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SILYLMANGANATION OF 1,3-DIENES. A FACILE SYNTHESIS OF FUNCTIONALIZED VINYLSILANES

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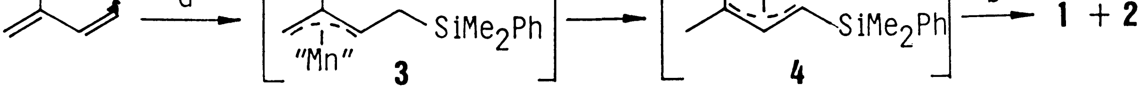
Treatment of 1,3-dienes with (R$_3$Si)$_3$MnMgMe provides silylated allylmanganese compounds which add to carbonyl moiety with high regioselectivity.

The manganese reagent (R$_3$Si)$_3$MnMgMe derived from R$_3$SiMgMe and MnCl$_2$ reacted with terminal acetylenes to give 1,2-disilylated 1-alkenes.$^{1)}$ In further extension of this new reactions, we have examined the reaction of 1,3-dienes with (R$_3$Si)$_3$MnMgMe to observe the selective formation of vinylsilanes after quenching with carbonyl compounds.

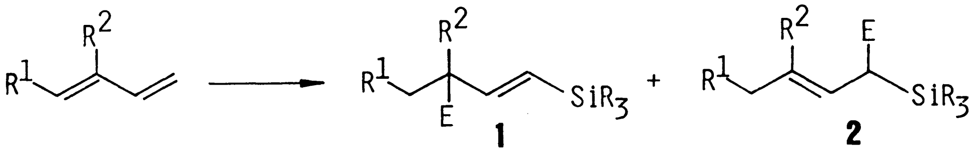
Treatment of isoprene with the reagent, (PhMe$_2$Si)$_3$MnMgMe gave a mixture of (E)-3-deuterio-1-dimethylphenylsilyl-3-methyl-1-butene (**1**) (E = D) and 1-deuterio-1-dimethylphenylsilyl-3-methyl-2-butene (**2**) (E = D) (1:5) after quenching with D$_2$O.$^{2)}$ Quenching with MeI gave a mixture of (E)-3,3-dimethyl-1-dimethylphenylsilyl-1-butene **1** (E = Me) and 4-dimethylphenylsilyl-2-methyl-2-pentene **2** (E = Me) (1:2) in 90% combined yield. In contrast, addition of aldehyde or ketone to the silylated allylmanganese intermediate gave (E)-vinylsilane **1** as a single product.

We are tempted to assume the following reaction mechanism. The reagent, (PhMe$_2$Si)$_3$MnMgMe adds to isoprene in 1,2-fashion (or 1,4-fashion) to give allylmanganese compound **3**. Reductive elimination of Mn-H and successive readdition produce isomeric allylmanganese compound **4** which reacts with some electrophiles.$^{3)}$ Alicyclic dienes such as cyclopentadiene and 1,3-cyclooctadiene were reluctant to react. The reagent, PhMe$_2$SiLi or PhMe$_2$SiMgMe did not add to isoprene and the manganese atom played a critical role in the reaction. The addition of MeMgI was essential for the complete isomerization of **3** into **4**. Treatment of isoprene with (PhMe$_2$Si)$_3$MnLi derived from PhMe$_2$SiLi and MnCl$_2$ gave 4-dimethylphenylsilyl-2-methyl-1-butene (30%) along with **1** (E = H, 10%) and **2** (E = H, 39%) after quenching with water.



a: (Me$_2$PhSi)$_3$MnMgMe "Mn": (Me$_2$PhSi)$_2$MnMgMe b: Electrophile

Table 1. Silylmanganation of 1,3-dienes with $(R_3Si)_3MnMgMe$



Entry	Diene		Reagent	Electrophile	Product Yield/%	
	R^1	R^2			1	2
1	H	H	$(PhMe_2Si)_3MnMgMe$	D_2O	44	25
2				MeI	11	69
3				PhCHO	70a)	0
4				Me_2CO	95	0
5	H	Me	$(PhMe_2Si)_3MnMgMe$	D_2O	13	65
6				MeI	30	60
7				BuCHO	85b)	0
8				PhCHO	78	0
9				PhCH=CHCHO	74c)	0
10			$(Me_3Si)_3MnMgMe$	$CH_3CH=CHCHO$	75c)	0
11				Me_2CO	76	0
12	Me	H	$(PhMe_2Si)_3MnMgMe$	D_2O	46	46
13				PhCHO	68a)	0

a) Erythro/threo = 1/1. b) See Ref. 4. c) Only 1,2-adducts were obtained.

Typical procedure is as follows. An ethereal solution of MeMgI (1.1 mol dm^{-3}, 4.1 cm^3, 4.5 mmol) was added to a THF solution of $PhMe_2SiLi$ (0.75 mol dm^{-3}, 6.0 cm^3, 4.5 mmol) and the resulting mixture was stirred at 0 °C for 15 min. A THF solution of Li_2MnCl_4 (1.0 mol dm^{-3}, 1.5 cm^3, 1.5 mmol) was added, and stirred for another 15 min. Isoprene (0.15 cm^3, 1.5 mmol) was added to the dark brown solution. After being stirred for 15 min, valeraldehyde (0.13 g, 1.5 mmol) was added and stirring was continued for 1 h. Extractive workup (1 mol dm^{-3} HCl and EtOAc) followed by purification by preparative tlc on silica-gel gave vinylsilane **1** (E = BuCHOH, 0.37 g) in 85% yield.

References

1) J. Hibino, S. Nakatsukasa, K. Fugami, S. Matsubara, K. Oshima, and H. Nozaki, J. Am. Chem. Soc., 107, 6416 (1985).

2) Silyltitanation of isoprene has been reported to give 4-dimethylphenylsilyl-2-methyl-1-butene. K. Tamao, M. Akita, R. Kanatani, N. Ishida, and M. Kumada, J. Organomet. Chem., 226, C9 (1982).

3) Grignard type carbonyl addition of allyl unit with $MnCl_2$-$LiAlH_4$ reagent has been reported. T. Hiyama, M. Sawahata, and M. Obayashi, Chem. Lett., 1983, 1237; T. Hiyama, M. Obayashi, and A. Nakamura, Organometallics, 1, 1249 (1982).

4) Bp 150 °C (1.0 Torr, bath temp); IR (neat) 3450, 2950, 1605, 1245, 1110, 840 cm^{-1}; NMR (CCl_4) δ 0.3 (s, 6H), 0.6-1.6 (m, 9H), 0.95 (s, 6H), 3.15 (t, J = 9 Hz, 1H), 5.70 (d, J = 17 Hz, 1H), 6.05 (d, J = 17 Hz, 1H), 7.1-7.4 (m, 5H). Found: C, 74.17; H, 10.60%. Calcd for $C_{18}H_{30}OSi$: C, 74.42; H, 10.41%.

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