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SILYL PHOSPHITES V.
THE REACTIONS OF TRIS(TRIMETHYLSILYL) PHOSPHITE WITH CARBONYL COMPOUNDS

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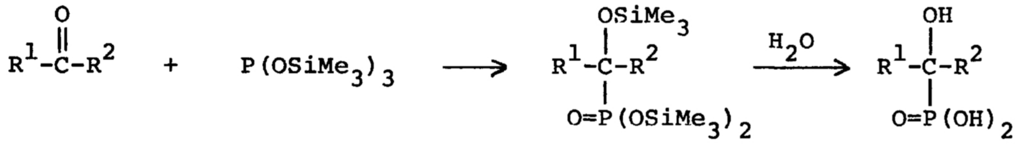
When tris(trimethylsilyl) phosphite (1) was treated with aldehydes, ketones, or α,β-unsaturated aldehydes at room temperature, the 1,2-adducts were obtained in high yields (75-94%). On the other hand, when α,β-unsaturated ketones or ethyl crotonate was used, the 1,4 -adducts were obtained in high yields (71-84%). The silylated products were smoothly hydrolyzed to the corresponding phosphonates in almost quantitative yields by addition of alcohol or water.

In order to extend the study on the reactions of tris(trimethylsilyl) phosphite (1)1), we have examined the reaction with the carbonyl compounds such as aldehydes, ketones, and α,β-unsaturated derivatives of aldehyde, ketone, and ester. The formation of "carbonyl adducts" by the use of phosphites is not unprecedented since trialkyl phosphites are known to react sluggishly with aldehydes, i.e., the reaction requires rather drastic conditions or much long reaction time and gives several addition compounds such as 1 : 1,2) 1 : 2,3) and 1 : 33a) in relatively low yields (20-60%). Pudovik and his coworkers reported that the 1 : 1 adducts were also obtained by the reaction of diethyl trimethylsilyl phosphite with carbonyl compounds.4)

We have found that the silyl phosphite (1) reacted smoothly with carbonyl compounds to give the 1 : 1 carbonyl addition products. According to this reaction, the 1 : 1 adducts were obtained as sole product in excellent yields and all the trimethylsilyl groups can be easily removed from the adducts by simple solvolysis using alcohols or water under very mild conditions. Therefore, the reaction by employing 1 provides a useful and very convenient method for the synthesis of α-hydroxyalkylphosphonic acids.

In the first place, the reactions of 1 with aldehydes and ketones are described: For example, when benzaldehyde (10 mmol) was allowed to react with one equiv. of 1 (10 mmol) in dry benzene (3 ml) at room temperature for 4 hr, the 1 : 1 adduct, bis(trimethylsilyl) α-trimethylsilyloxybenzylphosphonate (2; R^1= Ph, R^2= H) was obtained selectively in 88% yield. The structure of the adduct was confirmed by its NMR spectrum (CH-P: δ= 4.87 ppm, J = 14.4 Hz, COSiCH: δ= 0.20 ppm, POSiCH: δ= 0.33 ppm) and elemental analysis.



$$R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^2 + P(OSiMe_3)_3 \longrightarrow R^1\text{-}\underset{O=P(OSiMe_3)_2}{\underset{|}{\overset{OSiMe_3}{\overset{|}{C}}}}\text{-}R^2 \xrightarrow{H_2O} R^1\text{-}\underset{O=P(OH)_2}{\underset{|}{\overset{OH}{\overset{|}{C}}}}\text{-}R^2$$

(1) (2) (3)

Similarly, several aldehydes and ketones reacted with 1 to afford 2 in high yields.

When the adducts (2) prepared in the above experiments were treated with methanol, the corresponding α-hydroxylakylphosphonic acids (3) were obtained in almost quantitative yields as shown in Table 1.

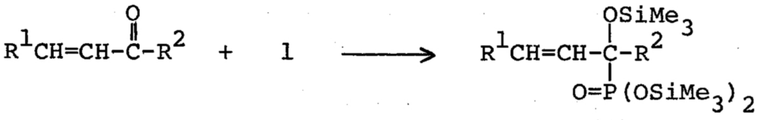
Table 1. Reaction of Aldehydes or Ketones with 1[a)]

R^1	R^2	Time (hr)	Yield of 2 (%)	Bp(°C/mmHg)	Yield of 3 (%)	Mp(°C)
Ph	H	4	88	126-130/2	98	179-180[b)]
$4\text{-}ClC_6H_4$	H	4	91	139-142/0.35	93	106-108[b)]
$4\text{-}MeOC_6H_4$	H	4	83	150-152/0.4	97	124-125[b)]
Et	H	2	85	91-95/0.2	quant.	159[b)]
iPr	H	4	82	106-108/0.8	quant.	166-168[b)]
Ph	CH_3	8	75	126-129/0.3	97	180-181[c)]
CH_3	CH_3	4	90	86-90/0.7	96	176-178[c)]

a) The reaction was carried out at room temperature except the case of acetone(under reflux). b) Free acid. c) Monoanilinium salt.

Next, the reactions of 1 with α,β-unsaturated carbonyl compounds were carried out. Kamai[5)] reported that the reaction of α,β-unsaturated aldehydes with triethyl phosphite at 120°C gave the addition products of the Michael's type, namely, the 1,4-addition products, in ca. 20% yields.

It was found that the reaction of 1 with α,β-unsaturated aldehydes afforded the 1,2-addition products (4) selectively in excellent yields as listed in Table 2.

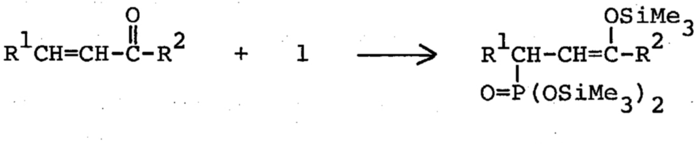


$$R^1CH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}R^2 + 1 \longrightarrow R^1CH{=}CH{-}\underset{O=P(OSiMe_3)_2}{\overset{OSiMe_3}{C}}{-}R^2$$

(4)

R^1= alkyl
R^2 = H

On the other hand, when α,β-unsaturated ketones and α,β-unsaturated ester were allowed to react with 1, the 1,4-addition products (5) were obtained exclusively as shown in Table 2.



$$R^1CH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}R^2 + 1 \longrightarrow R^1\underset{O=P(OSiMe_3)_2}{CH}{-}CH{=}\overset{OSiMe_3}{C}{-}R^2$$

(5)

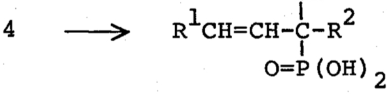
R^1= alkyl
R^2= alkyl or OC_2H_5

Table 2. Reaction of α,β-Unsaturated Aldehydes with 1[a)]

R^1	R^2	Reaction temp.	Reaction time (hr)	Yield of 4 (%)	Bp(°C/mmHg)	Yield of 5 (%)	Bp(°C/mmHg)
H	H	r.t.	4	94	97-103/1.1	—	—
CH_3	H	r.t.	4	89	93/0.23	—	—
Ph	H	r.t.	4	84	125-135/0.11	—	—
H	CH_3	r.t.	4	—	—	84	119-121/2.1
Ph	Ph	reflux	4	—	—	75	169-171/0.35
CH_3	OEt	reflux	7	—	—	45(71)[b)]	113-115/0.4

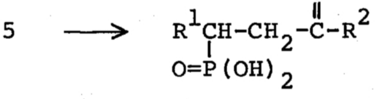
a) The reaction was carried out in dry benzene. b) Dioxane was used as solvent.

The 1,2- and 1,4-adducts (4 and 5) were converted successfully to monoanilinium or cyclohexylammonium salt (or free acid in some cases) of the corresponding alkylphosphonic acids (6 and 7) by treating with aqueous tetrahydrofuran followed by addition of aniline or cyclohexylamine in nearly quantitative yields as shown in Table 3.



$$4 \longrightarrow R^1CH{=}CH{-}\underset{O=P(OH)_2}{\overset{OH}{C}}{-}R^2$$

(6)



$$5 \longrightarrow R^1\underset{O=P(OH)_2}{CH}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}R^2$$

(7)

Table 3. Preparation of Phosphonates (6 and 7)

R^1	R^2	Yield of 6 (%)	Mp(°C)	Yield of 7 (%)	Mp(°C)
H	H	92	209-212[a]	—	—
CH_3	H	quant.	171-173[b]	—	—
Ph	H	quant.	107-109[c]	—	—
H	CH_3	—	—	92	197-200[a]
Ph	Ph	—	—	quant.	108-115[c]
CH_3	OEt	—	—	77	150-152[b]

a) Monocyclohexylammonium. b) Monoanilinium salt. c) Free acid.

It is noteworthy that the adducts mentioned above, viz., α-silyloxyalkylphosphonates, α-vinylphosphonates[6] and silyl enol ethers,[7] are valuable compounds since those might be applicable to the elongation of C-C bonds[8] and also to the synthesis of olefins. The extension of the study is now in progress.

References

1) (a) T.Hata and M.Sekine, J.Am.Chem.Soc.,96,7363(1974); Tetrahedron Lett.,3943 (1974); (b) M.Sekine and T.Hata, ibid., 1711(1975); (c) T.Hata, M.Sekine, and N.Kagawa, Chem.Lett.,635(1975); (d) T.Hata, M.Sekine, and N.Ishikawa, ibid., 645(1975); (e) T.Hata, I.Yamamoto, and J.Sekine, ibid., 601(1976).
2) V.S.Abramov, Kokl.Akad.Nauk SSSR,95,991(1954); Chem.Abst.,49,6084(1955).
3) (a) F.Ramirez, A.V.Patwardhan, and S.R.Heller, J.Am.Chem.Soc.,86,514(1964); (b) V.A.Ginsburg and A.Y.Yakubovich, Zh.Obshch.Khim.,30,3979(1960); Chem. Abstr.,55,22099(1961).
4) (a) I.V.Konovalova, L.A.Burnaeva, N.Sh.Saifullina, and A.N.Pudovik, Zh.Obshch. Khim.,46,18(1976); (b) Z.S.Novikova, S.N.Mashoshina, T.A.Sapozhnikova, and I.F. Lutsenko, ibid.,41,2662(1971); (b) Z.S.Novikova and I.F.Lutsenko, ibid.,40,2129 (1970); (c) L.V.Nesterov, N.E.Krepysheva, R.A.Sabirova, and G.N.Romanova, ibid., 41,2449(1971).
5) G.Kamai and V.A.Kukhtin, Zh.Obshch.Khim.,27,2376(1956); Chem.Abstr.,52,7127(1958).
6) (a) L.Horner, H.Hoffmann, and H.G.Wippel, Chem.Ber.,91,61(1958); (b) U. Schöllkopf, Angew.Chem.,71,260(1959); (c) W.S.Wadsworth and W.D.Emmons, J.Am.Chem. Soc.,83,1733(1961).
7) (a) G.Stork and P.F.Hudrlik, J.Am.Chem.Soc.,90,4462,4464(1968); (b) H.O.House, L.J.Czuba, J.Gall, H.D.Olmstead, J.Org.Chem.,34,2324(1969); (c) S.Murai, Y.Kuroki, T.Aya, N.Sonoda, and S.Tsutsumi, J.Chem.Soc.,Chem.Commun.,741(1972); (d) G.M.Rubottom, M.I.Lopez, J.Org.Chem.,38,2097(1973); (e) T.Mukaiyama, K.Narasaka, and K.Banno, Chem.Lett.,1011(1973); (f) T.Mukaiyama and M.Hayashi, ibid.,15,(1974); (g) K.Saigo, M.Osaki, and T.Mukaiyama, ibid.,163(1976); (h) K.Banno and T.Mukaiyama, ibid.,279(1976); (i) I.Kuwajima and E.Nakamura, J.Am.Chem.Soc.,97,3257(1975); (j) E.Nakamura, M.Shimizu, and I.Kuwajima, Tetrahedron Lett.,1699(1976); (k) Y.Ito, T.Konoike, and T.Saeguwa, J.Am.Chem.Soc., 97,649(1975).
8) (a) D.A.Evans and L.K.Truesdale, Tetrahedron Lett.,4929(1973); (b) D.A.Evans, K.G.Grimm, and L.K.Truesdale, J.Am.Chem.Soc.,97,3229(1975).

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