(isomer 2), 88441-98-9; **91**, 88441-81-0; **92**, 88441-82-1; **93**, 88441-83-2; **94** (isomer 1), 88441-84-3; **94** (isomer 2), 88494-69-3; **95** (isomer 1), 88494-70-6; **95** (isomer 2), 88494-71-7; **96**, 88441-85-4; **97**, 88441-86-5; **98**, 88441-87-6; **99**, 88441-88-7; **100**, 88441-89-8; $PhCH(OEt)_2$, 774-48-1; $PhCH(OMe)_2$, 1125-88-8; p-$ClC_6H_4CH(OMe)_2$, 3395-81-1; p-$CH_3C_6H_4CH(OMe)_2$, 3395-83-3; $PhCH{=}CHCH(OMe)_2$, 4364-06-1; (E)-n-$PrCH{=}CHCH(OMe)_2$, 18318-83-7; n-$C_5H_{11}CH(OMe)_2$, 1599-47-9; n-$C_9H_{19}CH(OMe)_2$, 7779-41-1; $(C_2H_5)_2C(OMe)_2$, 25636-49-1; $EtOCO(CH_2)_2COOEt$, 123-25-1; $ClIsMe_3$, 75-77-4; PhCHO, 100-52-7; PhSCl, 931-59-9; $Ph_3CH_3P^+Br^-$, 1779-49-3; cyclohexanone dimethyl ketal, 933-40-4; cyclohexanone diethyl ketal, 1670-47-9; cyclooctanone dimethyl ketal, 25632-03-5; cyclododecanone dimethyl ketal, 950-33-4; 2-allylcyclohexanone dimethyl ketal, 88441-90-1; norbornanone dimethyl ketal, 10395-51-4; 3-methylcyclohexanone dimethyl ketal, 18349-16-1; 2-methylcyclohexanone dimethyl ketal, 38574-09-3; dihydrojasmone, 1128-08-1; 2-((methoxycarbonyl)methyl)cyclohexanone, 13672-64-5; 4-methyl-3-cyclohexenone propylene ketal, 88441-96-7; 4-hydroxy-4-(4-methyl-3-cyclohexenyl)butanoic lactone, 88441-99-0; furfural, 98-01-1.

Base-Induced Rearrangement of 1-(Trimethylsilyl)allylic Alcohols. Stereo- and Regioselective Synthesis of Silyl Enol Ethers through Lithium Homoenolates[1]

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Abstract: 1-(Trimethylsilyl)allylic alcohols have been prepared and their conversions to silyl enol ethers have been examined. Under appropriate conditions, lithium alkoxides of the above alcohols are in equilibrium with lithium homoenolates, 3-(trimethylsiloxy)allyllithiums, which react with alkyl iodides to give the silyl enol ethers of defined stereo- and regiochemistry. Further, a catalytic amount of butyllithium induces the rearrangement of the alcohols to yield the corresponding silyl enol ethers in a highly stereo- and regiocontrolled manner via self-protolysis. Equilibrium composition between lithium alkoxides and lithium homoenolates has been shown to be greatly influenced by the steric factors around α carbons of allylic alcohols.

Since the works of Stork,[2] House,[3] and then Mukaiyama,[4] silyl enol ethers have been employed as one of the most promising nucleophilic substrates in organic synthesis. Use of this class of compounds has allowed the introduction of a variety of functional groups or carbon chains onto α carbons of the carbonyl compounds.[5] Most of the procedures described for their preparation have resorted to the same basic principle: generation of enolate anions from carbonyl compounds and their silylation with an appropriate reagent. The differences of kinetically and thermodynamically favorable enolate anions have been utilized to reserve the regiochemistry of the resulting silyl enol ethers.[3] However, much difficulty has been encountered in controlling regiochemical integrities where such differences are very small or negligible, typically with ketones of similar substitution patterns such as R^1CH_2–CO–CH_2R^2 or R^1R^2CH–CO–CHR^3R^4.

In addition to regiochemistry of enolates, much attention has recently been attracted to the geometry of an enol derivative because it often has a marked influence on the stereochemical outcome of reaction products, e.g., an aldol adduct.[6] A few methods have been described so far to control the stereochemistry of silyl enol ethers,[7] but the range of their application is restricted to symmetrically substituted ketones or carbonyl compounds enolizable on only one side.

Table I. Preparation of 1-(Trimethylsilyl)allylic Alcohols 4

R^1	R^2	R^3	method	yield, %
C_2H_5	H	H	A[a]	92
C_4H_9	H	H	A	96
C_6H_{13}	H	H	A	96
C_8H_{17}	H	H	A	90
$C_6H_5CH_2$	H	H	A	100
-$(CH_2)_5$-		H	A	80[b]
C_2H_5	H	CH_3	A	95
C_4H_9	H	CH_3	A	89
$C_6H_5CH_2$	H	CH_3	A	92
$C_6H_5CH_2$	H	C_4H_9	A	90
C_3H_7	CH_3	H	A	64[b]
C_2H_5	C_2H_5	H	A	58[b]
C_3H_7	CH_3	CH_3	A	80[b]
C_2H_5	C_2H_5	CH_3	A	76[b]
-$(CH_2)_5$-		C_4H_9	B[c]	93[d] × 85[e]
C_2H_5	C_2H_5	C_4H_9	B	87[d] × 92[e]

[a] Method A refers to the preparation from an acyltrimethylsilane and vinylmagnesium bromide. [b] A substantial amount of the silyl enol ether **5** was also formed in this case. [c] Method B refers to the preparation from the reaction of an acyltrimethylsilane with a magnesium acetylide followed by partial reduction. [d] Yield of the 1-(trimethylsilyl)propargyl alcohol. [e] Yield of the partial reduction of the propargyl alcohol.

By way of well-documented 1,2-migration of the silyl group from carbon to oxygen,[8] we have explored another indirect

(1) Preliminary reports dealing with certain aspects of this work: Kuwajima, I.; Kato, M. *J. Chem. Soc., Chem. Commun.* **1979**, 708. Kuwajima, I.; Kato, M. *Tetrahedron Lett.* **1980**, *21*, 2745.
(2) Stork, G.; Hudrlick, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4462, 4464.
(3) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.
(4) Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 817.
(5) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981; pp 198–287. Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983; pp 206–272. Brownbridge, P. *Synthesis* **1983**, *1*, 85.
(6) Evans, D. A.; Nelson, J. V.; Taber, T. R. "Topics in Stereochemistry"; Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds.; John Wiley & Sons: New York, 1982; pp 1–115. Heathcock, C. H. "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 2.
(7) (a) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. (b) Nakamura, E.; Hashimoto, K.; Kuwajima, I. *Tetrahedron Lett.* **1978**, 2079. (c) Fataftah, Z. A.; Kopka, I. E.; Rathke, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3959.
(8) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

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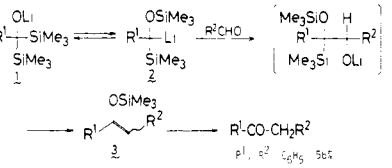
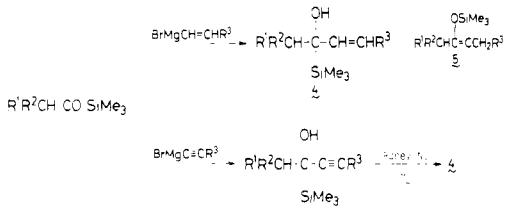
methodology for determining both regio- and stereochemistry of silyl enol ethers. At first, we attempted the reaction of a lithium alkoxide **1** of 1,1-bis(trimethylsilyl)alkanol[9] with an aldehyde, assuming that **1** may be used as an equivalent of nucleophilic species **2**. Under equilibrium conditions[8] such species may be expected to react with the aldehyde to yield the silyl enol ether **3** as depicted in eq 1. Various examinations revealed that benzylic



(1)

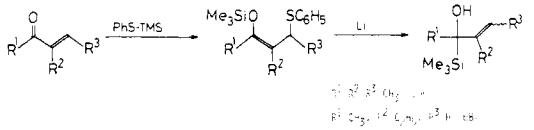
alkoxide **1** ($R^1 = C_6H_5$) reacted with an aldehyde as expected to give the corresponding aromatic ketone after hydrolytic workup, whereas saturated aliphatic alkoxides **1** (R^1 = alkyl) failed. Considering that an anion-stabilizing substituent such as the phenyl group may be needed to induce this type of rearrangement, we next turned to the examination of the rearrangement reaction of 1-(trimethylsilyl)allylic alcohols **4**.

Preparation of 1-(Trimethylsilyl)allylic Alcohols. 1-(Trimethylsilyl)allylic alcohols **4** are not available from the reactions of α,β-unsaturated ketones with (trimethylsilyl)lithium because the latter is a good nucleophile for conjugate addition.[10] However, they could be prepared easily by treating acyltrimethylsilanes[11,12] with vinylmagnesium bromide. β-Substituted vinyl Grignard reagents also reacted equally well to yield **4**. On using straight-chained acylsilanes, the resulting magnesium alkoxides are quite stable under reaction conditions to which afford the desired alcohols **4** in excellent yields (89–100%), whereas reactions with α-branched acylsilanes result in formation of silyl enol ethers **5** as side products along with alcohols **4**. Formation of these side products to which the equilibration mentioned above may be responsible appears to increase in a more polar solvent such as tetrahydrofuran (THF).[13] The two-step synthesis involving an addition reaction of magnesium acetylides[14] followed by partial reduction with Raney nickel seems to be useful for excluding this side reaction.



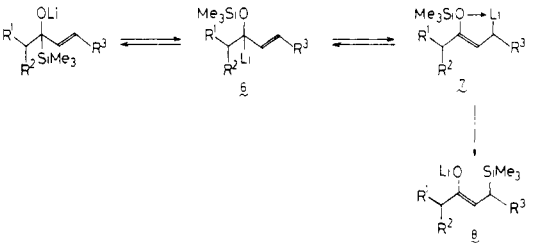
(2)

In the preparation of β-substituted allylic alcohols, α substituents on the vinyl group retarded addition reactions of the Grignard reagent to acylsilanes remarkably and further accelerated the rearrangement of the silyl group of the magnesium alkoxides produced, which led to formation of complex mixtures. The steric bulk of the trimethylsilyl group may account for these intractable results. A slightly modified procedure developed by Cohen[15] has also been employed as a good alternative, especially for preparation of β-substituted allylic alcohol.



(3)

Generation and Alkylation of Lithium Homoenolates. Judging from 1-(trimethylsilyl)benzyl alcohol, lithium alkoxides of **4** have been expected to be in equilibrium with the corresponding 1- or 3-(trimethylsiloxy)allyllithiums **6** or **7**, presumably the latter, namely lithium homoenolates, being favorable owing to internal coordination of the siloxy group to the metal cation.[16] Such equilibration may be influenced by the metal, the solvent, and the reaction temperature. By using butyllithium, we studied the



(4)

generation of homoenolate species **7** from alcohol **4**. To our surprise, it turned out to be very difficult to control the generation of the lithium alkoxide of **4** or homoenolate **7** when THF was used as the solvent as shown in the following example. A THF solution of **4** ($R^1 = C_6H_5CH_2$; $R^2 = R^3 = H$) was treated with an equimolar amount of butyllithium at −78 °C and methyl iodide was added to the resulting solution. After the reaction mixture was left to stand for 15 min at the same temperature, aqueous workup of the mixture afforded the corresponding methylation product[17] **9** ($R^1 = C_6H_5CH_2$; $R^2 = H$; $R = CH_3$) in 53% yield together with the silyl enol ether **5** ($R^1 = C_6H_5CH_2$; $R^2 = R^3 = H$) (46%). A prolonged reaction period did not improve the yield of methylated product, which may exclude a possibility that a certain amount of homoenolate **7** ($R^1 = C_6H_5CH_2$; $R^2 = R^3 = H$) survives the reaction conditions to give **5** ($R^1 = C_6H_5CH_2$; $R^2 = R^3 = H$) on quenching.

Alternatively, these results have strongly suggested that, before complete formation of the lithium alkoxide with butyllithium, a rapid equilibration has allowed the generation of the corresponding homoenolate **7** in THF, which undergoes protonation with the remaining alcohol **4** to yield **5**.

Several examinations have led to a finding that use of a nonpolar solvent such as hexane almost completely inhibits this equilibration. Such a complication as that in THF has never been observed and the alcohol **4** ($R^3 = H$) can be converted to its lithium alkoxide completely. Addition of THF to this hexane solution again effects a rapid equilibration between the alkoxide and **7** ($R^3 = H$). Although this system has contained at least two types of nucleophilic species, the lithium alkoxide and **7** ($R^3 = H$), the latter undergoes alkylation preferentially, on treatment with an alkyl iodide at about −40 °C, to afford the corresponding silyl enol ether **9** in good yields (63–74%) (see Table II). The silyl enol ethers **9** could be separated cleanly from other side products by MPLC. The reaction temperature is very critical in this alkylation since the alkoxide or anionic species **7** rearranges irreversibly to the enolate **8**[10] quite rapidly at about −20 °C (eq 4).[18] Because of

(9) Kuwajima, I.; Sato, T.; Minami, N.; Abe, T. *Tetrahedron Lett.* **1976**, 1591. Kuwajima, I.; Minami, N.; Abe, T.; Sato, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2391.

(10) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063. Still, W. C.; Mitra, A. *Tetrahedron Lett.* **1978**, 2659.

(11) Kuwajima, I.; Abe, T.; Minami, N. *Chem. Lett.* **1976**, 993. Kuwajima, I.; Arai, M.; Sato, T. *J. Am. Chem. Soc.* **1977**, *99*, 4181. Kuwajima, I.; Kato, M.; Sato, T. *J. Chem. Soc., Chem. Commun.* **1978**, 478. Kuwajima, I.; Mori, A.; Kato, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2368. About reactions of α-haloacyltrimethylsilanes with Grignard reagents, see: Sato, T.; Abe, T.; Kuwajima, I. *Tetrahedron Lett.* **1978**, 259.

(12) Reich et al. also reported a regioselective synthesis of silyl enol ethers with acyltrimethylsilanes. Reich, H. J.; Rusek, J. J.; Olson, R. E. *J. Am. Chem. Soc.* **1979**, *101*, 2225.

(13) On treating the acyltrimethylsilane (R^1, $R^2 = -(CH_2)_5-$) with vinylmagnesium bromide, the corresponding alcohol **4** and silyl enol ether **5** were formed as following: 80 and 10% yields in hexane, 75 and 25% yields in ether, and 50 and 50% yields in THF, respectively.

(14) Kuwajima, I.; Kato, M. *Tetrahedron Lett.* **1980**, *21*, 623.

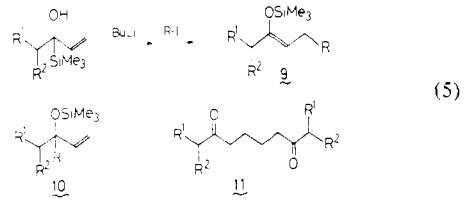
(15) Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900.

(16) For preparation of this kind of species from unsubstituted allyl ethers, see: (a) Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, *96*, 5560. (b) Still, W. C.; Macdonald, T. L. *Ibid.* **1974**, *96*, 5561. (c) Still, W. C.; Macdonald, T. L. *J. Org. Chem.* **1976**, *41*, 3620.

(17) Still reported alkylation of trialkylsilyl allyl ether via lithiation with *sec*-butyllithium followed by treating with an alkyl halide,[16b] but this method is not applicable to α-substituted allyl ethers.

(18) Alkoxides bearing β' substituents appear to rearrange to the corresponding enolates at a much lower temperature.

Table II. Alkylation Reaction of Homoenolate 7

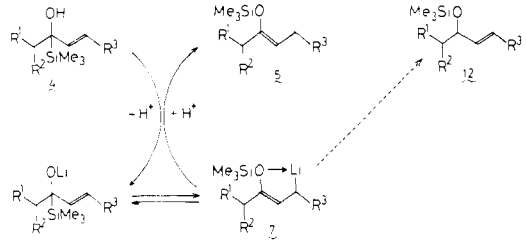


(5)

R¹	R²	R	yield, % 9[a]	10	11
C_2H_5	H	CH_3	63		
C_2H_5	H	C_4H_9	66		
C_8H_{17}	H	CH_3	66 (68)	0	28
C_8H_{17}	H	C_4H_9	72 (75)	4	21
C_8H_{17}	H	CH_2=$CHCH_2$	(65)	6	22
$C_6H_5CH_2$	H	CH_3	74 (70)	0	26
$C_6H_5CH_2$	H	C_4H_9	70 (68)	8	19
$C_6H_5CH_2$	H	CH_2=$CHCH_2$	(63)	6	23

[a] Numbers in parentheses represent yields of the parent ketones obtained after acidic workup.

Scheme I



this serious side reaction, use of less reactive alkyl chlorides or bromides is not recommended for satisfactory results. The alkylation with alkyl iodides or allyl bromides accompanies formation of two types of side products. After hydrolytic workup of the reaction mixture, these side product have been identified as **10** and **11**, resulting from an α-alkylation[19] and a dimerization of **7** (R^3 = H), respectively. Results are shown in Table II. With regard to γ- to α-selectivity, the former predominates over the latter in a ratio of 100:0 (with methyl iodide) to 95:5 or 90:10 (with butyl iodide or allyl bromide).[16b,20]

The ^{1}H NMR spectrum of each silyl enol ether **9** thus obtained has clearly suggested it to be homogeneous with respect to the geometry; each vinyl proton of **9** appears at δ 4.34–4.37 downfield from internal tetramethylsilane. This point has further been confirmed in a single case with the enol ether of 4-heptanone prepared by the present procedure. Authentic samples of (*Z*)- and (*E*)-4-(trimethylsiloxy)-3-heptenes were prepared as follows: fluoride-catalyzed silylation of 4-heptanone with ethyl (trimethylsilyl)acetate (ETSA) afforded the (*Z*) isomer exclusively,[7b] while a mixture of (*E*)-enriched enol ethers of the same ketone was obtained by using lithium diisopropylamide (LDA) and chlorotrimethylsilane.[3,7a] Complete absence of the (*E*) isomer demonstrated by comparison of their spectra has led to the conclusion that, in addition to defined regiochemistry, this alkylation reaction is highly stereoselective, probably due to fixed conformation of **7** (R^3 = H), giving the (*Z*) isomer exclusively.

Butyllithium-Catalyzed Self-Protolysis to Silyl Enol Ethers. Another important suggestion deduced from these experiments is that a small amount of base may transform the alcohol **4** into the corresponding silyl enol ether **5** or trimethylsilyl allyl ether **12** through the following four steps: (1) formation of the alkoxide, (2) generation of lithium homoenolate **7** via equilibration, (3) protonation of **7** with the remaining alcohol to yield **5** or **12**, and

(19) A numbering as α or γ is based on the structure of lithiated allylic ether.

(20) For an excellent review on reactions of allyl anionic species with electrophiles, see: Ono, M. *J. Synth. Org. Chem. Jpn.* **1980**, *38*, 836, 923.

Table III. Conversion of Alcohols **4** to the Silyl Enol Ethers **5**[a]

R¹	R²	R³	reaction temp, °C	yield, %	ratio of *Z*:*E*
C_4H_9	H	H	−20	95	96:4
C_6H_{13}	H	H	−20	91	95:5
C_8H_{17}	H	H	−20	98	96:4
$C_6H_5CH_2$	H	H	−20	96	95:5
$C_6H_5CH_2$	H	H	−40	91[b]	81:19
$-(CH_2)_5-$		H	−40	91	98:2
C_2H_5	H	CH_3	0	84[c]	94:6
C_4H_9	H	CH_3	0	85[c]	95:5
$C_6H_5CH_2$	H	CH_3	rt	81[c]	90:10
$C_6H_5CH_2$	H	CH_3	−20	83[c,d]	88:12
$C_6H_5CH_2$	H	C_4H_9	0	74[c]	89:11
C_3H_7	CH_3	H	−78	90	98:2
C_2H_5	C_2H_5	H	−78	92	98:2
C_3H_7	CH_3	CH_3	−30	94	97:3
C_2H_5	C_2H_5	CH_3	−30	95	98:2
$-(CH_2)_5-$		C_4H_9	−40	94	97:3
C_2H_5	C_2H_5	C_4H_9	−40	84	97:3

[a] All of the reactions were carried out in THF at the specified temperature, unless otherwise noted. [b] The reaction was performed in ether. [c] The corresponding isomers **12** were also formed in 5–15% in these cases. [d] The reaction was performed in dimethoxyethane.

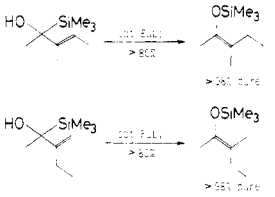
(4) regeneration of the alkoxide (Scheme I). Such consideration has prompted us to examine the fate of the alcohol **4** under the influence of a catalytic amount of butyllithium. At first, the alcohol **4** (R^1 = CH_3; R^2 = R^3 = H) was chosen as a substrate in order to determine the stereochemical outcome of the products. Treatment of this alcohol with 5 mol % of butyllithium in THF at −20 °C afforded, as expected, the corresponding silyl enol ether **5** (R^1 = CH_3; R^2 = R^3 = H) as a single product. Comparison of this product with authentic samples prepared by similar methods[3,7a,b] as described before was performed by GLC with a silicone OV-101 capillary column, and a ratio of (*Z*) and (*E*) isomer has been determined to be 95:5. In order to exclude the possibility that we might overlook the presence of the ether **12** due to its high volatility, another experiment was also performed with a higher homologue **4** (R^1 = C_4H_9; R^2 = R^3 = H). Under similar reaction conditions, it gave a mixture of two stereoisomers (*Z*:*E* = 96:4) of the silyl enol ether **5** (R^1 = C_4H_9; R^2 = R^3 = H) in excellent yield, and none of the corresponding allyl ether **12** could be detected in the reaction mixture.

In contrast to the high efficacy of butyllithium as a catalyst, a Grignard reagent such as ethylmagnesium bromide proved not to be sufficient for this conversion. With respect to higher stereoselectivity, THF is preferable to ether as the reaction solvent, although product yields are not so different. Contrary to the alkylation, control of the reaction temperature is not so important in the catalytic system presumably because of an extremely rapid quenching of **7** with **4**. Further, it should be noted here that highly pure alcohols **4** are usually required for complete conversion. Otherwise, the catalytic cycle is often destroyed, thus stopping the reaction by unknown factors. Various results are listed in Table III. From mechanistic points of view, formation of regioisomeric enol ethers of **5** is excluded, which has been verified by these experimental results.

A survey of Table III further reveals several interesting features on the relation of stereoselectivity to the structures of alcohols **4**. When one starts with γ-unsubstituted allylic alcohols **4** (R^1 = alkyl; R^2 = R^3 = H), the reaction usually proceeds at about −20 °C within 30 min to afford the corresponding silyl enol ether **5** in a ratio of *Z*:*E* = ca. 95:5. Introduction of substituents on the β' position enhances both reactivity and selectivity; the reaction of alcohols **4** (R^1 = alkyl; R^2 = alkyl; R^3 = H) takes place even at −78 °C with higher stereoselectivity (*Z*:*E* = ca. 98:2). Steric crowdedness around a carbon atom attached to silyl and oxido groups distinctly facilitates the rearrangement of alkoxide to the lithium homoenolate **7**. On the other hand, for complete conversion of γ-substituted allylic alcohols **4** ($R^3 \neq$ H), a higher reaction temperature is usually required and a slight loss of ste-

reoselectivity has sometimes been observed. Further, formation of the allyl ether **12** usually occurs in an appreciable amount (5–15%) with this type of alcohol. These findings may be attributable to both steric and electronic effects of substituents R^3.

Further, it is worthy of noting here that tetrasubstituted silyl enol ether can also be prepared easily from the corresponding allylic alcohols in a highly stereo- and regiocontrolled manner through the catalytic cycle. For example, 3-methyl-2-(trimethylsilyl)-3-penten-2-ol gave (*E*)-3-methyl-2-(trimethylsiloxy)-2-pentene, whereas its (*Z*) isomer was obtained from 3-ethyl-2-(trimethylsilyl)-3-buten-2-ol as shown in eq 6. Both of

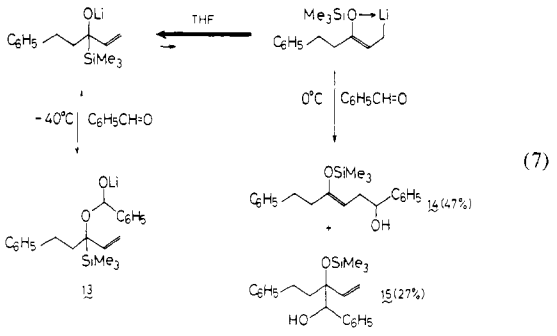


(6)

the enol ethers have been confirmed to be more than 98% isomerically pure by GLC analysis, and their geometries have been unambiguously determined by the difference of coupling constants between two methyl groups attached to olefinic linkages (J = 0.8 Hz in the (*Z*) isomer and 1.3 Hz in the (*E*) isomer).

Equilibrium Composition between Lithium Alkoxides and Lithium Homoenolates. Thus, 1-(trimethylsilyl)allylic alcohols **4** have proved to be excellent precursors of silyl enol ethers of defined stereo- and regiochemical integrities in two ways: one involves carbon chain homologation and the other a catalytic conversion. These enol ethers can be used efficiently for stereo- and regiocontrolled aldol synthesis via their boron enolates as shown already.[21]

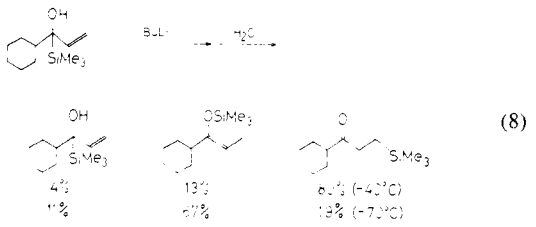
Besides such synthetic utilities, it is quite interesting to clarify, at equilibrium, which is the more favorable species, the lithium alkoxide or the lithium homoenolate **7**. In order to estimate roughly, a hexane–THF solution of lithium alkoxide of **4** (R^1 = $C_6H_5CH_2$; R^2 = R^3 = H) prepared as mentioned earlier was quenched with dilute hydrochloric acid, giving the parent alcohol exclusively. This result clearly indicates that the equilibrium is greatly favored by the alkoxide. Such equilibrium composition may also account for an unusual behavior of benzaldehyde whereby it does not react with this alkoxide–homoenolate system at a temperature (about −40 °C) at which alkylation takes place quite smoothly. The addition reaction occurs at a higher temperature to yield γ-adduct **14** and α-one **15** as shown in eq 7.



(7)

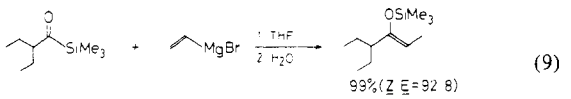
Considering the much higher reactivity of an aldehyde to such nucleophiles as **7**, it is reasonable to assume here that a concentration of homoenolate **7** is very low at this equilibrium and benzaldehyde is almost trapped with predominant alkoxide as a form of hemiacetal **13** to fix the equilibrium. Success of alkylation may only reflect such a great difference of reactivity of **7** from that of alkoxide toward alkyl iodides that the equilibrium may move to the homoenolate side as the reaction proceeds.

However, the equilibrium composition is greatly influenced by structure of alcohol **4**. As shown in eq 8, for example, similar



(8)

treatment of alcohol **4** (R^1, R^2 = $-(CH_2)_5-$; R^3 = H) at −70 °C afforded the corresponding silyl enol ether **5** (R^1, R^2 = $-(CH_2)_5-$; R^3 = H) as the major product together with the parent alcohol **4** and the β-trimethylsilyl ketone, whereas the last one was predominant at −40 °C. Further, on quenching the reaction mixture of α-ethylbutyryltrimethylsilane with vinylmagnesium bromide in THF, the corresponding silyl enol ether **5** (R^1 = R^2 = C_2H_5; R^3 = H) was obtained as a single product (eq 9).



(9)

This means that substituents on β and β' positions have a strong directing effect for both types of rearrangements, from an alkoxide to the lithium homoenolate **7** and from **7** to the β-silyl enolate anion **8**.

Thus, it has been concluded that, in addition to the anion-stabilizing effect of vinyl group, release from steric congestion around a central carbon atom should be an important factor in determining this equilibrium system, similarly to acceleration of the rearrangement in a catalytic system.

Experimental Section

General Methods. Boiling points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi EPI-G3 spectrometer; absorptions are reported in reciprocal centimeters. Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a Hitachi R-24B spectrometer; chemical shifts (δ) which are determined by comparison with that of bromoform (δ 6.87) are expressed in part per million downfield from tetramethylsilane. Analytical gas–liquid chromatography (GLC) was performed on a Hitachi 063 or 163 instrument with a flame-ionization detector and nitrogen carrier gas (1.0–1.3 kg/cm^2), using a OV-101 fused silica 20-m capillary column (Hitachi Chemi-Column). Microanalyses were performed with a Perkin-Elmer 240 at the Microanalytical Laboratory, Tokyo Institute of Technology.

Reactions involving air- or moisture-sensitive compounds were carried out in appropriate round-bottomed flasks with magnetic stirring bars under nitrogen or argon. Bulb-to-bulb distillation was performed with a Buchi Kugelrohr apparatus.

Ether, tetrahydrofuran (THF), and dimethoxyethane were distilled from sodium/benzophenone ketyl immediately before use.

Materials. Acyltrimethylsilanes were prepared from the corresponding trimethylsily enol ethers of benzene– or methane–thiol esters according to the method developed in our laboratory.[11e,d]

Preparation of 1-(Trimethylsilyl)allylic Alcohols 4. Method A. An acyltrimethylsilane (31 mmol) in ether (40 mL) was added to a THF solution of vinylmagnesium bromide (46 mL of a 1.02 M solution, 47 mmol) over 10 min at 0 °C with stirring in a nitrogen atmosphere. After the mixture was stirred for an additional 20 min at that temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted twice with ether. Then, the extracts were dried over anhydrous $MgSO_4$. Removal of the solvent followed by fractional distillation afforded the corresponding 1-(trimethylsilyl)allylic alcohol **4** (see Table I).

Method B. To ethylmagnesium bromide (32 mL of a 0.71 M THF solution, 22.5 mmol) diluted with ether (50 mL) was added an ethereal solution (25 mL) of a substituted acetylene (30 mmol) at 0 °C and the mixture was stirred for 30 min at room temperature. Then, an acyltrimethylsilane (15 mmol) in ether (25 mL) was added to the resulting solution and stirring was continued for 10 min at 0 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl and was extracted twice with ether. The extracts were washed with saturated aqueous NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent followed by distillation gave the corresponding 1-(trimethylsilyl)propargyl

(21) Kuwajima, I.; Kato, M.; Mori, A. *Tetrahedron Lett.* **1980**, *21*, 4291. See also: Wada, M. *Chem. Lett.* **1981**, 153.

(22) Evans, D. A.; Truesdale, L. K.; Grimm, K. G.; Nesbitt, S. L. *J. Am. Chem. Soc.* **1977**, *99*, 5009.

alcohol. The alcohol (5.0 mmol) thus obtained was dissolved in THF (50 mL) and treated with Raney nickel (W-2) (10 mL of 69 mg/mL in EtOH) under a hydrogen atmosphere for 30 h at room temperature. After elution through a hyfro-super cel, removal of the solvents followed by distillation gave the corresponding 1-(trimethylsilyl)allylic alcohol **4**.

3-(Trimethylsilyl)-1-hexen-3-ol: bp 72–3 °C (bath temperature) (20 mmHg); NMR (CCl_4) 0.00 (s, 9 H), 0.70–1.70 (m, 8 H including an OH signal at 1.03 as a singlet), 4.88 (dd, J = 17 and 2 Hz, 1 H), 4.92 (dd, J = 9 and 2 Hz, 1 H), 5.80 (dd, J = 17 and 9 Hz, 1 H); IR (neat) 3440, 1624, 1250 and 850. Anal. ($C_9H_{20}OSi$): C, H. **3-(Trimethylsilyl)-1-octen-3-ol**: bp 100–102 °C (bath temperature) (20 mmHg); NMR (CCl_4) 0.07 (s, 9 H), 0.68–1.80 (m, 12 H including an OH signal at 1.05 as a singlet), 4.90 (dd, J = 18 and 2 Hz, 1 H), 4.96 (dd, J = 10 and 2 Hz, 1 H), 5.83 (dd, J = 18 and 10 Hz, 1 H); IR (neat) 3400, 1610, 1245, and 840. Anal. ($C_{11}H_{24}OSi$): C, H. **3-(Trimethylsilyl)-1-decen-3-ol**: bp 90 °C (bath temperature) (10 mmHg); NMR (CCl_4) 0.20 (s, 9 H), 1.06–1.60 (m, 16 H), 5.08 (dd, J = 18 and 2 Hz, 1 H), 5.12 (dd, J = 9 and 2 Hz, 1 H), 5.90 (dd, J = 18 and 9 Hz, 1 H); IR (neat) 3400, 1620, 1238, 830. **3-(Trimethylsilyl)-1-dodecen-3-ol**: bp 99–100 °C (bath temperature) (0.28 mmHg); NMR (CCl_4) 0.01 (s, 9 H), 0.77–1.77 (m, 20 H including an OH signal at 1.11 as a singlet), 4.91 (dd, J = 17 and 2 Hz, 1 H), 4.95 (dd, J = 10 and 2 Hz, 1 H), 5.83 (dd, J = 17 and 10 Hz, 1 H). Anal. ($C_{15}H_{32}OSi$): C, H. **5-Phenyl-3-(trimethylsilyl)-1-penten-3-ol**: bp 91–2 °C (bath temperature) (0.05 mmHg); NMR (CCl_4) 0.00 (s, 9 H), 1.25 (s, 1 H), 1.53–2.10 (m, 2 H), 2.37–2.80 (m, 2 H), 4.93 (dd, J = 17 and 2 Hz, 1 H), 4.99 (dd, J = 10 and 2 Hz, 1 H), 5.87 (dd, J = 17 and 10 Hz, 1 H), 7.01 (s, 5 H); IR (neat) 3450, 3020, 1250, 845. Anal. ($C_{14}H_{22}OSi$): C, H. **1-Cyclohexyl-1-(trimethylsilyl)-2-propen-1-ol**: bp 94 °C (bath temperature) (84 mmHg); NMR (CCl_4) 0.23 (s, 9 H), 0.75–2.27 (m, 12 H), 5.07 (dd, J = 17 and 2 Hz, 1 H), 5.11 (dd, J = 9 and 2 Hz, 1 H), 6.03 (dd, J = 17 and 9 Hz, 1 H); IR (neat) 3420, 1620, 1245, 835. Anal. ($C_{12}H_{24}OSi$): C, H. **4-(Trimethylsilyl)-2-hepten-4-ol**: bp 94–5 °C (bath temperature) (30 mmHg); NMR (CCl_4) 0.03 and 0.07 (s, 9 H), 0.70–1.98 (m, 11 H including an OH signal at 1.04 as a singlet), 4.97–5.55 (m, 2 H); IR (neat) 3400, 1240, 840. **4-(Trimethylsilyl)-2-nonen-4-ol**: bp 103–4 °C (bath temperature) (5 mmHg); NMR (CCl_4) 0.00 (s, 9 H), 0.70–1.90 (m, 15 H including an OH signal), 4.92–5.50 (m, 2 H); IR (neat) 3410, 1242, 840. Anal. ($C_{12}H_{26}OSi$): C, H. **6-Phenyl-4-(trimethylsilyl)-2-hexen-4-ol**: 98–9 °C (bath temperature) (0.055 mmHg); NMR (CCl_4) 0.02 and 0.04 (s, 9 H), 1.07 (s, 1 H, OH), 1.50–1.94 (m, 5 H), 2.30–2.85 (m, 2 H), 5.00–5.52 (m, 2 H), 6.99 (s, 5 H); IR(neat) 3500, 3400, 1595, 1245, 840. **1-Phenyl-3-(trimethylsilyl)-4-nonen-3-ol**: bp 120–1 °C (bath temperature) (0.04 mmHg); NMR (CCl_4) 0.02 (s, 9 H), 0.77–1.53 (m, 8 H including an OH signal at 1.17 as a singlet), 1.57–1.94 (m, 2 H), 2.03–2.85 (m, 4 H), 4.95–5.50 (m, 2 H), 7.01 (s, 5 H); IR (neat) 3500, 1635, 1600, 1250, 843. Anal. ($C_{18}H_{30}OSi$): C, H. **4-Methyl-3-(trimethylsilyl)-1-hepten-3-ol**: bp 92 °C (bath temperature) (110 mmHg); NMR (CCl_4) 0.27 (s, 9 H), 0.75–2.09 (m, 12 H), 5.06 (dd, J = 18 and 2 Hz, 1 H), 5.11 (dd, J = 9 and 2 Hz, 1 H), 6.01 (dd, J = 18 and 9 Hz, 1 H). Anal. ($C_{11}H_{24}OSi$): C, H. **4-Ethyl-3-(trimethylsilyl)-1-hexen-3-ol**: NMR (CCl_4) 0.26 (s, 9 H), 0.65–2.09 (m, 12 H), 5.03 (dd, J = 17 and 2 Hz, 1 H), 5.07 (dd, J = 9 and 2 Hz, 1 H), 5.98 (dd, J = 18 and 9 Hz, 1 H); IR (neat) 3420, 1620, 1245, 835. **5-Methyl-4-(trimethylsilyl)-2-octen-4-ol**: bp 93 °C (bath temperature) (90 mmHg); NMR (CCl_4) 0.27 (s, 9 H), 0.75–2.09 (m, 15 H including a doublet (J = 6 Hz, 3 H) at 2.02), 5.15 (d, J = 15 Hz, 1 H), 5.47 (dq, J = 15 and 6 Hz, 1 H); IR (neat) 3420, 1620, 1245, 830. **5-Ethyl-4-(trimethylsilyl)-2-hepten-4-ol**: bp 93 °C (bath temperature) (72 mmHg); NMR (CCl_4) 0.30 (s, 9 H), 0.65–1.83 (m, 12 H), 2.05 (d, J = 5 Hz, 3 H), 5.15 (d, J = 15 Hz, 1 H), 5.47 (dq, J = 15 and 6 Hz, 1 H); IR(neat) 3420, 1630, 1240, 830. **Ethyl-4-(trimethylsilyl)-5-decen-4-ol**: bp 93–5 °C (bath temperature) (20 mmHg); NMR (CCl_4) 0.06 (s, 9 H), 0.8–1.5 (m, 20 H including an OH signal at 0.97), 2.2–2.5 (m, 1 H), 4.5–4.8 (m, 2 H); IR (neat) 3500, 1460, 1240, 840. Anal. ($C_{15}H_{32}OSi$): C, H. **1-Cyclohexyl-1-(trimethylsilyl)-2-hepten-1-ol**: bp 104–5 °C (bath temperature) (0.45 mmHg); NMR (CCl_4) 0.03 (s, 9 H), 0.9–2.0 (m, 20 H including an OH signal at 1.00), 2.0–2.5 (m, 1 H), 4.5–4.8 (m, 2 H); IR (neat) 3400, 1440, 1240, 840. Anal. ($C_{16}H_{32}OSi$): C, H.

Preparation of 3-Methyl-2-(trimethylsilyl)-3-penten-2-ol. Metallic lithium (126 mg) was treated with 1-(dimethylamino)naphthalene (90 μL) in THF (4 mL) at −70 °C. To the resulting dark green solution was added a THF (2 mL) solution of 3-methyl-4-(phenylthio)-2-(trimethylsiloxy)-2-pentene (332 mg, 1.2 mmol) prepared from 3-methyl-3-penten-2-one and phenylthiotrimethylsilane[22] and the mixture was stirred for 1.5 h at −70 °C. The reaction mixture was quenched with ice water and the aqueous layer was extracted with ether. The combined extracts were washed with 1 N HCl and were dried over anhydrous $MgSO_4$. Removal of the solvent followed by distillation afforded the title compound (205 mg, 100%): bp 138–140 °C (bath temperature); NMR (CCl_4) 0.04 (s, 9 H), 1.30 (s, 3 H), 1.59 (s, 3 H), 1.68 (m, 3 H), 5.27 (m, 1 H); IR (neat) 3400, 1240, 840. **3-Ethyl-2-(trimethylsilyl)-3-buten-2-ol** was also prepared in 68% yield by similar procedures. NMR (CCl_4) 0.03 (s, 9 H), 1.05 (t, J = 7 Hz, 3 H), 1.27 (s, 3 H), 1.97 (q, J = 7 Hz, 2 H), 4.64 (s, 1 H), 4.76 (s, 1 H); IR (neat) 3450, 1625, 1250, 840.

The Reaction of Lithium 1,1-Bis(trimethylsilyl)benzyl Alkoxide with Benzaldehyde. The lithium alkoxide was prepared by treating 1,1-bis-(trimethylsilyl)benzyl alcohol (324 mg, 1 mmol) with butyllithium (0.62 mL of a 1.78 M hexane solution, 1.1 mmol) in THF (5 mL) at 0 °C under nitrogen. To the resulting solution was added benzaldehyde (106 mg, 1 mmol) in THF (3 mL) at −40 °C and the solution was stirred for 1 h at that temperature. Then the reaction mixture was quenched with dilute HCl and extracted with ether. After the extracts were dried with anhydrous $MgSO_4$, removal of the solvents followed by separation with preparative TLC gave benzyl phenyl ketone (110 mg, 56%).

The Reaction of 5-Phenyl-3-(trimethylsilyl)-1-penten-3-ol with Butyllithium and Methyl Iodide in THF. To a THF (10 mL) solution of 5-phenyl-3-(trimethylsilyl)-1-penten-3-ol (468 mg, 2 mmol) was added butyllithium (1.24 mL of a 1.78 M hexane solution, 2.2 mmol) at −78 °C in nitrogen and the mixture was stirred for 15 min at the same temperature. Methyl iodide (284 mg, 2 mmol) in THF (5 mL) was added to the resulting solution and the mixture was stirred for 3 h at −78 °C. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl and was extracted with ether. GLC analysis of the ethereal solution showed formation of (*Z*)-5-phenyl-3-(trimethylsiloxy)-2-pentene (46%) and (*Z*)-6-phenyl-4-(trimethylsiloxy)-3-hexene (53%). Both of these products were confirmed by comparison with the samples prepared by the procedures shown later.

Alkylation of Lithium Homoenolates with Alkyl Iodides. General Procedures. To a hexane (2 mL) solution of 1-(trimethylsilyl)allylic alcohol **4** (2 mmol) was added butyllithium (1.24 mL of a 1.78 M hexane solution, 2.2 mmol) at 0 °C and the solution was stirred for 30 min at that temperature. Then, it was cooled to −78 °C and THF (10 mL) was added. After being stirred for a while, the THF (2 mL) solution of an alkyl iodide (2.4 mmol) was added and the mixture was stirred for 2–3 h at −30 °C. The reaction mixture was diluted with hexane (40 mL) precooled to −78 °C and was quenched with a buffered solution (KH_2PO_4–NaOH) precooled to 0 °C. The aqueous layer was extracted twice with hexane and the combined extracts were dried over anhydrous $MgSO_4$. Removal of the solvent followed by bulb-to-bulb distillation or chromatography using a Merck Lobar column (gross A LiChroprep Si 60) gave the corresponding alkylated silyl enol ethers **9**.

(*Z*)-4-(Trimethylsiloxy)-3-heptene: NMR (CCl_4) 0.16 (s, 9 H), 0.65–2.35 (m, 10 H), 4.35 (t, J = 7 Hz, 1 H); IR (neat) 1670, 1252, 850. **(*Z*)-4-(Trimethylsiloxy)-4-decene**: NMR (CCl_4) 0.16 (s, 9 H), 0.63–1.65 (m, 14 H), 1.70–2.16 (m, 4 H), 4.34 (t, J = 7 Hz, 1 H); IR (neat) 1665, 1250, 850. **(*Z*)-1-Phenyl-3-(trimethylsiloxy)-3-hexene**: NMR (CCl_4) 0.22 (s, 9 H), 0.91 (t, J = 7 Hz, 3 H), 1.67–2.40 (m, 4 H), 2.50–2.93 (m, 2 H), 4.36 (t, J = 7 Hz, 1 H), 7.07 (s, 5 H); IR (neat) 1675, 1600, 1250, 850. **(*Z*)-1-Phenyl-3-(trimethylsiloxy)-3-nonene**: NMR (CCl_4) 0.19 (s, 9 H), 0.73–1.50 (m, 9 H), 1.67–2.45 (m, 4 H), 2.57–2.91 (m, 2 H), 4.37 (t, J = 7 Hz, 1 H), 7.11 (s, 5 H); IR (neat) 1665, 1600, 1251, 850. **(*Z*)-4-(Trimethylsiloxy)-3-tridecene**: NMR (CCl_4) 0.16 (s, 9 H), 0.70–1.63 (m, 20 H), 1.72–2.27 (m, 4 H), 4.37 (t, J = 7 Hz, 1 H); IR (neat) 1670, 1252, 850. **(*Z*)-7-(Trimethylsiloxy)-6-hexadecene**: NMR (CCl_4) 0.15 (s, 9 H), 0.67–1.60 (m, 26 H), 1.66–2.17 (m, 4 H), 4.35 (t, J = 7 Hz, 1 H); IR (neat) 1670, 1253, 850. All of these products were further confirmed by conversion to their parent ketones through acidic treatment.

Conversion of 1-(Trimethylsilyl)allylic Alcohol 4 into the Corresponding Silyl Enol Ether 5 Catalyzed by Butyllithium. General Procedures. To a THF (10 mL) solution of 1-(trimethylsilyl)allylic alcohol **4** (2 mmol) was added butyllithium (0.08 mL of a 1.5 M hexane solution, 0.12 mmol) at −78 °C and the mixture was stirred at an ambient temperature (see Table III) for 30 min. Then, the reaction mixture was diluted with hexane (40 mL) precooled to −78 °C and quenched with a buffered solution (KH_2PO_4–NaOH). The aqueous layer was extracted twice with hexane and the combined extracts were dried over anhydrous $MgSO_4$. Removal of the solvent followed by bulb-to-bulb distillation or chromatography using a Merck Lobar column (gross A LiChroprep Si 60) gave the corresponding silyl enol ether **5**. The isomeric ratio was determined by GLC analysis.

(*Z*)-3-(Trimethylsiloxy)-2-octene: bp 92–5 °C (bath temperature) (9 mmHg); NMR (CCl_4) 0.17 (s, 9 H), 0.67–1.70 (m, 12 H), 1.70–2.17 (m, 2 H), 4.38 (q, J = 7 Hz, 1 H); IR (neat) 1662, 1245, 841. Anal. ($C_{11}H_{24}OSi$): C, H. **(*Z*)-3-(Trimethylsiloxy)-2-decene**: bp 74–6 °C (bath temperature) (5 mmHg); NMR (CCl_4) 0.21 (s, 9 H), 0.74–2.24 (m, 18 H), 4.49 (q, J = 7 Hz, 1 H); IR (neat) 1665, 1240, 840. **(*Z*)-3-(Trimethylsiloxy)-2-dodecene**: bp 100–104 °C (bath temperature) (0.2 mmHg); NMR (CCl_4) 0.13 (s, 9 H), 0.67–2.13 (m, 22 H), 4.30 (q, J

= 6 Hz, 1 H); IR (neat) 1660, 1245, 840. Anal. ($C_{15}H_{32}OSi$): C, H. **(*Z*)-5-Phenyl-3-(trimethylsiloxy)-2-pentene**: bp 79–80 °C (bath temperature) (0.04 mmHg); NMR (CCl_4) 0.20 (s, 9 H), 1.46 (dt, J = 6 and 1 Hz, 3 H), 2.00–2.46 (m, 2 H), 2.73–2.93 (m, 2 H), 4.44 (q, J = 7 Hz, 1 H), 7.07 (s, 5 H); IR (neat) 1670, 1251, 845. Anal. ($C_{14}H_{22}OSi$): C, H. **(*Z*)-1-Cyclohexyl-1-(trimethylsiloxy)-1-propene**: bp 108–9 °C (bath temperature) (5 mmHg); NMR (CCl_4) 0.15 (s, 9 H), 0.70–2.00 (m, 14 H), 4.33 (q, J = 7 Hz, 1 H); IR (neat) 1658, 1245, 1052, 838. Anal. ($C_{12}H_{24}OSi$): C, H. **(*Z*)-4-(Trimethylsiloxy)-3-heptene**: NMR (CCl_4) 0.16 (s, 9 H), 0.65–2.35 (m, 10 H), 4.35 (t, J = 7 Hz, 1 H); IR (neat) 1670, 1252, 850. **(*Z*)-4-(Trimethylsiloxy)-3-nonene**: NMR (CCl_4) 0.17 (s, 9 H), 0.65–2.23 (m, 16 H), 4.33 (t, J = 6.5 Hz, 1 H); IR (neat) 1660, 1248, 845. Anal. ($C_{12}H_{26}OSi$): C, H. **(*Z*)-4-(Trimethylsiloxy)-3-tridecene**: bp 95–6 °C (bath temperature) (0.17 mmHg); NMR (CCl_4) 0.16 (s, 9 H), 0.70–1.63 (m, 20 H), 1.72–2.27 (m, 4 H), 4.37 (t, J = 7 Hz, 1 H); IR (neat) 1670, 1252, 850. **(*Z*)-1-Phenyl-3-(trimethylsiloxy)-3-hexene**: bp 77–8 °C (bath temperature) (0.05 mmHg); NMR (CCl_4) 0.22 (s, 9 H), 0.91 (t, J = 7 Hz, 3 H), 1.67–2.40 (m, 4 H), 2.50–2.93 (m, 2 H), 4.36 (t, J = 7 Hz, 1 H), 7.07 (s, 5 H); IR (neat) 1675, 1250, 850. **(*Z*)-4-(Trimethylsiloxy)-4-decene**: NMR (CCl_4) 0.16 (s, 9 H), 0.63–1.65 (m, 14 H), 1.70–2.16 (m, 4 H), 4.34 (t, J = 7 Hz, 1 H); IR (neat) 1665, 1250, 850. **(*Z*)-7-(Trimethylsiloxy)-6-hexadecene**: NMR (CCl_4) 0.15 (s, 9 H), 0.67–1.60 (m, 26 H), 1.66–2.17 (m, 4 H), 4.35 (t, J = 7 Hz, 1 H); IR (neat) 1670, 1253, 850. **(*Z*)-1-Phenyl-3-(trimethylsiloxy)-3-nonene**: NMR (CCl_4) 0.19 (s, 9 H), 0.73–1.50 (m, 9 H), 1.67–2.45 (m, 4 H), 2.57–2.91 (m, 2 H), 4.37 (t, J = 7 Hz, 1 H), 7.11 (s, 5 H); IR (neat) 1665, 1600, 1251, 850. Anal. ($C_{18}H_{30}OSi$): C, H. **(*Z*)-4-Methyl-3-(trimethylsiloxy)-2-heptene**: bp 88 °C (bath temperature) (160 mmHg); NMR (CCl_4) 0.37 (s, 9 H), 0.90–2.37 (m, 14 H including a doublet (J = 6 Hz, 3 H) at 1.64), 4.52 (q, J = 6 Hz, 1 H); IR (neat) 1660, 1240, 825. **(*Z*)-4-Ethyl-3-(trimethylsiloxy)-2-hexene**: bp 80 °C (bath temperature) (95 mmHg); NMR (CCl_4) 0.39 (s, 9 H), 0.87–2.80 (m, 14 H including a doublet (J = 6 Hz, 3 H) at 1.73), 4.55 (q, J = 6 Hz, 1 H); IR (neat) 1665, 1240, 830. **(*Z*)-5-Methyl-4-(trimethylsiloxy)-3-octene**: bp 73 °C (bath temperature) (87 mmHg); NMR (CCl_4) 0.41 (s, 9 H), 0.85–2.37 (m, 16 H), 4.44 (t, J = 7 Hz, 1 H); IR (neat) 1660, 1240, 830. **(*Z*)-5-Ethyl-4-(trimethylsiloxy)-3-heptene**: bp 70 °C (bath temperature) (53 mmHg); NMR (CCl_4) 0.40 (s, 9 H), 0.77–2.77 (m, 16 H), 4.41 (t, J = 7 Hz, 1 H); IR (neat) 1660, 1245, 830. **(*Z*)-1-Cyclohexyl-1-(trimethylsiloxy)-1-heptene**: bp 75–7 °C (bath temperature) (0.50 mmHg); NMR (CCl_4) 0.13 (s, 9 H), 0.8–2.0 (m, 22 H), 4.23 (t, J = 7 Hz, 1 H); IR (neat) 1660, 1440, 1245, 840. Anal. ($C_{16}H_{32}OSi$): C, H. **(*Z*)-3-Ethyl-4-(trimethylsiloxy)-4-decene**: bp 62–4 °C (bath temperature) (0.12 mmHg); NMR (CCl_4) 0.17 (s, 9 H), 0.7–1.6 (m, 21 H), 1.8–2.1 (m, 1 H), 4.27 (t, J = Hz, 1 H); IR (neat) 1640, 1460, 1250, 840. **(*Z*)-3-Methyl-2-(trimethylsiloxy)-2-pentene**: NMR (CCl_4) 0.13 (s, 9 H), 0.88 (t, J = 7 Hz, 3 H), 1.53 (t, J = 0.8 Hz, 3 H), 1.70 (t, J = 0.8 Hz, 3 H), 1.97 (q, J = 7 Hz, 2 H); IR (neat) 1675, 1250, 840. **(*E*)-3-Methyl-2-(trimethylsiloxy)-2-pentene**: NMR (CCl_4) 0.13 (s, 9 H), 1.06 (t, J = 7 Hz, 3 H), 1.63 (t, J = 1.3 Hz, 3 H), 1.84 (t, J = 1.3 Hz, 3 H), 2.03 (q, J = 7 Hz, 2 H); IR (neat) 1685, 1255, 850.

The Reaction of the Lithium Alkoxide of 5-Phenyl-3-(trimethylsilyl)-1-penten-3-ol with Benzaldehyde. The alcohol (96 mg, 0.41 mmol) was treated with butyllithium (0.275 mL of a 1.51 M hexane solution) in hexane (0.1 mL) at 0 °C. Then, it was cooled to −78 °C and THF (4 mL) was added. After the solution was stirred for a few minutes, benzaldehyde (44 mg, 0.41 mmol) in THF (1 mL) was added and the mixture was gradually warmed up to 0 °C with stirring and then stirred for 30 min at that temperature. The reaction mixture was diluted with hexane and quenched with a buffer solution (KH_2PO_4–NaOH) precooled to 0 °C. The aqueous layer was extracted with ether and the combined extracts were dried over anhydrous $MgSO_4$. Removal of the solvent from the extracts followed by separation with column chromatography gave the γ-adduct **14** (66 mg, 47%) and the α-adduct **15** (38 mg, 27%). **14**: IR (neat) 3455, 1680, 1245, 845; NMR (CCl_4) 0.18 (s, 9 H), 1.98–2.88 (m, 7 H), 4.35 (t, J = 8 Hz, 1 H), 4.41 (t, J = 6 Hz, 1 H), 7.08 (s, 5 H), 7.13 (s, 5 H). **15**: IR (neat) 3450, 1245, 849; NMR (CCl_4) 0.00 (s, 9 H), 0.80–2.80 (m, 5 H), 4.45 (s, 1 H), 4.90–5.97 (m, 3 H), 7.03 (s, 5 H), 7.17 (s, 5 H).

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Registry No. 4 (R^1 = C_2H_5; R^2 = R^3 = H), 72551-25-8; **4** (R^1 = C_4H_9; R^2 = R^3 = H), 88766-72-7; **4** (R^1 = C_6H_{13}; R^2 = R_3 = H), 88766-73-8; **4** (R^1 = C_8H_{17}; R^2 = R_3 = H), 72551-27-0; **4** (R^1 = $C_6H_5CH_2$; R^2 = R^3 = H), 72551-26-9; **4** (R^1, R^2 = $-(CH_2)_5-$; R^3 = H), 76436-90-3; **4** (R^1 = C_2H_5; R^2 = H; R^3 = CH_3), 88766-74-9; **4** (R^1 = C_4H_9; R^2 = H; R^3 = CH_3), 88766-75-0; **4** (R^1 = $C_6H_5CH_2$; R^2 = H; R^3 = CH_3), 76436-92-5; **4** (R^1 = $C_6H_5CH_2$; R^2 = H; R^3 = C_4H_9), 88766-76-1; **4** (R^1 = C_3H_7; R^2 = CH_3; R^3 = H), 76436-88-9; **4** (R^1 = R^2 = C_2H_5; R^3 = H), 76436-89-0; **4** (R^1 = C_3H_7; R^2 = R^3 = CH_3), 76436-94-7; **4** (R^1 = R^2 = C_2H_5; R^3 = CH_3), 88766-77-2; **4** (R^1, R^2 = $-(CH_2)_5-$; R^3 = C_4H_9), 88766-79-4; **4** (R^1 = R^2 = C_2H_5; R^3 = C_4H_9), 88766-78-3; (*Z*)-**5** (R^1 = C_4H_9; R^2 = R^3 = H), 77189-64-1; (*E*)-**5** (R^1 = C_4H_9; R^2 = R_3 = H), 77189-58-3; (*Z*)-**5** (R^1 = C_6H_{13}; R^2 = R^3 = H), 88766-82-9; (*E*)-**5** (R^1 = C_6H_{13}; R^2 = R^3 = H), 88766-83-0; (*Z*)-**5** (R^1 = C_8H_{17}; R^2 = R_3 = H), 77189-65-2; (*E*)-**5** (R^1 = C_8H_{17}; R^2 = R_3 = H), 77189-59-4; (*Z*)-**5** (R^1 = $C_6H_5CH_2$; R^2 = R_3 = H), 70424-30-5; (*E*)-**5** (R^1 = $C_6H_5CH_2$; R^2 = R^3 = H), 70424-35-0; (*Z*)-**5** (R^1, R^2 = $-(CH_2)_5-$; R^3 = H), 76436-98-1; (*E*)-**5** (R^1, R^2 = $-(CH_2)_5-$; R^3 = H), 76437-07-5; (*Z*)-**5** (R^1 = C_2H_5; R^2 = H; R^3 = CH_3), 72551-28-1; (*E*)-**5** (R^1 = C_2H_5; R_2 = H; R^3 = CH_3), 77078-59-2; (*Z*)-**5** (R^1 = C_4H_9; R^2 = H; R_3 = CH_3), 88766-84-1; (*E*)-**5** (R^1 = C_4H_9; R^2 = H; R^3 = CH_3), 88766-85-2; (*Z*)-**5** (R^1 = $C_6H_5CH_2$; R^2 = H; R^3 = CH_3), 72551-30-5; (*E*)-**5** (R^1 = $C_6H_5CH_2$; R^2 = H; R^3 = CH_3), 76437-02-0; (*Z*)-**5** (R^1 = $C_6H_5CH_2$; R^2 = H; R^3 = C_4H_9), 72551-31-6; (*E*)-**5** (R^1 = $C_6H_5CH_2$; R^2 = H; R^3 = C_4H_9), 88766-86-3; (*Z*)-**5** (R^1 = C_3H_7; R^2 = CH_3; R^3 = H), 76436-96-9; (*E*)-**5** (R^1 = C_3H_7; R^2 = CH_3; R^3 = H), 76437-05-3; (*Z*)-**5** (R^1 = R^2 = C_2H_5; R^3 = H), 76436-97-0; (*E*)-**5** (R^1 = R^2 = C_2H_5; R^3 = H), 76437-06-4; (*Z*)-**5** (R^1 = C_3H_7; R^2 = R_3 = CH_3), 76437-01-9; (*E*)-**5** (R^1 = C_3H_7; R^2 = R^3 = CH_3), 76437-09-7; (*Z*)-**5** (R^1 = R^2 = C_2H_5; R^3 = CH_3), 88766-87-4; (*E*)-**5** (R^1 = R^2 = C_2H_5; R^3 = CH_3), 88766-88-5; (*Z*)-**5** (R^1, R^2 = $-(CH_2)_5-$; R^3 = C_4H_9), 88766-89-6; (*E*)-**5** (R^1, R^2 = $-(CH_2)_5-$; R^3 = C_4H_9), 88766-90-9; (*Z*)-**5** (R^1 = R^2 = C_2H_5; R^3 = C_4H_9), 88766-91-0; (*E*)-**5** (R^1 = R^2 = C_2H_5; R^3 = C_4H_9), 88766-92-1; **9** (R = C_4H_9, R^1 = C_2H_5; R^2 = H), 72551-29-2; **9** (R = CH_3; R^1 = C_8H_{17}; R^2 = H), 72551-32-7; **9** (R = C_4H_9; R^1 = C_8H_{17}; R^2 = H), 72551-33-8; 3-methyl-2-(trimethylsilyl)-3-penten-2-ol, 88766-80-7; 3-ethyl-2-(trimethylsilyl)-3-buten-2-ol, 88766-81-8; 1-(dimethylamino)-naphthalene, 86-56-6; 3-methyl-4-(phenylthio)-2-(trimethylsiloxy)-2-pentene, 88780-69-2; phenylthiotrimethylsilane, 4551-15-9; 3-methyl-3-penten-2-one, 565-62-8; 1,1-bis(trimethylsilyl)benzyl alcohol, 31129-63-2; benzaldehyde, 100-52-7; benzyl phenyl ketone, 451-40-1; (*Z*)-5-phenyl-3-(trimethylsiloxy)-2-pentene, 70424-30-5; (*Z*)-6-phenyl-4-(trimethylsiloxy)-3-hexene, 72551-30-5; butyllithium, 109-72-8; vinyl bromide, 593-60-2; ethyl bromide, 74-96-4.