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NEW SYNTHESES OF ALLYLSILANES AND VINYLSILANES BY MEANS OF $PhMe_2Si\text{-}AlEt_2$

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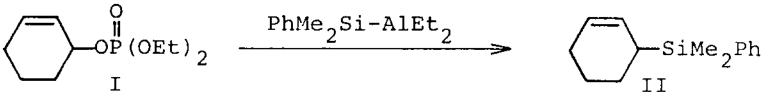
Abstract: The reaction of allylic phosphates with the title organoaluminium reagent ($PhMe_2Si\text{-}AlEt_2$) provides allylsilanes in good yields. Cross coupling of enol phosphates with $PhMe_2Si\text{-}Mtl$ (Mtl = $AlEt_2$ or MgMe) produces vinylsilanes regio- and stereoselectively in the presence of Pd(0) catalysts.

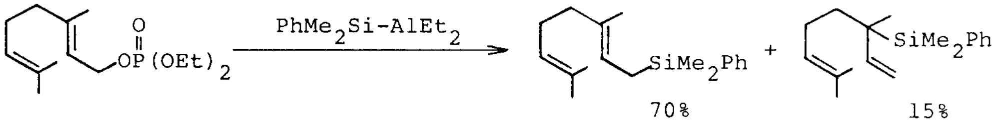
Much attention has been paid to the chemistry of allylsilanes and vinylsilanes as useful intermediates for organic synthesis.[1] Despite the availability of many methods for their synthesis, there still exists a need for new selective and convenient procedures. Trialkylaluminium compounds react with allylic phosphates or enol phosphates to give the corresponding alkylated products.[2,3] We report here further extension of this approach to the syntheses of these organosilicon compounds. Treatment of allylic phosphates or enol phosphates with organoaluminium reagent, $PhMe_2Si\text{-}AlEt_2$, provides allylsilanes or vinylsilanes, respectively.

A hexane solution of diethylaluminium chloride (1.0 *M*, 1.5 ml, 1.5 mmol) was added to a solution of $PhMe_2SiLi$[4] (1.5 mmol) in tetrahydrofuran (THF, 5 ml) at 0°C under argon atmosphere. After being stirred for 10 min, a solution of allylic phosphate I (0.24 g, 1.0 mmol) in THF (2 ml) was added and the whole was stirred for 1 h at 25°C. Workup (ether, 1*N* HCl) and purification by silica gel column chromatography gave allylic silane II[5] (0.17 g) in 79% yield.



I

II



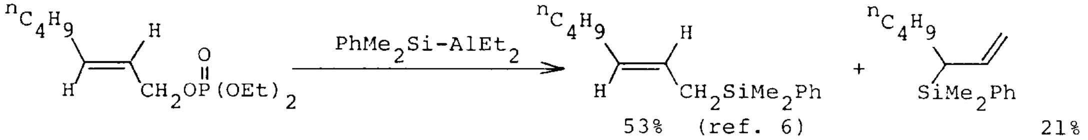
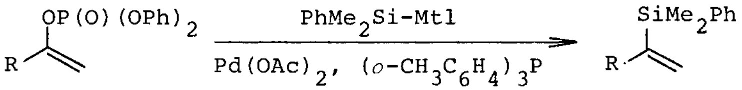
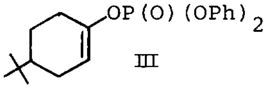
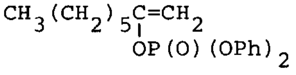
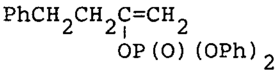
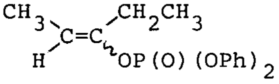
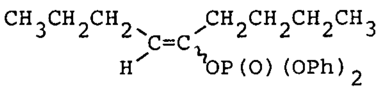


Table 1. Palladium catalyzed coupling reaction between enol phosphates and dimethylphenylsilylmetal reagents[a]



Enol Phosphate[b]	Reagent	Reaction Time (h)	Yield[c] of Vinylsilane (%)
 III	$PhMe_2Si-AlEt_2$	1.5	66
	$PhMe_2Si-MgMe$	1.0	74, 75[d,e]
 $CH_3(CH_2)_5C(OP(O)(OPh)_2)=CH_2$	$PhMe_2Si-AlEt_2$	1.0	55
	$PhMe_2Si-MgMe$	0.5	74
 $PhCH_2CH_2C(OP(O)(OPh)_2)=CH_2$	$PhMe_2Si-MgMe$	1.0	56[d,e]
 $CH_3CH=C(CH_2CH_3)OP(O)(OPh)_2$	$PhMe_2Si-MgMe$	3.0	65[d,e]
 $CH_3CH_2CH_2CH=C(CH_2CH_2CH_2CH_3)OP(O)(OPh)_2$	$PhMe_2Si-AlEt_2$	3.0	74
	$PhMe_2Si-MgMe$	1.5	72[d]

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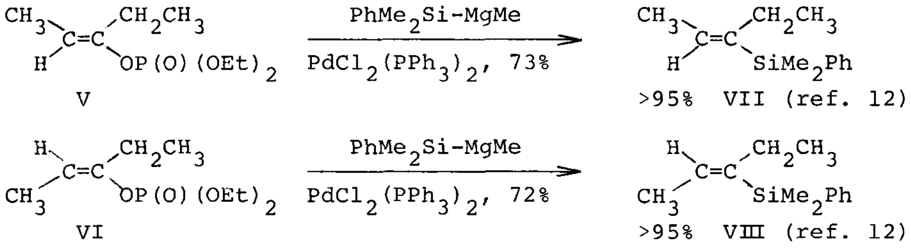
[a] Reactions were performed on 2.0 mmol scale at 25°C. [b] Prepared by the phosphorylation of the corresponding lithium enolates with diphenyl chlorophosphate. [c] Yields represent isolated, purified products. [d] THF was used as solvent instead of hexane. [e] $PdCl_2(PPh)_3$ (10 mol%) was used instead of $Pd(OAc)_2-(o-CH_3C_6H_4)_3P$ combination.

In the case of unsymmetrical allylic phosphates, mixtures of unrearranged, α attack products (S_N2) and rearranged, γ attack products (S_N2') were obtained. For instance, the reaction of diethyl geranyl phosphate with the organoaluminium reagent gave dimethylgeranylphenylsilane and the rearranged one in an 88:12 ratio.[7]

As shown in Table 1, vinylsilanes were obtained effectively by means of $PhMe_2Si-Mtl$ (Mtl = $AlEt_2$ or MgMe) only in the presence of palladium(0) catalyst. Dimethylphenylsilyl group is introduced selectively in preference to ethyl or methyl group, neither ethylated nor methylated products being detected. Organomagnesium compound was as effective as organoaluminium reagent. Meanwhile, $PhMe_2SiLi$ turned out to be too much nucleophilic to attack phosphorus atom of the esters and generated the enolates which gave the original ketones upon workup.[8]

In the absence of the metal phosphine catalyst the reaction did not proceed at all. Catalysts such as $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ were equally active, while $NiCl_2(PPh_3)_2$ and $PtCl_2(PPh_3)_2$ were inactive. The success of the procedure heavily depends on the nature of phosphine ligand of palladium. The reaction between enol phosphate III and $PhMe_2Si\text{-}AlEt_2$ was examined in the presence of palladium(II) acetate and various phosphine ligand,[9] phosphine, isolated yield of 1-silylated 4-*t*-butylcyclohexene IV[10] being $Ph_2PCH_2CH_2PPh_2$, 0%; $^nBu_3P$, 23%; Ph_3P, 62%; $(o\text{-}CH_3C_6H_4)_3P$, 66%.

High stereospecificity of the reaction was demonstrated in the transformation of (*E*) and (*Z*) phosphate (V and VI)[11] to silylated alkenes with $PhMe_2Si\text{-}MgMe$. All steps seem to proceed with retention of configuration similar to the reaction of enol phosphates with trialkylaluminium reagents.[3]



V

>95% VII (ref. 12)

VI

>95% VIII (ref. 12)

Palladium(II) acetate (68 mg, 0.2 mmol) and $(o\text{-}CH_3C_6H_4)_3P$ (0.24 g, 0.8 mmol) were combined in THF (10 ml). A solution of $PhMe_2Si\text{-}MgMe$ derived from $PhMe_2SiLi$ (6.0 mmol) and MeMgI (or Et_2AlCl) (6.0 mmol) in THF (10 ml) was added and the resulting mixture was stirred for 10 min at 0°C. Replacing THF with hexane was effected by evaporation of THF under reduced pressure, introduction of argon and addition of hexane (15 ml). Then enol phosphate III (0.76 g, 2.0 mmol) was added and the whole was stirred for another 1 h at 25°C Purification by preparative thin layer chromatography on silica gel gave silylated alkene IV[10] (0.40 g, 74% yield) as a colourless oil.[13]

References and Notes

1. For recent reviews, T. H. Chan and I. Fleming, *Synthesis*, 1979, 761; P. Magnus, *Aldrichim. Acta*, 13, 43 (1980).
2. S. Hashimoto, Y. Kitagawa, S. Iemura, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, 1976, 2615; A. Itoh, S. Ozawa, K. Oshima, S. Sasaki, H. Yamamoto, T. Hiyama, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 53, 2357 (1980).
3. K. Takai, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 21, 2531 (1980); M. Sato, K. Takai, K. Oshima, and H. Nozaki, *ibid.*, 22, 1609 (1981).

4. H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 607 (1958).
5. Bp 73-78°C (2 Torr, bath temp); IR (neat) 2950, 1660, 1431, 1252, 1112, 827, 802 cm^{-1}; NMR (CCl_4) δ0.27 (s, 6H), 1.05-2.03 (m, 7H), 5.51 (bs, 2H), 7.09-7.50 (m, 5H); exact mass spectrum *m/e* 216.1313. Calcd for $C_{14}H_{20}Si$: M, 216.1333.
6. Bp 72-74°C (2 Torr, bath temp); IR (neat) 2950, 1250, 825 cm^{-1}; NMR (CCl_4) δ0.27 (s, 6H), 0.69-1.06 (m, 3H), 1.06-1.48 (m, 4H), 1.57 (bd, 2H, *J* = 6.0 Hz), 1.91 (m, 2H), 5.20 (dt, 2H, *J* = 6.0 and 15.0 Hz), 7.12-7.48 (m, 5H). Found: C, 76.92; H, 10.32%. Calcd for $C_{15}H_{24}Si$: C, 76.99; H, 10.15%.
7. The reaction of Me_3SiLi with isoprenyl and geranyl chlorides leading to allylic silanes has been briefly mentioned. E. Negishi, F-T. Luo, and C. L. Rand, *Tetrahedron Lett.*, **23**, 27 (1982).
8. Yields of the desired vinylsilanes were less than 10%.
9. $Pd(OAc)_2$ (0.1 mmol) and phosphine (0.4 mmol) were employed per 1.0 mmol of enol phosphate III. In the case of $Ph_2PCH_2CH_2PPh_2$, the molar ratio of $Pd(OAc)_2$ and phosphine was 1:2.
10. Bp 93-97°C (2 Torr, bath temp); IR (neat) 2940, 1615, 1245, 817, 800 cm^{-1}; NMR (CCl_4) δ0.30 (s, 6H), 0.80 (s, 9H), 1.00-2.67 (m, 7H), 5.97 (m, 1H), 7.07-7.47 (m, 5H). Found: C, 79.08; H, 10.35%. Calcd for $C_{18}H_{28}Si$: C, 79.34; H, 10.36%.
11. Phosphorylation of lithium enolate derived from 3-pentanone by diethyl chlorophosphate in THF gave a mixture of V and VI (V/VI = 2.7/1). The addition of HMPA to the lithium enolate prior to the phosphorylation provided VI as a major product (V/VI = 5/95). The pure isomers were obtained by careful separation by silica gel column chromatography. R. E. Ireland and G. Pfister, *Tetrahedron Lett.*, **1969**, 2145; R. E. Ireland, R. H. Mueller, and A. K. Willard, *J. Am. Chem. Soc.*, **98**, 2868 (1976).
12. The *E* isomer VII: Bp 72-75°C (2 Torr, bath temp), IR (neat) 2945, 1608, 1420, 1245, 1100, 815, 795 cm^{-1}; NMR (CCl_4) δ0.32 (s, 6H), 0.83 (t, 3H, *J* = 7.5 Hz), 1.70 (d, 3H, *J* = 6.3 Hz), 2.11 (q, 2H, *J* = 7.5 Hz), 5.80 (q, 1H, *J* = 6.3 Hz), 7.08-7.52 (m, 5H). Found: C, 76.55; H, 10.00%. Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86%. The *Z* isomer VIII: NMR (CCl_4) δ0.33 (s, 6H), 0.97 (t, 3H, *J* = 7.5 Hz), 1.56 (d, 3H, *J* = 6.7 Hz), 2.06 (q, 2H, *J* = 7.5 Hz), 6.08 (q, 1H, *J* = 6.7 Hz), 7.10-7.50 (m, 5H).
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