours and ethyl chloride was detected.

The major reaction between chloroform and triethyl phosphite, which accounts for 90% of the latter, may be rationalised by assuming that they react slowly, either by a radical or an ionic route, to give diethyl dichloromethylphosphonate and ethyl chloride [reaction (i)]. As soon as a suitable, but small, concentration of the latter is produced, a competing and much more rapid Arbusov isomerisation of unreacted triethyl phosphite occurs to give diethyl ethylphosphonate with regeneration of ethyl chloride. The reaction is therefore a chain process initiated by the occurrence, but only to a small extent, of the reaction between phosphite and chloroform.



¹ Part XVII, Burn and Cadogan, *J.*, 1963, 5788.

² Kamai, *Doklady Akad. Nauk. S.S.S.R.*, 1951, **79**, 795.

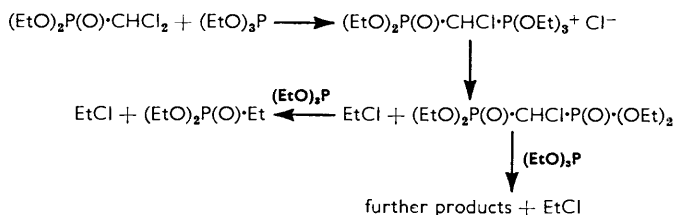
³ Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 5738.

⁴ Griffin, Abstract of 135th A.C.S. meeting, 1959, p. 69 O.

⁵ Burn, Cadogan, and Bunyan, *J.*, 1963, 1527.

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The correspondingly small amount of diethyl dichloromethylphosphonate so formed can also react with triethyl phosphite to give diethyl ethylphosphonate and ethyl chloride, thus providing a second mode of initiation of the isomerisation of the phosphite to the phosphonate, a postulate supported by experiment.



We have no evidence concerning the nature of reaction (i), reaction (ii) being assumed to proceed in the usual Arbusov fashion. The fact that the overall process is accelerated by the addition of di-*t*-butyl peroxide indicates only that reaction (i) *can* be radical-induced: it does not follow that it is homolytic in the absence of added peroxide.

In addition to the reactions so far described, that between triethyl phosphite and chloroform in the presence of ethanol was investigated at 130° both in the presence and absence of di-*t*-butyl peroxide. Much less phosphite could be accounted for in these cases and larger high-boiling residues were formed, but qualitatively the reaction took the same course in both cases giving triethyl phosphate, methylene chloride, and diethyl ethylphosphonate. A lower proportion of diethyl ethylphosphonate was formed in the peroxide-initiated reaction, presumably by the mechanism described in reactions (i) and (ii), whilst the reduction of chloroform to methylene dichloride by triethyl phosphite parallels the corresponding reduction of carbon tetrachloride to chloroform recently reported.^{1,6}

Finally, our observations on the reaction between triethyl phosphite and bromoform are recorded. Unlike Kamai,² who noted a "most vigorous reaction" with the isolation of ethyl bromide, diethyl phosphonate, and diethyl phosphorobromidate, we observed a smooth 84% conversion of pure triethyl phosphite into diethyl ethylphosphonate after 20 hours. The high-boiling products of the reaction, although unidentified, had the same g.l.c. retention times as those obtained from the corresponding reaction with chloroform. The reactions therefore are identical, except that that involving bromoform proceeds by way of ethyl bromide whereas the other involves ethyl chloride.

EXPERIMENTAL

G.l.c. was carried out using the Pye Argon and the Perkin-Elmer Fraktometer 116 (dual thermal-conductivity detector) instruments.

Reagents.—Diethyl dichloromethylphosphonate, b. p. 70–72°/1 mm., n_D^{26} 1.4510, was prepared as described by Bunyan and Cadogan⁷ who reported b. p. 82°/0.2 mm., n_D^{25} 1.4513. Triethyl phosphite in ether was washed with aqueous ferrous sulphate, *N*-sodium hydroxide, and water, dried over anhydrous magnesium sulphate and then sodium, and distilled under nitrogen. Tetraethyl methylenebisphosphonate was prepared by Cade's method⁸ and had b. p. 100–120°/0.1 mm., n_D^{25} 1.4351 (lit.,⁸ b. p. 122–124°/0.5 mm.; n_D^{20} 1.4308).

Reaction of Triethyl Phosphite with Chloroform.—(i) *Without added di-*t*-butyl peroxide.* Triethyl phosphite (6.64 g.; 1 mol.) and chloroform (9.52 g., 2 mol.) which had been previously saturated with nitrogen were kept at 130° under nitrogen for 93 hr. G.l.c. (Pye Argon QF1 column at 175°, and silicone column at 140°) indicated the presence of diethyl ethylphosphonate, triethyl phosphite, and three high-boiling components. Distillation gave (a) chloroform (7 g.), (b) diethyl ethylphosphonate (5.7 g., 86%), b. p. 80–92°/15 mm., n_D^{26} 1.4140 (correct infrared

⁶ Crofts and Downie, *J.*, 1963, 2559.

⁷ Bunyan and Cadogan, *J.*, 1962, 2953.

⁸ Cade, *J.*, 1959, 2266.

spectrum), and (c) a mixture of unidentified compounds (0.9 g.), b. p. 110—136°/0.1 mm., n_D^{26} 1.4333. Fraction (c) was redistilled to give two fractions, b. p. 110—112°/0.025 mm. (Found: C, 37.15; H, 7.95%) and b. p. 112—118°/0.025 mm. {Found: C, 36.4; H, 7.65. Calc. for $[(EtO)_2PO]_2CH_2$: C, 37.5; H, 7.7. Calc. for $[(EtO)_2PO]_3CH$: C, 36.8; H, 7.8. Calc. for $[(EtO)_2P(O)]_2CH \cdot CH_3$: C, 39.7; H, 8.0%}. The infrared spectrum of fraction (c) was identical with that of tetraethyl methylenebisphosphonate, but g.l.c. of the product indicated several components, only one of which had retention time equal to that of tetraethyl methylenebisphosphonate.

A large-scale experiment ($\times 10$) carried out to facilitate identification of the unknown products gave, in addition to diethyl ethylphosphonate, a product (0.9 g.), b. p. 110—130°/0.1 mm., n_D^{26} 1.4375, whose infrared spectrum and g.l.c. retention time were identical with that of tetraethyl methylenebisphosphonate, $[(EtO)_2P(O)]_2CH_2$. The sample, though pure (by g.l.c.), had an incorrect analysis however (Found: C, 35.9; H, 7.7; P, 21.1%; M, 295. Calc. for $C_9H_{22}O_6P_2$: C, 37.5; H, 7.7; P, 21.6%; M, 288).

(ii) *With di-t-butyl peroxide.* Triethyl phosphite (6.64 g., 1 mol.), chloroform (9.52 g., 2 mol.), and di-t-butyl peroxide (0.146 g., 0.025 mol.) were kept at 130° in a sealed tube for 23 hr. G.l.c. indicated the presence of ethyl chloride and diethyl ethylphosphonate, the latter being isolated by distillation.

(iii) *With ethanol.* Triethyl phosphite (40 g., 1 mol.), chloroform (57 g., 2 mol.), and ethanol (44 g., 4 mol.), freshly distilled and degassed with nitrogen, were kept at 130° in a sealed tube for 94 hr. Distillation gave a fraction (93.5 g.), b. p. <84°, containing ca. 10% methylene chloride (examined using a Perkin-Elmer g.l.c. 2 m. "U" column at 48°), and several fractions boiling in the range 81—105°/15 mm., n_D^{27} in the range 1.4055—1.4190 (total weight 30.4 g.), each containing triethyl phosphate and diethyl ethylphosphonate according to their infrared spectra. There was a residue (4.25 g.).

(iv) *With ethanol and di-t-butyl peroxide.* Triethyl phosphite (6.64 g., 1 mol.), chloroform (9.52 g.; 2 mol.) which had been degassed with nitrogen, ethanol (7.4 g., 4 mol.), and di-t-butyl peroxide (0.15 g.) were kept at 130° in a sealed tube for 23 hr. Pressure developed in the tube during the reaction. G.l.c. analysis (Perkin-Elmer 2 m. "U" column at 48°) showed that, in addition to ethyl chloride, methylene chloride was formed (5—10% based on remaining chloroform). After the lower-boiling fraction, b. p. <80°, (17.6 g.) had been removed, further distillation gave triethyl phosphate (0.8 g.), b. p. 60—96°/15 mm., n_D^{24} 1.4007, (correct infrared spectrum) and a high-boiling fraction, (1.7 g.), b. p. 60—120°/0.1 mm., n_D^{24} 1.4195, leaving an undistilled residue (2.2 g.). Diethyl ethylphosphonate was not isolated or detected, but less than 10% in the presence of triethyl phosphate would have escaped detection by our methods.

Reaction of Triethyl Phosphite with Diethyl Dichloromethylphosphonate.—Triethyl phosphite (10.0 g., 4 mol.) and diethyl dichloromethylphosphonate (3.3 g., 1 mol.) were boiled under reflux for 23 hr. Distillation gave diethyl ethylphosphonate (9.0 g., 90%), b. p. 86—102°/10 mm., n_D^{24} 1.4180 (correct infrared spectrum) and a fraction, b. p. 60—130°/0.05 mm., n_D^{24} 1.4420, containing unknown products (5—10%) and the bulk of diethyl dichloromethylphosphonate.

The Effect of Heat on Triethyl Phosphite.—Triethyl phosphite (3.0 g.) was kept at 130° in a sealed tube for 23 hr. G.l.c. (Pye Argon silicone column at 125°) showed that neither triethyl phosphate nor diethyl ethylphosphonate had been formed. The use of a W.F.1 column showed that none of the usual unknown compounds were formed. Identical results were obtained when triethyl phosphite (3.0 g.) and di-t-butyl peroxide (0.07 g.) were similarly kept at 130° for 23 hr.

Reaction of Bromoform with Triethyl Phosphite.—Bromoform (2.53 g., 1 mol.) was added dropwise to triethyl phosphite (8.3 g., 5 mol.) at 0°. Heat evolution did not occur. Work-up by distillation after 20 hr. under reflux gave diethyl ethylphosphonate (7.02 g., 84%), b. p. 76—82°/10 mm. (correct infrared spectrum) and the same high-boiling products obtained from the corresponding reaction with chloroform.

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