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Journal of Organometallic Chemistry 499 (1995) 155–157

Journal of Organometallic Chemistry

Preliminary communication

Ene preference in the reaction of allenylmethylsilanes with hetero-double bonds mediated by a Lewis acid ☆

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Received 11 January 1995; in revised form 22 February 1995

Abstract

Methylthio- and methoxy-substituted allenylmethylsilanes, a kind of allylsilanes, undergo the ene-type reaction, not the usual allylsilane-type reaction accompanying by desilylation, with carbonyl and azo compounds mediated by a Lewis acid. The corresponding 1-silyl-substituted functionalized 1,3-dienes are obtained in good yields.

Keywords: Silicon; Trimethylsilyl; Group 14; Aldehyde; Allene; Diolefin

Allylsilanes are one of the most useful and powerful reagents for the regiospecific allylation of a variety of electrophiles [2]. Such a reactivity has been applied to develop masked precursors of unstable and reactive species [3]. In contrast to these functionalized allylsilanes, we have previously reported that 1-methylthio-1-trimethylsilylmethylallene (**1a**), a kind of allylsilane, reacts with activated alkenes in a [2 + 2] cycloaddition fashion and can be viewed as a synthetically useful butatriene equivalent [4] (Eq. (1)). We now report another new reactivity of allenylmethylsilanes **1**, the ene reaction towards both carbonyl and azo compounds (Eq. (2)).

First, we found that allenylmethylsilane **1a** [4] reacted with ketomalonate in the same conditions as the [2 + 2] cycloaddition reaction with alkenes (using 1.4 equivalents of **1a** and 1.1 equivalents of $EtAlCl_2$ in CH_2Cl_2 at 0°C for 1 h) to afford a mixture of dienylsilane **2a** and diene **3a** in 14% and 29% yield, respectively. Unfortunately dienylsilane **2a** seems to be unstable and easily changed to the corresponding diene **3a** by loss of a trimethylsilyl group during the operation for workup and purification.

In this reaction, dienylsilane **2a** is a product of the ene reaction of allenylmethylsilane with a carbonyl compound, and diene **3a** is the product of the *formal* allylsilane-type reaction. However, **3a** seems to be produced by protodesilylation of vinylsilane **2a** because the ratio of **2a** to **3a** (monitored by GC in the beginning of the reaction) is larger than that in the high conversion and a prolonged period of workup and purification results in the formation of only **3a** along with a loss of **2a**. It is interesting to note that allenylmethylsilane **1a** possessing an allylsilane moiety reacts in an ene-mode, not in an ordinary allylsilane-mode [5] and that the difference between these two reactions is whether the migrating atom is a silicon or a hydrogen atom on the same allylic carbon atom [6]. Apparently introduction of a methylthio group on the β-carbon of the allenylmethylsilane promotes ene preference [7]. After several trial experiments, we found that $Ti(O\text{-}^iPr)_2Cl_2/Et_2O$ in the presence of molecular sieves was the best reaction system and a catalytic amount of the promoter was sufficient for the reaction. Results for the reactions of **1a** with carbonyl compounds as enophiles are summarized in Table 1 [8]. Reactions proceed efficiently, particularly with electron-deficient carbonyl compounds. Diazo compound also reacts with **1a** as an

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☆ Studies on organosilicon chemistry 127, for No. 126 see Ref. [1]. Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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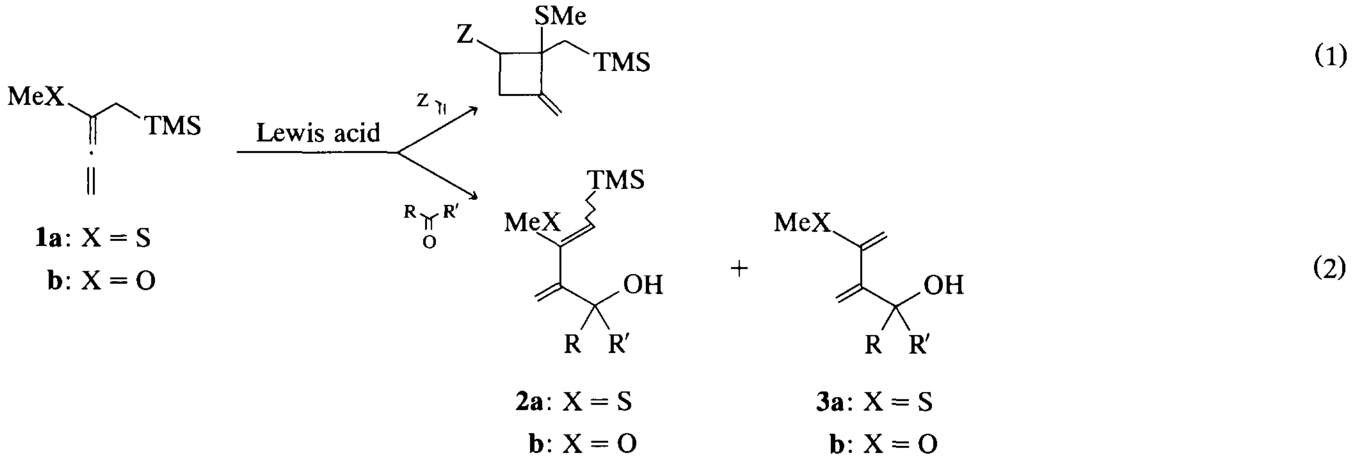
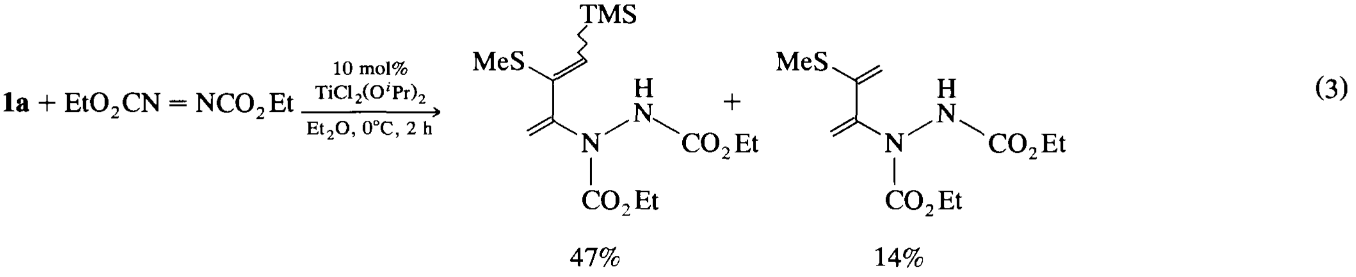
SSDI 0022-328X(95)00306-1



1a: X = S
b: X = O

2a: X = S
b: X = O

3a: X = S
b: X = O

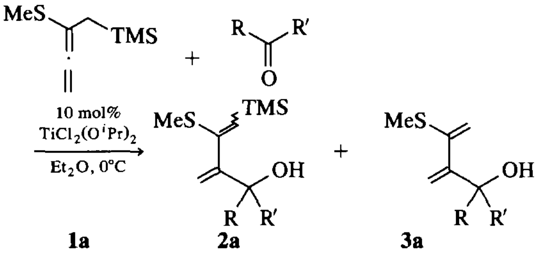


enophile (Eq. (3)). A typical procedure is as follows: to a well-dried flask containing molecular sieves 4 Å under nitrogen, **1a** (105 mg, 0.61 mmol), diethyl ketomalonate (87 mg, 0.5 mmol), and ether (2 ml) were introduced and the flask was cooled to 0°C. TiCl$_2$(O^{i}Pr)$_2$ (0.17 ml, 0.05 mmol) was added and the mixture was stirred at 0°C for 1 h. After hydrolysis with saturated aqueous NaHCO$_3$ solution, the mixture was extracted with ether and the ethereal solution was dried over Na$_2$SO$_4$. After evaporation of the solvent, a crude mixture (139 mg) was obtained and subjected to chromatography on silica gel (hexane/ethyl acetate = 5 : 1) to afford pure products **2a** (59 mg, 34%) and **3a** (38 mg, 28%), respectively.

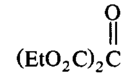
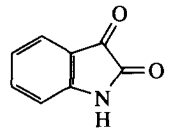
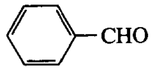
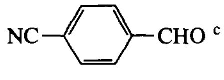
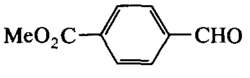
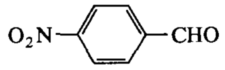
Similarly 1-methoxy-1-trimethylsilylmethylallene (**1b**) reacted with ketomalonate with ene preference under the same reaction conditions to give dienylsilane **2b** in 46% yield. However dienes **3b** were obtained in high yields from aldehydes and imines such as propanal (76%), benzaldehyde (95%), *p*-cyanobenzaldehyde (82%), and N-tosylphenylimine (57%). In these cases the products **3b** were derived only from the allylsilane-type reaction. The formation of **2b** was not observed in spite of careful investigations of the reaction mixture.

In conclusion, the present work provides a new and easy entry to the introduction of a silylbutadiene moiety in the nucleophilic process. It can safely be said that especially methylthio-substituted allenylmethylsilane **1a** possessing an allylsilane skeleton reacts with hetero-double bonds preferentially in the ene-mode over the allylsilane-mode. Since product **2** has both diene and vinylsilane moieties and is a highly functionalized synthon, further attempts to isolate purely dienylsilane **2**,

Table 1
Ene reaction of allenylmethylsilane **1a** with carbonyl compounds [a]



1a **2a** **3a**

Entry	Enophile	Conditions	%Yield (**2a** + **3a**) [b]
1	 $(EtO_2C)_2C=O$	0°C 1 h	62 (34 + 28)
2		0°C 2.5 h	48 (12 + 36)
3		0°C 2.5 h	53 (33.20)
4	 [c]	0°C 4 h	77 (43 + 34)
5		0°C 2 h	86 (47 + 39)
6		0°C 6 h	97 (55 + 42)

[a] Reaction conditions; carbonyl compound (0.5 mmol), allenylmethylsilane **1a** (1.2–1.3 equivalent), and TiCl$_2$(O^{i}Pr)$_2$ (0.1 equivalents) were stirred at 0°C under nitrogen in the presence of molecular sieves 4 Å.

[b] Isolated yield after purification by column chromatography on florisil.

[c] 1.37 equivalents of **1a** was used.

without changing to diene **3**, using more stable silyl groups under such acid conditions are now under way.

Acknowledgments

Financial support for this work is partly provided by Grants-in-Aid for Scientific Research, Grants-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture, Japan. We thank Dow Corning Toray Silicone, Co. Ltd., Chisso, Co. Ltd., and Shin-Etsu Chemical Industries, Co. Ltd., for a gift of organosilicon compounds.

References and notes

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[8] Products **2** were single isomers as identified by the spectrometric (^{1}H and ^{13}C NMR, GC-MS) and chromatographic (GC, TLC, and LC) analyses of the reaction mixture. They were isolated by column chromatography, but the geometry concerning the olefinic double bond was unclear. E.g., spectral and analytical data for **2a** (enophile = keto malonate) was as follows; ^{1}H NMR (CDCl$_3$) δ 0.03 (s, 9 H), 1.24 (t, $J = 6.9$ Hz, 6 H), 2.12 (s, 3 H), 4.22 (*q*, $J = 6.9$ Hz, 2 H), 4.23 (q, $J = 6.9$ Hz, 2 H), 5.36 (s, 1 H), 5.40 (s, 1 H), 5.42 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 0.2 (q), 13.5 (q), 15.8 (q), 62.4 (t), 79.7 (s), 121.0 (t), 126.2 (d), 143.4 (s), 149.7 (s), 168.9 (s); IR (solution in CHCl$_3$) 3500 (w), 3000 (m), 1738 (s), 1230 (s) cm^{-1}; Mass spectrum m/z (%relative intensity) 346 (M$^+$, 1), 273 (28), 181 (23), 155 (36), 73 (100), 45 (34). Anal. Calc. for C$_{15}$H$_{26}$O$_5$SSi: C, 51.99; H, 7.56. Found: C, 51.86; H, 7.48. Satisfactory spectral data (^{1}H and ^{13}C NMR, IR and MS) were obtained for all other new compounds in this work.