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Dealkylation Reaction of Acetals, Phosphonate, and Phosphate Esters with Chlorotrimethylsilane/Metal Halide Reagent in Acetonitrile, and Its Application to the Synthesis of Phosphonic Acids and Vinyl Phosphates[1)]

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A mild and efficient method has been developed for carbon-oxygen bond cleavage using chlorotrimethylsilane/sodium iodide in acetonitrile. It was applied to synthetic transformation under nonaqueous and neutral conditions, such as acetal deprotection and the synthesis of phosphonic acids from the corresponding dialkyl phosphonates *via* methanolysis of their silyl esters. Effectiveness of various kinds of metal or ammonium iodides for this type of dealkylation was examined in the acetonitrile solution by ^{1}H NMR. Satisfactory results were also obtained with lithium or potassium iodide in place of sodium iodide. However, copper(I) or quarternary ammonium iodide was ineffective. Chlorotrimethylsilane/lithium bromide in acetonitrile is effective for selective dealkylation of multifunctional phosphonic esters or dialkyl vinyl phosphates.

Organosilicon compounds have been extensively developed and applied to organic synthesis as reagents, reactive intermediates, and protective groups.[2)] Attention was drawn to a new and efficient method for carbon-oxygen bond cleavage using organosilicon compounds under nonaqueous and neutral conditions, bromotrimethylsilane and iodotrimethylsilane in particular being versatile reagents for synthetic transformation of many functional groups. The chemistry of iodotrimethylsilane has been developed by Olah *et al.*[3)] and Jung *et al.*[4)] with regard to the reactions of carboxylic esters, ethers, acetals, alcohols, carbamates, and sulfoxides. Mckenna *et al.* and Rudinskas *et al.* reported the usefulness of bromotrimethylsilane for the conversion of dialkyl phosphonates into the silyl esters,[5)] sulfoxides into sulfides,[3b)] alcohols into bromides and orthoesters into the corresponding esters.[6)] However, bromotrimethylsilane is of little use for the cleavage of carboxylic esters, ethers, and acetals.

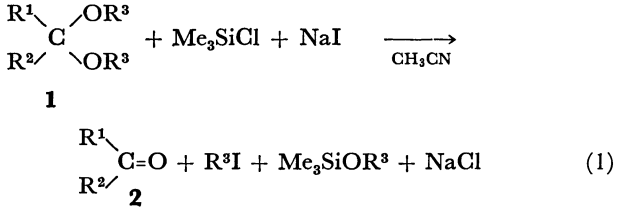
The preparation of bromotrimethylsilane[7)] or iodotrimethylsilane[8)] requires two steps *via* hexamethyldisiloxane from chlorotrimethylsilane, these fuming compounds being easily hydrolyzed in the atmospheric moisture. To overcome the disadvantages inherent in the use of iodotrimethylsilane, two improve methods have been worked out for the preparation of the reagent *in situ* using phenyltrimethylsilane/iodine[9)] or allyltrimethylsilane/iodine[10)] in the presence of carboxylic esters or ethers. The high reactivity of these reagents can be rationalized by the hard and soft acids and base principle,[11)] since they contain both hard acid and soft bases in their molecules. Chlorotrimethylsilane itself is essentially ineffective,[12)] although it is the most easily available reagent and frequently employed as a starting material for many reactive organosilicon compounds in organic synthesis.

In the course of studies on synthesis and biological properties of various phosphonic acids, we have sought a new and mild method for carbon-oxygen bond cleavage in the phosphonic esters with use of the most inexpensive chlorotrimethylsilane itself. In a preliminary communication, we demonstrated that chlorotrimethylsilane/sodium iodide in acetonitrile is an extremely effective reagent for dealkylation of esters, ethers *etc.*[13,14)] Olah *et al.* independently reported a similar use of the reagent in the same reactions.[15)]

In order to avoid an overlap of results, this paper describes the scope and limitation of dealkylation of dialkyl phosphonates and acetals with chlorotrimethylsilane/sodium iodide and the effectiveness of various iodides for this type of reaction. A novel reaction of chlorotrimethylsilane/lithium bromide as a selective dealkylating agent of phsophonic esters having other labile functional groups, and dialkyl vinyl phosphates is also described.

Results and Discussion

Dealkylation of Acetal with Chlorotrimethylsilane/Sodium Iodide. Dealkylation of acetals (**1**) with chlorotrimethylsilane/sodium iodide in acetonitrile was performed under mild and nonaqueous conditions. In most cases, the reaction was virtually complete at 45 °C within 0.5—2.5 h, affording the parent carbonyl compounds (**2**) in one step quantitatively (Eq. 1). The results are summarized in Table 1.



$$\underset{\mathbf{1}}{R^1R^2C(OR^3)_2} + Me_3SiCl + NaI \xrightarrow[CH_3CN]{} \underset{\mathbf{2}}{R^1R^2C{=}O} + R^3I + Me_3SiOR^3 + NaCl \qquad (1)$$

The present method is applicable to both dimethyl and diethyl acetals. However, the case of the ethylene acetal (**1c**) results in relatively poor yield, a similar result being reported on ethylene acetal cleavage with iodotrimethylsilane by Jung *et al.*[4c)] It was found that the acetal cleavage is significantly influenced by the ratio of the reagent to the substrate used. For example, treatment of benzaldehyde dimethyl acetal (**1a**) with 1.5 equiv. of chlorotrimethylsilane/sodium iodide gave a mixture of the acetal (**1a**) and benzaldehyde (**2a**) (14:86) at 45 °C for 0.5 h, in spite of the complete disappearance of the chlorotrimethylsilane signal. The complete conversion of **1a** into **2a** could be achieved by using 2.0 equiv. of the reagent at 45 °C for 0.5 h, the formation ratio of methyl iodide:

Table 1. Acetal dealkylation with chlorotrimethylsilane/sodium iodide

Compound	R^1	R^2	R^3	Temp °C	Time h	Yield[a] of **2** %
1a	Ph	H	Me	45	0.5	88
1b	Ph	H	Et	45	1.5	85
1c	Ph	H	$-CH_2-$	45	2.5	30
1d	$Me(CH_2)_5$	H	Me	45	0.5	91
1e	*p*-$MeOC_6H_4$	H	Me	45	2.5	95
1f	$-(CH_2)_5-$		Me	45	0.5	84
1g	Ph	Me	Me	45	0.5	82

a) Isolated yield. The products were characterized by comparison with authentic samples.

methyl trimethylsilyl ether being 6:1. The results indicate that further dealkylation of the initially formed methyl trimethylsilyl ether occurs competitively.

$$Me_3SiOMe + Me_3SiCl + NaI \xrightarrow[CH_3CN]{} MeI + (Me_3Si)_2O + NaCl \quad (2)$$

A report was given on the useful application of chlorotrimethylsilane/sodium iodide to the conversion of alcohols into iodides *via* their trimethylsilyl ethers.[16]

Effect of Other Iodide. In order to elucidate the effectiveness of various iodides for the dealkylating method using chlorotrimethylsilane, the effect of the salts on the yield was examined, **1a** being selected as a typical substrate and acetonitrile as solvent. The results are summarized in Table 2.

$$\underset{\textbf{1a}}{PhCH(OMe)_2} + Me_3SiCl + MI \xrightarrow[CH_3CN]{} \underset{\textbf{2a}}{PhCHO} + MeI + Me_3SiOMe + MCl \quad (3)$$

We see that the reaction yield is greatly influenced by the kind of salt used, lithium, sodium, and potassium iodide being very effective and giving an excellent yield of **2a** at 45 °C for 0.5 h. However, other salts such as copper(I) or quarternary ammonium iodides are unsatisfactory, the yields of **2a** being invariably lower than 40%, even for the prolonged reaction. This can be explained by the difference in solubility of the chloride (MCl) produced as a by-product in acetonitrile. With the progress of reaction, lithium, sodium, and potassium chloride immediately precipitate, but the ammonium chlorides are highly soluble in the solvent. For the sake of confirmation, we carried out a control experiment in which acetonitrile-soluble phenyltrimethylammonium chloride was added to the acetonitrile solution of chlorotrimethylsilane/phenyltrimethylammonium iodide (entry 9, Table 2). The chloride added prevented the formation of **2a**.[17] The effect of various solvents (carbon tetrachloride, chloroform, or *N*,*N*-dimethylformamide) on acetal dealkylation using chlorotrimethylsilane/sodium iodide was also examined. Acetonitrile was found to be the most suitable, the reaction in other solvents being slightly slower than that in acetonitrile.

Table 2. Acetal dealkylation with chlorotrimethylsilane in the presence of various iodide salts

Entry	MI	Temp °C	Time h	Yield[a] of **2a** %
1	LiI	45	0.5	100
2	NaI	45	0.5	100
3	KI	45	0.5	100
4	CuI	45	3.0	25
5	Me_4NI	45	3.0	11
6	Bu_4NI	45	3.0	36
7	$PhNMe_3I$	45	3.0	33
8	$PhNMe_3I$	45	5.0	38
9	$PhNMe_3I$[b]	45	3.0	6

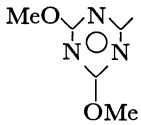
a) Determined by ^1H NMR. b) Control experiment: **1a** (7 mmol), Me_3SiCl (14 mmol), $PhNMe_3I$ (14 mmol), and $PhNMe_3Cl$ (7 mmol) in CH_3CN (5 ml).

Dealkylation of Phosphonic Esters with Chlorotrimethylsilane/Sodium or Potassium Iodide. Phosphonic acids were prepared from the corresponding dialkyl esters by acid-catalyzed hydrolytic dealkylation, by refluxing them with 6 mol dm^{-3} hydrochloric acid for several hours. Many multifunctional phosphonic esters are frequently subjected to undesirable reactions under these acidic conditions.[18]

The exothermic reaction of dimethyl phosphonates (**3**) with chlorotrimethylsilane/sodium iodide occurred rapidly at room temperature to give the corresponding bis(trimethylsilyl) phosphonates (**4**) and methyl iodide quantitatively.[19] The dealkylation monitored by ^1H NMR spectroscopy proceeded to completion within 15 min. The rate of dealkylation of dialkyl phosphonates with the reagent decreases according to the bulkiness of the alkyl group in the order: R^2=Me> Et>*i*-Pr.[20] Treatment of the silyl esters (**4**) with methanol at room temperature gave the corresponding

$$\underset{\textbf{3}}{R^1P(OR^2)_2} + 2\,Me_3SiCl + 2\,NaI \xrightarrow[CH_3CN]{} \underset{\textbf{4}}{R^1P(OSiMe_3)_2} + 2\,R^2I + 2\,NaCl \xrightarrow{MeOH} \underset{\textbf{5}}{R^1P(OH)_2} \quad (4)$$

Table 3. Phosphonic ester dealkylation with chlorotrimethylsilane/sodium or potassium iodide

Compound	R^1	R^2	Iodide salt	Dealkylation conditions		Yield[a] of salt of **5**
				Temp °C	Time min	%
3a	$PhCH_2$	Me	NaI	25	15	92[b]
3b	$PhCH_2$	Et	NaI	25—35	30	81[b]
3c	$PhCH_2$	*i*-Pr	NaI	25—35	60	78[b]
3d	CCl_3	Me	NaI	25	15	87
3e	$NCCH_2$	Et	NaI	25—35	30	85
3f	MeCO	Et	NaI	25—35	30	83[c]
3g	$MeOCOCH_2$	Et	NaI	25—35	30	74
3h	$EtOCOCH_2$	Et	KI	25—35	30	85
3i	*t*-$BuOCOCH_2$	Me	NaI	25	15	77
3j	$PhCH_2OCOCH_2$	Et	NaI	25—35	30	84
3k	EtOCO	Et	KI	25—35	30	85
3l	Et_2NCO	Et	NaI	25—35	30	88
3m		Me	NaI	25	15	91
3n	MeCOOCHPh	Me	NaI	25	15	90
3o	$PhCOCH_2$	Me	KI	25	15	89
3p	$MeOCH_2$	Et	KI	25—35	30	76
3q	$(MeO)_2CHCH_2$	Et	KI	25—35	30	82
3r	$(MeO)_2CH$	Me	NaI	25	15	93

a) Isolated yield. The phosphonic acids were isolated as anilinium salts unless otherwise indicated. b) Free acid. c) Cyclohexylammonium salt.

phosphonic acids (**5**), which were readily isolated as anilinium or cyclohexylammonium salts. Use of potassium iodide in place of sodium iodide was also effective for the phosphonic ester dealkylation under the same conditions. The reaction conditions and results are given in Table 3.

The new and mild route for dealkylation of phosphonic ester using chlorotrimethylsilane/sodium or potassium iodide caused pronounced improvement in the original Rabinowitz method.[12] Phosphonic acid (**5m**) having triazine ring was prepared for the first time in high yield.[21] An acid-catalyzed hydrolytic cleavage of the dimethyl ester (**3m**) was unsuccessful because of the lability of the ring.

We have demonstrated the most facile cleavage of *t*-butyl and benzyl acetate in various alkyl acetates using chlorotrimethylsilane/sodium iodide at 45 °C for 0.5 h.[13b] In order to clarify the functional group selectivity, we examined a competitive dealkylation of phosphonic esters (**3i**, **3j**) having other labile functional groups using twice the molar quantity of chlorotrimethylsilane/sodium iodide. The formation of **4i** and **4j** in high yield (>95%) was confirmed by means of

$$\underset{\textbf{3i}}{t\text{-}BuOCCH_2P(OMe)_2} + 2\,Me_3SiCl + 2\,NaI \xrightarrow[CH_3CN]{} \underset{\textbf{4i}}{t\text{-}BuOCCH_2P(OSiMe_3)_2} + 2\,MeI + 2\,NaCl \quad (5)$$

$$\underset{\textbf{3j}}{PhCH_2OCCH_2P(OEt)_2} + 2\,Me_3SiCl + 2\,NaI \xrightarrow[CH_3CN]{} \underset{\textbf{4j}}{PhCH_2OCCH_2P(OSiMe_3)_2} + 2\,EtI + 2\,NaCl \quad (6)$$

the ^1H NMR spectra of the reaction mixture. The results indicate that the only dealkylation of the dialkoxyphosphinyl group proceeds with complete selectivity owing to the difference of reactivity between carboxylic and phosphonic esters.

Dealkylation of Phosphonic Ester with Chlorotrimethylsilane/Lithium Bromide. High selectivity of bromotrimethylsilane is observed for the dealkylation of phosphonic esters having other functional groups.[22] Gross *et al.*[23] and Mckenna and Schmidhauser[24] reported similar results with regard to multifunctional phosphonic ester cleavage. Since a certain metal bromide might also promote a Rabinowitz type reaction, we studied the combination of chlorotrimethylsilane and bromide salts.

When dialkyl phosphonate (**3**) was treated with chlorotrimethylsilane/lithium bromide in acetontrile, dealkylation immediately took place to afford the corresponding bis(trimethylsilyl) phosphonate (**4**) and alkyl bromide, accompanied by the precipitation of lithium chloride.

The reaction monitored by ^1H NMR spectroscopy was almost complete at 45—75 °C within 2—5 h.

$$\underset{\mathbf{3}}{R^1P(OR^2)_2} + 2\,Me_3SiCl + 2\,LiBr \xrightarrow[CH_3CN]{} \underset{\mathbf{4}}{R^1P(OSiMe_3)_2} + 2\,R^2Br + 2\,LiCl \quad (7)$$

The results for several phosphonates are given in Table 4.

Other salts such as KBr, $MgBr_2$, NEt_4Br, and $PhNMe_3Br$ are ineffective. The rate of dealkylation by the present method is slightly smaller than that with bromotrimethylsilane. The dealkylation of phosphonic ester moiety with chlorotrimethylsilane/lithium bromide proceeds with higher functional group selectivity than that with chlorotrimethylsilane/sodium iodide, indicating no cleavage of other functional groups even when a large excess of the reagent is used. Benzyl acetate hardly reacted at all with this reagent at 75 °C for 9 h.

Dealkylation of Dialkyl Vinyl Phosphate with Chlorotrimethylsilane/Lithium Bromide. From our studies on dealkylation of phosphonic and phosphoric ester using bromotrimethylsilane, we find that no C=COP bond cleavage occurs in dialkyl vinyl or dialkyl phenyl phosphates.[25] The C=COP bond cleavage in the hydrolysis of dialkyl vinyl phosphate under acidic or basic conditions occurs predominantly to yield dialkyl phosphate and carbonyl compounds.[26] Hata *et al.* as well as our group have prepared many kinds of unesterified enolphosphates of biologically interest from the corresponding dialkyl esters by means of bromotrimethylsilane.[27] In order to extend our methodology, the reaction of dialkyl vinyl phosphates with chlorotrimethylsilane/lithium bromide in acetonitrile solution was undertaken.

When dialkyl vinyl phosphates (**6**) reacted with chlorotrimethylsilane/lithium bromide in acetontrile, the corresponding bis(trimethylsilyl) vinyl phosphates (**7**) were obtained in high yields.

$$\underset{\mathbf{6}}{R^1OP(OR^2)_2} + 2\,Me_3SiCl + 2\,LiBr \xrightarrow[CH_3CN]{} \underset{\mathbf{7}}{R^1OP(OSiMe_3)_2} + 2\,R^2Br + 2\,LiCl \quad (8)$$

The silyl esters (**7**), treated with methanol at room temperature, were immediately converted into the corresponding phosphates (**8**) which were isolated as anilinium salts. The results are given in Table 5.

$$\mathbf{7} \xrightarrow{MeOH} \underset{\mathbf{8}}{R^1OP(OH)_2} \quad (9)$$

Alcoholysis of the silyl ester (**7a**) was unsuccessful. No desirable anilinium salt of **8a** could be isolated, resulting in the C=COP bond cleavage.

We have developed a mild and versatile method for carbon-oxygen bond cleavage using easily accessible and inexpensive chlorotrimethylsilane/metal halides, and have demonstrated the applicability of this method to synthetic transformation.

Experimental

Boiling points are uncorrected. Melting points were determined on a Yanagimoto micromelting apparatus and are uncorrected. ^1H NMR spectra were obtained with a JNM FX 100 using TMS or DSS as an internal standard, and IR spectra with a Shimadzu IR-400. GLC analyses were performed on a Shimadzu GC-3AF using stainless steel

Table 4. Phosphonic ester dealkylation with chlorotrimethylsilane/lithium bromide

Compound	R^1	R^2	Temp °C	Time h	Yield[a] of **4** %
3a	$PhCH_2$	Me	45—55	1.5	89
3b	$PhCH_2$	Et	70—75	3.0	90
3g	$MeOCOCH_2$	Et	70—75	4.5	87
3i	*t*-$BuOCOCH_2$	Me	45—50	1.5	83
3j	$PhCH_2OCOCH_2$	Et	70—75	4.5	85
3p	$MeOCH_2$	Et	70—75	4.0	88
3r	$(MeO)_2CH$	Me	45—50	1.5	92

a) Isolated yield.

Table 5. Phosphoric ester dealkylation with chlorotrimethylsilane/lithium bromide

Compound	R^1	R^2	Dealkylation conditions: Temp °C	Dealkylation conditions: Time h	Yield[a] of **7** %	Yield[a] of salt of **8** %
6a	$H_2C{=}CMe$	Et	70—75	3.0	84	—
6b	$Me_2C{=}CPh$	Et	70—75	3.5	81	93
6c	$Cl_2C{=}CH$	Me	45—50	1.5	86	95

a) Isolated yield.

columns packed with 25% Silicone DC 550 on Shimalite.

Materials. Commercial chlorotrimethylsilane was dried over CaH_2 and distilled. Acetonitrile and other solvents were dried and distilled by the usual method. Commercial anhydrous inorganic halides were stored in a desiccator. Hygroscopic lithium bromide was dried *in vacuo* at 100 °C just use. All substrates (phosphonic esters, acetals, and phosphoric esters) were prepared by the usual method. All the dialkyl phosphonates (**3a**—**3q**, except **3n** and **3r**) were prepared by the Arbuzov reaction of the corresponding halides with trialkyl phosphite.[18] The phosphonate (**3m**) was prepared from 2-chloro-4,6-dimethoxy-1,3,5-triazine[28] and trimethyl phosphite: yield 80%; viscous oily product; NMR (CCl_4): δ 3.93 (6H, d, J=10.6 Hz, CH_3OP), 4.02 (6H, s, CH_3O); Found: P, 12.31%. Calcd for $C_7H_{12}N_3O_5P$: P, 12.43%. The phosphonate (**3n**) was prepared by the reaction of benzaldehyde with dimethyl phosphonate, followed by acetylation with acetyl chloride in the presence of triethylamine.[18] The phosphonate (**3r**) was prepared from PCl_3 and trimethyl orthoformate.[29] All the phosphates (**6a**—**6c**) were prepared by the Perkow reaction of the corresponding α-halogenocarbonyl compounds with trialkyl phosphite.[26]

General Procedure for Dealkylation of Acetal with Chlorotrimethylsilane/Sodium Iodide. A mixture of acetal (30 mmol), chlorotrimethylsilane (60 mmol), and anhydrous sodium iodide (60 mmol) in dry acetonitrile (15 ml) was heated at 45 °C with stirring, the reaction being monitored by ^1H NMR. When the reaction was completed, the mixture was poured into 5% aqueous solution of $NaHCO_3$ (50 ml), followed by deiodinization with sodium thiosulfate. The resulting organic layer was extracted with ether (50 ml×3), the combined extract being dried over Na_2SO_4. After the removal of low-boiling materials on an evaporator (below 50 °C), the residue was distilled *in vacuo* to afford the pure product.

Effect of Iodide Salts on Dealkylation of Acetal. ^1H NMR analysis was carried out according to the same procedure as that described above. A mixture of benzaldehyde dimethyl acetal (7 mmol), chlorotrimethylsilane (14 mmol), and anhydrous iodide salt (14 mmol) was stirred at 45 °C in dry acetonitrile (5 ml). Conversion of the dimethyl acetal into benzaldehyde was determined by measurement of ^1H NMR spectra of the reaction mixture.

General Procedure for Dealkylation of Dialkyl Phosphonate with Chlorotrimethylsilane/Sodium or Potassium Iodide. Chlorotrimethylsilane (60 mmol) was added dropwise to a mixture of phosphonate (30 mmol) and anhydrous sodium or potassium iodide (60 mmol) in dry acetonitrile (30 ml). The mixture was stirred at 25—35 °C for 15—30 min, the progress of reaction being monitored by ^1H NMR spectroscopy. After complete disappearance of the chlorotrimethylsilane signal, the resulting sodium or potassium chloride was filtered off rapidly and washed with dry ether (20 ml×2). On removing low-boiling materials from the filtrate with an evaporator (below 50 °C), the corresponding silyl esters were obtained as oily residue. The residue was dissolved in methanol (30 ml) containing aniline or cyclohexylamine (60 mmol) and the mixture was concentrated to dryness under reduced pressure to give a white solid, amine salt of phosphonic acid. The crude salts were purified by recrystallization. Some known products were identified by comparison with authenitic samples prepared from dialkyl phosphonates and bromotrimethylsilane.[22] The structures of new compounds were identified by ^1H NMR spectra and elemental analysis.

*Anilinium (Ethoxycarbonylmethyl)phosphonate (Salt of **5h**).* The salt was recrystallized from acetone: yield 85%; mp 134—136 °C; NMR (D_2O): δ 1.27 (3H, t, CH_3C), 4.14 (2H, q, CH_2O), 2.84 (2H, d, J=20.9 Hz, CH_2P), 7.4—7.6 (5H, m, C_6H_5N); Found: C, 46.05; H, 6.29; N, 5.44; P, 11.72%. Calcd for $C_{10}H_{16}NO_5P$: C, 45.98; H, 6.17; N, 5.36; P, 11.86%.

*Anilinium (t-Butoxycarbonylmethyl)phosphonate (Salt of **5i**).* The salt was recrystallized from acetone: yield 77%; mp 115—117 °C; NMR (D_2O): δ 1.46 (9H, s, C_4H_9OCO), 2.74 (2H, d, J=20.8 Hz, CH_2P), 7.4—7.6 (5H, m, C_6H_5N); Found: C, 49.56; H, 6.65; N, 4.95; P, 11.77%. Calcd for $C_{12}H_{20}NO_5P$: C, 49.83 H, 6.97; N, 4.84; P, 10.71%.

*Anilinium (Benzyloxycarbonylmethyl)phosphonate (Salt of **5j**).* The salt was recrystallized from acetone: yield 84%; mp 123—125 °C; NMR (D_2O): δ 2.89 (2H, d, J=20.8 Hz, CH_2P), 5.18 (2H, s, $PhCH_2O$), 7.3—7.6 (10H, m, C_6H_5C, C_6H_5N); Found: C, 55.87; H, 5.50; N, 4.46; P, 8.89%. Calcd for $C_{15}H_{18}NO_5P$: C, 55.73; H, 5.61; N, 4.33; P, 9.58%.

*Anilinium (Ethoxycarbonyl)phosphonate (Salt of **5k**).* The salt was recrystallized from ethanol: yield 85%; mp 143—145 °C; NMR (D_2O): δ 1.28 (3H, t, CH_3C), 4.19 (2H, q, CH_2O), 7.3—7.6 (5H, m, C_6H_5N); Found: C, 44.23; H, 5.89, N, 5.73; P, 12.70%. Calcd for $C_9H_{14}NO_5P$: C, 43.73; H, 5.71; N, 5.67; P, 12.53%.

*Anilinium (Diethylcarbamoyl)phosphonate (Salt of **5l**).* The salt was recrystallized from acetone–ethanol (5/1): yield 88%; mp 142—144 °C; NMR (D_2O): δ 1.10 (3H, t, CH_3C), 1.19 (3H, t, CH_3C), 3.31 (2H, q, CH_2N), 3.69 (2H, q, CH_2N), 7.4—7.7 (5H, m, C_6H_5N); Found: C, 48.32; H, 7.44; N, 10.05; P, 10.95%. Calcd for $C_{11}H_{19}N_2O_4P$: C, 48.18; H, 6.99; N, 10.21; P, 11.29%.

*Anilinium (4,6-Dimethoxy-1,3,5-triazine-2-yl)phosphonate (Salt of **5m**).* The salt was recrystallized from ethanol: yield 91%; dec. 153—155 °C; NMR (D_2O): δ 4.02 (6H, s, CH_3O), 7.3—7.6 (5H, m, C_6H_5N); Found: C, 42.24; H, 4.82; N, 17.82; P, 9.63%. Calcd for $C_{11}H_{15}N_4O_5P$: C, 42.02; H, 4.81; N, 17.83; P, 9.86%.

*Anilinium (α-Acetoxybenzyl)phosphonate (Salt of **5n**).* The salt was recrystallized from methanol: yield 90%; mp 159—161 °C; NMR (D_2O): δ 2.81 (3H, s, CH_3C), 5.82 (1H, d, J=13.0 Hz, CHP), 7.3—7.6 (10H, m, C_6H_5C, C_6H_5N); Found: C, 55.79; H, 5.71; N, 4.24; P, 8.93%. Calcd for $C_{15}H_{18}NO_5P$: C, 55.73; H, 5.61; N, 4.33; P, 9.58%.

*Anilinium (Benzoylmethyl)phosphonate (Salt of **5o**).* The salt was recrystallized from acetone–methanol (10/1): yield 89%; mp 103—104 °C; NMR (D_2O): δ 3.57 (2H, d, J=21.3 Hz, CH_2P), 7.3—8.1 (10H, m, C_6H_5C, C_6H_5N); Found: C, 57.31; H, 5.51; N, 4.81; P, 10.49%. Calcd for $C_{14}H_{16}NO_4P$: C, 57.34; H, 5.50; N, 4.78; P, 10.56%.

*Anilinium (Methoxymethyl)phosphonate (Salt of **5p**).* The salt was recrystallized from acetone: yield 76%; mp 114—116 °C; NMR (D_2O): δ 3.43 (3H, s, CH_3O), 3.59 (2H, d, J=8.5 Hz, CH_2P), 7.3—7.6 (5H, m, C_6H_5N); Found: C, 43.56; H, 6.33; N, 6.37; P, 14.23%. Calcd for $C_8H_{14}NO_4P$: C, 43.84; H, 6.44; N, 6.39; P, 14.13%.

*Anilinium (2,2-Dimethoxyethyl)phosphonate (Salt of **5q**).* The salt was recrystallized from acetone–methanol (10/1): yield 82%; mp 86—88 °C; NMR (D_2O): δ 2.03 (2H, dd, J=18.1 Hz, CH_2P, J=5.9 Hz, $CHCH_2$), 3.36 (6H, s, CH_3O), 7.3—7.6 (5H, m, C_6H_5N); Found: C, 45.28; H, 6.32; N, 5.65; P, 11.52%. Calcd for $C_{10}H_{18}NO_5P$: C, 45.63; H, 6.89; N, 5.32; P, 11.77%.

General Procedure for Dealkylation of Dialkyl Phosphonate with Chlorotrimethylsilane/Lithium Bromide. A mixture of phosphonate (20 mmol), chlorotrimethylsilane (44 mmol for R^2=Me, 56 mmol for R^2=Et) and anhydrous lithium bromide (44 mmol for R^2=Me, 56 mmol for R^2=Et) in dry

acetontrile (15 ml) was vigorously stirred at 45—75 °C for several hours, the reaction being monitored by ^{1}H NMR. When the reaction was completed, the reaction mixture was cooled to room temperature and resulting lithium chloride and the excess of lithium bromide were filtered off. After the removal of low-boiling materials on an evaporator, the residue was distilled under reduced pressure to give the pure trimethylsilyl ester. The products were identified by comparison with authentic samples prepared by use of bromotrimethylsilane.[22]

*Bis(trimethylsilyl) Benzylphosphonate (**4a**).* Yield 89%; bp 95—97 °C/0.1 mmHg† (lit,[23] 88—90 °C/0.04 mmHg); IR (neat): 1245 cm^{-1} (P=O); NMR (CCl_4): δ 3.00 (2H, d, J=22.2 Hz, CH_2P), 7.22 (5H, m, C_6H_5C), 0.15 (18H, s, $OSiMe_3$).

*Bis(trimethylsilyl) (t-Butoxycarbonylmethyl)phosphonate (**4i**).* Yield 83%; bp 82—84 °C/0.01 mmHg; IR (neat): 1725 (C=O) and 1250 cm^{-1} (P=O); NMR (CCl_4): δ 1.46 (9H, s, C_4H_9O), 2.72 (2H, d, J=22.5 Hz, CH_2P), 0.28 (18H, s, $OSiMe_3$); Found: P, 9.31%. Calcd for $C_{12}H_{29}O_5PSi_2$: P, 9.10%.

*Bis(trimethylsilyl) (Benzyloxycarbonylmethyl)phosphonate (**4j**).* Yield 85%; bp 123—125 °C/0.002 mmHg; IR (neat): 1730 (C=O) and 1260 cm^{-1} (P=O); NMR (CCl_4): δ 2.87 (2H, d, J=22.5 Hz, CH_2P), 5.11 (2H, s, $PhCH_2O$), 7.31 (5H, m, C_6H_5C), 0.26 (18H, s, $OSiMe_3$); Found: P, 7.69%. Calcd for $C_{15}H_{27}O_5PSi_2$: P, 8.27%.

*Bis(trimethylsilyl) (Methoxymethyl)phosphonate (**4p**).* Yield 88%; bp 123—124 °C/8 mmHg (lit,[23] 73—75 °C/0.02 mmHg); IR (neat): 1250 cm^{-1} (P=O); NMR (CCl_4): δ 3.55 (2H, d, J=8.5 Hz, CH_2P), 3.43 (3H, s, CH_3O), 0.29 (18H, s, $OSiMe_3$).

General Procedure for Dealkylation of Dialkyl Vinyl Phosphate with Chlorotrimethylsilane/Lithium Bromide. Dealkylation of the phosphoric esters (20 mmol) was carried out by the same procedure as that in the case of dialkyl phosphonate. The silyl ester was isolated by distillation *in vacuo*. When the silyl ester (10 mmol) was added to a methanol solution (30 ml) of aniline (20 mmol) and the solution was concentrated to dryness on an evaporator (below 50 °C), anilinium salt was obtained as a white crystalline solid. After recrystallization the structures of the products were characterized by ^{1}H NMR, IR spectra, and elemental analysis.

*Bis(trimethylsilyl) 1-Methylethenyl Phosphate (**7a**).* Yield 84%; bp 90—92 °C/8 mmHg (lit,[27] 75—77 °C/1.25 mmHg).

*Bis(trimethylsilyl) 2-Methyl-1-phenyl-1-propenyl Phosphate (**7b**).* Yield 81%; bp 110—111 °C/0.01 mmHg; IR (neat): 1680 (C=C) and 1245 cm^{-1} (P=O); NMR (CCl_4): δ 1.70 (3H, d, J=3.0 Hz, CH_3C=COP), 1.88 (3H, d, J=2.4 Hz, CH_3C=COP), 7.2—7.4 (5H, m, C_6H_5C), 0.11 (18H, s, $OSiMe_3$); Found: P, 8.56%. Calcd for $C_{16}H_{29}O_4PSi_2$: P, 8.31%.

*Bis(trimethylsilyl) 2,2-Dichloroethenyl Phosphate (**7c**).* Yield 86%; bp 79—81 °C/1 mmHg; IR (neat): 1630 (C=C) and 1245 cm^{-1} (P=O); NMR (CCl_4): δ 6.84 (1H, d, J=5.9 Hz, C=CHOP), 0.30 (18H, s, $OSiMe_3$); Found: P, 9.41. Calcd for $C_8H_{19}O_4PSi_2Cl_2$: P, 9.18%.

*Anilinium 2-Methyl-1-phenyl-1-propenyl Phosphate (Salt of **8b**).* The salt was recrystallized from acetone: yield 93%; mp 142—143 °C; NMR (D_2O): δ 1.71 (3H, d, J=3.1 Hz, CH_3C=COP), 1.75 (3H, d, J=2.2 Hz, CH_3C=COP), 7.3—7.6 (10H, m, C_6H_5C, C_6H_5N); Found: C, 60.16; H, 6.75; N, 4.83; P, 9.85%. Calcd for $C_{16}H_{20}NO_4P$: C, 59.81; H, 6.27; N, 4.83; P, 9.64%.

*Dianilinium 2,2-Dichloroethenyl Phosphate (Salt of **8c**).* The salt was recrystallized from water: yield 95%; dec. 143—147 °C; NMR (CD_3OD): δ 6.9—7.4 (11H, m, C=CHOP, C_6H_5N); Found: C, 44.22; H, 4.58 N, 7.24 P, 8.02; Cl, 18.80%. Calcd for $C_{14}H_{17}N_2O_4PCl_2$: C, 44.34; H, 4.52; N, 7.39; P, 8.17; Cl, 18.70%.

† 1 mmHg=133.3 Pa.

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$$ROH \longrightarrow ROSiMe_3 \xrightarrow[CH_3CN]{Me_3SiCl/NaI} RI$$

17) There is probably an equilibrium shifting toward the left

$$Me_3SiCl + I^- \rightleftarrows Me_3SiI + Cl^-$$

The reaction proceeds *via* the formation of a small amount of iodotrimethylsilane (in equilibrium). This seems to be an acceptable explanation. An alternative mechanism was proposed for phosphonic ester dealkylation.[13a] Olah *et al.* pointed out that the active compound formed from chlorotrimethylsilane/sodium iodide in acetonitrile is silylnitrilium iodide, $[CH_3C{\equiv}N^+\text{-}SiMe_3]\ I^-$.[15a] We believe that the mechanism involves the initial formation of Me_3SiI from Me_3SiCl and NaI, subsequent rapid silylation of CH_3CN by the Me_3SiI, and the dealkylation of organic substrate by silylnitrilium iodide.

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