The Reaction of Butatrienolates with Aldehydes for the Syntheses of α-Vinylidene Acylsilanes

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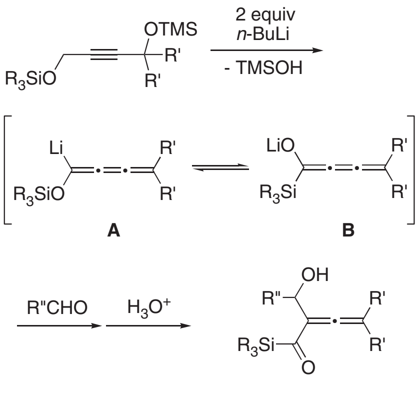
Lithium butatrienolates were prepared in situ by the 1,4-elimination from 2-butynyl trimethylsilyl ethers along with a retro-Brook rearrangement. The addition reaction of the enolates with the aldehydes afforded β-hydroxy-α-vinylidene acylsilanes.

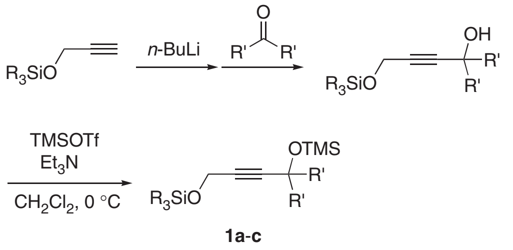
The aldol addition of enolates with aldehydes is one of the most important carbon–carbon forming reactions. In particular, the addition of α-silyl-substituted enolates gives acylsilanes,[1] which are useful synthetic intermediates for various transformations.[2] When α-silyl-substituted allenolates (propadienolates), which were prepared by the retro-Brook rearrangement of allenyllithiums, were used, the reaction with aldehydes gave α-methylene acylsilanes.[3,4] Here we disclose that the addition reaction of α-silyl-substituted butatrienolates with aldehydes affords α-vinylidene acylsilanes.

The 1,4-elimination of trimethylsilanol from 1,4-disiloxy-2-butyne using 2 equivalent amounts of base gives the lithiated butatriene **A**.[5] *C*-lithium **A** is known to exist in equilibrium with *O*-lithium **B** through a (retro-)Brook rearrangement.[6] We subjected the in situ prepared lithium butatrienolates to a reaction with aldehydes (Scheme 1).

1,4-Disiloxy-2-butynes **1a–c**, the precursors for butatrienolates, were readily available from the addition of the lithium salt of 1-siloxy-2-propyne to ketones along with the trimethylsilyl-protection of the obtained alcohols (Scheme 2).

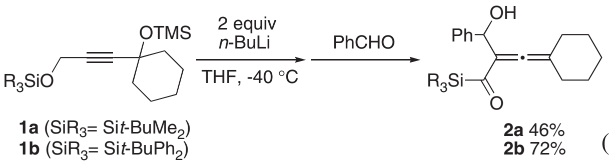


Scheme 1.



Scheme 2.

When the reaction of the *t*-butyldimethylsilyl-protected ether **1a** with benzaldehyde was examined, the corresponding β-hydroxy-α-vinylidene acylsilane **2a** was obtained in moderate yield along with the formation of several unidentified products derived from **1a**. The *t*-butyldiphenylsilyl ether **1b** gave the better result, a 72% yield. The more bulky silyl group probably stabilized the lithium salt. Actually, at the higher reaction temperature (−20 °C), the butatrienolate decomposed to give a complex mixture.



(1)

The reaction of aldehydes with two butatrienolates was examined (Table 1). Alkyl and α,β-unsaturated aldehydes were also substrates and the corresponding β-hydroxy-α-vinylidene acylsilanes **2c**, **d** were obtained in good yields (Entries 1, 2). Only a trace amount of the 1,4-adduct was obtained in Entry 2. The dimethyl-substituted butatrienolate prepared from **1c** also reacted with aldehydes to give α-vinylidene acylsilanes **2e–g** in acceptable yields (Entries 3–5).

The unique reactivity of the cumulated carbon–carbon double bond is anticipated, which could not be realized in simple alkenes or conjugate systems. Recently, allenes (propadienes) were comprehensively studied as unique reagents for transition metal-catalyzed reactions, however, the synthetic use of the butatriene component is limited.[7] This paper discloses that the aldol reaction of lithium butatrienolate with aldehydes proceeded, and that β-hydroxy-α-vinylidene acylsilanes were obtained.

Experimental

General. ^{1}H NMR spectra were measured with a JNM AL-400 spectrometer and ^{13}C NMR spectra were measured with a JEOL Lambda 500 spectrometer using tetramethylsilane as an internal standard and $CDCl_3$ as a solvent. IR spectra were recorded with a Horiba FT730 spectrophotometer. High-resolution mass spectral analyses (FAB) were performed on a JEOL JMS-SX102A. All reactions were examined using an Ar balloon.

1-[3-(*t*-Butyldimethylsiloxy)prop-1-ynyl]-1-trimethylsiloxycyclohexane (1a). Pale yellow oil. ^{1}H NMR δ 0.09 (s, 6H), 0.15 (s, 9H), 0.88 (s, 9H), 1.19–1.22 (m, 1H), 1.40–1.64 (m, 7H), 1.78–1.81 (m, 2H), 4.33 (s, 2H); ^{13}C NMR δ −5.1, 2.1, 18.3, 23.1, 25.3, 25.8, 41.1, 51.8, 69.9, 83.6, 88.6; IR (neat) 1094 cm^{-1}; HRMS m/z calcd for $C_{18}H_{35}O_2Si_2$ ($M^+ - 1$): 339.2176. Found: 339.2151.

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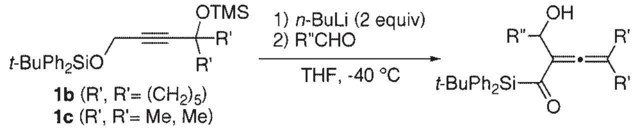
Table 1. The Reaction of in Situ Prepared Lithium Butatrienolates with Aldehydes



Entry	1	R″	Yield/%
1	**1b**	*n*-Pr	71 (**2c**)
2	**1b**	$CH_3CH{=}CH$	85 (**2d**)
3	**1c**	Ph	72 (**2e**)
4	**1c**	*n*-Pr	65 (**2f**)
5	**1c**	$CH_3CH{=}CH$	60 (**2g**)

1-[3-(*t*-Butyldiphenylsiloxy)prop-1-ynyl]-1-trimethylsiloxycyclohexane (1b). Pale yellow oil. ^{1}H NMR δ 0.18 (s, 9H), 1.05 (s, 9H), 1.19–1.25 (m, 2H), 1.44–1.60 (m, 6H), 1.79–1.82 (m, 2H), 4.37 (s, 2H), 7.37–7.76 (m, 10H); ^{13}C NMR δ 2.2, 19.3, 23.2, 25.4, 26.7, 41.2, 52.8, 70.0, 83.4, 88.7, 127.6, 129.6, 133.0, 135.4; IR (neat) 1097 cm^{-1}; HRMS m/z calcd for $C_{28}H_{39}O_2Si_2$ ($M^+ - 1$): 463.2489. Found: 463.2446.

1-(*t*-Butyldiphenylsiloxy)-4-methyl-4-trimethylsiloxypent-2-yne (1c). Pale yellow oil. ^{1}H NMR δ 0.17 (s, 9H), 1.05 (s, 9H), 1.43 (s, 6H), 4.34 (s, 2H), 7.37–7.72 (m, 10H); ^{13}C NMR δ 1.9, 19.2, 26.7, 32.8, 52.7, 66.5, 81.1, 90.0, 127.7, 129.7, 133.2, 135.6; IR (neat) 1113 cm^{-1}; HRMS m/z calcd for $C_{25}H_{35}O_2Si_2$ ($M^+ - 1$): 423.2176. Found: 423.2199.

1-(*t*-Butyldimethylsilyl)-2-(cyclohexylidenemethylene)-3-hydroxy-3-phenylpropan-1-one (2a). Yellow oil. ^{1}H NMR δ 0.17 (s, 6H), 0.90 (s, 9H), 1.02–1.10 (m, 1H), 1.21–1.30 (m, 1H), 1.46–1.65 (m, 4H), 1.89–2.02 (m, 3H), 2.10–2.15 (m, 1H), 3.79 (d, $J = 2.4$ Hz, 1H), 5.66 (d, $J = 2.4$ Hz, 1H), 7.23–7.33 (m, 5H); ^{13}C NMR δ −5.4, −5.3, 16.8, 25.4, 26.0, 26.1, 26.6, 30.4, 30.4, 72.0, 108.9, 117.5, 126.4, 127.1, 128.0, 141.9, 210.1, 235.9; IR (neat) 3487, 1946, 1575 cm^{-1}; HRMS (FAB) m/z calcd for $C_{22}H_{31}O_2Si$ ($M^+ - 1$): 355.2094. Found: 355.2090.

1-(*t*-Butyldiphenylsilyl)-2-(cyclohexylidenemethylene)-3-hydroxy-3-phenylpropan-1-one (2b). To a THF solution (2 mL) of silyl ether **1b** (139.4 mg, 0.30 mmol) was added BuLi (0.72 mmol, 1.59 mol/L hexane solution) dropwise at −40 °C, and the mixture was stirred for 10 min. To the resulting mixture was added benzaldehyde (95.5 mg, 0.90 mmol) at −40 °C. After being stirred for 10 min, the reaction mixture was quenched with sat. NH_4Cl (aq), and the organic materials were then extracted with Et_2O. The extracts were then washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (hexane/ethyl acetate = 10/1). Yellow oil. ^{1}H NMR δ 1.00 (s, 9H), 0.52–0.60 (m, 1H), 0.66–0.77 (m, 1H), 0.79–0.92 (m, 3H), 1.07–1.16 (m, 4H), 1.26–1.32 (m, 1H), 3.77 (d, $J = 4.0$ Hz, 1H), 5.71 (d, $J = 4.0$ Hz, 1H), 7.18–7.73 (m, 15H); ^{13}C NMR δ 18.6, 25.0, 25.6, 25.7, 26.8, 28.5, 28.6, 71.9, 110.7, 116.8, 126.3, 127.0, 127.6, 127.6, 127.9, 128.3, 129.3, 133.2, 133.2, 135.6, 135.7, 142.0, 210.1, 233.3; IR (neat) 3459, 1943, 1583 cm^{-1}; HRMS m/z calcd for $C_{32}H_{37}O_2Si$ ($M^+ + 1$): 481.2563. Found: 481.2565.

1-(*t*-Butyldiphenylsilyl)-2-(cyclohexylidenemethylene)-3-hydroxyhexan-1-one (2c). Yellow oil. ^{1}H NMR δ 0.86–0.93 (m, 3H), 1.00 (s, 9H), 1.03–1.13 (m, 6H), 1.23–1.43 (m, 5H), 1.47–1.55 (m, 3H), 3.18 (d, $J = 5.5$ Hz, 1H), 4.52 (dt, $J = 5.5$, 5.5 Hz, 1H), 7.34–7.73 (m, 10H); ^{13}C NMR δ 14.0, 18.6, 18.9, 25.2, 26.1, 26.1, 26.8, 28.8, 29.0, 37.2, 68.8, 110.4, 115.5, 127.6, 127.7, 128.3, 129.3, 129.4, 133.3, 133.4, 135.7, 209.0, 233.9; IR (neat) 3444, 1941, 1577 cm^{-1}; HRMS m/z calcd for $C_{29}H_{39}O_2Si$ ($M^+ + 1$): 447.2719. Found: 447.2711.

1-(*t*-Butyldiphenylsilyl)-2-(cyclohexylidenemethylene)-3-hydroxyhex-4-en-1-one (2d). Yellow oil. ^{1}H NMR δ 1.01 (s, 9H), 1.03–1.06 (m, 2H), 1.19–1.25 (m, 4H), 1.40–1.42 (m, 3H), 1.49–1.52 (m, 1H), 1.69 (d, $J = 6.4$ Hz, 3H), 3.38 (d, $J = 5.5$ Hz, 1H), 5.00 (dd, $J = 5.5$, 5.5 Hz, 1H), 5.49 (dd, $J = 5.5$, 15.2 Hz, 1H), 5.65–5.73 (m, 1H), 7.30–7.70 (m, 10H); ^{13}C NMR δ 17.7, 18.7, 25.3, 26.3, 26.3, 26.9, 29.0, 29.0, 70.2, 110.6, 115.3, 126.9, 127.7, 127.7, 129.4, 129.4, 131.2, 133.3, 133.3, 135.7, 135.8, 209.4, 233.4; IR (neat) 3451, 1942, 1577 cm^{-1}; HRMS m/z calcd for $C_{29}H_{36}O_2Si$ (M^+): 444.2485. Found: 444.2483.

1-(*t*-Butyldiphenylsilyl)-3-hydroxy-2-(isopropylidenemethylene)-3-phenylpropan-1-one (2e). Yellow oil. ^{1}H NMR δ 0.70 (s, 3H), 0.77 (s, 3H), 0.98 (s, 9H), 3.64 (d, $J = 5.8$ Hz, 1H), 5.61 (d, $J = 5.8$ Hz, 1H), 7.22–7.60 (m, 15H); ^{13}C NMR δ 17.8, 18.0, 18.6, 26.8, 71.9, 105.1, 116.4, 126.1, 127.2, 127.7, 127.7, 127.9, 128.4, 129.4, 133.0, 133.0, 135.6, 135.6, 142.3, 212.8, 233.4; IR (neat) 3515, 1954, 1593 cm^{-1}; HRMS m/z calcd for $C_{29}H_{33}O_2Si$ ($M^+ + 1$): 441.2250. Found: 441.2217.

1-(*t*-Butyldiphenylsilyl)-3-hydroxy-2-(isopropylidenemethylene)hexan-1-one (2f). Yellow oil. ^{1}H NMR δ 0.82 (s, 3H), 0.86 (s, 3H), 0.90 (t, $J = 7.2$ Hz, 3H), 1.01 (s, 9H), 1.25–1.65 (m, 4H), 3.08 (d, $J = 5.8$ Hz, 1H), 4.49 (dt, $J = 5.8$, 5.8 Hz, 1H), 7.33–7.66 (m, 10H); ^{13}C NMR δ 14.0, 18.1, 18.2, 18.7, 18.9, 26.8, 37.4, 68.9, 104.5, 115.8, 127.7, 127.7, 129.4, 129.4, 133.1, 133.2, 135.6, 212.2, 234.0; IR (neat) 3451, 1947, 1585 cm^{-1}; HRMS m/z calcd for $C_{26}H_{35}O_2Si$ ($M^+ + 1$): 407.2406. Found: 407.2409.

1-(*t*-Butyldiphenylsilyl)-3-hydroxy-2-(isopropylidenemethylene)hex-4-en-1-one (2g). Yellow oil. ^{1}H NMR δ 0.83 (s, 3H), 0.87 (s, 3H), 1.01 (s, 9H), 1.69 (d, $J = 6.0$ Hz, 3H), 3.21 (d, $J = 6.3$ Hz, 1H), 4.93 (dd, $J = 6.3$, 6.3 Hz, 1H), 5.51 (dd, $J = 6.3$, 15.0 Hz, 1H), 5.66–5.74 (m, 1H), 7.33–7.67 (m, 10H); ^{13}C NMR δ 17.7, 18.1, 18.2, 18.7, 26.8, 70.2, 104.7, 115.4, 127.1, 127.7, 127.7, 129.4, 131.3, 133.1, 133.1, 135.6, 135.6, 135.7, 212.3, 233.4; IR (neat) 3451, 1947, 1587 cm^{-1}; HRMS m/z calcd for $C_{26}H_{31}O_2Si$ ($M^+ - 1$): 403.2094. Found: 403.2082.

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