*Tetrahedron*. Vol. 29, pp. 1089 to 1094. Pergamon Press 1973. Printed in Great Britain

# ORGANOPHOSPHORUS ESTERS—IV*

## NOVEL APPROACH TO MONOALKYL HYDROGEN PHOSPHITES

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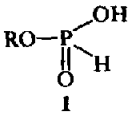
(*Received in the UK* 29 *September* 1972; *Accepted for publication* 28 *November* 1972)

**Abstract**—Tetramethylammonium t-butyl hydrogen phosphite (2), readily available from the reaction between di-t-butyl phosphite and aqueous tetramethylammonium hydroxide, was found to be a convenient phosphorylating agent for organic halides. It reacts easily with alkyl iodides and some alkyl bromides in boiling acetone affording the corresponding alkyl t-butyl phosphites (3). On treatment with trifluoroacetic acid at room temperature these compounds can be readily converted into monoalkyl hydrogen phosphites (1), isolated and characterized as S-*p*-chlorobenzylthiouronium derivatives (4).

Many methods have been proposed for the preparation of dialkyl hydrogen phosphates as models for the formation of the internucleotide linkage.[1] In contrast to various procedures employing the suitable "activation" of a phosphate monoester in phosphorylation of alcohols only a few methods utilizing nucleoside phosphites as intermediates in oligonucleotide synthesis have been reported. This situation is evidently due to rather limited accessibility of the corresponding nucleoside phosphites.[2-4]

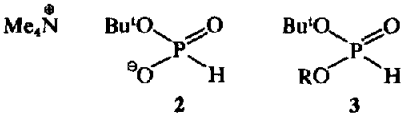
The first objective of the present study was the general, novel approach to various monoalkyl hydrogen phosphites (1).



1

Numerous synthetic procedures leading to 1 and involving basic[5,6] or acidic[7] hydrolysis as well as dealkylation of the corresponding dialkyl phosphites by means of suitably selected nucleophiles[8] have been reported. None of these methods, however, meets the requirement of simplicity and convenience in the case of 1 containing complex, polyfunctional alkyl groups in the molecule.

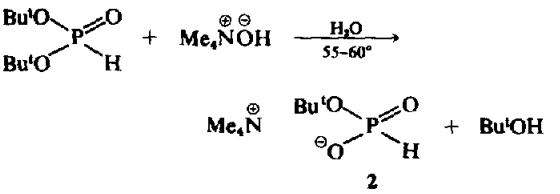
Very recently, we have found[9] that monoalkyl phosphates can be obtained in high yields by direct phosphorylation of the corresponding alkyl halides with tetramethylammonium di-t-butyl phosphate followed by subsequent removal of t-butyl groups in acidic medium. Consequently, the use of a suitably protected phosphorous acid derivative, i.e. tetramethylammonium t-butyl hydrogen phosphite (2), as a phosphorylating agent for alkyl halides seemed to fulfil the requirement of simplicity in the synthesis of monoalkyl hydrogen phosphites (1). In this paper we describe the preparation of alkyl t-butyl phosphites (3) and their easy acid cleavage which offers an attractive route to 1.



2 3

Incidentally a simple approach to mixed dialkyl phosphites (3), not available until now, and containing a chiral center at the P atom, may be also of considerable interest from a stereochemical point of view.

Tetramethylammonium t-butyl hydrogen phosphite (2) can be obtained in almost quantitative yield and analytical purity by the action of aqueous tetramethylammonium hydroxide solution on di-t-butyl phosphite at 55–60°:



2

The salt (2) is a colourless, crystalline solid (m.p. 198–200°) which, although very hygroscopic, is perfectly stable and can be stored indefinitely in a sealed vessel.

The phosphorylation of alkyl halides, some of them containing additional functional groups in the molecule (Table 1, compounds 8–11), was readily

*Part III: A. Zwierzak, *Phosphorus* 2, 19 (1972); Paper CLXXVIII on organophosphorus compounds.

Table 1. t-Butyl alkyl phosphites ($Bu^tO$)(RO)P(O)H

| Compound No. | Alkyl halide | Yield % | $n_D^{22}$ | Analyses (%) Required C | H | P | Found C | H | P |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $CH_3I$ | 82 | 1·4141 | 39·5 | 8·6 | 20·4 | 39·6 | 8·6 | 20·7 |
| 2 | $C_2H_5I$ | 82 | 1·4197 | 43·4 | 9·1 | 18·6 | 43·7 | 9·2 | 18·6 |
| 3 | n-$C_3H_7I$ | 78 | 1·4184 | 46·7 | 9·5 | 17·2 | 46·9 | 9·3 | 16·7 |
| 4 | i-$C_3H_7I$ | 55·5 | 1·4192 | 46·7 | 9·5 | 17·2 | 47·0 | 9·3 | 16·8 |
| 5 | n-$C_4H_9I$ | 83 | 1·4210 | 49·5 | 9·9 | 15·9 | 49·5 | 9·9 | 15·6 |
| 6 | sec-$C_4H_9I$ | 31 | 1·4230 | 49·5 | 9·9 | 15·9 | 49·3 | 9·8 | 16·0 |
| 7 | $CH_2{=}CH{-}CH_2Br$ | 79 | 1·4321 | 47·2 | 8·5 | 17·4 | 46·9 | 8·3 | 17·0 |
| 8 | Br-$(CH_2)_4$-Br | 84* | 1·4647 | 35·2 | 6·6 | 11·35 | 34·6 | 6·6 | 11·2 |
| 9 | $C_2H_3O{\cdot}CO{\cdot}CH_2Br$ | 60 | 1·4317 | 42·9 | 7·65 | 13·8 | 42·9 | 7·2 | 13·3 |
| 10 | $Ph{\cdot}CO{\cdot}CH_2Br$ | 82 | — | 56·3 | 6·7 | 12·1 | 56·4 | 6·8 | 12·3 |
| 11 | p-Br—$C_6H_4$—$CH_2Br$ | 87 | 1·5102 | 43·0 | 5·25 | 10·1 | 43·5 | 5·35 | 10·6 |

*Only t-butyl 4-bromobutyl phosphite (monophosphorylated product) was obtained even when 100% excess of tetramethylammonium t-butyl hydrogen phosphite has been used.

Table 2. IR and NMR spectral assignments of t-butyl alkyl phosphites ($Bu^tO$)(RO)P(O)H

| No. | Compound R | IR (film)[a] $cm^{-1}$ | NMR ($CCl_4$ with TMS as int. ref.) chemical shifts (δ, ppm; J, Hz)[b] |
|---|---|---|---|
| 1 | $CH_3$ | 2425s [P-H], 1400s, 1377vs [$Bu^t$], 1270vs [P=O], 1175vs [C—O—(P)], 1048vs, 992vs [P—O—(C)] | δ = 1·49 (s, 9H, $Bu^t$), 3·65 (d, 3H, $^3J_{P-H}$ = 12·3), 6·62 (d, 1H, $J_{P-H}$ = 684) |
| 2 | $C^BH_3{-}C^AH_2$ | 2428m [P—H], 1400m, 1376vs [$Bu^t$], 1269vs [P=O], 1176s [C—O—(P)], 1046s, 980vs [P—O—(C)] | δ = 1·30 (t, 3$H_B$, $J_{H_A-H_B}$ = 7·5), 1·47 (s, 9H, $Bu^t$), 4·04 (dq, 2$H_A$, $J_{H_A-H_B}$ = 7·5, $^3J_{P-H_A}$ = 9·6), 6·68 (d, 1H, $J_{P-H}$ = 680) |
| 3 | $C^CH_3{-}C^BH_2{-}C^AH_2$ | 2425s [P—H], 1399s, 1375vs [$Bu^t$], 1266vs [P=O], 1175vs [C—O—(P)], 1046vs, 980vs [P—O—(C)] | δ = 0·99 (t, 3$H_C$, $J_{H_B-H_C}$ = 7·5), 1·47 (s, 9H, $Bu^t$), 1·40–2·05 (m, 3$H_B$), 3·92 (dt, 2$H_A$, $J_{H_A-H_B}$ = 6·3, $^3J_{P-H_A}$ = 8·8), 6·66 (d, 1H, $J_{P-H}$ = 682) |
| 4 | $(C^BH_3)_2C^AH$ | 2424m [P—H], 1392s, 1378vs [$Bu^t$], 1269vs [P=O], 1180s, 1145s, 1114s [C—O—(P)], 1025vs, 980vs [P—O—(C)] | δ = 1·32 (d, 6$H_B$, $J_{H_A-H_B}$ = 6·45), 1·47 (s, 9H, $Bu^t$), 4·63 (dsp, 1$H_A$, $J_{H_A-H_B}$ = 6·45, $^3J_{P-H_A}$ = 9·0), 6·68 (d, 1H, $J_{P-H}$ = 680) |
| 5 | $C^DH_3{-}C^CH_2{-}C^BH_2{-}C^AH_2$ | 2425m [P—H], 1399m, 1375s [$Bu^t$], 1269vs [P=O], 1175s [C—O—(P)], 1042s, 980vs [P—O—(C)] | δ = 0·96 (distorted t, 3$H_D$, $J_{H_C-H_D}$ = 5·4), 1·47 (s, 9H, $Bu^t$), 1·10–1·95 (m, 4$H_{BC}$), 3·99 (dt, 2$H_A$, $J_{H_A-H_B}$ = 6·3, $^3J_{P-H_A}$ = 8·7), 6·68 (d, 1H, $J_{P-H}$ = 684) |
| 6 | $C^DH_3{-}C^CH_2{-}C^AH(C^BH_3)$ | 2420m [P—H], 1399m, 1375vs [$Bu^t$], 1267vs [P=O], 1176s, 1129m, 1116m [C—O—(P)], 1040vs, 980vs [P—O—(C)] | δ = 0·97 (distorted t, 3$H_D$, $J_{H_C-H_D}$ = 6·6), 1·31 (d, 3$H_B$, $J_{H_A-H_B}$ = 6·4), 1·16–1·80 (m, 2$H_C$), 1·48 (s, 9H, $Bu^t$), 4·42 (dsx, 1$H_A$, $J_{H_A-H_B} \simeq J_{H_A-H_C}$ = 6·4, $^3J_{P-H_A}$ = 6·72 (d, 1H, $J_{P-H}$ = 680) |
| 7 | $^AH(^BH){=}C(^XH){-}C^YH_2$ | 2425m [P—H], 1400m, 1378s [$Bu^t$], 1270vs [P=O], 1176s [C—O—(P)], 1042vs, 980vs [P—O—(C)] | ABXY$_2$ system:[c] $\delta_Y$ = 4·47 (12 lines, 2$H_Y$), $\delta_A$ = 5·19, $\delta_B$ = 5·31 (AB part, 8 lines, 2$H_{AB}$), $\delta_X$ = 5·97 (12 lines, 1$H_X$); $J_{AX}$ = 10·0, $J_{BX}$ = 17·4, $J_{AB}$ = 2·4, $J_{Y(AB)}$ = 1·4, $J_{XY}$ = 5·3, $^3J_{P-H_Y}$ = 9·4; δ = 1·50 (s, 9H, $Bu^t$), 6·74 (d, 1H, $J_{P-H}$ = 684) |

Table 2. (Contd.)

| No. | Compound R | IR (film)[a] $cm^{-1}$ | NMR ($CCl_4$ with TMS as int. ref.) chemical shifts (δ, ppm; J, Hz)[b] |
|---|---|---|---|
| 8 | $Br—C^DH_2—C^CH_2—C^BH_2—C^AH_2$ | 2425m [P—H], 1400s, 1376vs [$Bu^t$], 1265vs [P=O], 1173vs [C—O—(P)], 1045vs, 980vs [P—O—(C)] | δ = 1·49 (s, 9H, $Bu^t$), 1·64–2·18 (m, $4H_{BC}$), 3·45 (distorted t, $2H_D$, $J_{H_C-H_D} = 6·4$), 4·02 (dt, $2H_A$, $J_{H_A-H_B} = 6·0$, $^3J_{P-H_A} = 8·6$), 6·90 (d, 1H, $J_{P-H} = 684$) |
| 9 | $C^DH_3—C^CH_2—O—\overset{O}{\overset{\|}{C}}—C\begin{matrix}{}^B H\\ {}^A H\end{matrix}$ | 2435m [P—H], 1760vs [C=O], 1401s, 1378vs [$Bu^t$], 1269vs [P=O], 1175vs [C—O—(P)], 1030vs, 980vs [P—O—(C)] | δ = 1·30 (t, $3H_D$, $J_{H_C-H_D} = 7·5$), 1·50 (s, 9H, $Bu^t$), 4·28 (q, $2H_C$, $J_{H_C-H_D} = 7·5$), 4·54 (d, $1H_A$, $^3J_{P-H_A} = 14·6$, $J_{H_A-H_B} = 0$), 4·59 (d, $1H_B$, $^3J_{P-H_B} = 11·8$), 6·94 (d, 1H, $J_{P-H} = 714$)[d] |
| 10 | $Ph—\overset{O}{\overset{\|}{C}}—C\begin{matrix}{}^B H\\ {}^A H\end{matrix}$ | 2440s [P—H], 1710vs [C=O], 1400s, 1378vs [$Bu^t$], 1265vs [P=O], 1171vs [C—O—(P)], 1047vs, 980vs [P—O—(C)] | δ = 1·50 (s, 9H, $Bu^t$), 5·37 (d, $1H_A$, $^3J_{P-H_A} = 14·4$, $J_{H_A-H_B} = 0$), 5·39 (d, $1H_B$, $^3J_{P-H_B} = 10·8$), 7·06 (d, 1H, $J_{P-H} = 720$), 7·30–7·92 (m, 5H arom.)[d] |
| 11 | $p$-Br—$C_6H_4$—$CH_2$ | 2425 [P—H], 1399m, 1375s [$Bu^t$], 1266vs [P=O], 1171s [C—O—(P)], 1044vs, 980vs [P—O—(C)] | δ = 1·46 (s, 9H, $Bu^t$), 4·92 (d, 2H, $^3J_{P-H} = 9·8$), 6·80 (d, 1H, $J_{P-H} = 690$), 7·06–7·52 (m, 4H arom.) |

[a]Only characteristic absorption bands are included.
[b]Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dq, double quartet; dt, double triplet; dsx, double sextet; dsp, double septet.
[c]First order treatment was applied.
[d]Magnetic nonequivalence of geminal methylene protons ($H_A$ and $H_B$) was confirmed by heterodecoupling of $^{31}P$ nucleus.

effected in boiling acetone with one molecular equivalent or a slight excess (up to 25%) of tetramethylammonium t-butyl hydrogen phosphite (2). The reaction and subsequent removal of the t-butyl group leading to the final phosphorylation product (1) is given by the equation:

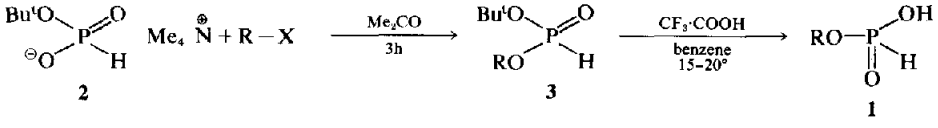



Table 3. S-$p$-Chlorobenzylthiuronium salts of monoalkyl hydrogen phosphites

$(RO)(H)P(O)O^{\ominus}$ $p$-Cl—$C_6H_4$—$CH_2$—$\overset{\oplus}{S}$=$C(NH_2)_2$

| Compound No. | R | M.p. °C | Analyses (%) Required N | Required P | Found N | Found P |
|---|---|---|---|---|---|---|
| 1a | $CH_3$ | 146–8 | 9·4 | 10·4 | 9·5 | 10·4 |
| 2a | $C_2H_5$ | 140–2 | 9·0 | 10·0 | 8·9 | 10·1 |
| 3a | n-$C_3H_7$ | 139–41 | 8·6 | 9·5 | 8·6 | 9·6 |
| 4a | i-$C_3H_7$ | 166–8 | 8·6 | 9·5 | 8·5 | 9·3 |
| 5a | n-$C_4H_9$ | 150–2 | 8·3 | 9·1 | 8·2 | 8·7 |
| 6a | sec-$C_4H_9$ | 169–71 | 8·3 | 9·1 | 7·9 | 9·1 |
| 7a | $CH_2$=CH—$CH_2$ | 145–7 | 8·7 | 9·6 | 8·7 | 9·6 |
| 8a | Br-$(CH_2)_4$ | 130–2 | 6·7 | 7·4 | 6·6 | 7·3 |
| 9a | $C_2H_5O$·CO·$CH_2$ | 178–80 | 7·6 | 8·4 | 7·5 | 8·3 |
| 10a | Ph·CO·$CH_2$ | 150–2 | 7·0 | 7·7 | 6·8 | 7·4 |
| 11a | p-Br—$C_6H_4$·$CH_2$ | 170–2 | 6·2 | 6·9 | 6·25 | 6·8 |

Crude alkyl t-butyl phosphites (3), isolated in high yields, were in all cases analytically pure. Their yields, physical constants, and elemental analysis data are listed in Table 1. The structure of all compounds was unambiguously confirmed by IR and NMR spectroscopy, the relevant data being compiled in Table 2.

The influence of the leaving group and the solvent on the yield of alkyl t-butyl phosphites (3) was studied, n-butyl halides ($Bu^nX$, X = Cl,

Table 4. IR and NMR spectral assignments of S-*p*-chlorobenzylthiuronium salts of monoalkyl hydrogen phosphites

$(RO)(H)P(O)O^{\ominus}$ *p*-Cl—$C_6H_4$—$CH_2$—$\overset{\oplus}{S}$=$C(NH_2)_2$

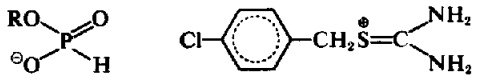
| Compound No. | IR (KBr)[a] $cm^{-1}$ | NMR ($CD_3SOCD_3$ with TMS as int. ref.) chemical shifts (δ, ppm; *J*, Hz)[b] |
|---|---|---|
| **1a** | 2390m [P—H], 1498s [C=S], 1209vs, 1062vs [$PO_2^{\ominus}$?], 1163vs [C—O—(P)], 1021s, 1005vs [P—O—(C)] | δ = 3·41 (d, 3H, $CH_3O$, $^3J_{PH}$ = 12·4), 4·58 (s, 2H, $CH_2$), 6·65 (d, 1H, $J_{PH}$ = 598), 7·55 (s, 4H arom.) |
| **2a** | 2408m [P—H], 1499s [C=S], 1201vs, 1060vs [$PO_2^{\ominus}$?], 1158s [C—O—(P)], 1025vs, 1011vs [P—O—(C)] | δ = 1·15 (t, 3H, $CH_3$, $J_{HH}$ = 7·6), 3·80 (dq, 2H, $CH_2$—O, $J_{HH}$ = 7·6, $^3J_{PH}$ = 9·2), 4·55 (s, 2H, $CH_2$), 6·69 (d, 1H, $J_{PH}$ = 597), 7·55 (s, 4H arom.) |
| **3a** | 2390m [P—H], 1499s [C=S], 1208vs, 1064vs [$PO_2^{\ominus}$?], 1158s [C—O—(P)], 1020s, 1004vs [P—O—(C)] | δ = 0·88 (t, 3H, $CH_3$, $J_{HH}$ = 7·4), 1·25–1·95 (m, 2H, $CH_3$—$CH_2$—$CH_2O$), 3·72 (dt, 2H, $CH_2$—O, $J_{HH}$ = 6·6, $^3J_{PH}$ = 8·4), 4·58 (s, $CH_2$), 6·70 (d, 1H, $J_{PH}$ = 599), 7·55 (s, 4H arom.) |
| **4a** | 2392m [P—H], 1498vs [C=S], 1201vs, 1070vs [$PO_2^{\ominus}$?], 1152, 1120vs, 1098vs [C—O—(P)], 1030s, 1018s, 988vs [P—O—(C)] | δ = 1·14 (d, 6H, $CH_3$, $J_{HH}$ = 7·2), 3·80–4·50 (m, 1H, CH), 4·58 (s, 2H, $CH_2$), 6·72 (d, 1H, $J_{PH}$ = 598), 7·58 (s, 4H arom.) |
| **5a** | 2389m [P—H], 1498s [C=S], 1190vs, 1065vs [$PO_2^{\ominus}$?], 1145vs [C—O—(P)], 1020vs, 1000vs [P—O—(C)] | δ = 0·89 (distorted t, 3H, $CH_3$, $J_{HH}$ = 6·0), 1·10–1·66 (m, 4H, —$CH_2$—$CH_2$—), 3·50–3·95 (m, 2H, —$CH_2$—O—), 4·54 (s, 2H, $CH_2$), 6·68 (d, 1H, $J_{PH}$ = 597), 7·56 (s, 4H arom.) |
| **6a** | 2389m [P—H], 1498s [C=S], 1200vs, 1072vs [$PO_2^{\ominus}$?], 1157s [C—O—(P)], 1040vs, 992vs [P—O—(C)] | δ = 0·82 (t, 3H, $CH_3$—$CH_2$—, $J_{HH}$ = 6·8), 1·12 (d, 3H, $CH_3$—CH—, $J_{HH}$ = 6·5), 1·10–1·63 (m, 2H, $CH_2$—CH—), 4·05 (dsx, 1H, CH, $J_{HH}$ = 6·5, $^3J_{PH}$ = 10·6), 4·47 (s, 2H, $CH_2$), 6·59 (d, 1H, $J_{PH}$ = 590), 7·43 (s, 4H arom.) |
| **7a** | 2405 [P—H], 1498s [C=S], 1203vs 1085vs [$PO_2^{\ominus}$?], 1154s [C—O—(P)], 1022vs, 996vs [P—O—(C)] | δ = 4·15–4·44 (m, 2H, —$CH_2$—O), 4·58 (s, 2H, $CH_2$), 5·04–5·55 (m, 2H, $CH_2$=), 5·74–6·37 (m, 1H, =CH), 6·76 (d, 1H, $J_{PH}$ = 603), 7·57 (s, 4H arom.) |
| **8a** | 2370m [P—H], 1498s [C=S], 1198vs, 1058vs [$PO_2^{\ominus}$?], 1149s [C—O—(P)], 1020s, 970s [P—O—(C)] | δ = 1·45–2·00 (m, 4H, —$CH_2$—$CH_2$—), 3·30–4·10 (m, 4H, Br-$CH_2$, $CH_2$—O), 4·55 (s, 2H, $CH_2$), 6·69 (d, 1H, $J_{PH}$ = 597), 7·55 (s, 4H arom.). |
| **9a** | 2390s [P—H], 1668vs [C=O?], 1499s [C=S], 1194vs, 1078vs [$PO_2^{\ominus}$?], 1145vs [C—O—(P)], 1040vs, 1020vs, 1004vs [P—O—(C)] | δ = 1·24 (t, 3H, $CH_3$, $J_{HH}$ = 7·2), 3·90–4·42 (m, 4H, $CH_2$—O), 4·57 (s, 2H, $CH_2$), 6·82 (d, 1H, $J_{PH}$ = 594), 7·56 (s, 4H arom.) |
| **10a** | 2365m [P—H], 1712vs, 1654vs [C=O?], 1499s [C=S], 1218vs 1072vs [$PO_2^{\ominus}$?], 1150m [C—O—(P)], 1034s, 972vs [P—O—(C)] | δ = 4·56 (s, 2H, $CH_2$), 5·21 (d, 2H, $CH_2$—O, $^3J_{PH}$ = 10·7), 6·91 (d, 1H, $J_{PH}$ = 613), 7·4–8·2 (m, 9H arom.) |
| **11a** | 2389s [P—H], 1498s [C=S], 1203vs, 1084vs [$PO_2^{\ominus}$?], 1135s [C—O—(P)], 1060vs, 1002vs [P—O—(C)] | δ = 4·56 (s, 2H, $CH_2$), 4·82 (d, 2H, $CH_2$—O, $^3J_{PH}$ = 9·3), 6·82 (d, 1H, $J_{PH}$ = 602), 7·25–7·75 (m, 8H arom.) |

[a]Only characteristic absorption bands are included.

[b]Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet; dt, double triplet; dq, double quartet; dsx, double sextet.

Br, I) being used as model compounds. In boiling acetone distinct differences in the yield of nucleophilic displacement were observed in all cases. n-Butyl t-butyl phosphite (3, R = n-Bu) was formed in 83% yield from n-butyl iodide, but only in 33·5% yield from the corresponding bromide. n-Butyl chloride was found to be almost unreactive towards (2) under comparable conditions. The yield of n-butyl t-butyl phosphite obtained from n-butyl bromide could be effectively improved (up to 61%) by using more polar acetonitrile instead of acetone as a reaction medium. This change of solvent was, however, meaningless in the case of more reactive n-butyl iodide. Inferior results obtained in dimethoxyethane (33·5% yield of the corresponding (3) from n-butyl iodide) were probably due to the low solubility of the salt (2) in this solvent.

Alkyl t-butyl phosphites (3) could be easily and quantitatively converted into the corresponding monoalkyl hydrogen phosphites (1). The free acids (1) are colourless, syrupy oils, relatively unstable even at ambient temperature. It was found that S-*p*-chlorobenzylthiuronium chloride[10] is an excellent reagent for the conversion of sodium salts of 1 into crystalline S-*p*-chlorobenzylthiuronium derivatives (4). These derivatives, which show characteristic, relatively sharp m.ps, were found to be quite useful for the purification and identification of 1.



4

M.ps and elemental analysis data of 4 are compiled in Table 3. Characteristic IR absorption bands of these compounds and their NMR spectral assignments are summarized in Table 4.

The reaction between alkyl halides and tetramethylammonium t-butyl hydrogen phosphite (2) is the first example of mixed dialkyl phosphite synthesis by means of $S_N$-type nucleophilic displacement. Further studies on this and related transformations are now being continued in our laboratory.

## EXPERIMENTAL

Solvents and reagents were purified by conventional methods. Light petroleum refers to the fraction boiling at 60–80°. All solns were evaporated under reduced press. M.ps (taken in capillaries) are uncorrected. NMR spectra were measured at 60 MHz with a Jeol JNM-C-60 HL spectrometer in $CCl_4$ or $CD_3{\cdot}SO{\cdot}CD_3$ solns using TMS as internal standard. IR spectra were recorded using a Spectromom 2000 spectrophotometer (MOM, Budapest). Measurements were made on samples of analytical purity.

Tetramethylammonium hydroxide (*ca* 5% aqueous soln) was prepared as described previously.[9]

Di-t-butyl phosphite was obtained in 80–85% yield according to Goldwhite and Saunders.[11]

*Tetramethylammonium t-butyl hydrogen phosphite* (2). A soln of di-t-butyl phosphite (97·1 g, 0·5 mole) in EtOH (100 ml) was placed in a 2 litre 3-necked flask equipped with a stirrer, thermometer and dropping funnel. A *ca* 5% aqueous soln of freshly prepared tetramethylammonium hydroxide (0·5 mole) was added quickly with efficient stirring at 55–58°. The soln was kept at this temp until it became neutral or slightly alkaline* On evaporation at slightly elevated temp (40–50°) a colourless, crystalline residue was obtained, which weighed 101·4 g (96%) when dried *in vacuo* over $P_2O_5$. The crude salt (2) was analytically pure, m.p. 198–200°. (Found: C, 45·5; H, 10·4; N, 7·1; P, 14·4; $C_8H_{22}O_3NP$ requires: C, 45·5; H, 10·5; N, 6·6; P, 14·7%). The IR spectrum (KBr) showed characteristic bands at: 2382s (P-H), 1491s ($Me_4\overset{\oplus}{N}$), 1396s, 1370s ($Bu^t$), 1090vs, 1042s ($PO_2^{\ominus}$?), 950vs [P-O-(C)] $cm^{-1}$. The NMR spectrum (in $D_2O$ with DSS as internal reference) showed signals at: $\delta = 1{\cdot}41$ ppm (s, 9H, C-$CH_3$), 3·20 ppm (s, 12H, N-$CH_3$), and 6·82 ppm (d, 1H, $J_{P\text{-}H} = 624$ Hz, P-H).

*Phosphorylation of alkyl halides with* 2*—General procedure*

1. *Preparation of alkyl t-butyl phosphites* (3). A mixture of alkyl halide (0·02 mole) and 2 (4·2 g, 0·02 mole) was refluxed with stirring for 3 hr in acetone soln (30 ml). The ppt of tetramethylammonium halide was filtered off on cooling and washed with acetone. The filtrate was evaporated, diluted with light petroleum (30 ml), filtered once more and evaporated again. The residue was kept at 30–40°/2 mmHg for 1 hr in order to remove traces of solvent, yields, physical properties, analytical and spectral data of 3 thus prepared are listed in Tables 1 and 2.

2. *Removal of t-butyl group—Monoalkyl hydrogen phosphites* (1). Trifluoroacetic acid (1·4 g, 0·012 mole) was added to the soln of crude 3 (0·01 mole) in benzene (10 ml) and the mixture was set aside for 18 hr at room temp. Crude 1, obtained as a thick oil on evaporation of the soln, was dissolved in water (5 ml) and neutralized with 20% NaOHaq. The soln of *p*-chlorobenzylisothiuronium chloride (2·37 g, 0·01 mole) in EtOH (10 ml) was then added at 95° and the resulting mixture evaporated to dryness. The residue was crystallized from anhyd EtOH, sodium chloride ppt being removed by filtration. M.ps, analytical, and spectral data of 4 thus obtained in almost quantitative yields are summarized in Tables 3 and 4.

*Caution – Slow addition of $Me_4\overset{\oplus}{N}\overset{\ominus}{O}H$ soln may cause temporary acidification of the mixture resulting in considerable removal of both $Bu^t$ groups.

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