BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (1), 337—338 (1978)

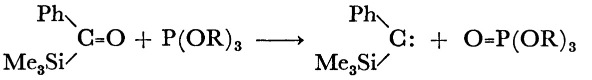
Formation of Dialkyl α-Siloxybenzylphosphonate *via* 1,2-Anionic Rearrangement of a Silyl Group

Akira Sekiguchi, Masayuki Ikeno, and Wataru Ando
Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki 300-31

(Received July 8, 1977)

Synopsis. The reactions of silyl phenyl ketones with trialkyl phosphites and dialkyl sodiophosphonates gave dialkyl α-siloxybenzylphosphonates in good yields. The mechanism involves the migration of a silyl group from carbon to anionic oxygen. No deoxygenation of silyl ketone with trialkyl phosphite was observed.

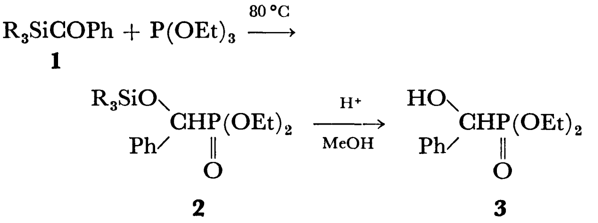
Silylcarbenes have recently been found to be one of the most interesting species for the formation of silicon-carbon double bond. A report was given on the intermolecular and intramolecular reactions of silylcarbenes generated by either photolysis or thermolysis of silyl diazo compounds.[1)] On the other hand, trialkyl phosphite is known to deoxygenate or desulfurate to give carbene intermediates.[2)] We attempted to generate a silylcarbene by deoxygenation of a silyl phenyl ketone.



$$\mathrm{Ph(Me_3Si)C{=}O} + \mathrm{P(OR)_3} \longrightarrow \mathrm{Ph(Me_3Si)C{:}} + \mathrm{O{=}P(OR)_3}$$

However, we found 1,2-anionic rearrangement of a silyl group in the reaction of silyl phenyl ketone with trialkyl phosphite instead of the formation of silylcarbene.

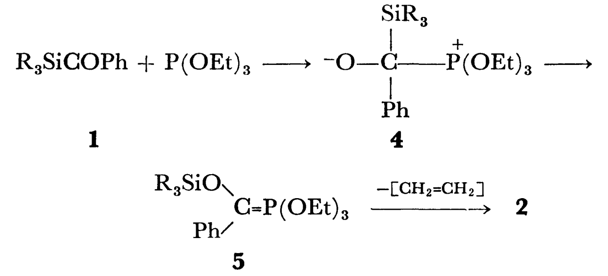
A mixture of trimethylsilyl phenyl ketone **1a**(5.72 mmol) and triethyl phosphite(60 mmol) was heated at 80 °C with stirring for 12 h. Distillation of the reaction mixture afforded **2a**(1.09 g, 60%, bp 142 °C/2 mmHg), which was found to be diethyl α-trimethylsiloxybenzylphosphonate from analysis of the spectra. The phosphonate **2a** was desilylated by refluxing methanol followed by crystallization from cyclohexane to give diethyl α-hydroxybenzylphosphonate **3** in 86% yield. Phosphonate **3** was also obtained from a variety of other silyl ketones, **1b**, **1c**, and **1d** in 72, 43, and 38% yields, respectively.



$$\underset{\mathbf{1}}{\mathrm{R_3SiCOPh}} + \mathrm{P(OEt)_3} \xrightarrow{80\,^\circ\mathrm{C}} \underset{\mathbf{2}}{\mathrm{R_3SiO(Ph)CHP(O)(OEt)_2}} \xrightarrow[\mathrm{MeOH}]{\mathrm{H^+}} \underset{\mathbf{3}}{\mathrm{HO(Ph)CHP(O)(OEt)_2}}$$

a: $R_3=Me_3$, **b**: $R_3=Et_3$,
c: $R_3=PhMe_2$, **d**: $R_3=Ph_3$.

The low yields of product **3** in the case of **1c** and **1d** may be ascribed to the steric hindrance on the silicon having phenyl groups. The formation of the products may be explained as resulting from the addition of triethyl phosphite to the carbonyl group to give betaine **4**, which may rearrange to triethoxymethylenephosphorane **5** by 1,2-anionic rearrangement of the silyl group.[3)] However, no Wittig-type products expected from the reaction of the methylenephosphorane with the starting silyl ketone were observed. An attempt to trap the methylenephosphorane with benzaldehyde was unsuccessful. Thus, the reaction of **1a**(5.76 mmol) with triethyl phosphite(60 mmol) in the presence of benzaldehyde(8.07 mmol) also led to the formation of **2a** in 65% yield under the above conditions.



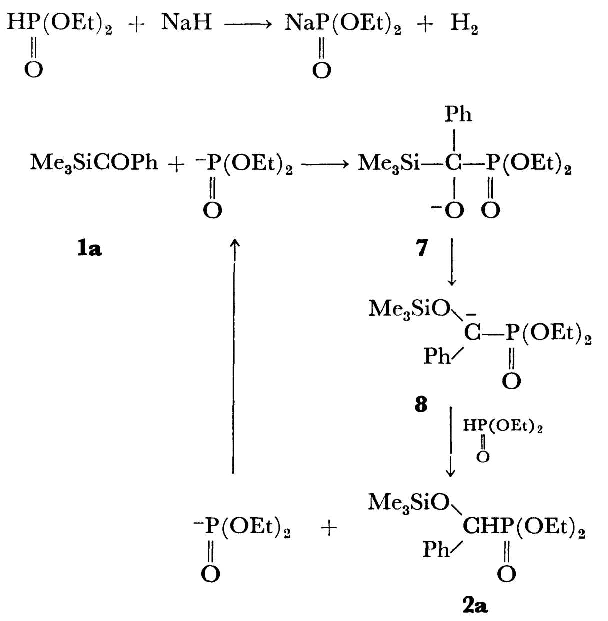
$$\underset{\mathbf{1}}{\mathrm{R_3SiCOPh}} + \mathrm{P(OEt)_3} \longrightarrow \underset{\mathbf{4}}{{}^-\mathrm{O{-}C(SiR_3)(Ph){-}\overset{+}{P}(OEt)_3}} \longrightarrow \underset{\mathbf{5}}{\mathrm{R_3SiO(Ph)C{=}P(OEt)_3}} \xrightarrow{-[\mathrm{CH_2{=}CH_2}]} \mathbf{2}$$

Scheme 1.

Methylenephosphorane **5** also decomposes to phosphonate **2** with cyclic elimination of ethylene under the reaction conditions (Scheme 1). Generation of ethylene was ascertained by trapping with a solution of bromine in 1,2-dibromoethane, but the yield was only 22% based on the silyl ketone **1a**.[4)]

Dimethyl α-trimethylsiloxybenzylphosphonate **6** was produced in the reaction of **1a** with an excess trimethyl phosphite under the above conditions, probably with elimination of methylene. However, **1a** did not react with triphenyl phosphite under the same conditions, probably because of the incapability of olefin elimination.

Extended studies on the 1,2-anionic rearrangement of the silyl group were carried out by the reaction of the silyl ketone with dialkyl sodiophosphonate. Diethyl sodiophosphonate reacts with the silyl ketone under mild conditions. Catalytic amount of sodium hydride (1.07 mmol) was added to the mixture of the silyl ketone **1a**(5.91 mmol) and diethyl phosphite(36 mmol) with stirring. An exothermic reaction took place with evolution of hydrogen, phosphonate **2a** being produced in 59% yield. However, **2a** was not formed in the absence of sodium hydride even if a mixture of **1a** and diethyl phosphite was heated at 100 °C for 16 h (Scheme 2). Adduct **7** can be formed initially by the addition of diethyl sodiophosphonate to the silyl ketone **1a** followed by rearrangement to anion **8** which may abstract hydrogen from diethyl phosphite to produce **2a** and diethyl sodiophosphonate. Diethyl sodiophosphonate produced again reacts with the silyl ketone as shown in Scheme 2. The phosphonate **6** was also obtained in 56% yield in the reaction of **1a** with dimethyl phosphite in the presence of catalytic sodium hydride.



Scheme 2.

Experimental

General. NMR data were obtained on a Varian A-60D spectrometer, IR spectra on a Hitachi EP-1-G3 spectrometer and mass spectra on a Nippon Denshi JMF-07 at 20 eV. All silyl ketones were prepared by the hydrolysis of the corresponding dibromides with silver acetate in water-acetone-ethanol system using the method of Brook.[5] Melting points are uncorrected.

*Reaction of **1a** with Triethyl Phosphite.* A mixture of **1a** (5.72 mmol) and triethyl phosphite(60 mmol) was heated at 80 °C for 12 h. After removal of excess triethyl phosphite *in vacuo*, **2a**[6] was obtained by vacuum distillation in 60% yield, bp 142 °C/2mmHg; IR(NaCl) 1250, 1070—1020 cm^{-1}; NMR(CCl_4) δ 0.08(s, 9H, SiMe), 1.20(t, J=7Hz, 6H, $OCCH_3$), 3.6—4.2(m, 4H, OCH_2), 4.80(d, J=14Hz, 1H, POCH), and 7.0—7.6(m, 5H, ArH). Phosphonate **2a** was desilylated in refluxing methanol. Crystallization from cyclohexane after removal of the methanol yielded **3** in 86% yield, mp 83 °C; IR(KBr) 3250, 1230, 1205, 1050, and 1030 cm^{-1}; Mass *m/e*: M^+ 244(rel. int. 39), 138(100), 111(56), and 106(28); NMR($CDCl_3$) δ 1.1—1.4(m, 6H, $OCCH_3$), 3.7—4.3(m, 4H, OCH_2), 4.51(br. s, 1H, OH), 5.01(d, J=12 Hz, 1H, POCH), and 7.2—7.7(m, 5H, ArH); Found: C, 53.93; H, 7.27%. Calcd for $C_{11}H_{17}O_4P$: C, 54.10; H, 7.02%.

*Reaction of Other Silyl Ketones, **1b**, **1c**, and **1d** with Triethyl Phosphite.* The reactions of **1b**(5.70 mmol), **1c**(6.12 mmol), and **1d**(5.22 mmol) with triethyl phosphite(60 mmol) were performed under the same conditions as described above. Desilylation in refluxing methanol containing one drop of hydrochloric acid yielded **3** in 72, 43, and 38% yields, respectively.

*Reaction of **1a** with Trimethyl Phosphite.* A mixture of **1a**(7.08 mmol) and trimethyl phosphite(80 mmol) was heated at 80 °C for 12 h. Phosphonate **6** was obtained in 50% yield, bp 128 °C/2 mmHg; IR(NaCl) 1260, 1060—1020 cm^{-1}; NMR(CCl_4) δ 0.08(s, 9H, SiMe), 3.45(d, J=10Hz, 6H, POMe), 4.75(d, J=14 Hz, 1H, POCH), and 7.2(m, 5H, ArH). Desilylation of **6** in refluxing methanol gave dimethyl α-hydroxybenzylphosphonate, mp 98—99 °C; IR(KBr) 3620, 1205, 1060, and 1020 cm^{-1}; Mass *m/e*: M^+ 216(12), 111(13), 110(100), 107(19), 106(36), 105(35), and 104(25); NMR($CDCl_3$) δ 3.67(d, J=11 Hz, 3H, POMe), 3.75(d, J=11 Hz, 3H, POMe), 5.07(d, J=11 Hz, 1H, POCH), 5.17(br. s, 1H, OH), and 7.2—7.7(m, 5H, ArH); Found: C, 50.49; H, 6.14%. Calcd for $C_9H_{13}O_4P$: C, 50.01; H, 6.06%.

*Reaction of **1a** with Diethyl Phosphite in the Presence of Sodium Hydride.* Sodium hydride(1.07 mmol) was added to a mixture of **1a**(5.91 mmol) and diethyl phosphite(36 mmol) with stirring. Exothermic reaction occurred with evolution of hydrogen. After the reaction ceased, the reaction mixture was distilled under reduced pressure to give **2a** in 59% yield.

*Reaction of **1a** with Dimethyl Phosphite in the Presence of Sodium Hydride.* Sodium hydride(1.60 mmol) was added to a mixture of **1a**(9.07 mmol) and dimethyl phosphite(45 mmol) with stirring. Phosphonate **6** was obtained in 56% yield.

References

1) W. Ando, A. Sekiguchi, and T. Migita, *Chem. Lett.*, **1976**, 779, and references cited therein.

2) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963); F. Ramirez, H. Yamanaka, and O. H. Basedow, *ibid.*, **83**, 173 (1961); F. Ramirez, S. B. Bhatia, and C. P. Smith, *J. Org. Chem.*, **31**, 4105 (1966).

3) A. G. Brook, *Acc. Chem. Res.*, **7**, 77 (1974).

4) 1,2-Dibromoethane was estimated with a NMR spectrometer.

5) A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957); A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, **82**, 5102 (1960).

6) A. Hashizume, M. Sekine, and T. Hata, 36th National Meeting of Chemical Society of Japan, Osaka, April 1977.