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SELECTIVE PREPARATION OF 1,3-BIS(TRIMETHYLSILYL)-1-, -2-PROPENYL, AND 3-TRIMETHYLSILYL-1,2-PROPADIENYL FUNCTIONAL GROUPS

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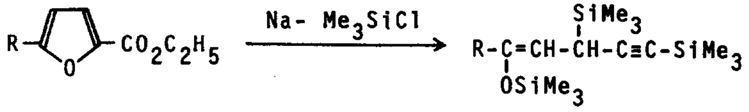
It has recently been reported that vinyl-[1] and allylsilane[2] types of compounds have exhibited nucleophilic reactivities toward cationic center, which is attributable to stabilization of the resulting positively charged β-carbon of the intermediate through σ-π hyperconjugative effect[3] of silyl group.

In the previous paper, we described that ethyl 2-furoates undergo facile reductive silylation followed by ring opening to afford the corresponding silyl enol ether 1 possessing 1,3-bis(trimethylsilyl)-2-propynyl side chain.[4]



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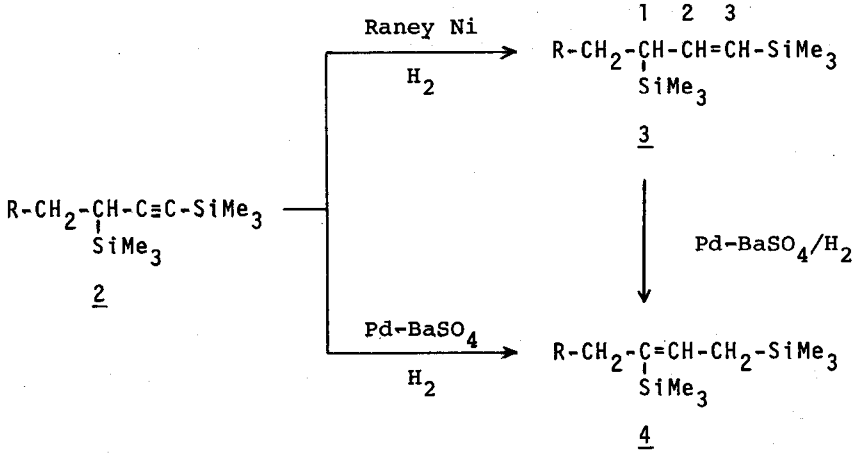
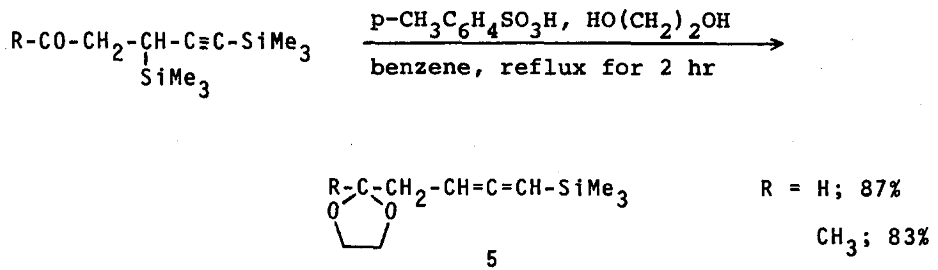
In the present paper, we wish to report on selective conversion of the side chain into 1,3-bis(trimethylsilyl)-1-, -2-propenyl, and 3-trimethylsilyl-1,2-propadienyl groups. The first and the second ones appear to be especially useful, because they are expected to show much enhanced reactivities toward electrophile at C-1 and C-3 carbonic sites, respectively, by double activation with two silyl groups and will add another synthetic utility in addition to the characteristic features of 1. Since partial hydrogenation of silyl acetylenes catalyzed by Raney nickel[5] or palladium[6] has been reported, we have examined these procedures for hydrogenation of 1,3-bis(trimethylsilyl)propynyl group of 2 derived easily from 1. It was established that the side chain was cleanly hydrogenated to afford the corresponding desired product 3 in good yield when 2 was exposed to hydrogen in ethyl acetate in the presence of Raney nickel. Only exceptional case was that with the aldehyde 2a, which afforded a rather complicated mixture accompanied with the products resulting from reduction of aldehyde moiety (see the note in the Table). It should also be noted that hydrogenation reactions usually take place smoothly under atmospheric pressure of hydrogen, contrary to the reported result employing high pressure of hydrogen.[5]

On the other hand, when Pd-$BaSO_4$ was employed as the hydrogenation catalyst, hydrogenation accompanied with double bond migration usually took place to give the product having 1,3-bis(trimethylsilyl)-1-propenyl side chain 4 selectively or exclusively, unless the starting materials possess reactive functional groups such as hydroxyl or formyl toward the catalyst.[7] In the latter case, however, protection of such group in conventional manner followed by hydrogenation catalyzed by Pd-$BaSO_4$ led to the formation of the desired product 4c. Further, it has been established that hydrogenation products 3 undergo facile isomerization into 4 in the presence of Pd-$BaSO_4$ under hydrogen atmosphere.



In the course of studies on acetalization of carbonyl group of 2, it was also found that an interesting derivation of the side chain was realized. Thus, when 2a or 2b was treated with a catalytic amount of p-toluenesulfonic acid in appropriate alcohol, it resulted in the formation of the acetal having silylallenic side chain 5, accompanied with protonation followed by removal of silyl group. For effecting acetalization of such compounds, it was neccesary to employ a system of ammonium nitrate--trimethyl orthoformate, which afforded the corresponding acetal cleanly.



$$R\text{-}CO\text{-}CH_2\text{-}\underset{SiMe_3}{CH}\text{-}C{\equiv}C\text{-}SiMe_3 \xrightarrow[\text{benzene, reflux for 2 hr}]{p\text{-}CH_3C_6H_4SO_3H,\ HO(CH_2)_2OH}$$

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Table. Conversion of 2 into 3[a] or 4[a], and 3 into 4.

R	Catalyst	Solvent	Yield, (%) 3	Yield, (%) 4
2a; HCO	Raney Ni (W-2)	Ethyl Acetate	60[b,c,d]	--
2b; CH_3CO	"	"	85[e]	--
2c; $HC(OCH_3)_2$	"	"	96[e]	--
2d; $C_6H_5CH_2CH_2CH(OAc)$	"	"	99[e,f]	--
2a; HCO	$Pd\text{-}BaSO_4$	Hexane	47[g]	20
2b; CH_3CO	"	"	--	88[g]
2c; $HC(OCH_3)_2$	"	"	9	80[g]
2e; C_2H_5	"	"	<1	90[g,h]
3b; CH_3CO	"	"	--	99[i]
3e; C_2H_5	"	"	<0.5	98[j,k]

[a] Satisfactory (ir, nmr, and mass) spectral data have been obtained for all of the products. [b] The reaction was carried out for 5 hr. [c] The aldehyde (5%) was recovered. [d] A mixture consisting from nearly equal amounts of 3,5-bis(trimethylsilyl)pent-4-en-1-ol and 3,5-bis(trimethylsilyl)pent-4-yn-1-ol was also formed in 18% yield. [e] The reaction was carried out for 2 hr. [f] The same hydrogenation product 3d was obtained in 95% yield even if $Pd\text{-}BaSO_4$ was used as the catalyst. [g] The reaction was carried out overnight. [h] The corresponding saturated product was formed in 9% yield. [i] $Pd\text{-}BaSO_4$ pre-treated with hydrogen was used and the isomerization experiment was performed under argon atmosphere for 3 hr. [j] The reaction was carried out under hydrogen atmosphere for 5 hr. [k] The corresponding saturated product was formed in 2% yield.

Two typical examples are described in the following. 4,6-Bis(trimethylsilyl)hex-5-en-2-one (3b); 4,6-bis(trimethylsilyl)hex-5-yn-2-one (2b) (1 mmol) was treated with atmospheric pressure of hydrogen in ethyl acetate (10 ml) in the presence of a catalytic amount of Raney nickel (W-2) for 2 hr. From the reaction mixture, 4,6-bis(trimethylsilyl)hex-5-en-2-one 3b was isolated in 85% yield by silica gel-silver nitrate column chromatography. 3b, ir(neat); 2950, 1720, 1600, 1250, and 850 cm^{-1}. nmr (CCl_4, benzene as internal standard); δ 0.11 (s, 9H, $(C\underline{H}_3)_3Si$), 0.21 (s, 9H, $(C\underline{H}_3)_3Si$), 2.11 (s, 3H, $C\underline{H}_3CO$), 2.3$\sim$2.6 (m, 3H, $Si-C\underline{H}-C\underline{H}_2-CO$), 5.29 (d, J = 14 Hz, 1H, $Si-C\underline{H}=CH-$), 5.8$\sim$6.3 (d.m, J = 14 Hz, 1H, $Si-CH=C\underline{H}-$).

4,6-Bis(trimethylsilyl)hex-4-en-2-one (4b); 2b (1 mmol) was treated with hydrogen in hexane in the presence of a catalytic amount of $Pd-BaSO_4$ (5% Pd) overnight. From the reaction mixture, the title compound was isolated in 88% yield by similar procedure described above. 4b, ir(neat); 2950, 1715, 1602, 1250, and 840 cm^{-1}. nmr (CCl_4, benzene as internal standard); δ 0.18 (s, 9H, $(C\underline{H}_3)_3Si$), 0.21 (s, 9H, $(C\underline{H}_3)_3Si$), 1.77 (d, J = 9 Hz, 1H, $Si-C\underline{H}_2-CH=C$), 2.15 (s, 3H, $C\underline{H}_3CO$), 3;28 (s, 2H, $C=C(SiMe_3)-C\underline{H}_2-CO$), and 6.17 (t, J = 9 Hz, 1H, $CH_2-C\underline{H}=C$).

We are currently exploring synthetic utilities of the types of compounds such as 3, 4, and 5 in addition to 1.

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