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

Keigo FUGAMI, Shigeki NAKATSUKASA, Koichiro OSHIMA,<sup>\*</sup> Kiitiro UTIMOTO, and Hitosi NOZAKI Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

Treatment of 1,3-dienes with  $(R_3Si)_3MnMgMe$  provides silylated allylmanganese compounds which add to carbonyl moiety with high regioselectivity.

The manganese reagent  $(R_3Si)_3MnMgMe$  derived from  $R_3SiMgMe$  and  $MnCl_2$  reacted with terminal acetylenes to give 1,2-disilylated 1-alkenes.<sup>1</sup>) In further extension of this new reactions, we have examined the reaction of 1,3-dienes with  $(R_3Si)_3MnMgMe$  to observe the selective formation of vinylsilanes after quenching with carbonyl compounds.

Treatment of isoprene with the reagent,  $(PhMe_2Si)_3MnMgMe$  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  $D_2O.^{(2)}$  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)-vinyl-silane 1 as a single product.

We are tempted to assume the following reaction mechanism. The reagent,  $(PhMe_2Si)_3MnMgMe$  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.<sup>3)</sup> Alicyclic dienes such as cyclopentadiene and 1,3-cyclooctadiene were reluctant to react. The reagent,  $PhMe_2SiLi$  or  $PhMe_2SiMgMe$  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  $(PhMe_2Si)_3MnLi$  derived from  $PhMe_2SiLi$  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<sub>2</sub>PhSi)<sub>3</sub>MnMgMe "Mn": (Me<sub>2</sub>PhSi)<sub>2</sub>MnMgMe b: Electrophile

R	$\mathbb{R}^2$	// -	$ R^1 \xrightarrow{R^2}_{E}$	$rac{1}{siR_3} + R^1$		iR <sub>3</sub>
Entry	Di R <sup>1</sup>	ene R <sup>2</sup>	Reagent	Electrophile	Product 1	Yield/% 2
1 2 3 4	Н	Н	(PhMe <sub>2</sub> Si) <sub>3</sub> MnMgMe	D <sub>2</sub> O MeI PhCHO Me <sub>2</sub> CO	44 11 70 <sup>a</sup> ) 95	25 69 0 0
5 6 7 8 9 10	Н	Me	(PhMe <sub>2</sub> Si) <sub>3</sub> MnMgMe (Me <sub>3</sub> Si) <sub>3</sub> MnMgMe	D <sub>2</sub> O MeI BuCHO PhCHO PhCH=CHCHO CH <sub>3</sub> CH=CHCHO MecCO	13 30 85b) 78 74 <sup>c</sup> ) 75 <sup>c</sup> ) 76	65 60 0 0 0 0
12 13	Ме	н	(PhMe <sub>2</sub> Si) <sub>3</sub> MnMgMe	D <sub>2</sub> O PhCHO	46 68 <sup>a</sup> )	46 0

Table 1. Silylmanganation of 1,3-dienes with (R<sub>3</sub>Si)<sub>3</sub>MnMgMe

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<sup>-3</sup>, 4.1 cm<sup>3</sup>, 4.5 mmol) was added to a THF solution of PhMe<sub>2</sub>SiLi (0.75 mol dm<sup>-3</sup>, 6.0 cm<sup>3</sup>, 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<sup>-3</sup>, 1.5 cm<sup>3</sup>, 1.5 mmol) was added, and stirred for another 15 min. Isoprene (0.15 cm<sup>3</sup>, 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<sup>-3</sup> HCl and EtOAc) followed by purification by preparative tlc on silica-gel gave vinylsilane 1 (E = BuCHOH, 0.37 g) in 85% yield.

References

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- Grignard type carbonyl addition of allyl unit with MnCl<sub>2</sub>-LiAlH<sub>4</sub> reagent has been reported. T. Hiyama, M. Sawahata, and M. Obayashi, Chem. Lett., <u>1983</u>, 1237; T. Hiyama, M. Obayashi, and A. Nakamura, Organometallics, <u>1</u>, 1249 (1982).
- 4) Bp 150 °C (1.0 Torr, bath temp); IR (neat) 3450, 2950, 1605, 1245, 1110, 840 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) 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<sub>18</sub>H<sub>30</sub>OSi: C, 74.42; H, 10.41%.

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