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Fluoride Ion-Induced Horner–Emmons Reaction of α-Silylalkylphosphonic Derivatives with Carbonyl Compounds

Takayuki Kawashima,* Takafumi Ishii, and Naoki Inamoto*
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113
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Dimethyl α-trimethylsilylbenzylphosphonate was allowed to react with carbonyl compounds in the presence of fluoride ion to give the corresponding olefins in fairly good yields. Use of CsF in tetrahydrofuran gave the best result. On the other hand, dimethyl trimethylsilylmethylphosphonate was allowed to react similarly with benzophenone to afford 1,1-diphenylethylene, dimethyl methylphosphonate, and dimethyl 2,2-diphenylethenylphosphonate. A similar result was obtained by using *O,O*-diethyl trimethylsilylmethylphosphonothioate. But, reaction of trimethylsilylmethylphosphonic bis(diethylamide) afforded only the protodesilylation product.

Since Si–F bond energy is high,[1] fluoride-induced desilylation has been utilized as a powerful tool for the generation of stabilized carbanions under neutral and relatively mild conditions.[2] The first application to the Wittig reaction was demonstrated by Vedejs and Martinez during the investigation on the generation and reaction of a carbanion stabilized by positively charged nitrogen, sulfur, or phosphorus.[3] Recently, this desilylation of α-silylalkylphosphonium salts has been studied in detail and shown to be a useful method for trisubstituted olefins by Bestmann and Bomhard.[4] If this fluoride ion-induced desilylation can be applied to α-silylalkylphosphonates, it is possible to undergo to Horner–Emmons reaction under neutral and mild conditions. A few of the results have already been described in a previous report.[5] In this paper we wish to report the detailed results.

Results and Discussion

Preparation of α-Trimethylsilylalkylphosphonic Derivatives 1. Dimethyl α-trimethylsilylbenzylphosphonate (**1a**) was prepared in 92% yield by α-lithiation of dimethyl benzylphosphonate (**2a**) and subsequent silylation with chlorotrimethylsilane.

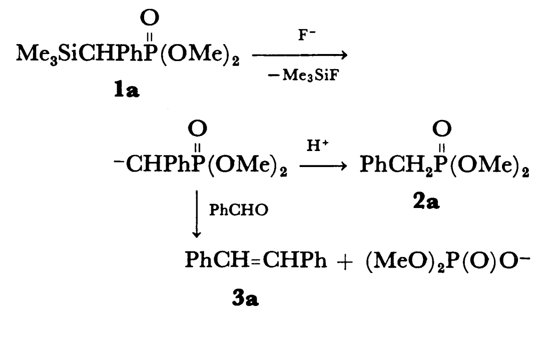
$$\underset{\mathbf{2}}{X_2P(O)CH_2R} \xrightarrow[\text{2) Me}_3\text{SiCl}]{\text{1) BuLi}} \underset{\mathbf{1}}{X_2P(O)CHRSiMe_3}$$

a: R=Ph, X=OMe; b: R=H, X=OMe;
c: R=H, X=NEt$_2$

Dimethyl trimethylsilylmethylphosphonate (**1b**) was obtained similarly in 27% yield. The formation of dimethyl α,α-bis(trimethylsilyl)methylphosphonate could not be inhibited since the reaction was carried out under conditions where the quencher existed in more excess than the reactant (See Experimental). Very efficient distillation with a spinning band was necessary for removal of the by-product. According to the literature,[6] **1b** can be prepared by the Arbuzov reaction of trimethyl phosphite with trimethylsilylmethyl halide. Trimethylsilylmethylphosphonic bis(diethylamide) (**1c**) was also prepared in 43% yield by the same method as described above. *O,O*-Diethyl trimethylsilylmethylphosphonothioate (**1d**) was given in 74% yield by reaction of chlorodiethoxyphosphine with trimethylsilylmethylmagnesium chloride, followed by sulfurization.

$$(EtO)_2PCl + Me_3SiCH_2MgCl \longrightarrow \xrightarrow{S_8} \underset{\mathbf{1d}}{(EtO)_2P(S)CH_2SiMe_3}$$

Reaction of 1a with Benzaldehyde in the Presence of Various Fluoride Ion Sources. Dimethyl α-trimethylsilylbenzylphosphonate (**1a**) was allowed to react with benzaldehyde in tetrahydrofuran (THF) in the presence of various fluoride ion sources to give stilbene (**3a**) and a protodesilylation product, dimethyl benzylphosphonate (**2a**). The reaction proceeds as shown in the following scheme. The results are summarized in Table 1.



$$\underset{\mathbf{1a}}{Me_3SiCHPh\overset{O}{\overset{\|}{P}}(OMe)_2} \xrightarrow[-Me_3SiF]{F^-} {}^-CHPh\overset{O}{\overset{\|}{P}}(OMe)_2 \xrightarrow{H^+} \underset{\mathbf{2a}}{PhCH_2\overset{O}{\overset{\|}{P}}(OMe)_2}$$

$$\downarrow PhCHO$$

$$\underset{\mathbf{3a}}{PhCH{=}CHPh} + (MeO)_2P(O)O^-$$

When cesium fluoride dried freshly by a heat gun under vacuum was used, the best result was obtained. Use of acetonitrile as a solvent gave a similar result, but in toluene the reaction became very slow. Potassium fluoride was less effective even in the presence of 18-crown-6. On the other hand, ammonium fluorides could undergo desilylation efficiently even at room temperature, however, the

Table 1. Reaction of **1a** with Benzaldehyde in the Presence of Various Fluoride Ion Sources

Fluoride	Reaction condition			Stilbene	
	Solvent	Temp	Time	Yield[a]/%	E/Z[b]
CsF[c]	THF	RT	overnight		
		Reflux	40 min	32	100/0
CsF[d]	THF	RT	2.5 h		
		Reflux	overnight	36	100/0
CsF[e]	THF	50 °C	overnight		
		Reflux	2 h	64	100/0
CsF[f]	THF	Reflux	6 h	52	100/0
CsF[g]	THF	Reflux	1 d	85	100/0
CsF[g]	CH_3CN	50 °C	overnight	64	100/0
CsF[g]	Toluene	75 °C	1 d		
		90 °C	12 h	60	100/0
CsF[g]	DME	RT	6 h		
		Reflux	2.5 h	51	100/0
KF[h]-18-crown-6	THF	Reflux	1 d	9.5	100/0
Freeze dry KF[i]	THF	Reflux	2 d	40	100/0
Freeze dry KF[i]	CH_3CN	Reflux	2 d	57	100/0
TBAF[j]	THF	RT	2.5 h	65	90/10
TBAF[k]	THF	RT	3.5 h	26	90/10
TMAF[l]	THF	RT	1.5 h	30	90/10

a) Isolated yields based on **1a**. b) By ^{1}H NMR analysis. c) Heated at 120 °C under vacuum. d) Dried by heating at 115 °C over P_2O_5 under vacuum. e) Dried by benzene azeotrope. f) Dried with molecular sieves 4A. g) Heated with a heat gun under vacuum. h) Heated at 120 °C over P_2O_5 under vacuum. i) Heated at 180 °C under vacuum. j) Commercially available one. k) Half mol equivalent of TBAF was used with molecular sieves 4A. l) Heated at 110 °C under vacuum.

yield of **3a** was rather poor. It seems to be due to the difficulty in drying because of its thermal instability and/or the existence of acidic hydrogens easily abstractable by the resulting carbanion. Considering that the yield of **3a** was less than 60% in spite of drying of tetrabutylammonium fluoride (TBAF) by various procedures such as absorption of water with molecular sieves 4A, removal of water as the benzene azeotrope and so on, the latter reason seems more likely.

It is interesting to point out that when metal fluorides were used only (*E*)-**3a** was obtained, while use of ammonium fluorides afforded a mixture of (*E*)- and (*Z*)-**3a** in a ratio of 90:10. In general the Horner–Emmons reaction using the phosphonates with substituents stabilizing carbanion at the α-position gives selectively thermodynamically more stable (*E*)-olefins through a reversible addition of the carbanion to the carbonyl compound at the first step of the reaction.[7] Therefore, it can reasonably be explained as follows: Ammonium cation makes counter anion more naked so that the second step of the reaction, cycloelimination of the phosphate ion, proceeds more readily to give kinetically (*Z*)-stilbene. Such an acceleration of the second step has been alternatively achieved by stabilizing a pentavalent intermediate by use of five-membered phosphonates[8] or electronegative group such as 2,2,2-trifluoroethyl.[9]

The following labeling experiment indicates that **1a** can not act as a proton source for the formation of **2a**, and that the resulting carbanion seems to be protonated by water which still remained in the system: A similar reaction using dimethyl α-deuterio-α-trimethylsilylbenzylphosphonate (**1a**-*d*) gave stilbene-*d* and dimethyl α-deuteriobenzylphosphonate (**2a**-*d*). No evidence was obtained for the formation of dimethyl α,α-dideuteriobenzylphosphonate. It can be concluded that the carbanion generated by desilylation does not abstract the α-proton of **1a**. Therefore, if water could be removed completely, the yield of the olefin is expected to increase.

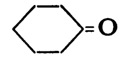
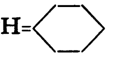
The reaction can be followed by ^{31}P NMR spectroscopy. As the signal at δ_P 31.4 due to **1a** decreased gradually, the peak at δ_P 28.5 assignable to protodesilylation product **2a** appeared in a low intensity, but no peak of the phosphate ion could be observed around δ_P 0 except for use of TBAF, because of low solubility of metal phosphate.

Reactions of 1a with Other Carbonyl Compounds in the Presence of CsF. A mixture of **1a** and carbonyl compounds was refluxed overnight in THF in the presence of CsF to give the corresponding olefins in moderate yields. The results are shown in Table 2.

It is noteworthy that 1,2-diphenylpropene (**3c**) was obtained by reaction of **1a** with acetophenone in 67% yield, whereas the reaction using the lithio derivative caused mainly deprotonation of acetophenone and gave **3c** only in 8% yield, suggesting that the carbanion generated by the present desilylation is less basic than the lithio derivative. However, in the case of reactions with more easily enolizable carbonyl compounds such as cyclohexanone and isobutyraldehyde, the corresponding olefins were obtained in quite low yields. The latter result shows the limitation of the present reaction.

Determination of geometry of olefins was done by comparing their ^{1}H NMR spectra with those reported in the literature.[10,11] In the case of 3-methyl-1-phenyl-1-butene (**3e**) the upper field doublet due to the isopropyl group was assigned to Z-isomer based on shielding effect of benzene ring. This assignment is also supported by the fact that, on irradiating the minor peak due to the methine proton of the isopropyl group, the upper doublet became singlet and double doublet at δ 5.44 changed to a doublet with J=11.5 Hz, a typical vicinal coupling constant between the Z-protons. Considering that the Z-isomer formed predominantly in the case of **3c**, while the E-

Table 2. Reaction of **1a** with Other Carbonyl Compounds in the Presence of CsF in Refluxing THF

Carbonyl compound	/ mmol	**1a** / mmol	CsF$^{a)}$ / mmol	Time	Olefin **3**	Yield$^{b)}$ / %	E/Z$^{c)}$
$Ph_2C=O$	4.00	1.90	2.70	5 h	b : $PhCH=CPh_2$	79	
PhCOMe	4.21	1.80	5.20	Overnight	c : PhCH=CMePh	67	1/3
	4.83	2.50	3.65	5 h	d : PhCH= 	35	
i-PrCHO	6.06	2.06	3.62	5.5 h	e : PhCH=CH-Pr^i	35	70/30
PhCH=CHCHO	5.80	2.48	4.94	Overnight	f : PhCH=CH-CH=CHPh$^{d)}$	67	

a) Heated with a heat gun under vacumm. b) Isolated yields based on **1a**. c) By ^{1}H NMR analysis. d) Only E,E-isomer was obtained.

isomer predominated over the Z-isomer in the case of **3e**, what determines stereochemistry of the olefin remains unclear.

Reaction of Dimethyl Trimethylsilylmethylphosphonate (1b) with Benzophenone in the Presence of CsF. A mixture of **1b**, benzophenone, and CsF in THF was refluxed for 1 d to afford 1,1-diphenylethylene (**3g**), dimethyl 2,2-diphenylethenylphosphonate (**4a**), and dimethyl methylphosphonate (**2b**) in 20, 30, and 50% yields, respectively. The following two mechanisms can be considered for the formation of **4a**: (i) Elimination of CsOH from the adduct **6** of the α-phosphinyl carbanion with benzophenone (Path a) and (ii) the Peterson reaction of α-trimethylsilyl-α-phosphinylmethylide anion (**7**) with benzophenone (Path b).[12]

$$\begin{aligned}
&(MeO)_2P(O)CH_2^-\ Cs^+ \\
&\xrightarrow{Ph_2C=O} \underset{\mathbf{6}}{(MeO)_2P(O)CH_2CPh_2O^-\ Cs^+} \\
&\xrightarrow[-CsOH]{} \underset{\mathbf{4a}}{(MeO)_2P(O)CH=CPh_2} \qquad \text{(Path a)} \\
&\mathbf{5} + \mathbf{1b} \longrightarrow \mathbf{2b} + Cs^+\ \underset{\mathbf{7}}{^-CH(SiMe_3)P(O)(OMe)_2} \\
&\xrightarrow{Ph_2C=O} \underset{\mathbf{8}}{(MeO)_2P(O)CH(SiMe_3)CPh_2O^-\ Cs^+} \\
&\xrightarrow[-Me_3SiOCs]{} \underset{\mathbf{4a}}{(MeO)_2P(O)CH=CPh_2} \qquad \text{(Path b)}
\end{aligned}$$

In order to decide which mechanism is operative, an attempt to generate the intermediate β-oxido phosphonate (**6**) alternatively was done. Namely, dimethyl 2,2-diphenyl-2-(trimethylsiloxy)ethylphosphonate (**9**) was treated with CsF to afford 1,1-diphenylethylene (**3g**) in high yield and no 2,2-diphenylethenylphosphonate (**4**), indicating that path a can be ruled out. Therefore, the resulting carbanion **5** by desilylation may abstract a proton from **1b** in competition with an attack on a carbonyl compound to give α-silylalkylphosphonate carbanion (**7**) which undergoes the Peterson reaction with benzophenone to afford **3g**.

$$\underset{\mathbf{9}}{(MeO)_2P(O)CH_2CPh_2OSiMe_3} \xrightarrow[THF,\ reflux]{CsF} \underset{\mathbf{3g}}{CH_2=CPh_2}$$

It has been reported by Ando and Sekiguchi that dimethyl α-trimethylsilylalkylphosphonates such as **1b** are heated at 250 °C to give alkylidenedimethoxy(trimethylsiloxy)phosphoranes (**10**) through 1,3-silyl shift from carbon to oxygen atom, which undergo the Wittig-type olefination with carbonyl compounds.[13]

$$\begin{aligned}
&(MeO)_2P(O)CHRSiMe_3 \xrightarrow[\bigcirc]{250\,^\circ C} \underset{\mathbf{10}}{(MeO)_2(Me_3SiO)P=CHR} \\
&\xrightarrow{Ph_2C=O} RCH=CPh_2 + (MeO)_2P(O)OSiMe_3
\end{aligned}$$

From the fact that the thermal reaction of **1b** with benzophenone affords **3g** in good yield and no Peterson reaction product,[13] it can reasonably be concluded that methylenephosphorane (**10**), which was proposed as an intermediate in the above reaction, is less basic than the carbanion **7** formed by an attack of fluoride ion on **1b**.

Reaction using other trimethylsilylmethylphosphonic derivatives, trimethylsilylphosphonic bis(diethylamide) (**1c**) and *O,O*-diethyl trimethylsilylmethylphosphonothioate (**1d**), failed to raise the yield of the methylene derivative. Use of **1c** caused mainly protodesilylation because strong hygroscopic property of **1c** made it difficult to remove water. Use of **1d** gave a result similar to that for **1b**, and the yield of the olefin was also quite poor, in marked contrast to the fact that reaction of dimethyl lithiomethylphosphonothioate with carbonyl compounds gives the corresponding methylene derivatives in good yields.[14] Two phase reaction in the presence of phase-transfer catalyst does not work in this system, either.

Experimental

All melting points and boiling points are not corrected. ^{1}H NMR spectra were measured with a Varian EM-390 (90 MHz), a Hitachi R-24B (60 MHz), and a JEOL FX-90Q (90 MHz) spectrometers using tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were taken with a JEOL FX-90Q (22.53 MHz) specrometer using TMS as internal standard. ^{31}P NMR spectra were recorded with a JEOL FX-90Q (36.28 MHz) spectrometer using 85% H_3PO_4 as external standard. Mass spectra were measured at 70 eV with a JEOL 300-D mass spectrometer.

Preparation of α-Trimethylsilylalkylphosphonic Derivatives 1. Dimethyl α-Trimethylsilylbenzylphosphonate (1a). Dimethyl benzylphosphonate (**2a**) was prepared as described previously.[15] To a solution of **2a** (18.3 g, 91.7 mmol) in THF (300 ml), distilled over benzophenone ketyl, was added butyllithium (commercially available, 1.5 M (1 M=1 mol dm^{-3}) solution in hexane, 101 mmol) at −78 °C under argon. After 5 min chlorotrimethylsilane (16.3 g, 150 mmol) was added to the reaction mixture. The solution was allowed to warm to room temperature. After neutralization with aq $NaHCO_3$ THF was removed under reduced pressure, then the residue was treated with water and dichloromethane. Organic layers were collected and aq solution was extracted four times with dichloromethane. All extracts were combined, dried over anhydrous $MgSO_4$, and then the solvent was evaporated to give a colorless oil which was distilled under vacuum to afford 22.9 g (92%) of **1a**. Bp 90—92 °C/0.05 Torr (1 Torr=133.322 Pa). ^{1}H NMR ($CDCl_3$) $\delta=0.11$ (9H, s, $Si(C\underline{H}_3)_3$), 2.71 (1H, d, $J=24.6$ Hz, P-C$\underline{H}$-Si), 3.59 (3H, $J=10.7$ Hz, $P(OC\underline{H}_3)(OCH'_3)$), 3.66 (3H, d, $J=11.0$ Hz, $P(OCH_3)(OC\underline{H}'_3)$), and 7.2 (5H, br s, Ph). ^{13}C NMR ($CDCl_3$) $\delta_C=-1.35$ (d, $^3J_{C,P}=2.4$ Hz, $Si(\underline{C}H_3)_3$), 36.84 (d, $^1J_{C,P}=125.7$ Hz, P-$\underline{C}H_2Si$), 51.78 (d, $^2J_{C,P}=6.7$ Hz, $P(O\underline{C}H_3)(OC'H_3)$), 52.98 (d, $^2J_{C,P}=7.3$ Hz, $P(OCH_3)(O\underline{C}'H_3)$), 125.76 (d, $^5J_{C,P}=2.4$ Hz, para-C), 128.46 (d, $^3J_{C,P}=1.8$ Hz, ortho-C), 129.53 (d, $^4J_{C,P}=8.5$ Hz, meta-C), and 135.08 (d, $^2J_{C,P}=7.3$ Hz, ipso-C). ^{31}P NMR ($CDCl_3$) $\delta_P=31.4$. MS m/z (rel intensity) 272 (M^+; 49), 257 (43), 167 (33), 151 (96), and 105 (100). Found: C, 53.04; H, 7.80%. Calcd for $C_{12}H_{21}O_3PSi$: C, 52.92; H, 7.77%.

Dimethyl α-Deuterio-α-trimethylsilylbenzylphosphonate (1a-*d*). To a solution of **1a** (2.1 g, 7.7 mmol) in 50 ml of THF was added *n*-BuLi (9.2 mmol) at −78 °C. After 5 min a solution of D_2O (0.55 g, 27.7 mmol) in THF (10 ml) was added to the reaction mixture. The reaction mixture was allowed to warm to room temperature, neutralized with aq NH_4Cl, and extracted with dichloromethane. After removal of the solvent the residue was distilled under vacuum with Kugelrohr to give 1.79 g (85%) of **1a-*d***. Bp 100 °C/0.01 Torr. ^{1}H NMR ($CDCl_3$) $\delta=0.114$ (9H, s, $Si(C\underline{H}_3)_3$), 3.55 (3H, d, $^3J_{H,P}=10.8$ Hz, $P(OC\underline{H}_3)(OCH'_3)$), 3.66 (3H, $^3J_{H,P}=11.0$ Hz, $P(OCH_3)(OC\underline{H}'_3)$), and 7.24 (5H, br s, $C_6\underline{H}_5$). ^{31}P NMR ($CDCl_3$) $\delta_P=31.4$. High resolution mass spectrum (HRMS) m/z Found: 273.1064. Calcd for $C_{12}H_{20}DO_3PSi$: 273.1061. D contents was estimated to be 98 and 87% by ^{1}H NMR and mass spectroscopies, respectively.

Dimethyl Trimethylsilylmethylphosphonate (1b). To a solution of dimethyl methylphosphonate (**2b**) (20.0 g, 160 mmol) in THF (200 ml) was added *n*-BuLi (176 mmol) at −78 °C. After 5 min chlorotrimethylsilane (34.7 g, 320 mmol) was added dropwise to the solution, the cooling bath was taken off. After aq $NaHCO_3$ was added, THF was evaporated, and the residue was extracted with dichloromethane. Organic layer was dried over anhydrous $MgSO_4$, then the solvent was evaporated to give 32.4 g of an equimolar mixture of **1b**, **2b**, and dimethyl α,α-bis(trimethylsilyl)methylphosphonate. Fractional distillation with a spinning band gave 8.42 g (27%) of **1b**. **1b**; bp 100 °C/12 Torr (lit,[6] 111—114 °C/21.5 Torr). ^{1}H NMR ($CDCl_3$) $\delta=0.1$ (9H, s, $Si(C\underline{H}_3)_3$), 1.1 (2H, d, $J=20$ Hz, P-$C\underline{H}_2$), and 3.7 (6H, d, $J=13$ Hz, $P(OC\underline{H}_3)_2$). ^{13}C NMR ($CDCl_3$) $\delta_C=-0.42$ (d, $^3J_{C,P}=4.3$ Hz, $Si(\underline{C}H_3)_3$), 13.65 (d, $^1J_{C,P}=128.2$ Hz, P-$\underline{C}H_2$), and 51.83 (d, $^2J_{C,P}=6.7$ Hz, $(O\underline{C}H_3)_2$). ^{31}P NMR ($CDCl_3$) $\delta_P=35.6$.

Trimethylsilylmethylphosphonic bis(diethylamide) (1c). Methylphosphonic bis(diethylamide) (**2c**) was prepared by the Arbuzov reaction of ethoxybis(diethylamino)phosphine with iodomethane in 85.5% yield. Bp 120 °C/0.9 Torr. (lit,[16] bp 166 °C/33 Torr). To a solution of methylphosphonic bis(diethylamide) (0.4 ml, 1.88 mmol) in THF (10 ml) was added butyllithium (1.2 equiv) at −78 °C, and the mixture was allowed to warm to 0 °C. To a cooled solution of chlorotrimethylsilane (1.5 equiv) was added by means of a syringe the solution of α-lithio derivative of methylphosphonic bis(diethylamide) at −40 °C for 30 min. After stirring was continued overnight aq NH_4Cl was added, the organic layer was extracted with dichloromethane, dried over anhydrous $MgSO_4$. The solvent was evaporated to give colorless oil, which was distilled with Kugelrohr to give **1c** as a colorless oil in 43% yield. Bp 70 °C/0.03 Torr. ^{1}H NMR ($CDCl_3$) $\delta=0.16$ (9H, s, $Si(C\underline{H}_3)_3$), 1.08 (12H, t, $J=7.0$ Hz, $(N(CH_2C\underline{H}_3)_2)_2$), 1.15 (2H, d, $J=17.2$ Hz, P-$C\underline{H}_2$), and 2.70—3.35 (8H, m, $(N(C\underline{H}_2CH_3)_2)_2$). ^{13}C NMR ($CDCl_3$) $\delta_C=0.36$ (d, $^3J_{C,P}=4.3$ Hz, $Si(\underline{C}H_3)_3$), 14.44 (d, $^3J_{C,P}=2.2$ Hz, $N(CH_2\underline{C}H_3)_2$), 15.72 (d, $^1J_{C,P}=106.4$ Hz, P-$\underline{C}H_2$), and 39.05 (d, $^2J_{C,P}=4.4$ Hz, $N(\underline{C}H_2CH_3)_2$). ^{31}P NMR ($CDCl_3$) $\delta_P=35.41$. HRMS m/z Found: 278.1952. Calcd for $C_{12}H_{31}N_2PSi$: 278.1942.

***O,O*-Diethyl Trimethylsilylmethylphosphonothioate (1d).** Diethoxychlorophosphine was prepared as described in a previous paper[16] in 40% yield, which was contaminated with about less than 8% of ethoxydichlorophosphine. Ten ml of trimethylsilylmethylmagnesium chloride solution, prepared from chloromethyltrimethylsilane (4.39 g, 35.8 mmol) and Mg (0.933 g, 38.4 mmol) in ether (27 ml), was added to a solution of diethoxychlorophosphine (1.64 g, 10.47 mmol) in ether (20 ml) with stirring at −78 °C under argon atmosphere, then dry excess amount of sulfur (0.4 g) was added by portions to the solution. The reaction mixture was allowed to warm to room temperature, the reaction was quenched by adding aq NH_4Cl. The organic layer was extracted with dichloromethane, dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was distilled fractionally under vaccum to give 1.869 g (74%) of **1d** as a colorless oil. Bp 115 °C/7 Torr. ^{1}H NMR ($CDCl_3$) $\delta=0.17$ (9H, s, $Si(C\underline{H}_3)_3$), 1.29 (6H, t, $J=7.1$ Hz, $(OCH_2C\underline{H}_3)_2$), 1.53 (2H, d, $J=20.0$ Hz, P-$C\underline{H}_2$), and 3.75—4.42 (4H, m, $(OC\underline{H}_2CH_3)_2$). ^{13}C NMR ($CDCl_3$) $\delta_C=-0.12$ (d, $^3J_{C,P}=3.9$ Hz, $Si(\underline{C}H_3)_3$), 16.19 (d, $^3J_{C,P}=7.3$ Hz, $P(OCH_2\underline{C}H_3)_2$), 25.47 (d, $^1J_{C,P}=100.1$ Hz, P-$\underline{C}H_2$), and 61.97 (d, $^2J_{C,P}=6.8$ Hz, $P(O\underline{C}H_2CH_3)_2$). ^{31}P NMR ($CDCl_3$) $\delta_P=97.80$. HRMS: m/z Found: 240.0768. Calcd for

$C_8H_{21}O_2PSSi$: 240.0768.

Preparation of Dimethyl 2,2-Diphenyl-2-(trimethylsiloxy)ethylphosphonate (9). To a solution of dimethyl methylphosphonate (**1b**) (1.74 g, 14 mmol) in THF (50 ml) was added dropwise n-BuLi (15.4 mmol) at −78 °C. After 5 min a solution of benzophenone (2.80 g, 15.4 mmol) in THF (5 ml) was added to the solution, and the reaction mixture was allowed to warm gradually to room temperature. After cooling the reaction mixture at −78 °C again was added chlorotrimethylsilane (2.28 g, 21 mmol) by means of a syringe. The reaction mixture was allowed to warm to room temperature and it was neutralized with aq NaHCO$_3$. After removal of the solvent the residue was treated with water, and extracted with dichloromethane. The extracts were dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure to give crude **4**, which was recrystallized from hexane to afford 4.97 g (97%) of pure **9**. **9**: Mp 86—88 °C (hexane). ^{1}H NMR (CDCl$_3$) $\delta=-0.04$ (9H, s, Si(C$\underline{H}_3$)$_3$), 3.05 (2H, d, J=19.6 Hz, PC$\underline{H}_2$), 3.42 (6H, d, J=11.0 Hz, P(OC$\underline{H}_3$)$_2$), and 7.1—7.3 (10H, m, 2×Ph). ^{31}P NMR (CDCl$_3$) δ_P=29.0. MS (70 eV) m/z (rel intensity) 378 (M$^+$; 2), 363 (59), 301 (33), and 255 (100). HRMS (70 eV) m/z Found: 378.1413. Calcd for $C_{19}H_{27}O_4PSi$: 378.1414. Found: C, 60.02; H, 7.07%. Calcd for $C_{19}H_{27}O_4PSi$: C, 60.30; H, 7.19%.

Reaction of 1a with Benzaldehyde in the Presence of CsF. 1) In a 30 ml two-necked flask was placed CsF (0.354 g, 2.33 mmol), dried at 120 °C under vacuum for 2 h. Into the flask were added benzaldehyde (0.24 ml, 2.37 mmol) and THF (10 ml) under argon atmosphere, and a solution of **1a** (0.708 g, 2.60 mmol) in THF (10 ml) was added to the mixture cooled at −19 °C. The reaction mixture was stirred at room temperature overnight, and refluxed for 40 min. Thin-layer chromatography (SiO$_2$, CCl$_4$) showed the existence of unreacted benzaldehyde and (E)-stilbene (**3a**). After evaporating the solvent the residue was treated with water and dichloromethane, and the organic layer was dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure to give 0.477 g of an oil, which was subjected to dry column chromatography (DCC)(SiO$_2$, CCl$_4$) to afford 0.13 g (32%) of (E)-**3a**. Identification of this compound was done by comparing its ^{1}H NMR spectrum with that previously reported[10] and R_f value with that of authentic sample.

2) A mixture of CsF (0.349 g, 2.3 mmol), which was dried overnight at 115 °C over phosphorus pentaoxide under vacuum, benzaldehyde (0.35 ml, 3.46 mmol), and **1a** (0.476 g, 1.75 mmol) in THF (20 ml) was stirred at room temperature for 2.5 h, and refluxed overnight. The work-up as described above gave a mixture of **2a**, unreacted benzaldehyde, and (E)-**3a**, which was subjected to DCC (SiO$_2$, CCl$_4$) to give 0.113 g (36%) of (E)-**3a** and 0.23 g (66%) of crude **2a**.

3) In a 30 ml two-necked flask were placed CsF (0.410 g, 2.70 mmol) and dry benzene (15 ml), and water was removed as an azeotrope with benzene. Into the flask were added THF (20 ml), benzaldehyde (0.210 g, 1.98 mmol), and **1a** (0.204 g, 0.75 mmol), the mixture was stirred overnight at 50 °C and refluxed for 2 h. The usual work-up gave 0.087 g (64%) of (E)-**3a**.

4) A mixture of CsF (0.340 g, 2.24 mmol) and molecular sieves 4A (1 g) was refluxed for 1 h in THF (20 ml). After cooling was added benzaldehyde (0.29 ml, 2.87 mmol) and **1a** (0.463 g, 1.70 mmol) to the suspension, and the reaction mixture was refluxed for 6 h. The usual work-up afforded (E)-**3a** in 52% yield.

5) In a 30 ml flask was placed CsF (0.347 g, 2.29 mmol) and dried by heating with a 400 W heat-gun under vacuum. After adding THF (20 ml), benzaldehyde (0.51 ml, 5.05 mmol), and **1a** (0.558 g, 2.05 mmol) the mixture was refluxed for 1 d, and was treated as described above. DCC (SiO$_2$, CCl$_4$) of the residue gave 0.311 g (85%) of (E)-**3a**.

6) CsF dried as described in 5) was used, the reaction was carried out in acetonitrile at 50 °C overnight, in toluene at 75 °C for 1 d plus at 90 °C for 12 h, and in 1,2-dimethoxyethane at room temperature for 6 h plus at reflux for 2.5 h to afford (E)-**3a** in 64, 60, and 51% yields after usual work-up, respectively.

Reaction of Dimethyl α-Deuterio-α-trimethylsilylbenzylphosphonate (1a-*d*) with Benzaldehyde in the Presence of CsF. Dimethyl α-deuterio-α-trimethylsilylbenzylphosphonate (**1a**-d) (0.625 g, 2.29 mmol) was allowed to react with benzaldehyde (0.740 g, 6.97 mmol) in the presence of CsF (0.896 g, 5.90 mmol) in THF (8 ml) as described above to give (E)-**3a**-d (0.29 g, 70%) and dimethyl α-deuteriobenzylphosphonate (**2a**-d) (0.15 g, 33%). (E)-**3a**-d: ^{1}H NMR (CDCl$_3$) δ=7.09 (1H, br s, -CD=C$\underline{H}$-) and 7.18—7.62 (10H, m, aromatic). HRMS m/z Found: 181.1007. Calcd for $C_{14}H_{11}D$: 181.1002. D contents was estimated to be 95% by the ^{1}H NMR spectrum. **2a**-d: ^{1}H NMR (CDCl$_3$) δ=3.16 (1H, br d, $^2J_{H,P}$=21.5 Hz, P-CD$\underline{H}$), 3.65 (6H, d, $^3J_{H,P}$=10.7 Hz, P(OC$\underline{H}_3$)$_2$), and 7.29 (5H, br s, aromatic). HRMS m/z Found: 201.0665. Calcd for $C_9H_{12}DO_3P$: 201.0665. D contents was estimated to be 95 and 86% by ^{1}H NMR and mass spectroscopies, respectively.

Reaction of 1a with Benzaldehyde in the Presence of Other Fluorides. 1) In a 30 ml two-necked flask was weighted potassium fluoride (0.14 g, 2.41 mmol), and it was dried at 120 °C over phosphorus pentaoxide under vacuum overnight. Drying was continued at 200 °C for additional 5 h. Into the flask were added benzaldehyde (0.41 ml, 4.06 mmol), THF (20 ml), and **1a** (0.409 g, 1.50 mmol), and the mixture was refluxed for 1 d. As the ^{31}P NMR showed that **1a** still remained in a significant amount, a trace of 18-crown-6 was added to the reaction mixture. After stirring at room temperature for 1 d the usual work-up gave 0.034 g (9.5%) of (E)-**3a**.

2) Freeze dry KF (0.67 g, 11.5 mmol), which was prepared according to the literature,[18] was dried at 180 °C under vacuum for 1 h in a 50 ml two-necked flask, and THF (40 ml), benzaldehyde (1.04 ml, 10.3 mmol), and **1a** (2.124 g, 7.80 mmol) were added into the flask, and then the mixture was refluxed for 2 d. (E)-Stilbene (**3a**) and crude **2a** were obtained in 40 and 69% yields after the usual work-up, respectively.

3) Reaction of **1a** (1.69 g, 6.20 mmol) with benzaldehyde (1.24 ml, 12.2 mmol) in the presence of freeze dry KF (0.71 g, 12.2 mmol) in refluxing acetonitrile (40 ml) afforded 0.58 g (57%) of (E)-**3a**.

4) To a solution of **1a** (0.43 g, 1.59 mmol) and benzaldehyde (0.32 ml, 3.18 mmol) in THF (18 ml) was added dropwise commercially available tetrabutylammonium fluoride (TBAF)(1 M THF solution, 1.91 ml) at room temperature. Stirring was continued for 2.5 h. In the ^{31}P NMR spectrum of the reaction mixture two peaks were

observed at δ_P=27.7 and 0.87 in almost same ratio, which can be assignable to the signals due to **2a** and tetrabutylammonium dimethyl phosphate, respectively. The usual work-up afforded a mixture of (*E*)- and (*Z*)-**3a** (0.168 g, 65%) and crude **2a** (0.128 g, 44%). The ratio of (*E*)- to (*Z*)-stilbene was determined to be 90:10 by ^{1}H NMR spectroscopy.[10]

5) A mixture of benzaldehyde (0.41 ml, 4.06 mmol), TBAF (1 ml, 1 mmol), and molecular sieves 4A (1 g) in THF (5 ml) was stirred overnight at room temperature. To the suspension was added a solution of **1a** (0.54 g, 1.98 mmol) in THF (15 ml), and the mixture was stirred for 3.5 h at room temperature. The usual work-up afforded (*E*)- and (*Z*)-**3a** (0.085 g, 26%) in the same ratio and crude **2a** (0.30 g, 80%).

6) A mixture of benzaldehyde (0.41 ml, 4.06 mmol), tetramethylammonium fluoride (TMAF) (0.372 g, 4.00 mmol), and **1a** (0.368 g, 1.35 mmol) in THF (15 ml) was stirred for 1.5 h at room temperature. The usual work-up gave (*E*)- and (*Z*)-**3a** in 30% yield. The ratio of (*E*)- and (*Z*)-**3a** was 90:10.

Reaction of Dimethyl α-Trimethylsilylbenzylphosphonate (1a) with Other Carbonyl Compounds in the Presence of CsF. Benzophenone. Cesium fluoride (0.410 g, 2.70 mmol) was dried in a 30 ml two-necked flask as described above, and a solution of dry benzophenone (0.729 g, 4.00 mmol) in THF (18 ml) and **1a** (0.518 g, 1.90 mmol) were added into the flask, and then the mixture was refluxed for 5 h and stirred at 50 °C overnight. The usual work-up gave a mixture (0.870 g) of 1,1,2-triphenylethylene (**3b**), **2a**, and unreacted benzophenone, which was subjected to DCC (SiO_2, CCl_4) to afford **3b** (0.385 g, 79%) as a viscous oil. ^{1}H NMR ($CDCl_3$) δ=6.87 (1H, s, $C=C\underline{H}Ph$), 6.97 (5H, s, Ph), and 7.06—7.40 (10H, m, 2×Ph).

Acetophenone. In a 30 ml two-necked flask was weighted CsF (0.790 g, 5.20 mmol), dried as described above. After subsequent addition of acetophenone (0.49 ml, 4.21 mmol), THF (20 ml), and **1a** (0.490 g, 1.80 mmol), the mixture was refluxed overnight. The usual DCC (SiO_2, CCl_4) afforded a mixture of (*E*)- and (*Z*)-1,2-diphenylpropenes (**3c**) (0.234 g, 67%) as a colorless oil. (*E*)-**3c**: ^{1}H NMR ($CDCl_3$) δ=2.19 (3H, d, *J*=1.5 Hz, $=CC\underline{H}_3$), 6.46 (1H, q, *J*=1.5 Hz, $=C\underline{H}Ph$), and 6.90—7.62 (10H, m, Ph). (*Z*)-**3c**: ^{1}H NMR ($CDCl_3$) δ=2.26 (3H, d, *J*=1.2 Hz, $=CC\underline{H}_3$), 6.83 (1H, q, *J*=1.2 Hz, $=C\underline{H}Ph$), and 6.90—7.62 (10H, m, Ph). The ratio of (*E*)- and (*Z*)-**3c** was determined to be 1:3 from the integral ratio between the doublet at δ 2.26 due to E-isomer and the doublet at δ 2.19 due to Z-isomer.[11]

Cyclohexanone. In a 30 ml two necked flask was placed CsF (0.544 g, 3.65 mmol), and dried. Into the flask were added cyclohexanone (0.50 ml, 4.83 mmol), THF (20 ml), and **1a** (0.681 g, 2.50 mmol), and the mixture was refluxed for 5 h, and then it was stirred at 50 °C overnight. The residue obtained after the usual work-up was submitted to DCC (SiO_2, CCl_4) to give 0.146 g (35%) of benzylidenecyclohexane (**3d**). ^{1}H NMR ($CDCl_3$) δ=1.37—1.87 (6H, m, $-CH_2-(C\underline{H}_2)_3-CH_2-$), 2.01—2.47 (4H, m, $-C\underline{H}_2-(CH_2)_3-C\underline{H}_2-$), 6.10 (1H, br s, $=C\underline{H}Ph$), and 6.90—7.40 (5H, m, Ph).

Isobutyraldehyde. Cesium fluoride (0.55 g, 3.62 mmol) was dried, mixed with isobutyraldehyde (0.55 ml, 6.06 mmol), THF (30 ml), and **1a** (0.561 g, 2.06 mmol) and the mixture was refluxed for 5.5 h. The reaction mixture was treated as described above to give 0.535 g of an oil which was subjected to DCC (SiO_2, CCl_4) to afford a mixture of (*E*)- and (*Z*)-3-methyl-1-phenyl-1-butenes (**3e**) (0.10 g, 35%). (*E*)-**3e**: ^{1}H NMR ($CDCl_3$) δ=1.07 (6H, d, *J*=6.6 Hz, $CH(C\underline{H}_3)_2$), 2.18—2.67 (1H, m, $C\underline{H}(CH_3)_2$), 6.12 (1H, dd, *J*=5.4, 16 Hz, $=C\underline{H}CH(CH_3)_2$), 6.36 (1H, d, *J*=16 Hz, $=C\underline{H}Ph$), 6.9—7.6 (5H, m, Ph). (*Z*)-**3e**: ^{1}H NMR ($CDCl_3$) δ=1.02 (6H, d, *J*=6.6 Hz, $CH(C\underline{H}_3)_2$), 2.67—3.14 (1H, m, $C\underline{H}(CH_3)_2$), 5.44 (1H, dd, *J*=10.0, 11.5 Hz, $=C\underline{H}CH(CH_3)_2$), 6.29 (1H, d, *J*=11.5 Hz, $=C\underline{H}Ph$), and 6.9—7.6 (5H, m, Ph). The ratio of (*E*)- and (*Z*)-**3e** was determined to be 70:30 from the integral ratio of the doublet at δ 1.07 due to E-isomer to the doublet at δ 1.02 due to Z-isomer.

Cinnamaldehyde. A mixture of **1a** (0.675 g, 2.48 mmol), cinnamaldehyde (0.73 ml, 5.80 mmol), and CsF (0.75 g, 4.94 mmol) in THF (25 ml) was refluxed overnight. After removal of the solvent the residue was treated with water and extracted several times with dichloromethane. The extracts were combined, dried over anhydrous $MgSO_4$, and then the solvent was evaporated. The residue was subjected to DCC (SiO_2, CCl_4) to afford (*E,E*)-1,4-diphenyl-1,3-butadiene (**3f**) (0.326 g, 67%). Mp 151—152 °C (EtOH) (lit,[19] 152—153 °C).

Reaction of Trimethylsilylmethylphosphonic Derivatives (1b—d) with Benzophenone in the Presence of CsF. Dimethyl Trimethylsilymethylphosphonate (1b). A mixture of CsF (0.744 g, 4.90 mmol), dried as described above, benzophenone (1.35 g, 7.40 mmol), **1b** (0.420 g, 2.14 mmol), and THF (20 ml) was refluxed for 1 d with stirring. The usual work-up afforded 1,1-diphenylethylene (**3g**), dimethyl 2,2-diphenylethenylphosphonate (**4a**), and dimethyl methylphosphonate (**2b**) in 20, 30, and 50% yields, respectively. **4a**: ^{1}H NMR ($CDCl_3$) δ=3.49 (6H, d, *J*=11 Hz, $P(OC\underline{H}_3)_2$), 6.18 (1H, d, *J*=15 Hz, $=C\underline{H}$), and 7.3—7.5 (10H, m, 2×Ph). ^{31}P NMR ($CDCl_3$) δ_P=19.32. HRMS: *m/z* Found: 288.0913. Calcd for $C_{16}H_{17}O_3P$: 288.0914.

Trimethylsilylmethylphosphonic Bis(diethylamide) (1c). A mixture of CsF (0.559 g, 3.68 mmol), benzophenone (0.399 g, 2.19 mmol), and **1c** (0.381 g, 1.37 mmol) in THF (20 ml) was refluxed overnight to give methylphosphonic bis(diethylamide) (**2c**) almost quantitatively after usual work-up.

***O,O*-Diethyl Trimethylsilylmethylphosphonothioate (1d).** A mixture of CsF (0.577 g, 3.80 mmol), benzophenone (0.292 g, 1.60 mmol), and **1d** (0.250 g, 1.05 mmol) in THF (20 ml) was refluxed overnight. The usual work-up afforded **3g**, *O,O*-diethyl 2,2-diphenylethenylphosphonothioate (**4b**), and *O,O*-diethyl methylphosphonothioate (**2d**) in 30, 25, and 42% yields, respectively, from analysis of ^{1}H NMR and ^{31}P NMR spectra of the mixture. **4b**: Bp 175 °C/0.05 Torr. ^{1}H NMR ($CDCl_3$) δ=1.08 (6H, t, *J*=7.1 Hz, $C\underline{H}$), 3.51—4.19 (4H, m, $OC\underline{H}_2$), 6.36 (1H, d, *J*=20.3 Hz, $=C\underline{H}$), 7.25 (5H, br s, Ph), and 7.35 (5H, br s, Ph). ^{31}P NMR ($CDCl_3$) δ_P=80.16. HRMS: *m/z* Found: 332.1008. Calcd for $C_{18}H_{21}O_2PS$: 332.1000.

Reaction of Dimethyl 2,2-Diphenyl-2-(trimethylsiloxy)-ethylphosphonate (9) with CsF. A mixture of CsF (0.749 g, 4.93 mmol) and **9** (0.867 g, 2.29 mmol) in THF (20 ml) was refluxed for 3 d. The usual work-up gave 1,1-diphenylethylene (0.351 g) in 85% yield.

Reaction of Dimethyl α-Lithiobenzylphosphonate with Acetophenone. To a solution of dimethyl benzylphosphonate (**2a**) (0.544 g, 2.72 mmol) in THF (20 ml) was added *n*-BuLi (2.0 ml, 1.64 M) at −78 °C. After 5 min a solution of acetophenone (0.63 ml, 2.0 equiv) in THF (5 ml) was added to the solution at the same temperature and the reaction mixture was allowed to warm to room temperature, and then was stirred for 1 d. The usual work-up gave 0.856 g of crude mixture, which was chromatographed on silica gel (DCC, CCl_4) to give 0.043 g (8.1%) of **3c**.

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