The Dealkylation of Phosphate and Phosphonate Esters by Iodotrimethylsilane: A Mild and Selective Procedure

By G. Michael Blackburn * and David Ingleson, Department of Chemistry, The University, Sheffield S3 7HF

Iodotrimethylsilane transforms alkyl esters of phosphorus oxyacids into their corresponding trimethylsilyl esters and alkyl iodide. The reaction is rapid and quantitative at room temperature. The reagent has no effect on aryl phosphate ester functions or upon alkyl carboxylate, ether, bromoalkane, vinyl, and ethynyl functions under the conditions employed for transesterification. The trimethylsilyl esters can be isolated by distillation or solvolysed without purification using methanol or water to afford dealkylated phosphate and phosphonate species. Selective monodealkylation of dialkyl phosphonates cannot be achieved using only one equivalent of the reagent, which leads to the formation of mixed products.

THE chemistry of esters of phosphoric and phosphorous acids derives much of its importance from the role of the former in oligonucleotide syntheses [1] and of the latter as precursors for phosphonate analogues of biological phosphates.[2] A key step in the final stages of syntheses in either of these fields is the partial or complete de-esterification of fully esterified phosphorus oxyacids. Some selectivity has been achieved through use of the alkaline-lability of aryl esters,[3] *via* the hydrogenolysis of benzylic and phenolic esters,[4] by virtue of special properties of specifically designed alkyl esters, such as 2-cyanoethyl [1,5] or 2,2,2-trichloroethyl [1,6] species, or by anionic debenzylations.[7] However, no readily available method has been to hand for the mild dealkylation of partially or fully esterified phosphorus oxyacids, which has usually been accomplished under forcing conditions, typically by means of concentrated hydrochloric acid under reflux or at higher temperature [8] and often resulting in poor yields.[9]

Voronkov [10] and Schwarz [11] showed that bromo- and chloro-trialkylsilanes interact with trialkyl phosphates or with alkyl phosphinates to give the corresponding trialkylsilyl esters which, in turn, could be hydrolysed readily to afford the parent phosphorus acids. This initiative was later developed in work by Rabinowitz [12] and by others,[13–15] which established that the use of bromotrimethylsilane is superior to that of chlorotrimethylsilane.

It appeared likely that iodotrimethylsilane would exhibit even greater reactivity towards phosphate and phosphonate alkyl esters and its ready availability from disiloxan by a simple and efficient procedure [16] led us to investigate its suitability for this purpose. Since the publication of our preliminary results,[17] the use of this reagent has been described for the dealkylation of dialkyl phosphoro-chloridates, -bromidates, and -amidates, and trialkyl phosphorothiolates,[18] of dialkyl oxoalkane-phosphonates,[19] and of dimethyl enol phosphates.[20] In addition, the use of chlorotrimethylsilane in conjunction with sodium iodide has been advocated for de-esterification of dialkyl phosphonates.[21]

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R34 instrument at 220 MHz in $CDCl_3$ for silyl esters and in [$^2H_5$]-pyridine or deuterium oxide for the ammonium salts with Me_4Si or t-butyl alcohol as internal reference.

Iodotrimethylsilane.—This reagent was obtained as a clear, colourless liquid, b.p. 106—110°, by the method of Jung and Lyster.[16] It can be stored conveniently under nitrogen in a polythene-capped bottle for up to 1 year at 0 °C in the dark (though it attacks rubber rapidly).

Dealkylation of Dialkyl Phosphonates.—The dialkyl phosphonate ester † (10 mmol) in dry carbon tetrachloride (10 ml) was stirred magnetically under dry nitrogen in a flask fitted with a polythene septum-sealed side-arm and with external cooling. Iodotrimethylsilane (3 ml, *ca.* 22 mmol) was added dropwise using a glass syringe and steel hypodermic needle to maintain the temperature between 0 and 10 °C. After complete addition, a sample (0.5 ml) was removed for examination by n.m.r. to establish completion of reaction. The reaction solution was evaporated *in vacuo* and the brownish residue treated with water (20 ml). At this stage only benzylphosphonic acid gave a crystalline solid. Other phosphonates were isolated by lyophilisation, dissolution in t-butyl alcohol (50 ml), and treatment with *p*-anisidine (10 mmol) in dry ether. The precipitated crystalline anisidinium salt was collected and recrystallised from ethanol.

Thus, benzylphosphonic acid (1a) was obtained as white needles, m.p. 167—168° (from water) (lit.,[22] 167—169°) by dealkylation of its dimethyl ester (1b)[4b] (Found: C, 48.9; H, 6.25; P, 3.8. Calc. for $C_7H_9O_3P$: C, 49.05; H, 6.45; P, 4.1%), δ (C_5D_5N) 7.61 (d, 2 H, *J* 7 Hz, *o*-ArH), 7.20 (2 H, t, *J* 7 Hz, *m*-ArH), 7.08 (1 H, t, *J* 7 Hz, *p*-ArH), and 3.46 (2 H, d, J_{PH} 21 Hz, $ArCH_2P$). Benzoylphosphonic acid (7a) was isolated as its *p*-anisidinium salt by dealkylation of the corresponding dimethyl ester (2b) as pale yellow plates, m.p. 134° (from ethanol) (Found: C, 54.2; H, 5.1; N, 4.65. $C_{14}H_{16}NO_5P$ requires C, 54.4; H, 5.2; N, 4.55%), δ (C_5D_5N) 8.82 (d, 2 H, *J* 8 Hz, *o*-C_6H_5CO), 7.40 (3 H, m, *m*,*p*-C_6H_5CO), 7.22 and 6.82 (4 H, AB, *J* 8 Hz, $MeOC_6H_4$), and 3.60 (3 H, s, *Me*OAr). *Prop-1-ynylphosphonic acid* (7) was isolated as its *p*-anisidinium salt by dealkylation of diethyl prop-2-ynylphosphonate (3b) [23] at −30 to 0 °C as lustrous tan plates, m.p. 207° (from ethanol) (Found: C, 47.05; H, 5.9; N, 5.75. $C_{16}H_{14}NO_4P\cdot0.5H_2O$ requires C, 47.6; H, 6.0; N, 5.55%), δ (CD_3OD) 7.40 and 7.15 (4 H, AB, *J* 8 Hz, $MeOC_6H_4$), 3.90 (3 H, s, MeO), and 1.95 (3 H, d, J_{PH} 4 Hz, $CH_3C{\equiv}C{-}P$). *2-Bromoethylphosphonic acid* (4a) was isolated as its *p*-anisidinium salt by dealkylation of the diethyl ester (4b) as pale pink prisms, m.p. 165° (from aqueous ethanol) (Found: C, 33.2; H, 4.55; N, 4.5. $C_9H_{15}BrNO_4P\cdot0.5H_2O$ requires C, 33,65; H, 5.05; N, 4.35%), δ (C_5D_5N) 7.02 and

† For methods of preparation see ref. 4*b*.

6.88 (4 H, AB, J 8 Hz, $MeOC_6H_4$), 4.03 (2 H, dt, J_{HH} 7 Hz, J_{PH} 11 Hz, $BrCH_2CH_2P$), 3.61 (3 H, s, *Me*OAr), and 2.72 (2 H, dt, J_{HH} 7, J_{PH} 16 Hz, CH_2CH_2P). *Vinylphosphonic acid* (5a) was isolated as its *p*-anisidinium salt by dealkylation of

$C_6H_5CH_2P(O)(OR^1)(OR^2)$ (1) a, $R^1 = R^2 = H$; b, $R^1 = R^2 = Me$; c, $R^1 = R^2 = Me_3Si$; d, $R^1 = Me$, $R^2 = Me_3Si$

$C_6H_5COP(O)(OR)_2$ (2) a, R = H; b, R = Me; c, $R = Me_3Si$

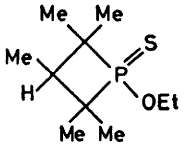
$BrCH_2CH_2P(O)(OR)_2$ (3)
$HC{\equiv}CCH_2P(O)(OEt)_2$ (4)
$H_2C{=}CHP(O)(OR)_2$ (5)
$(EtO_2C)_2CHCH_2P(O)(OR)_2$ (6)
$CH_3C{\equiv}CP(O)(OR)_2$ (7)
a, R = H; b, R = Et; c, $R = Me_3Si$

$C_6H_5OP(O)(OR^1)(OR^2)$ (8) a, $R^1 = R^2 = H$; b, $R^1R^2 =$ $Me_2C(CH_2^-)_2$; c, $R^1 = R^2 = Me_3Si$

p-$ClC_6H_4OP(O)(OR)_2$ (9)
p-$MeOC_6H_4OP(O)(OR)_2$ (10)
p-$EtO_2CC_6H_4OP(O)(OR)_2$ (11)
a, R = H; b, R = Et; c, $R = Me_3Si$

$(C_6H_5O)_2P(O)(OR)$ (12) a, R = H; b, R = Me_2CH; c, $R = Me_3Si$

(13)



the diethyl ester (5b) as mauve prisms, m.p. 250° (from ethanol–ether) (Found: C, 43.3; H, 5.9; N, 5.4. $C_9H_{14}NO_4P{\cdot}H_2O$ requires C, 43.4; H, 6.4; N, 5.35%), δ 6.98 and 6.73 (4 H, AB, J 8 Hz, $MeOC_6H_4$), 6.69 (1 H, ddd, H-1), 6.47 (1 H, ddd, *Z*-H-2), and 5.90 (1 H, ddd, *E*-H-2; $J_{HH_{gem}}$ 2, $J_{HH_{cis}}$ 12, $J_{HH_{trans}}$ 18, $J_{PH_{gem}}$ 20, $J_{PH_{cis}}$ 22, and $J_{PH_{trans}}$ 46 Hz), and 3.57 (3 H, s, MeOAr). 2,2-*Bisethoxycarbonylethylphosphonic acid* (6a) was isolated as its *p*-anisidinium salt by dealkylation of the ethyl ester (6b) as colourless needles, m.p. 127° (from ethanol) (Found: C, 48.05; H, 6.45; N, 4.1. $C_{15}H_{22}NO_8P$ requires C, 47.75; H, 6.35; N, 3.7%), δ (C_5D_5N) 6.92 and 6.58 (4 H, AB, J 8 Hz, $MeOC_6H_4$), 4.32 (1 H, dt, J_{HH} 8, J_{PH} 13 Hz, $CHCH_2P$), 4.19 and 4.18 (4 H, 2q, J 8 Hz, OCH_2Me), 3.62 (s, 3 H, *Me*OAr), 2.85 (2 H, dd, J_{HH} 8, J_{PH} 17 Hz, $CHCH_2P$), and 1.10 (6 H, t, J 8 Hz, OCH_2CH_3).

*General Procedure for the Dealkylation of Dialkyl Aryl Phosphates.**—The same procedure was used as for the phosphonates with solvolysis of the aryl bistrimethylsilyl phosphate using water or methanol. At this stage 4-chlorophenyl phosphate gave a crystalline solid. Other aryl phosphates were dissolved in 95% ethanol (50 ml) and treated with cyclohexylamine (2.2 equiv.). The cyclohexylammonium salt was obtained on lyophilisation and purified by crystallisation. Thus, *phenyl phosphate* (8a) was isolated as its biscyclohexylammonium salt by dealkylation of 5,5-dimethyl-2-phenoxy-2-oxo-1,3,2-dioxaphosphorinan (8b) as colourless prisms, m.p. 190° (from ethanol–water 1 : 1 v/v) (Found: C, 57.8; H, 8.6; N, 7.45. $C_{18}H_{33}N_2O_4P$ requires C, 58.05; H, 8.95; N, 7.5%), δ (D_2O–DCl) 6.64 and 6.46 (5 H, m, C_6H_5O), 2.40br (2 H, m, 2 $CH\overset{+}{N}H_3$), and 1.20—0.55 (20 H, m, 2 $[CH_2]_5$). 4-Chlorophenyl phosphate (9a) was isolated as the dibasic acid by de-esterification of the diethyl ester (9b) as colourless prisms, m.p. 125.5° (from benzene) (lit.,[24] 93°) (Found: C, 33.5; H, 3.25; Cl, 16.9. Calc. for $C_6H_6ClO_4P{\cdot}0.5H_2O$: C, 33.15; H, 3.25; Cl, 16.3%), δ (D_2O) 7.10 and 6.85 (4 H, AB, J 7 Hz, ClC_6H_4O). 4-*Methoxyphenyl phosphate* (10a) was isolated as its biscyclohexylammonium salt by dealkylation of the corresponding diethyl ester (10b) as colourless prisms from 95% ethanol, m.p. 188—189° (Found: C, 56.95; H, 8.5; N, 7.15. $C_{19}H_{35}N_2O_5P$ requires C, 56.65; H, 8.75; N, 6.95%), δ (D_2O–DCl) 7.02 and 6.82 (4 H, AB, J 7 Hz, $MeOC_6H_4O$), 3.80 (3 H, s, MeOAr), 2.40br (m, 2 H, 2 $CH\overset{+}{N}H_3$), and 1.20—0.55 (m, 20 H, 2 $[CH_2]_5$). 4-*Ethoxycarbonylphenyl phosphate* (11a) was isolated as its biscyclohexylammonium salt from the diethyl ester (11b) as colourless prisms, m.p. 163—164° (from 95% ethanol) (Found: C, 56.5; H, 8.4; N, 6.15. $C_{21}H_{37}N_2O_6P$ requires C, 56.55; H, 8.4; N, 6.3%), δ (D_2O–DCl) 7.05 and 6.35 (4 H, AB, J 7 Hz, $-COC_6H_4O$), 3.40 (2 H, q, J 6.5 Hz, OCH_2Me), 2.45br (2 H, m, 2 $CH\overset{+}{N}H_3$), 1.44(3 H, t, J 6.5 Hz, OCH_2CH_3), and 1.20—0.60 (m, 20 H, 2 $[CH_2]_5$). Diphenyl phosphate (12a) was isolated as its cyclohexylammonium salt by dealkylation of the isopropyl ester (12b) as colourless needles, m.p. 195° (from ethanol) (lit.,[25] 199—200°) (Found: C, 61.6; H, 6.75; N, 3.75. Calc. for $C_{18}H_{24}NO_4P$: C, 61.9; H, 6.9; N, 4.0%), δ ([$^2H_6$]DMSO–C_5D_5N) 7.26 (8 H, m, ArH), 7.00 (2 H, t, J Hz, 2 *p*-ArH), 2.82 (1 H, m, $CH\overset{+}{N}H_3$), and 1.95—1.22 (10 H, m, $[CH_2]_5$).

Partial and Complete Silylation of Dimethyl Benzylphosphonate.—(*a*) Iodotrimethylsilane (22 mmol) and dimethyl benzylphosphonate (10 mmol) were allowed to react in dry CCl_4 as described above. Evaporation of volatiles *in vacuo* gave bistrimethylsilyl benzylphosphonate as the sole product (g.l.c.; OV17 column), δ ($CDCl_3$) 7.13 (5 H, s, C_6H_5), 3.00 (2 H, d, J_{PH} 21 Hz, $ArCH_2P$), and 0.18 (18 H, s, 2 Me_3SiO).

(*b*) Iodotrimethylsilane (11 mmol) and dimethyl benzylphosphonate (10 mmol) under the same conditions led to a mixture of three products in the ratio 39 : 26 : 35 (g.l.c.). The first was identified as dimethyl benzylphosphonate and the last as bistrimethylsilyl benzylphosphonate by peak enhancement. The second peak was identified as methyl trimethylsilyl benzylphosphonate, δ ($CDCl_3$) 7.13 (5 H, s, C_6H_5), 3.58 (3 H, d, J_{PH} 11 Hz, MeOP), 3.04 (2 H, d, J_{PH} 21 Hz, $ArCH_2P$), and 0.18 (9 H, s, Me_3SiO).

DISCUSSION

In every case examined, iodotrimethylsilane has been found to effect transesterification of methyl and ethyl esters of phosphonic acids (1b)—(6b) under the mildest of conditions. The reaction appears to proceed to completion in all cases as gauged by n.m.r. analysis of the bistrimethylsilyl phosphonate esters (1c)—(3c) and (5c)—(7c) in the reaction solutions. In turn, solvolysis of these products is quantitative so that the yields of phosphonic acid products (1a)—3a) and (5a)—(7a) are only limited by the efficiency of their purification, variously achieved by transformation into anisidinium, cyclohexylammonium, or lithium salts. In the case of 1-oxoethylphosphonate, its diethyl ester was smoothly transesterified yielding the distillable bistrimethylsilyl ester but attempts to purify an anisidinium salt subsequent to solvolysis were unsuccessful. The acid does, however, form a biscyclohexylammonium salt.[19] In similar fashion, the mixed alkyl aryl phosphate triesters examined [(8b)—(12b)] all experienced transformation

* For methods of preparation see ref. 4*a*.

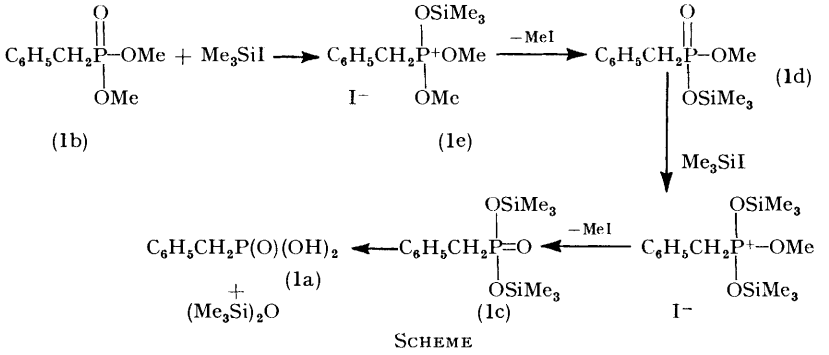
into their trimethylsilyl aryl esters (8c)—(12c) in essentially quantitative yield. While in some cases these esters could be isolated by distillation, they were generally transformed by solvolysis in water or methanol into the parent aryl esters which were purified either directly (9a) or as their cyclohexylammonium salts (8a) and (10a)—(12a).

This selectivity for hydrolysis of alkyl as against aryl phosphate ester functions provides a valuable complement to the variety of methods generally available for the converse process, *i.e.* the selective cleavage of aryl ester functions. It is obviously closely related to the preferential cleavage of alkyl esters in mixed alkyl enol phosphates recently described by Hata using bromotrimethylsilane,[20] though it is interesting to note that this reagent failed in the case of diethyl 1-(4-methoxyphenyl)vinylphosphate. It would clearly be of advantage to investigate dealkylation of this substance using iodotrimethylsilane.

phonate ester functions led to the suggestion that iodotrimethylsilane showed a greater selectivity than bromotrimethylsilane for phosphonate esters,[17] but more detailed investigations in the present work have not supported that opinion.[27]

It appeared possible that the greater reactivity of iodotrimethylsilane might prove advantageous for the low-temperature dealkylation of phosphonates with labile multiple bonds and the case of diethyl prop-2-ynylphosphonate (4b) was selected for investigation. However, transesterification of this material with iodotrimethylsilane at −30 to 0 °C followed by solvolysis in methanol gave only the prop-1-ynylphosphonic acid (7a). Recourse to a lower reaction temperature would require the use of a different solvent system.

It is interesting to note that attempts to dealkylate the small-ring phosphorothionate ester (13) were unsuccessful and inspection (n.m.r.) of the silylation mixture suggested that a complex variety of products was formed



SCHEME

Iodotrimethylsilane is unquestionably superior in use to the combination of chlorotrimethylsilane and sodium iodide as described by Morita,[21] both with respect to the facility of the operations involved and with regard to its greater specificity. McKenna has reported [26] that the chlorotrimethylsilane–sodium iodide treatment of diethyl bromomethylphosphonate leads to a mixture of halogenomethylphosphonates. By contrast, the reaction of iodotrimethylsilane with the 2-bromoethylphosphonate ester (3b) gave only trace amounts of iodinated phosphonate in the crude reaction product and these were readily removed on crystallisation.

The differing characteristics of bromotrimethylsilane and iodotrimethylsilane may be employed with advantage in appropriate circumstances. Both reagents operate without adverse effect on halogenoalkyl, carboxylic ester, ether, olefin, and acetylene functions. The lesser reactivity of bromotrimethylsilane can be used to differentiate between methyl and isopropyl esterolysis [24] whereas at 0 °C iodotrimethylsilane *rapidly* dealkylates primary [*e.g.* (1b)—(4b), secondary (7b),[19] tertiary,[19] and neoalkyl (8b)] alkyl ester linkages to phosphoryl species. This greater reactivity may be decisive in the dealkylation of phosphonate esters resistant by bromotrimethylsilane without resort to elevated temperatures.[14,26] Preliminary work on the selective dealkylation of species having multiple carboxylate and phos-

with some evidence suggestive of ring-opening. It may be pertinent that the work of Chojnowski [18] suggests that there is reduced reactivity for thionophosphoryl systems which may be accentuated in this case by ring-size effects.

The mechanistic course of the transesterification process with silyl halides is clear from their exclusive selectivity for alkyloxy-cleavage and from the formation of mixed alkyl trimethylsilyl phosphonate esters observed here and elsewhere,[17,26,28] and is shown in the Scheme in the case of dimethyl benzylphosphonate (1b).

It is apparent that the overall velocity of the steps leading to the formation of the mixed ester (1d) is comparable to that for its transesterification into the bistrimethylsilyl ester (1c). The fact that enol and phenol esters are resistant to cleavage is wholly consistent with this Scheme. The observation that iodotrimethylsilane shows apparently equally rapid transesterification for primary, secondary, tertiary, and neopentyl functions suggests that the rate-determining step is the formation of (1e) and that its dealkylation by iodide anion to (1d) is rapid. [In the case of (8b), n.m.r. analysis of the silylation mixture indicated that there was some skeletal rearrangement accompanying the opening of the phosphorinan ring.] This situation may well be reversed in the case of bromotrimethylsilane and may also have some relevance to the useful selective and stepwise dealkyl-

ation of alkyl phosphates and phosphonates achieved by the use of phenylthiotrimethylsilane.[26]

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