Phase-Transfer-Catalysed Halogenation of Di-*t*-butyl Phosphite. Preparation of Di-*t*-butyl Phosphorohalidates[1]

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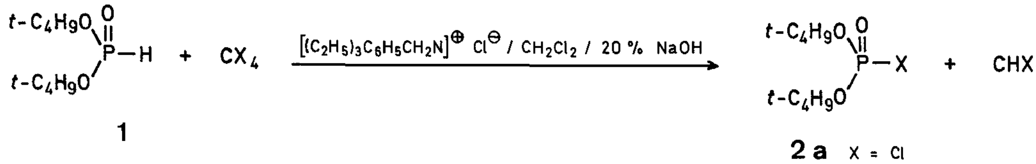
In view of the well recognised ease of dealkylation under mild acidic conditions[2,3], di-*t*-butyl phosphorohalidates (**2a, b**), possible attractive reagents for phosphorylation of alcohols and amines, cannot be prepared by standard halogenation[4] of di-*t*-butyl phosphite (**1**). Di-*t*-butyl phosphorochloridate (**2a**) was, however, obtained in an impure state when di-*t*-butyl phosphite (**1**) was treated with *N*-chlorosuccinimide at 65° in tetrachloromethane solution[2]. Di-*t*-butyl phosphorobromidate (**2b**) has not been hitherto described although some other dialkyl phosphorobromidates are readily available from the reaction between the corresponding phosphites and *N*-bromosuccinimide[5].

Incidental to our studies on the application of phase-transfer-catalysed two-phase system for Atherton-Todd phosphorylation of amines[1] and alcohols[6] we have noticed that this technique creates remarkably advantageous circumstances for the preparation of pure **2**. The reaction medium is constantly kept strongly alkaline during halogenation of di-*t*-butyl phosphite (**1**) with an excess of the corresponding tetrahalomethane, thus preventing acid-catalysed dealkylation. Considerable steric hindrance at phosphorus due to the bulk of the *t*-butyl groups renders the consecutive transformation of **2** into tetra-*t*-butyl pyrophosphate practically impossible. Our expectations have found full experimental support.



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2a X = Cl

b X = Br

We wish to report now a new convenient synthetic procedure leading to pure **2**. When di-*t*-butyl phosphite (**1**) was reacted with an excess of tetrachloromethane at 20–25° in a two-phase system consisting of dichloromethane/20% aqueous sodium hydroxide solution in the presence of about 5 mol-% of triethylbenzylaminium chloride (TEBA), analytically pure di-*t*-butyl phosphorochloridate (**2a**) was formed in 88% yield. Similarly, bromination of **1** with stoichiometric amounts of tetrabromomethane in the two-phase system described above afforded analytically pure di-*t*-butyl phosphorobromidate (**2b**) in 90% yield. Di-*t*-butyl phosphorohalidates (**2a, b**) are unstable liquids, decomposing spontaneously at room temperature after several hours. They can be, however, stored at +5° for about 12 h without any sign of decomposition. At lower temperature (−10°) they remain practically unchanged for at least 3 days.

Attempted application of the modified Atherton-Todd two-phase bromination of dialkyl phosphites for the preparation of other dialkyl phosphorobromidates failed. The above mentioned treatment of diethyl phosphite with tetrabromomethane in dichloromethane – 20% aqueous sodium hydroxide solution containing 5 mol% of triethylbenzylaminium chloride at 0–5° resulted in the formation of a mixture consisting of tetraethyl pyrophosphate (83%; ^{31}P-N.M.R.: $\delta = +13.75$ ppm from 85% H_3PO_4), diethyl hydrogen phosphate (17%; ^{31}P-N.M.R.: $\delta = +1.2$ ppm from 85% H_3PO_4), and only minute amounts of the desired diethyl phosphorobromidate (^{31}P-N.M.R.: $\delta = +9.39$ ppm from 85% H_3PO_4). All compounds referred to were unequivocally identified by comparing their ^{31}P-N.M.R. spectra with those of authentic samples. The latter observation is in full accord with the Steinberg's statement[7] that dialkyl phosphorobromidates cannot be obtained by bromination of the corresponding dialkyl phosphites with tetrabromomethane in the presence of tertiary amines.

Preparation of Di-*t*-butyl Phosphorochloridate (2a):

A solution of di-*t*-butyl phosphite (**1**[2]; 9.7 g, 0.05 mol) in dichloromethane (15 ml) was added dropwise to a stirred two-phase system consisting of tetrachloromethane (30 ml), 20% aqueous sodium hydroxide (30 ml), and benzyltriethylaminium chloride (0.5 g). The temperature of the slightly exothermic reaction was kept at 20–25°. After the addition had been completed, stirring was continued for 3 h at room temperature. The mixture, which acquired a dark-brown coloration, was then diluted with dichloromethane (50 ml), the organic layer was separated, washed with water (3 × 30 ml), and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was kept at 20°/0.6 torr for 1 h to remove traces of volatile impurities. The residual pale-yellow liquid was an analytically pure sample of **2a**; yield: 10.1 g (88%); $n_D^{20} = 1.4286$.

$C_8H_{18}ClO_3P$	calc.	C 42.05	H 7.9	P 13.5
(228.7)	found	42.0	8.05	13.3

I.R. (film): $\nu_{max} = 2995, 2950, 1480$ (CH_3); 1398, 1374 [$(CH_3)_3C$]; 1290 (P=O), 1168 [C—O—(P)]; 1040, 995 cm^{-1} [P—O—(C)].

^{1}H-N.M.R. (CCl_4): $\delta = 1.45$ ppm (s, 9H, C$\underline{H}_3$).

^{31}P-N.M.R. (CCl_4): $\delta = +6.62$ ppm (from 85% H_3PO_4).

Preparation of Di-*t*-butyl Phosphorobromide (2b):

A solution of di-*t*-butyl phosphite (**1**[2]; 9.7 g, 0.05 mol) in dichloromethane (15 ml) was added dropwise with efficient stirring to a two-phase system consisting of dichloromethane (30 ml), tetrabromomethane (8.3 g, 0.025 mol), 20% aqueous sodium hydroxide (20 ml), and triethylbenzylaminium chloride (0.5 g, ~5 mol-%) at 20–25°. The mixture was then stirred at this temperature for a further 3 h. The pale-yellow solution was diluted with dichloromethane (50 ml), the organic layer was separated, washed with water (2 × 50 ml), and dried over anhydrous sodium sulfate. The liquid obtained after evaporation of the solvent and removal of volatile impurities in vacuo (1h at 0.5 torr) was an analytically pure sample of **2b**; yield: 12.2 g (90%); $n_D^{20} = 1.4490$.

$C_8H_{18}BrO_3P$	calc.	C 35.2	H 6.65	P 11.35
(273.1)	found	35.25	6.7	11.4

I.R. (film): $\nu_{max} = 2990, 2940, 1480$ (CH_3); 1397, 1373 (t-C_4H_9); 1285 (P=O); 1170 [C—O—(P)]; 1040, 995 cm^{-1} [P—O—(C)].

^{1}H-N.M.R. (CCl_4): $\delta = 1.475$ ppm (s, 9H, CH_3).

^{31}P-N.M.R. (CCl_4): $\delta = +22.85$ ppm (from 85% H_3PO_4).

Received: December 23, 1975

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