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Preparation of (Triphenylsilyl)allyl Anion and (Triphenylgermyl)allyl Anion from 1-Propenyltriphenylsilane and 1-Propenyltriphenylgermane and Their Reactions with Electrophiles

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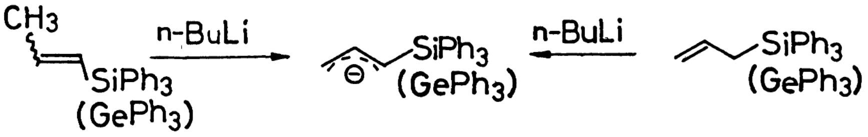
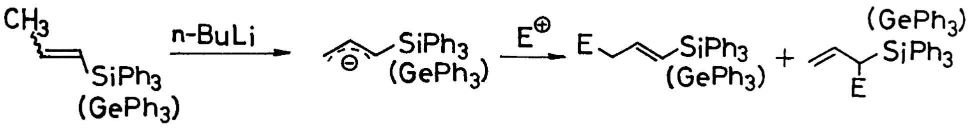
Treatment of 1-propenyltriphenylsilane with n-BuLi in THF-HMPA provides (triphenylsilyl)allyl anion which is identical with an anion derived from 2-propenyltriphenylsilane and base. Generation of (triphenylgermyl)allyl anion is also described. Addition of alkyl halides or carbonyl compounds to these anions gives the corresponding adducts regioselectively.

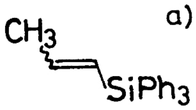
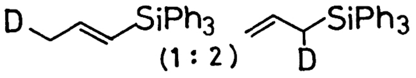
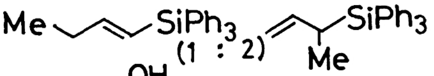
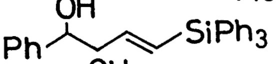
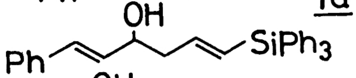
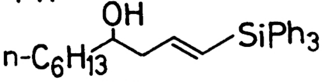
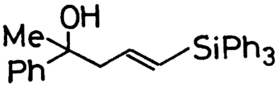
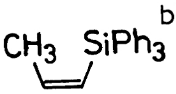
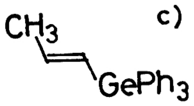
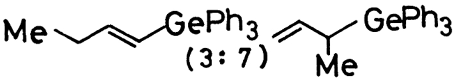
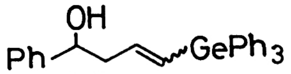
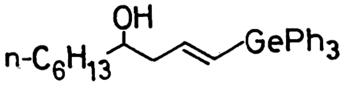
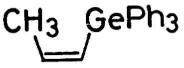
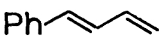
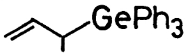
1-Alkenylsilanes and 2-alkenylsilanes are recognized to be versatile synthetic intermediates and their use for the organic synthesis is widely studied.1) Allyltrialkylsilane is conveniently deprotonated by treatment with bases such as t-BuLi, n-BuLi, or t-BuOK/n-BuLi to give (trialkylsilyl)allyl anion which reacts with various electrophiles.2) On the other hand, the reaction of 1-alkenylsilanes with bases has been hardly investigated.3) Here we wish to report that treatment of 1-propenyltriphenylsilane with n-BuLi in THF-HMPA (10:1) gives the title α-silyl carbanion which reacts with electrophiles such as alkyl halides and carbonyl compounds to afford the corresponding adducts.



Butyllithium (1.5 M hexane solution, 1 M = 1 mol dm^{-3}, 0.8 ml, 1.2 mmol) was added to a solution of 1-propenyltriphenylsilane (0.30 g, 1.0 mmol) in THF (8 ml)-HMPA (0.8 ml) at -78 °C under an argon atmosphere. The color of the solution turned dark red immediately. Stirring was continued at this temperature for 30 min, then a solution of benzaldehyde (0.11 g, 1.0 mmol) in THF (2 ml) was added dropwise. The resulting mixture was stirred at -78 °C for 30 min and allowed to warm to 0 °C. Workup (AcOEt, 1.0 M HCl) followed by purification by thin layer chromatography on silica gel gave (E)-1-phenyl-4-triphenylsilyl-3-buten-1-ol (0.37 g, 90% yield).

Table 1. Reaction of (triphenylsilyl)allyl anion and (triphenylgermyl)allyl anion with various electrophiles

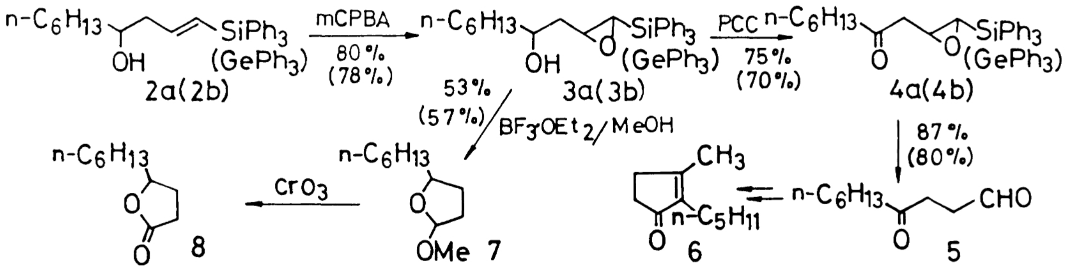


Run	Starting material	Additive	E^+	Y/%	Product
1	 a)		D_2O	78	 (1 : 2)
2			MeI	92	 (1 : 2)
3			PhCHO	90	 1a
4			PhCH=CHCHO	62	
5		MeMgI	$n-C_6H_{13}CHO$	72	 2a
6		MeMgI	$PhCOCH_3$	55	
7		Et_2Zn	PhCHO	74	
8	 b)		PhCHO	70	1a
9	 c)		MeI	75	 (3 : 7)
10			PhCHO	69	 1b[d)]
11			$n-C_6H_{13}CHO$	65	 2b
12			PhCHO	70	1b[d)]
13			$n-C_6H_{13}CHO$	63	2b
14		Et_2Zn	PhCHO	72	  1b[d)] (11 : 75 : 14)
15			$n-C_6H_{13}CHO$	70	2b

a) Prepared from $CH_3CH=CHMgBr$ and Ph_3SiCl. E/Z = 6/4. b) Prepared by reduction of $CH_3C≡CSiPh_3$ with $i-Bu_2AlH$. c) Prepared by hydrogermylation of propyne. d) E/Z = 4/1. e) see Ref. 4.

The representative results containing the reaction of (triphenylgermyl)allyl anion are summarized in Table 1. Several comments are worth noting. (1) Stereochemistry of the starting 1-propenyltriphenylsilane did not affect the reaction. Thus, both (E)-1-propenyltriphenylsilane and (Z)-isomer were easily deprotonated with n-BuLi to give the same allyl anion which is identical with the carbanion derived from 2-propenyltriphenylsilane.$^{5)}$ (2) The reaction does not seem to vary significantly with the change of the substitution on silicon. For instance, an addition of n-BuLi to 1-propenyltriethylsilane gave an allyl anion which afforded the corresponding adducts, (E)-1-phenyl-4-triethylsilyl-3-buten-1-ol in 65% yield upon treatment with benzaldehyde. (3) (Triphenylgermyl)allyl anion was produced from 1-propenyltriphenylgermane in similar fashion and easily reacted with electrophiles such as MeI and PhCHO. The same (triphenylgermyl)allyl anion was obtained on treatment of allyltriphenylgermane with n-BuLi (Run 15 in Table 1). (4) Regioselectivity of the reaction depends on the nature of the electrophile and counterion of the anion. Alkylation of allyllithium with methyl iodide gave a mixture of α- and γ-adducts, whereas the reaction with carbonyl compounds provided γ-adducts exclusively. Change of the counterion to zinc increased the α-selectivity in the reaction with carbonyl compounds. (5) The double bonds of the produced alkenylsilanes or alkenylgermanes were exclusively trans$^{6)}$ from ^{1}H NMR studies (J = ca. 19 Hz).

The adduct **2a** or **2b** was epoxidized to provide the corresponding α,β-epoxysilane **3a** or epoxygermane **3b**.$^{7)}$ Oxidation with PCC followed by treatment with (1) concd H_2SO_4 in MeOH and (2) aq. $CH_3COOH^{8)}$ gave δ-ketoaldehyde **5** which was converted into dihydrojasmone according to the reported procedure.$^{9)}$ Treatment of epoxide **3a** or **3b** with $BF_3 \cdot OEt_2$ in MeOH$^{2c)}$ gave lactol **7**.$^{10,11)}$



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Corriu, C. Guerin, and J. M'boula, Tetrahedron Lett., 22, 2985 (1981); e) Y. Yamamoto, Y. Saito, K. Maruyama, ibid., 23, 4597 (1982); f) J. M. Muchowski, R. Naef, and M. L. Maddox, ibid., 26, 5375 (1985); g) K. Koumaglo and T. H. Chan, ibid., 25, 717 (1984); h) K. Tamao, E. Nakajo, and Y. Ito, J. Org. Chem., 52, 957 (1987).

3) The addition of Grignard reagents or organolithium compounds to the C-C double bond of vinylsilanes has been known to form a carbanion adjacent to silicon. C. F. Cason, H. G. Brooks, J. Am. Chem. Soc., 74, 4582 (1952); G. R. Buell, R. Corriu, C. Guerin, and L. Spialter, ibid., 92., 7424 (1970); K. Tamao, R. Kanatani, and M. Kumada, Tetrahedron Lett., 25, 1905 (1984).

4) (E)-1-Triphenylgermyl-1-decen-4-ol (**2b**): bp 190 °C (bath temp, 2.0 Torr); IR (neat) 3400, 3080, 2940, 2860, 1620, 1490, 1440, 1100, 1000, 740, 700 cm^{-1}; H-NMR ($CDCl_3$, 200 MHz) δ 0.91 (bt, 3H), 1.23-1.55 (m, 10H), 1.60 (bs, 1H), 2.38 (ddd, J = 14.0, 7.5, 6.5 Hz, 1H), 2.51 (ddd, J = 14.0, 6.5, 5.0 Hz, 1H), 3.65-3.83 (m, 1H), 6.16 (dt, J = 18.5, 6.5 Hz, 1H), 6.40 (d, J = 18.5 Hz, 1H), 7.38-7.68 (m, 15H). Found: C, 73.54; H, 7.57%. Calcd for $C_{28}H_{34}OGe$: C, 73.24; H, 7.46%.

5) Three allylic anions derived from (E)-1-propenyltriphenylsilane, (Z)-isomer, and allyltriphenylsilane gave exactly same products upon treatment with alkyl halides or carbonyl compounds.

6) The reaction of (triphenylgermyl)allyl anion with PhCHO was an exception and gave a mixture of (E)- and (Z)-1-phenyl-4-triphenylgermyl-3-buten-1-ol (E:Z = 4:1).

7) **3b**: bp 190 °C (bath temp, 2.0 Torr); IR (neat) 3450, 3050, 2940, 2860, 1740, 1490, 1440, 1250, 1100, 870, 740, 700 cm^{-1}; H-NMR ($CDCl_3$, 200 MHz) δ 0.90 (bt, 3H), 1.23-2.13 (m, 13H), 3.03 (d, J = 3.0 Hz, 0.5H), 3.05-3.18 (m, 1H), 3.19 (d. J = 3.0 Hz, 0.5H), 3.75-3.95 (m, 1H), 7.35-7.65 (m, 15H). Found: C, 71.18; H, 6.79%. Calcd for $C_{28}H_{34}O_2Ge$: C, 71.08; H, 6.82%.

8) G. Stork and E. Colvin, J. Am. Chem. Soc., 93, 2080 (1971).

9) K. Oshima, H. Yamamoto, and H. Nozaki, J. Am. Chem. Soc., 95, 4446 (1973).

10) Treatment of (Z)-1-triphenylsilyl-1-dodecene or (Z)-1-triphenylgermyl-1-dodecene with n-BuLi followed by the addition of PhCHO gave the corresponding γ-adduct in only 15% or 18% yield along with the recovered starting material (60-70%) under the same reaction conditions.

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