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STEREO- AND REGIO-SELECTIVE CONVERSION OF 1-TRIMETHYLSILYLALLYLIC ALCOHOLS INTO THE SILYL ENOL ETHERS CATALYZED BY BUTYLLITHIUM

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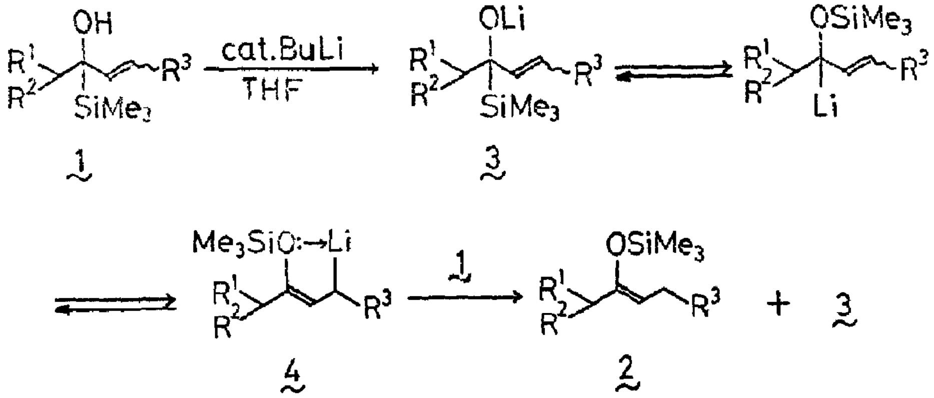
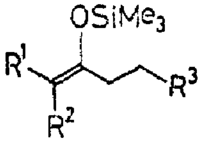
Summary: (Z)-Silyl enol ethers can be prepared selectively with complete regio-specificity by treating 1-trimethylsilylallylic alcohols with a catalytic amount of butyllithium.

Since silyl enol ethers of ketones have been recognized as versatile reagents for regioselective carbon chain homologation or functionalization of ketones,[1] various procedures have been developed for their preparation.[2∿5] In most of them, silylation of ketones has been achieved with moderate or sufficient regioselectivity by generating the corresponding enolates under kinetically or thermodynamically controlled reaction conditions.[2] Further, appropriate choice of reagents[3] or reaction conditions[4] has sometimes enabled their stereoselective preparation. However, problems still remain undissolved in such a case where two types of methylene groups neighboring to carbonyl group can not be differentiated satisfactorily under the reaction conditions employed.

We have recently reported an efficient method for generation of homoenolate equivalents starting from 1-trimethylsilylallylic alcohols 1.[6] In the present paper, we wish to describe a direct stereo- and regio-selective conversion of 1 into the corresponding silyl enol ethers 2 catalyzed by butyllithium.

1-Trimethylsilylallylic alcohols 1 can be prepared almost quantitatively by treating the corresponding acyltrimethylsilanes with vinylmagnesium bromide (1.2 equiv)[6] or by Raney nickel catalyzed partial reduction of 1-trimethylsilylpropargyl alcohols easily obtained by the reaction of acyltrimethylsilanes with magnesium acetylides. Treatment of 1 with a catalytic amount of butyllithium (ca. 5 mol%) in tetrahydrofuran led to the stereo- and regio-selective formation of the corresponding silyl enol ethers 2. The reaction may proceed through an initial formation of the lithium alkoxide 3, which is in equilibrium with allyllithiums.[6,7] Proton abstraction of the intermediate 4 stabilized by coordination to the siloxy group from the starting alcohol 1 affords the desired 2 accompanied with regeneration of lithium alkoxide 3. Thus, the net reaction is considered to proceed totally under the catalytic influence of butyllithium as shown in the following equations.

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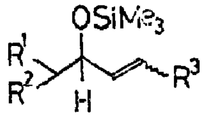
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As shown in the Table, all of the allylic alcohols 1 examined gave the corresponding silyl enol ethers 2 in good to excellent yields without any concomitant formation of their regio-isomers 5. In contrast to the high efficacy of butyllithium, Grignard reagent such as ethylmagnesium bromide is not usually sufficient for this conversion. Tetrahydrofuran is preferable as the reaction solvent. Employment of ether appears to reduce the stereo-selectivity as shown in run 3.

Further, results obtained here have suggested some interesting features on the stereo-selectivity of this reaction. When started from 3-unsubstituted allylic alcohols 1 $(R^1 \neq H, R^2,R^3 = H)$, the reaction usually proceeds at -20 °C within 30 min and the corresponding 2 can be obtained with high stereo-selectivity (Z:E = ca. 95:5). Such kind of tendency appears to be enhanced with the alcohols 1 $(R^1,R^2 = H)$ possessing α-substituents:[8] the reaction takes place even at -78∿-40 °C and excellent stereo-selectivity (Z:E = ca. 98:2) can be attained as shown in runs 4,5,6, and 11. Steric crowdness around the carbon atom attached to silyl and oxido groups may facilitate the rearrangement of 3 into 4. On the other hand, with 3-substituted allylic alcohols 1 $(R^3 \neq H)$, higher reaction temperature is usually required for the complete conversion and the decrease in the stereo-selectivity has sometimes been observed. Further, the corresponding trimethylsilyl allyl ethers 6 were also formed in appreciable amounts as the by-products in these cases. This may be attributable to both of steric and electronic effects of substituents R^3. The former may reduce the regio-selectivity in the protonation process, and the latter may retard the rearrangement of the lithium alkoxide 3 into the intermediate 4 due to its destabilizing effect.

Table. Preparation of Silyl Enol Ethers 2.

Run	R^1	R^2	R^3	Temp.(°C)	Yield(%) of 2[a]	Ratio(Z:E)[b]
1	C_5H_{11}	H	H	-20	95	96:4
2	$C_6H_5CH_2$	H	H	-20	96	95:5
3	$C_6H_5CH_2$	H	H	-40	91[c]	81:19
4	C_3H_7	CH_3	H	-78	95	98:2
5	C_2H_5	C_2H_5	H	-78	93	99:1
6	$-(CH_2)_5-$		H	-40	91	98:2
7	C_5H_{11}	H	CH_3	0	85[d]	95:5
8	$C_6H_5CH_2$	H	CH_3	R.T.	81[d]	90:10
9	$C_6H_5CH_2$	H	CH_3	-20	83[d,e]	88:12
10	$C_6H_5CH_2$	H	C_5H_{11}	0	74[d]	89:11
11	C_3H_7	CH_3	CH_3	-30	94	97:3

[a] All of the reactions were carried out in THF, otherwise noted. The products 2 were isolated by fractional distillation or by chromatography using Merck Lobar column. [b] The isomeric ratios were determined by glpc analyses using Hitachi Chemi-column (Silicone OV-101, 0.25mm x 20m). [c] The reaction was carried out in ether. [d] In these cases, formation of the corresponding isomers 6 was observed in 5∿15% yields by nmr analyses of the crude reaction mixtures. [e] The reaction was carried out in dimethoxyethane.

Typical example is as follows. 3-Trimethylsiloxy-5-phenyl-2-pentene: To THF (10 ml) solution of 3-trimethylsilyl-5-phenyl-1-penten-3-ol (0.468 g, 2 mmol) was added butyllithium (0.08 ml of 1.5 M hexane solution, 0.12 mmol) at -78°C. Then, the reaction temperature was gradually raised to -20°C and it was stirred for 20 min at that temperature. Hexane (40 ml) pre-cooled to -78°C was added to the reaction mixture and was poured into buffer (KH_2PO_4-NaOH) solution. After extracted twice with hexane (10 ml) and drying, removal of the solvent followed by fractional distillation afforded the title compound (0.449 g, 96%), which exhibited the following spectral data. ir(neat): 1670, 1251, and 845 cm^{-1}. nmr(CCl_4, dichloromethane as an internal standard): δ 0.20 (s, 9H, $\underline{Me}_3Si$), 1.46 (d.t., J = 1 and 6 Hz, 3H, $C\underline{H}_3C{=}C$), 2.00∿2.46 (m, 2H, $C\underline{H}_2C{=}C$), 2.73∿2.93 (m, 2H, $C_6H_5C\underline{H}_2$), 4.44 (q, J = 7 Hz, 1H, $C\underline{H}{=}C$), and 7.07 (s, 5H, $C_6\underline{H}_5$).

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8) In these cases, the rearrangement appears to take place even with magnesium alkoxides. For example, the reaction of the acyltrimethylsilane with vinylmagnesium bromide in ether gave a mixture of the corresponding 1 and the ketone resulting from the rearrangement followed by hydrolysis. When the same reaction was carried out in hexane, the corresponding 1 was obtained in ca. 80% yield along with the ketone (ca. 10%).

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