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# The Reaction of Diphenyl(trimethylsilylmethyl)phosphine with Carbonyl Compounds in the Presence of Fluorides

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**Synopsis.** Diphenyl(trimethylsilylmethyl)phosphine (**1**) was allowed to react with benzophenone in the presence of CsF in *N,N*-dimethylformamide to give a mixture of methyldiphenylphosphine (**2**), (2,2-diphenyl-2-trimethylsiloxyethyl)diphenylphosphine (**3**) and (2-hydroxy-2,2-diphenylethyl)diphenylphosphine (**4**) in good yield. The use of about 10 mol% of CsF gave **3** with fairly good selectivity. The reaction with benzaldehyde gave a similar result, but only protodesilylation occurred in the reaction with enolizable carbonyl compounds.

The direct deprotonation of methyldiphenylphosphine was achieved successfully by using organolithium compounds with a help of *N,N,N′,N′*-tetramethylethylenediamine. However, it was accompanied by the substitution reaction at the phosphorus atom because of their nucleophilicity enhanced by the disaggregation.[1] In the course of our studies on the Horner–Emmons reaction, we uncovered the fluoride induced Horner–Emmons reaction.[2] We decided to examine the generation of diphenylphosphinomethyl anion by the fluoride-induced desilylation and the olefination via quaternalization from its carbonyl adduct. In this paper we wish to report on the results.

## Results and Discussion

**The Reaction of Diphenyl(trimethylsilylmethyl)phosphine (1) with Carbonyl Compounds in the Presence of CsF.** Diphenyl(trimethylsilylmethyl)phosphine (**1**) was allowed to react with benzophenone in the presence of CsF in *N,N*-dimethylformamide (DMF) to afford a mixture of methyldiphenylphosphine (**2**), a protodesilylation product of **1**, (2,2-diphenyl-2-trimethylsiloxyethyl)diphenylphosphine (**3**), and (2-hydroxy-2,2-diphenylethyl)diphenylphosphine (**4**). The results are shown in Table 1. Sulfurization of the reaction mixture followed by usual workup gave a mixture of methyldiphenylphosphine sulfide (**5**) and (2-hydroxy-2,2-diphenylethyl)diphenylphosphine sulfide (**6**).[3] The signal due to **3** decreased with an increase in that of **4** with the elapse of the reaction time, indicating the hydrolysis of **3** occurred under the conditions. About 10 mol% of CsF is enough to complete the reaction, indicating that the present reaction proceeds as shown in the following scheme. An alternative mechanism where the resulting **8** reacts with **1** to afford **3** and **7** cannot be ruled out. It is interesting to point out that the carbanion **7** can be generated in the present system in spite of the lack of carbanion-stabilizing ability compared with cases of phosphonio[4,5] or phosphoryl derivatives[2] and that the yield of **7** is very high, though a part of **7** reacts with water existing in the system to give **2**.

$$\underset{\mathbf{1}}{Ph_2PCH_2SiMe_3} + F^- \longrightarrow (Ph_2PCH_2\underset{F}{\overset{-}{Si}}Me_3) \longrightarrow \underset{\mathbf{7}}{Ph_2PCH_2^-} + Me_3SiF$$

$$\mathbf{7} + Ph_2C{=}O \longrightarrow \underset{\mathbf{8}}{Ph_2PCH_2CPh_2O^-}$$

$$\mathbf{8} + Me_3SiF \longrightarrow \underset{\mathbf{3}}{Ph_2PCH_2CPh_2OSiMe_3} + F^-$$

$$\mathbf{7} + H_2O \longrightarrow \underset{\mathbf{2}}{Ph_2PCH_3}$$

$$\mathbf{8} + H_2O \longrightarrow \underset{\mathbf{4}}{Ph_2PCH_2CPh_2OH}$$

$$\mathbf{3} + H_2O + F^- \longrightarrow \mathbf{4}$$

The use of LiF or NaF as a fluoride ion source gave no adduct (**3** or **4**) besides a small amount of **2**, presumably because of its poorer solubility. The use of HMPA as a solvent gave almost the same results, but the reaction using an ethereal solvent such as tetrahydrofuran or diethylene glycol dimethyl ether was unsuccessful. An addition of molecular sieves 4A to remove water caused a decrease in the yields of the products as well as a reduction in the rate of the reaction.

In the case of the reaction of **1** with 1,5-diphenyl-3-pentanone in the presence of CsF the resulting carban-

Table 1. The Reaction of **1** with Benzophenone in the Presence of CsF in DMF

| Entry | **1**/mmol | CsF[a]/mmol | Temp/°C | Time/h | **2**:**3**:**4**[b] |
|---|---|---|---|---|---|
| 1 | 1.5 | 2.6 | 40 | 24 | 60:10:30 |
| 2 | 0.75 | 0.79 | 90 | 3 | 29:40:31 |
| 3 | 0.75 | 0.38 | 60 | 2 | 24:72:4 |
| 4 | 0.75 | 0.10 | 60 | 4 | 14:82:4 |
| 5 | 0.75 | 0.10 | 50 | 6 | 19:75:7[c] |

a) Dried by heating with a heat gun under vacuum. b) The ratio of peak heights of signals at $\delta_P$=−27.7, −26.3, and −24.8 due to **2**, **3**, and **4**, respectively. c) About 9% of **1** ($\delta_P$=−22.7) remained.

ion acts as a base to afford only protodesilylation product **2**. Considering the fact that the reaction of dimethyl lithiomethylphosphonate gives the corresponding adduct in 95% yield,[6] it is concluded that unexpectedly low nucleophilicity for the present reactive species is probably attributed to the following reason: It may not be a free carbanion but solvated one, or it exists in equilibrium with "silicon ate complex".

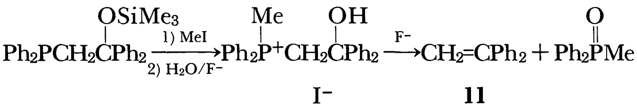
$$\underset{\mathbf{1}}{\mathrm{Ph_2PCH_2SiMe_3}} + \mathrm{Me_2NCHO} \xrightarrow{\mathrm{F^-}}$$

$$\mathrm{Ph_2PCH_2CH(NMe_2)OSiMe_3} \xrightarrow{-\mathrm{Me_3SiOH}}$$

$$\underset{\mathbf{9}}{\mathrm{Ph_2PCH{=}CHNMe_2}} \xrightarrow{\mathrm{S_8}} \underset{\mathbf{10}}{\mathrm{Ph_2P(S)CH{=}CHNMe_2}}$$

In the reaction with sterically hindered carbonyl compounds such as (−)-fenchone the desired adduct was not obtained, but a new peak appeared at $\delta_P=-14.0$ besides −27.7 in the $^{31}$P NMR spectrum, which is assignable to 1-dimethylamino-2-diphenylphosphinoethylene (**9**), a reaction product with DMF, from the following facts: 1) The chemical shift ($\delta_P=-14.0$) is similar to that of diphenylvinylphosphine ($\delta_P=-11.7$).[7] 2) Sulfurization of the reaction mixture gave **5** and trans-1-dimethylamino-2-(diphenylphosphinothioyl)ethylene (**10**).[8]

**Olefination via P-Methylation.** The reaction mixture which was obtained by the reaction of **1** with benzophenone in the presence of CsF was treated with iodomethane (1.1 equiv) and subsequent CsF-$H_2O$ (1 equiv) to give 1,1-diphenylethylene (**11**). The isolated yield of **11** and the reaction conditions are summarized in Table 2.



$$\mathrm{Ph_2PCH_2\overset{OSiMe_3}{\overset{|}{C}}Ph_2} \xrightarrow[2)\ \mathrm{H_2O/F^-}]{1)\ \mathrm{MeI}} \mathrm{Ph_2\overset{Me}{\overset{|}{P}}{}^{+}CH_2\overset{OH}{\overset{|}{C}}Ph_2}\ \mathrm{I^-} \xrightarrow{\mathrm{F^-}} \underset{\mathbf{11}}{\mathrm{CH_2{=}CPh_2}} + \mathrm{Ph_2\overset{O}{\overset{\|}{P}}Me}$$

Besides the desired olefination side reactions such as the C-C bond cleavage (Entry 2) and the dehydration (Entry 3) occurred depending on the reaction conditions. Interestingly, an addition of more than 1.5 equivalents of water gave good results. A similar effect of water was reported in the case of the conversion of β-hydroxyalkylphosphonates into the corresponding olefins.[6,9] The $^{31}$P NMR shows siloxyphosphonium salt is converted into the hydroxyphosphonium salt before the olefination.

## Experimental

All melting points and boiling points are not corrected. $^{1}$H NMR and $^{31}$P NMR spectra were measured with a JEOL FX-90Q using tetramethylsilane as an internal standard and 85% $H_3PO_4$ as an external standard, respectively.

**Preparation of Diphenyl(trimethylsilylmethyl)phosphine (1).** To a solution of chlorodiphenylphosphine (5.1 g, 23 mmol) in dry ether (50 ml) was added dropwise an ethereal solution[10] of trimethylsilylmethylmagnesium chloride (1 M, 1 M=1 mol dm$^{-3}$, 23 mmol) at −78 °C under Ar. The reaction mixture was allowed to warm to room temperature and the resulting precipitates were filtered under Ar. The filtrate was evaporated under reduced pressure and the residue was distilled under vacuum with Kugelrohr to give **1** in 76% yield. Bp 105—110 °C/0.03 Torr (1 Torr=133.322 Pa) (lit,[11] bp 139—143 °C/0.6 Torr). $^{31}$P NMR ($CDCl_3$) $\delta_P=-21.6$. $^{1}$H NMR ($CDCl_3$) $\delta=-0.05$ (9H, s, Si(C$\underline{H}_3$)$_3$), 1.3 (2H, d, $J$=1 Hz, P-C$\underline{H}_2$-Si), and 7.0—7.5 (m, 10H, 2×Ph).

**Reaction of 1 with Carbonyl Compounds in the Presence of CsF. Benzophenone:** In a two-necked flask CsF (0.03 g, 0.1 mmol) was placed and heated by a heat gun under vacuum. A mixed solution of **1** (0.20 g, 0.75 mmol) and benzophenone (0.24 g, 1.3 mmol) in dry DMF (10 ml) was added to the flask and the mixture was heated at 60 °C for 4 h. The $^{31}$P NMR spectrum of the reaction mixture showed three signals at $\delta_P=-27.7$, −26.3, and −24.8 due to methyldiphenylphosphine (**2**), (2,2-diphenyl-2-trimethylsiloxyethyl)-diphenylphosphine (**3**), and (2-hydroxy-2,2-diphenylethyl)-diphenylphosphine (**4**) in a ratio of peak heights of 14 : 82 : 4, respectively.[12] Sulfurization of the reaction mixture by treatment with excess of sulfur, followed by usual workup afforded a mixture of methyldiphenylphosphine sulfide (**5**) and (2-hydroxy-2,2-diphenylethyl)diphenylphosphine sulfide (**6**), which could be separated by preparative high-pressure liquid chromatography (LC) (Japan Analytical Industries: JAIGEL 1H, 2H).

**5** (10%):[13] $^{1}$H NMR ($CDCl_3$) $\delta=2.27$ (3H, d, $^{2}J_{H,P}=13.4$ Hz, PC$\underline{H}_3$), 7.39—7.54 (6H, m, para and meta), and 7.65—7.97 (4H, m, ortho). $^{31}$P NMR ($CDCl_3$) $\delta_P=35.81$.

**6** (80%): mp 151—152.5 °C (hexane) (lit,[1] mp 142—145 °C). $^{1}$H NMR ($CDCl_3$) $\delta=3.64$ (2H, d, $^{2}J_{H,P}=10.3$ Hz, PC$\underline{H}_2$), 6.63 (1H, s, O$\underline{H}$), 6.98—7.18 (5H, m, Ph), 7.18—7.50 (11H, m, Ph′ and para and meta of PPh), and 7.50—7.80 (4H, m, ortho of PPh). $^{31}$P NMR ($CDCl_3$) $\delta_P=34.66$. The results of the reactions carried out under various conditions are shown in Table 1.

**Benzaldehyde:** A mixture of **1** (0.10 g, 0.38 mmol), benzaldehyde (0.04 g, 0.38 mmol), and CsF (0.03 g, 0.19 mmol) was heated in DMF (8 ml) at 0 °C for 2 h. The $^{31}$P NMR spectrum of the reaction mixture showed three signals at $\delta_P=-27.7$, −22.3, and −21.6 due to **2**, (2-phenyl-2-trimethyl-

Table 2. Isolated Yield of **11** and the Reaction Conditions

| Entry | CsF$^{a)}$/mmol | $H_2O$/mmol | Temp/°C | Time/h | **11**$^{b)}$/% |
|---|---|---|---|---|---|
| 1 | 0.79 | — | R.T. | 24 | 49 |
| 2 | 0.79 | — | 60 | 1.5 | 28$^{c)}$ |
| 3 | 0.79 | — | 0 | 12 | —$^{d)}$ |
| 4 | 0.79 | 1.19 | R.T. | 2 | 60 |
| 5 | 0.83 | 2.49 | R.T. | 12 | 53 |
| 6 | 0.83 | 7.47 | R.T. | 12 | 58 |

a) Dried by heating with a heat gun under vacuum. b) Isolated yield based on **1**. c) The formations of benzophenone and dimethyldiphenylphosphonium iodide[14] were observed. d) Methyl(2,2-diphenylethenyl)diphenylphosphonium iodide was formed.[15]

siloxyethyl)diphenylphosphine, (2-hydroxy-2-phenylethyl)diphenylphosphine in a ratio of peak heights of 12 : 15 : 74, respectively. Sulfurization of the mixture as described above, followed by LC gave (2-hydroxy-2-phenylethyl)diphenylphosphine sulfide (**12**) in 83% yield.

**12:** Mp 90—91 °C (hexane). $^1$H NMR ($CDCl_3$) $\delta$=2.88 (2H, dd, $^3J_{H,H}$=6.0 Hz, $^2J_{H,P}$=9.6 Hz, $PC\underline{H}_2$), 4.29 (1H, s, $O\underline{H}$), 5.15 (1H, dt, $^3J_{H,H}$=6.0 Hz, $^3J_{H,P}$=11.8 Hz, $C\underline{H}OH$–), 7.24—7.33 (5H, m, CPh), 7.38—7.59 (6H, m, meta and para of PPh), and 7.61—8.06 (4H, m, ortho of PPh). $^{31}$P NMR ($CDCl_3$) $\delta_P$=38.43. High-resolution mass spectrum (HRMS) (70 eV): *m/z* Found: 338.0913. Calcd for $C_{20}H_{19}OPS$: 338.0895.

**(−)-Fenchone:** The reaction using **1** (0.20 g, 0.75 mmol), (−)-fenchone (0.14 g, 0.93 mmol), and CsF (0.05 g, 0.33 mmol) in DMF (10 ml) gave a mixture of **2** and trans-2-dimethylamino-1-diphenylphosphinoethylene (**9**), which was sulfurized and subjected to LC to afford trans-dimethylamino-1-diphenylphosphinothioylethylene (**10**) in 36% yield.

**9:** $^{31}$P NMR (DMF) $\delta_P$=−14.0.

**10:** Mp 99—101 °C (hexane). $^1$H NMR ($CDCl_3$) $\delta$=2.92 (6H, s, $NMe_2$), 4.48 (1H, dd, $^2J_{H,P}$=13.5 Hz, $^3J_{H,H}$=17.2 Hz, $PC\underline{H}$=CH), 7.24 (1H, dd, $^3J_{H,P}$=14.0 Hz, $^3J_{H,H}$=17.2 Hz, $=C\underline{H}NMe_2$), 7.31—7.56 (6H, m, meta and para), and 7.62—7.96 (4H, m, ortho). $^{31}$P NMR ($CDCl_3$) $\delta_P$=37.49. HRMS (70 eV): *m/z* Found: 287.0907. Calcd for $C_{16}H_{18}NPS$: 287.0897.

**Olefination via P-Methylation.** To the reaction mixture which was obtained by the reaction of **1** (0.20 g, 0.75 mmol) with benzophenone (0.20 g, 1.1 mmol) in the presence of CsF (0.06 g, 0.38 mmol) were added iodomethane (1.1 equiv), CsF (0.20 g, 0.75 mmol), and $H_2O$ (1.19 mmol). After stirring for 2 h at room temperature the reaction was quenched with water, and then the reaction mixture was extracted with dichloromethane. After removal of the solvent the residue was subjected to dry column chromatography ($SiO_2$) to give 1,1-diphenylethylene (**11**) in 60% yield. The isolated yield of **11** and the reaction conditions are summarized in Table 2.

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15) The structure was estimated by the following NMR spectral data: $^1$H NMR ($CDCl_3$) $\delta$=2.3 (3H, d $^2J_{H,P}$=14 Hz, $PC\underline{H}_3$) and 6.7—7.9 (21H, m, $C\underline{H}$=$CPh_2$ and 4×Ph). $^{31}$P NMR ($CDCl_3$) $\delta_P$=12.9.