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A SIMPLE SYNTHESIS OF 2,4-DIENALS FROM 1-TRIMETHYLSILYL-1,3-DIENES

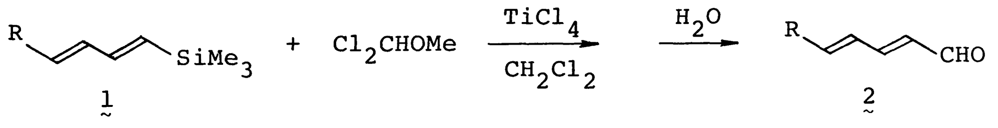
Keiji YAMAMOTO, Mitsuaki OHTA, and Jiro TSUJI
Department of Chemical Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152

Reaction of 1-trimethylsilyl-1,3-dienes with dichloromethyl methyl ether in the presence of titanium(IV) chloride afforded, after hydrolysis, 2,4-dienals in good yields. Convenient preparative route to the 1-trimethylsilyl-1,3-dienes starting from allylsilanes was also described.

We have recently reported a simple method for the synthesis of α,β-unsaturated aldehydes (2-alkenals) which involves 1-chloromethoxymethylation of various vinylsilanes with dichloromethyl methyl ether promoted by titanium(IV) chloride.[1] A synthetic application of the facile formylation of vinylsilanes to two naturally occurring substances has also been presented.[2]

Attempted formylation of allyltrimethylsilane and of trimethylsilylphenylacetylene was, however, found to be unsuccessful, because the chloromethoxymethylation of these more reactive silanes resulted in giving undesired final products.[3]

We wish to report here that 1-trimethylsilyl-1,3-dienes (**1**) readily undergo formylation with replacement of the silyl group on treatment with dichloromethyl methyl ether and titanium(IV) chloride to give the corresponding conjugated dienyl aldehydes (2,4-dienals) (**2**) (eq. 1).

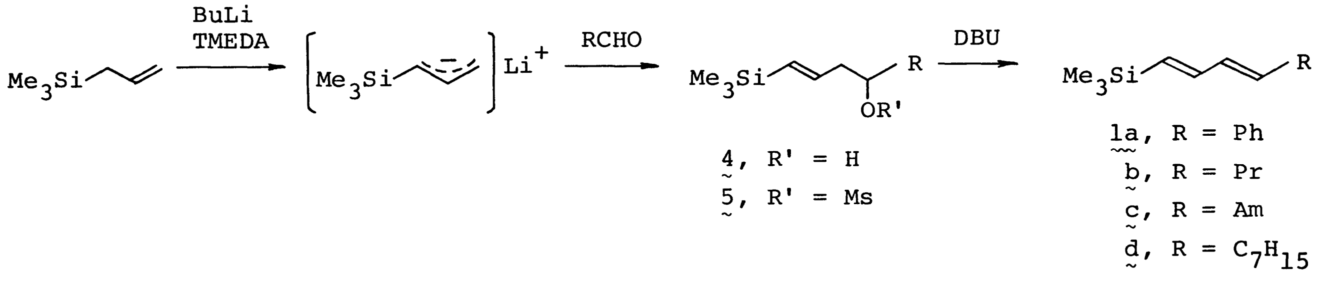


(1)

2,4-Dienals are fairly unstable but often useful intermediates in organic synthesis,[4] being conveniently prepared by the present procedure in good yields.

We have also devised a simple route to the general preparation of requisite 1-trimethylsilyl-1,3-dienes (**1**)[5] starting from allyltrimethylsilane (**3**) based on the sequence of reactions shown in the scheme.

Scheme

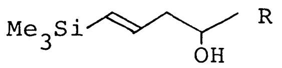
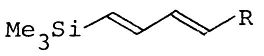


Corriu and his coworkers[6] have previously reported the formation of allyl carbanion from allyltriphenylsilane and its reactions with such electrophiles as ethylene oxide and benzophenone to take place preferentially at γ-position of the allyl group. More recently, Magnus *et al.*[7] have prepared γ-lactones derived from δ-hydroxyvinylsilanes which can be obtained by a reaction of the allylanion of allyltrimethylsilane with cyclohexanone or *p*-tolualdehyde. Therefore, it has been found that α-silylallyl carbanions react with carbonyl compounds to give exclusively the γ-products, the regioselectivity being changed in giving α-products in the presence of magnesium bromide.[8]

Similar reactions of the α-trimethylsilylallyl carbanion with 1-alkanals were thus carried out. The following procedure is typical: To a stirred solution of allyltrimethylsilane (2.28 g, 20 mmol) and tetramethylethylenediamine (TMEDA) (2.32 g, 20 mmol) in anhydrous THF (60 ml) with cooling in an ice-water bath was added dropwise *n*-butyllithium (1.80 M in hexane, 11.2 ml). Stirring was continued at this temperature for 4 h, and the mixture was cooled to -30°C. To this cold solution was added dropwise 1-hexanal (1.80 g, 18 mmol) dissolved in dry THF (5 ml) and the reaction mixture was then allowed to warm to 0°C. Usual hydrolytic work-up followed by column chromatographic purification (silica gel, gradient elution with hexane-ether) gave 1-trimethylsilyl-1-nonen-4-ol[9] (1.93 g, 50%) and a little 1,3-nonadiene.[10]

A solution of the homoallylic alcohol (2.14 g, 10 mmol) in dry pyridine (10 ml) was treated with 1.3 equivalent amounts of methanesulfonyl chloride at 0°C. This was followed by stirring with two fold excess 1,8-diazabicyclo[5.4.0]undecene (DBU) without isolation of the mesylate. The reaction mixture was diluted with hexane, centrifuged to remove voluminous salts, and the organic layer separated was filtered through a silica gel column. The filtrate was concentrated by evaporation and finally purified by column chromatography to give 1.06 g (56%) of 1-trimethylsilyl-1,3-nonadiene (1c). NMR: δ 0.05 (s, 9H), 0.90 (m, 3H), 1.10-1.60 (m, 6H), 2.03 (broad q, 2H), and 5.23-6.57 ppm (m, 4H). IR (neat): 1645 (m), 1580 (m), 1460 (m), 1250 (s), 1005 (s), 870 (s), and 840 (s) cm^{-1}.

Table 1 Preparation of δ-Hydroxyvinyltrimethylsilanes (4) and 1-Trimethylsilyl-1,3-dienes (1) from Allyltrimethylsilane and Aldehydes.

Aldehyde R =	Yield (%)[a]	
	 (4)	 (1)
Ph	45	40 (25)[b]
Pr	54	43 (42)[c]
Am	50	56 (36)[c]
C_7H_{15}	—	— (30)[c]

[a] After purification by column chromatography.

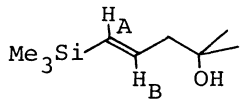
[b] Overall yields by one-pot reactions are given in parentheses.

[c] Isolated an ether by-product arising from alcohol 4 (Note 11).

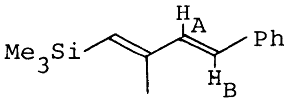
Isolation of the homoallyl alcohol could be omitted. Thus sequencial addition of 1-hexanal, methanesulfonyl chloride, and DBU to the trimethylsilylallyl carbanion in one-pot reaction was found to give the diene 1 in comparative yield.[11]

Table 1 shows the results obtained for four aldehydes. Although the overall yields of 1-trimethylsilyl-1,3-dienes (1) are only moderate, it was confirmed that neither the aldol formation of 1-alkanals used nor the formation of non-conjugated 1,4-dienes from intermediate homoallylic mesylates, if not neglegible, interfered seriously with the present procedure. Also, ready availability of reagents and simple manipulations would be competent for the new route to 1.

Stereochemistry of 1 is most likely (1*E*,3*E*), because a δ-hydroxyvinylsilane obtained by the same reaction as above is reported to have the *E* configuration,[7] and β-elimination of the homoallylic mesylates in the presence of a strong base is the anti one. This stereochemistry was confirmed to be the case by examining the NMR spectrum of 1-trimethylsilyl-4-methyl-1-penten-4-ol (5), obtained from the allyl anion and acetone in 35% yield, and that of 1-trimethylsilyl-2-methyl-4-phenyl-1,3-butadiene (6) which was prepared from the reaction of methallyl-trimethylsilane with benzaldehyde in 41% overall yield.

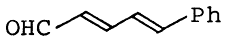
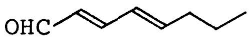
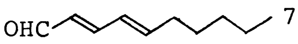
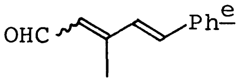


(5), J_{AB} = 18.5 Hz



(6), J_{AB} = 15.5 Hz

Table 2 Preparation of 2,4-Dienals (2) from 1-Trimethylsilyl-1,3-dienes (1 and 6)

Diene	Dienal (2)	Isolated Yield(%)	^{1}H NMR; IR[a] (ppm) (cm^{-1})	2,4-DNP mp(°C)
1a		50	6.13 (dd, J=15, 7.5 Hz, 1H), 6.77-7.75 (m, 8H), 9.51 (d, J=7.5 Hz, 1H); 2730, 1680, 1620.	208-209[b]
1b		71	0.95 (t, J=7.0 Hz, 3H), 1.41 (m, 2H), 2.23 (q, J=7.0 Hz, 2H), 6.00 (dd, J=15, 7.5 Hz, 1H), 6.20-7.40 (m, 3H), 9.51 (d, J=7.5 Hz, 1H); 2730, 1685, 1640.	147-149[c]
1c		72	0.90 (t, J=6.5 Hz, 3H), 1.10-1.90 (m, 6H), 2.20 (q, J=6.5 Hz, 2H), 5.96 (dd, J=15, 7.5 Hz, 1H), 6.15-7.25 (m, 3H), 9.48 (d, J=7.5 Hz, 1H); 2730, 1685, 1640.	140-142[d]
6		68	(2*E*) 2.15 (s, 1H), 5.94 (d, J=7.5 Hz, 1H), 6.75-7.55 (m, 7H), 10.12 (d, J=7.5 Hz, 1H); 2760, 1665, 1615. (2*Z*) 2.35 (s, 1H), 5.84 (d, J=7.5 Hz, 1H), 6.75-7.55 (m, 7H), 10.26 (d, =7.5 Hz, 1H); 2720, 1665, 1590.	—

[a] Characteristic of HCO, HCO, and C=C. [b] Semicarbazone. [c] 154-156°C.[4]
[d] 143-145°C.[4] [e] Geometrical mixture, 2*E* : 2*Z* (3 : 1).

The 1-trimethylsilyl-1,3-dienes (1) were allowed to react with an equivalent amount of dichloromethyl methyl ether and titanium(IV) chloride in dichloromethane at -70°C for 20 min.[1] Hydrolysis of the reaction mixture with 50% aqueous methanol at -20°C was followed by usual work-up. Column chromatographic purification of the crude product (silica gel, *n*-hexane-ether) afforded respective 2,4-dienals (2) in satisfactory yields. Results are summarized in Table 2.

2,4-Dienals (2) obtained as pale yellow-green oils appear to undergo facile polymerization on exposure to air at room temperature.

Crucial assignment of the geometry of pure (2*E*,4*E*)-decadienal could be made by comparison of the retention time on GLC (PEG 20 M on celite 545, 3 m, at 170°C) with that of authentic samples which were prepared in this laboratory by an alternative route as a mixture of (2*E*,4*E*)- and (2*E*,4*Z*)-isomer in a ratio 90 : 10.[12,13]

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References and Notes:

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2) K. Yamamoto, J. Yoshitake, N. T. Qui, and J. Tsuji, Chem. Lett., 859 (1978).
3) α-Chlorohomoallyl ether formed by the reaction of allyltrimethylsilane with dichloromethyl methyl ether was even more reactive than the dichloromethyl ether, reacting with another molecule of allylsilane to give 1-(trimethylsilyl)methyl-3-methoxy-5-chlorocyclohexane. Reaction of trimethylsilylphenylacetylene with the dichloromethyl ether gave α-chloro-β-trimethylsilylcinnamaldehyde, an addition product, under the reaction conditions employed.
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5) Preparation of 1-trimethylsilyl-1,3-butadiene and branched derivatives has been reported: J-P. Pillot, J. Dunoguès, and R. Calas, J. Chem. Res. (S), 268 (1977), and references cited therein.
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8) P. W. K. Lau and T. H. Chan, Tetrahedron Lett., 2383 (1978).
9) NMR: δ 0.05 (s, 9H), 0.67-1.63 (m, 11H), 1.80-2.33 (m, 2H), 3.20-3.70 (m, 1H), 5.60 (d, J = 18.5 Hz, 1H), and 5.90 ppm (dt, J = 18.5 and 5.5 Hz, 1H).
10) Reaction at α-position of the allylic carbanion with spontaneous β-elimination of Me_3SiO^- gave 1,3-nonadiene (less than 10% by GLC analysis) which was readily separated by column chromatography.
11) In the one-pot reaction we have isolated an ether compound (7) as by-product. These ethers arise presumably from the reaction of mesylate of 4 with lithium alcoholate of 4 both formed *in situ*.
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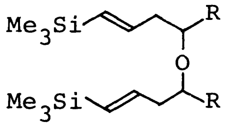

(7)

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