Table X. Product Ratios from Reaction of 8 with trans,trans-2,4-Hexadiene

solvent	GC column	X	Y	23	25	24	26
benzene	G	1.0	2.9	12.5	8.9	2.6	2.6
	H	1.0	7.0	29.8	28.2		6.2

pound is not sufficiently separated from the other components of the mixture to allow inspection of its fragmentation pattern.

cis-1-((*E*)-1-Propenyl)-2-methyl-5-hydroxyindan (26): retention time (column H) 10.0 min, (column G) 18.32 min; ¹H NMR (500 MHz, CDCl₃) 6.98 (d, 1 H, *J* = 8.00 Hz, aromatic), 6.62 (s, 1 H, aromatic), 6.60 (br, s, 1 H, aromatic), 5.50 (m, 1 H, vinyl), 5.32 (d, 1 H, *J* = 11.44 Hz, vinyl), 4.48 (s, 1 H, ArOH), 3.73 (m, 1 H, ArCH–propenyl), 3.17 (dd, 1 H, *J* = 13.44, 3.78 Hz, ½ArCH₂), 2.69 (dd, 1 H, *J* = 13.41, 6.77 Hz, ½ArCH₂), 2.51 (m, 1 H, CHMe), 1.39 (d, 3 H, *J* = 7.33 Hz, vinyl CH₃), 0.95 (d, 3 H, *J* = 7.18 Hz, CH₃); GC/MS [100, 1, 10, 200, 6.2] 188 (39, M), 173 (100, –CH₃), 159 (21), 146 (18), 145 (73), 131 (31), 155 (42), 107 (7), 105 (6).

Table X shows the product ratios.

Hydrogenation of *cis*-1-((*Z*)-1-Propenyl)-2-methyl-7-hydroxyindan (20) and *trans*-1-((*E*)-1-Propenyl)-2-methyl-7-hydroxyindan (23). Several milligrams of GC-purified 20 (column A, 100 °C isothermal) were dissolved in 5 mL of methylene chloride and stirred magnetically at room temperature. Potassium azodicarboxylate (650 mg, 3.5 mmol) was added to the solution. Glacial acetic acid (200 μL, 3.5 mmol) was added over a period of 20 min via a syringe and syringe pump. The mixture was stirred for 20 min after the addition was complete. This cycle was repeated twice by adding additional portions of potassium azodicarboxylate and glacial acetic acid. After three cycles the solid was filtered and the filter cake washed with copious amounts of methylene chloride. The filtrate and the washings were combined, the solvent was removed in vacuo, and the entire process was repeated.

In this same manner 23 was also reduced by using potassium azodicarboxylate and glacial acetic acid. These two samples of hydrogenated major products along with unreacted starting material were shown to be different by GC (column G, 165 °C isothermal). This shows that the major adducts from *cis,cis*- and *trans,trans*-2,4-hexadiene differ in the relative configurations of the indan ring substituents.

cis-1-(1-Propyl)-2-methyl-7-hydroxyindan (from 20): retention time 10.58 ± 0.03 min; GC/MS [100, 1, 20, 200, 6.1] 190 (14, M⁺), 147 (100); exact mass calcd for C₁₃H₁₈O 190.1358, obsd 190.1360.

trans-1-(1-Propyl)-2-methyl-7-hydroxyindan (from 23): retention time 8.34 ± 0.03 min; GC/MS [100, 1, 20, 200, 5.8] 190 (14, M⁺), 147 (100).

Supplementary Material Available: Details of structural assignments to the dimethoxyethene adducts, Table S-I, and Scheme S-I (7 pages). Ordering information is given on any current masthead page.

On the Origin of the Configurational Instability of (1-Silyl-1-alkenyl)lithiums and Related Alkenylmetals

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Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received August 30, 1985

Abstract: The origin of the remarkably facile configurational isomerization of 1-silyl-1-metalloalkenes was investigated by using 1-(trimethylsilyl)-1-lithio-1-octene (5) as a representative example. Of seven mechanisms considered, those involving disproportionation via metal–metal exchange (mechanism I), addition–elimination (mechanism II), simple ionization of the Li–C bond (mechanism III), and polarization of the C=C bond (mechanisms IV and VI) have been firmly or tentatively ruled out. Two most plausible mechanisms (mechanisms V and VII) involve a synergistic or "push–pull" interaction of the Li–C σ bond and an empty orbital of Si, the main difference between the two lying in the extent to which the Li–C bond ionizes. The rates of configurational isomerization of (*Z*)-1-lithio-1-(trimethylsilyl)-1-octene (5a), generated by treating (*E*)-1-iodo-1-(trimethylsilyl)-1-octene (6a) with 2 equiv of *t*-BuLi in ether–pentane at −78 °C, were determined by ¹H NMR spectroscopy over the temperature range −40–0 °C. The first-order rate constants (min⁻¹) were 2.9 × 10⁻² (−40 °C), 1.5 × 10⁻¹ (−20 °C), 2.2 × 10⁻¹ (−10 °C), and 5.0 × 10⁻¹ (0 °C). The enthalpy and entropy of activation calculated from these data were Δ*H*‡ = 8.4 ± 1.0 kcal/mol and Δ*S*‡ = −37 ± 3 cal/(mol·K). The rate of isomerization of (1-(trimethylsilyl)-1-octenyl)metals is dependent on the metals and appears to be roughly proportional to the electropositivity of the metals. Four (*Z*)-β-lithio-β-(trimethylsilyl)styrenes with the *p*-H, *p*-MeO, *p*-Me, and *p*-Cl substituents were synthesized. The first-order rate constants (min⁻¹) for their configurational isomerization in ether–pentane at −20 °C were MeO 0.220 ± 0.010, Me 0.205 ± 0.015, H 0.200 ± 0.010, and Cl 0.185 ± 0.015. The ρ value calculated from these data is −0.1. Although 5 is configurationally much less stable than 1-lithio-1-ethoxyethylene (14), ethyl vinyl ether is considerably more acidic than 1-(trimethylsilyl)-1-octene (7), indicating that the configurational instability of alkenyllithiums does not necessarily correlate with the acidity of their conjugate acids. The configurational isomerization of 5 is facile (*t*₁/₂ < 4 min at 0 °C) even in hydrocarbon solvents, although Li–I exchange requires 6–9 h for ≥90% completion. In sharp contrast with the results obtained in ether–pentane, the major product (ca. 90%) was the *Z* isomer (5a), suggesting that aggregation plays an important role in hydrocarbons. If the mechanism of isomerization does not significantly change in going from ether to hydrocarbons, mechanism VII would be strongly favored over mechanism V. However, the validity of assumption is unclear at present.

An increasing number of 1,1-dimetalloalkenes, such as 1-silyl-1-metalloalkenes (1) containing Li,[1] Mg,[2] Zn,[3] or Al,[4] as well as 1-alumino-1-titanoalkenes[5] (2), have been shown to be configurationally unstable. Furthermore, theoretical studies predict
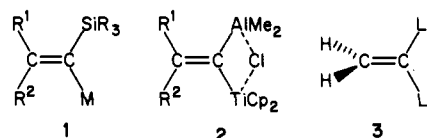
(1) (a) Zweifel, G.; Murray, R. E.; On, H. P. *J. Org. Chem.* 1981, 46, 1292. (b) Knorr, R.; Roman, T. v. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 366.

(2) Sato, F.; Watanabe, H.; Tanaka, Y.; Sato, M. *J. Chem. Soc., Chem. Commun.* 1982, 1126.

that certain 1,1-dimetalloalkenes, such as 1,1-dilithioethylene (3), possess anti van't Hoff structures.[6] Besides being of theoretical interest, the configurational instability of 1-lithio-1-silylalkenes has proved to be of considerable synthetic utility.[1a,7] These findings prompted us to investigate the origin of their configurational instability. In the present study, we have chosen 1-lithio-1-silylalkenes as the representative 1,1-dimetalloalkenes possessing configurationally unstable structures for the following reasons. Their configurational instability in ether even at room temperature has been clearly established.[1] And yet, the Z isomers of 1-lithio-1-silylalkenes can be generated as isomerically pure species via Li–halogen exchange at low temperatures in ether.[8]

In principle, 1,1-dimetalloalkenes (4) can configurationally isomerize by many different mechanisms. Disproportionation via metal–metal exchange (mechanism I) provides an intermolecular
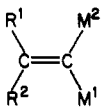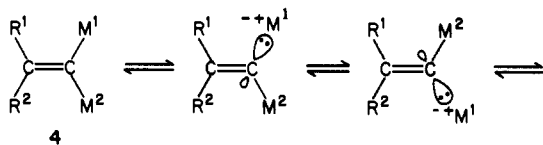
mechanism I
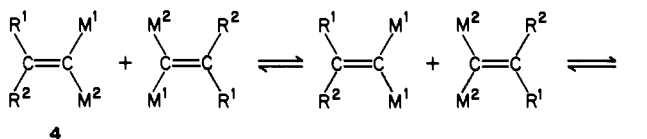
mechanism for isomerization. Another intermolecular process involving addition–elimination (mechanism II) has been considered as a possible mechanism for isomerization of alkenylalanes.[4]

mechanism II
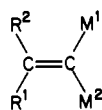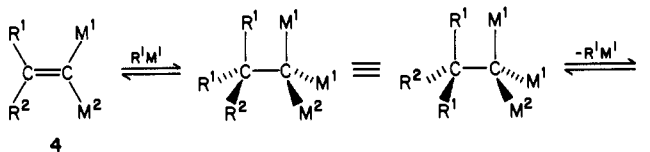
Several intramolecular processes are conceivable. Configurational isomerization may involve ionization of 4 and isomerization of carbanionic intermediates, which will be hereinafter referred to as the simple ionization mechanism (mechanism III). Al-

mechanism III

ternatively, one or both metals of 4 may act as electron acceptors

to induce polarization of the alkene π system. Configurational isomerization of 4 may then occur via rotation about the C–C single bond (mechanism IV). This may be termed here the simple polarization mechanism which has been considered for 1-silyl-1-aluminoalkenes.[4]

mechanism IV
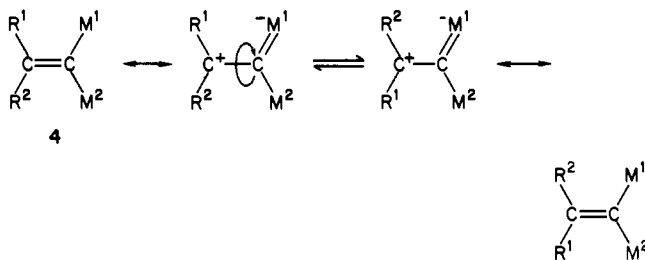
The ready availability of low-lying empty orbitals and the σ donor property of metals render the following synergistic or "push-pull" mechanisms attractive. In mechanism V, isomeri-

mechanism V
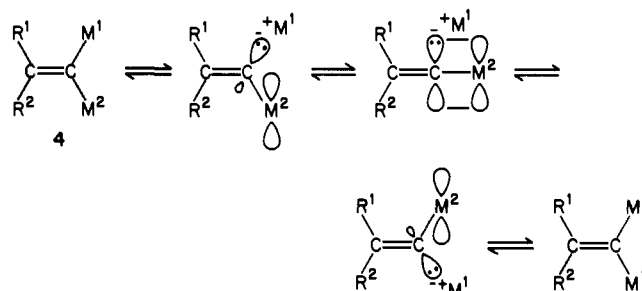
zation of the carbanionic intermediate is assisted by a low-lying empty metal orbital. On the other hand, a polar metal–carbon bond stabilizes the polar intermediates, thereby promoting isomerization in mechanism VI. One critical difference between these

mechanism VI
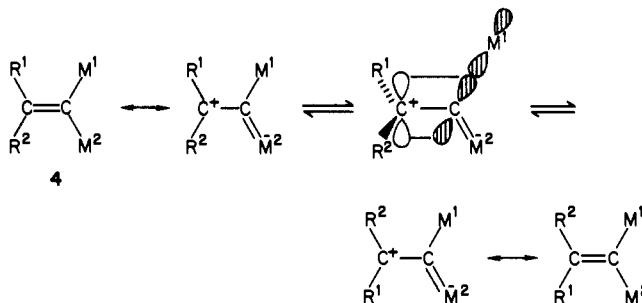
two mechanisms is that, whereas the π electrons extensively participate in mechanism VI, they do not in mechanism V. Similarly, mechanism VII does not involve the alkene π electrons,

mechanism VII
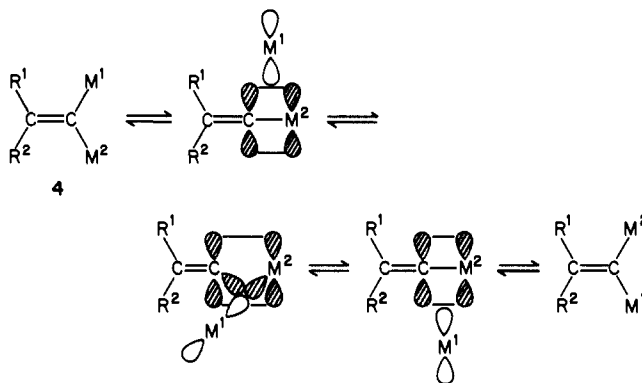
nor does it require ionization of the M^1–C bond. Instead, con-

(3) (a) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761. (b) Molander, G. A. *J. Org. Chem.* **1983**, *48*, 5409.

(4) (a) For a review containing many pertinent references, see: Eisch, J. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1. (b) Miller, J. A.; Negishi, E. *Isr. J. Chem.* **1984**, *24*, 76.

(5) Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 1276.

(6) For a review, see: Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151.

(7) (a) Negishi, E.; Boardman, L. D.; Tour, J. M.; Sawada, H.; Rand, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 6344. (b) Boardman, L. D.; Bagheri, V.; Sawada, H.; Negishi, E. *Ibid.* **1984**, *106*, 6105.

(8) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2739.

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figurational isomerization by this mechanism critically depends on the ability of an empty orbital to participate in the three-center two-electron bonding.

The main goal of this study is to evaluate the plausibility of these mechanisms with respect to the configurational isomerization of 1 with emphasis on 1-lithio-1-silylalkenes.

Results and Discussion

1-Lithio-1-(trimethylsilyl)-1-octene (5) was chosen as a representative 1,1-dimetalloalkene that is configurationally unstable and was generated by treating (*E*)-1-iodo-1-(trimethylsilyl)-1-octene[8] (6a) dissolved in ether with 2 equiv of a pentane solution
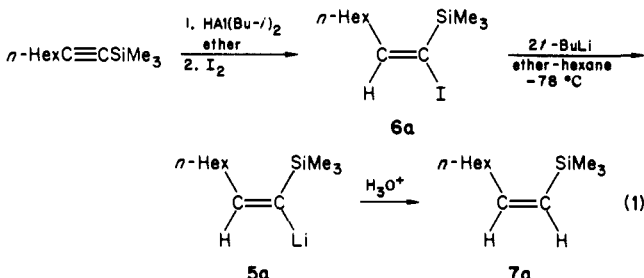
of *t*-BuLi at -78 °C according to a literature procedure.[8] Protonolysis of 5a (*Z* isomer) cleanly produced (*Z*)-1-(trimethylsilyl)-1-octene (7a) in essentially quantitative yield as an isomerically >98% pure species,[1a] indicating that 5a was also isomerically >98% pure. These results support a notion that no radical species which might induce facile configurational isomerization was generated in the Li-I exchange step. The preparation of 6b and 7b was achieved as reported in the literature.[8] The *E* and *Z* isomers of 6 and 7 were readily detected by GLC (SE-30) as base line separated peaks.
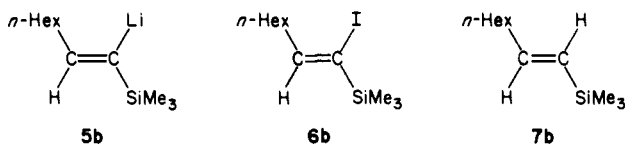
In an analogous manner, (*E*)-1-iodo-1-(triethylsilyl)-1-hexene (8a) was prepared and isomerized into its *Z* isomer (8b). When a 1:1 mixture of 6a and 8a was treated with 4 equiv of *t*-BuLi
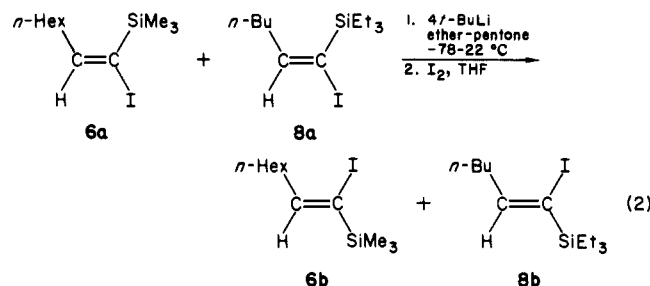
in ether-pentane (-78-22 °C) and the reaction quenched with I_2 in THF, a mixture consisting mostly of 6b and 8b in a 1:1 ratio was obtained. There was no indication for the formation of crossover products, such as 9 and 10. The results clearly rule out the disproportionation mechanism (mechanism I) for this case.
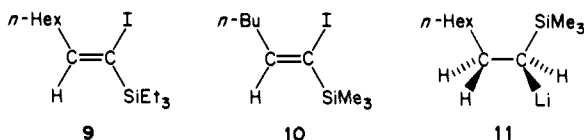
Configurational isomerization of 6a to 6b took place even with a deficient amount of *t*-BuLi.[1a] Treatment of 5a with 3 equiv of *t*-BuLi did not produce 11, as judged by the absence of *n*-octyltrimethylsilane in the protonolysis product. Some addition and/or elimination reactions of alkyllithiums and LiH are known.[9]

Table I. Isomerization of (*Z*)-1-Lithio-1-(trimethylsilyl)-1-octene[a] (5a)

temp, °C	rate constant, min^{-1}	half-life, min
-40	2.9×10^{-2}	24
-20	1.5×10^{-1}	4.7
-10	2.2×10^{-1}	3.2
0	5.0×10^{-1}	1.4

[a] 0.42 M in ether-pentane (10:9).

In particular, *t*-BuLi is known to add to vinyltrimethylsilane even at low temperature.[9b] However, there was no indication for addition of *t*-BuLi to either 5b or 6b.[9b] Furthermore, the rate of isomerization of 5a in the presence of a 100% or 200% excess of *t*-BuLi at -10 °C was essentially the same (0.18 ± 0.02 min^{-1}) as that with only the stoichiometric amount of *t*-BuLi (2 equiv). These results clearly rule out the addition-elimination mechanism (mechanism II).

Turning our attention to the intramolecular mechanisms, we measured the rate of isomerization of 5a in ether-pentane (10:9) by ^1H NMR spectroscopy. The reaction obeys the first-order rate law over the temperature range -40-0 °C. The results of rate measurements are summarized in Table I. The enthalpy and entropy of activation calculated from these data were $\Delta H^* = 8.4 \pm 1.0$ kcal/mol and $\Delta S^* = -37 \pm 3$ cal/(mol·K). These values are similar to those reported recently[1b] for the diastereotopomerization of 1-lithio-1-(trimethylsilyl)-ethylene, i.e., $\Delta H^* = 7.4 \pm 1.5$ kcal/mol and $\Delta S^* = -32 \pm 4$ cal/(mol·K).
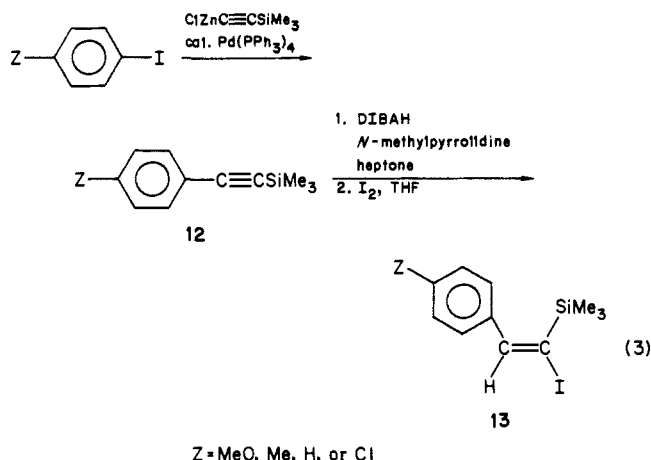
To probe the effects of countercations we treated 5a at -78 °C with KOBu-*t* (3 equiv), EtMgBr (1 equiv), EtZnCl (1 equiv), or Et_2AlCl (1 equiv) in THF-ether-pentane and measured the rates of their configurational isomerization at appropriate temperatures. The experimental results summarized in Table II indicate that addition of KOBu-*t* to 5a accelerates the rate of isomerization, while that of organometals containing Mg, Zn, and Al drastically retards the rate. Although the relative rates of isomerization of the Mg- and Zn-containing species counter our anticipation on the basis of the relative electronegativity values of Mg and Zn, the results summarized in Table II suggest that, the more electropositive the countercation is, the more facile is the configurational isomerization of 1. This tends to support mechanisms III, V, VI, and VII but does not discriminate one from the others.

To examine the plausibility of the mechanisms involving extensive polarization of the alkene π system, i.e., mechanisms IV and VI, a series of para-substituted (arylethynyl)trimethylsilanes (12), where Z = MeO, Me, H, and Cl, were prepared by the Pd-catalyzed reaction[10] of ((trimethylsilyl)ethynyl)zinc chloride with the appropriately substituted aryl iodides. Treatment of 12 with DIBAH and *N*-methylpyrrolidine in heptane and then with I_2 in THF gave 13, the isomeric purity of which was >98% in each case. Conversion of 13 into the lithio derivatives with 2 equiv of *t*-BuLi in ether-pentane (6:7) and configurational isomerization of the resultant lithio derivatives were carried out at -20 °C at the concentration of 0.47 M. The first-order rate constants (min^{-1}) are as follows: MeO 0.220 ± 0.010, Me 0.205 ± 0.015, H 0.200 ± 0.010, and Cl 0.185 ± 0.015. The ρ value calculated from these data is -0.1, which clearly disfavors mechanisms IV and VI. We conclude that the configurational isomerization of 5a does not depend on polarization of the C=C bond.

The difference between mechanism III and mechanism V lies in the extent to which the carbanionic intermediates are stabilized by the π-accepting ability of Si. To probe the significance of Si

(9) (a) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: New York, 1974. (b) For a facile reaction of vinyltrimethylsilane with *t*-BuLi, however, see: Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* 1977, *99*, 8447. We have found that the reaction of 1-octenyltrimethylsilane (7b) with *t*-BuLi (1 equiv) in ether-hexane at room temperature followed by protonolysis produces, after 12 h, (2-*tert*-butyloctyl)trimethylsilane in ca. 40% yield. However, this compound was not formed when the corresponding 1-iodo-1-octenylsilane (6b) was treated with 3 equiv of *t*-BuLi under comparable conditions. The results indicate that 5b must be much less reactive toward *t*-BuLi than 7b.

(10) King, A. O.; Negishi, E.; Villani, F. J., Jr.; Silveira, A., Jr. *J. Org. Chem.* 1978, *43*, 358.

Configurational Instability of (1-Silyl-1-alkenyl)lithiums

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Z = MeO, Me, H, or Cl

Table II. Isomerization of 1-Metallo-1-(trimethylsilyl)-1-octenes[a]

metal	temp, °C	initial $Z/E^{b,c}$	time, h	$Z/E^{b,d}$
Li	-78	97/3	3	87/13
K	-78	97/3	3	30/70
ZnEt	50	77/23	1	20/80
MgEt	50	82/18	3	79/21
			18	56/44
AlEt$_2$	50	74/26	1	72/28
			12	72/28

[a] All of these compounds were prepared from (Z)-1-lithio-1-(trimethylsilyl)-1-octene (5a) as described in the Experimental Section. The initial concentration was 0.17 M based on 5a in THF-ether-pentane (4:1:1). [b] The Z/E ratios of 1-(trimethylsilyl)-1-octene were determined by GLC after hydrolysis. [c] The initial Z/E ratio at the indicated temperature. [d] The Z/E ratios after the indicated reaction times.

Table III. Reaction of (Z)-1-Iodo-1-(trimethylsilyl)-1-octene (6b) with *tert*-Butyllithium in Hexane[a]

time, min	6b,[b] %	7a,[b] %	7b,[b] %	7a/7b
0	91			
5	75	11	4	74/26
15	78	15	4	80/20
30	70	22	5	81/19
60	54	32	6	84/16
180	32	54	7	88/12
540	4	77	8	91/9

[a] At 0 °C. The initial concentration of 6b was 0.46 M. Two equivalents of *tert*-butyllithium was used. [b] Determined by GLC after hydrolysis at 0 °C with *n*-nonane as an internal standard. 6b = (Z)-1-iodo-1-(trimethylsilyl)-1-octene; 7a = (Z)-1-(trimethylsilyl)-1-octene; 7b = (E)-1-(trimethylsilyl)-1-octene.

as a π acceptor, we compared the solution-phase acidity of 1-(trimethylsilyl)-1-octene (7) with that of ethyl vinyl ether. It has been reported that 1-ethoxy-1-lithioethylene (14) and 1-ethoxy-1-lithiopropene are configurationally stable for days at 25 °C in THF and are far more stable to isomerization than 1-lithio-1-(trimethylsilyl)ethylene,[1b] the configurational stability of which has been shown to be comparable to that of 5 (vide supra).

When a 1:1 mixture of (E)-1-(trimethylsilyl)-1-octene (7b) and ethyl vinyl ether was treated with 1 equiv of *t*-BuLi in THF-pentane (10:3) for 1 h at 22 °C, 14 was formed in about 50% yield,
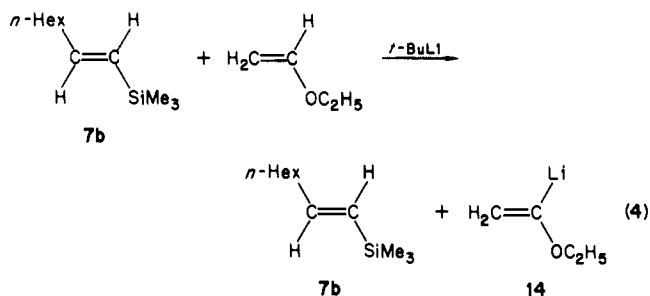
with about 50% of ethyl vinyl ether remaining unreacted. There was no indication for the conversion of 7b into 5b, with essentially 100% of 7b remaining unchanged. Therefore, the kinetic acidity of ethyl vinyl ether is higher than that of 7b under these conditions.

To further probe their relative acidities, 14 was generated by treating ethyl vinyl ether with *t*-BuLi, as described in the literature.[11] When 14 was added to 1 equiv of 6b in THF-pentane at 23 °C, no change was detected by either ^{1}H NMR analysis or GLC analysis of the protonolysis products. On the other hand, treatment of 1-ethoxy-1-iodoethylene (15) with 1 equiv of 5b in THF-ether-pentane at 23 °C gave 6b in 86% yield along with 14 formed in 84% yield (eq 5). These results imply that even
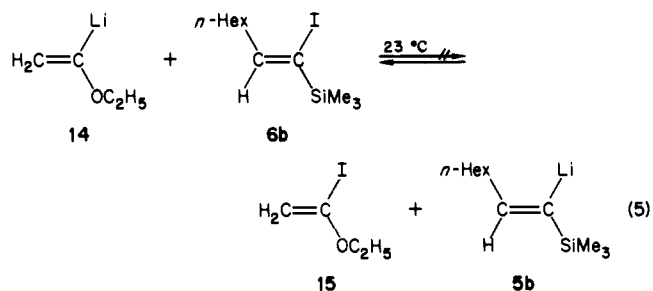
the thermodynamic acidity of ethyl vinyl ether is higher than that of 7. These results further indicate that the configurational instability of alkenyllithiums does not necessarily correlate with the acidity of their conjugate acids. This, in turn, disfavors the simple ionization mechanism (mechanism III). Thus, even if
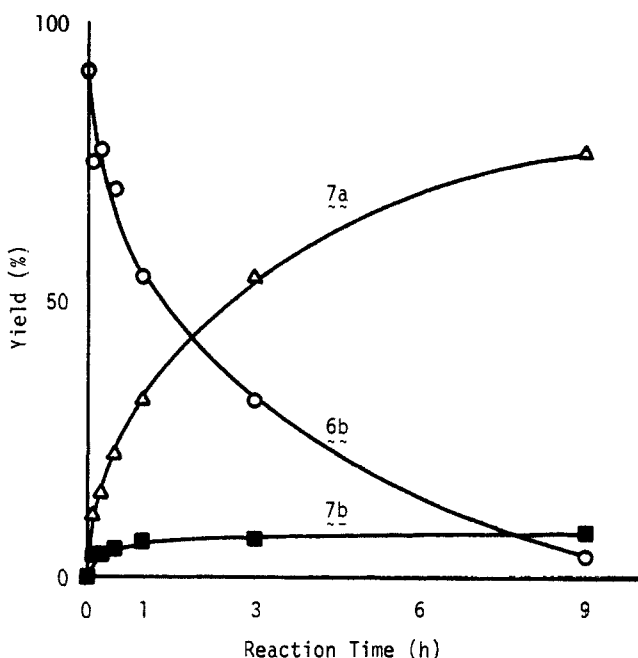

Figure 1. Reaction of (Z)-1-iodo-1-(trimethylsilyl)-1-octene (6b) with *tert*-butyllithium in hexane-pentane at 0 °C. The results were obtained by GLC analysis after hydrolysis.

ionization of the Li-C bond were a necessary condition for facile isomerization of alkenyllithiums, it does not appear to be a sufficient condition. This conclusion is in accord with the relatively high barrier (27.5-50 kcal/mol) to isomerization calculated for the free vinyl anion $^-C_2H_3$.[12] It now appears eminently reasonable to conclude that the π-accepting ability of Si must be essential to the configurational instability of 1, such as 5. It is worth mentioning here that mechanism V, in essence, corresponds to some mechanistic interpretations previously advanced to account

(11) Baldwin, J. E.; Hofle, G.; Lever, O. W., Jr. *J. Am. Chem. Soc.* 1974, *96*, 7125.

(12) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1981, *103*, 5609 and references cited therein.

Table IV. Reaction of (*E*)-1-Iodo-1-(trimethylsilyl)-1-octene (6a) with *tert*-Butyllithium in Hexane[a]

time, min	6a,[b] %	6b,[b] %	7a,[b] %	7b,[b] %	7a/7b
0	97	3			
2	54	24	16	1	94/6
7	50	28	21	1	95/5
15	42	29	21	1	96/4
30	39	32	27	1	96/4
60	30	38	33	1	96/4
180	1	41	51	5	91/9
360	2	15	71	9	89/11
540	tr	9	76	9	90/10

[a] At 0 °C. The initial concentration of 6a was 0.46 M. Two equivalents of *tert*-butyllithium was added. [b] Determined by GLC after hydrolysis at 0 °C with *n*-nonane as an internal standard. 6a = (*E*)-1-iodo-1-(trimethylsilyl)-1-octene; 6b = (*Z*)-1-iodo-1-(trimethylsilyl)-1-octene; 7a = (*Z*)-1-(trimethylsilyl)-1-octene; 7b = (*E*)-1-(trimethylsilyl)-1-octene.

for the configurational instability of certain α-substituted alkenyllithiums.[1,13]

The data presented thus far are consistent with both the π-stabilized carbanion mechanism (mechanism V) and the metal-bonded metal–carbene complex mechanism (mechanism VII). Mechanism V requires ionization of the Li–C bond, whereas mechanism VII does not, even though both are facilitated by the highly polar Li–C bond. To further probe the significance of ionization of the Li–C bond we examined the effect of solvent polarity. Treatment of 6b with 2 equiv of *t*-BuLi in hexane–pentane at 0 °C induced a relatively slow Li–I exchange reaction requiring between 6 and 9 h for 90% completion. Quite unexpectedly, the products obtained after protonolysis mainly consisted of 7a (the *Z* isomer) along with a minor amount of 7b (the *E* isomer); the ratio of 7a to 7b increased from 74/26 after 5 min to 90/10 after 9 h. The experimental results summarized in Table III and Figure 1 clearly indicate that *configurational isomerization of 5b into 5a is very rapid, requiring less than 4 min for 50% isomerization*, despite the slow Li–I exchange process. That the product of the reaction before protonolysis was indeed 5 was indicated by nearly 100% incorporation of deuterium in the α position upon treatment with D₂O. The ¹H NMR spectrum of the α-deuterated product showed a triplet for the β alkenyl proton which was further split by D at 6.2 ppm (J_{H-H} = 8 Hz, J_{H-D} = 2 Hz). The predominant formation of the *Z* isomer of 5, i.e., 5a, is in sharp contrast with the results obtained in the presence of etherial solvents. The results are, however, unquestionable, since addition of ether (10 equiv) to the reaction mixture containing mostly 5a (after 9 h) at 0 °C caused immediate isomerization of 5a into 5b. We conclude that, in hydrocarbon solvent, e.g., hexane–pentane, 5a must be more stable than 5b. It is reasonable to speculate that 5 is more highly aggregated in hydrocarbons than in ethers and that highly aggregated alkenyllithiums tend to force the β substituent, i.e., *n*-Hex, to be trans to Li or outside the alkenyllithium cluster. The above conclusion that 5b must be more stable than 5b in hydrocarbons was further supported by the results obtained by treating 6a with 2 equiv of *t*-BuLi in hexane–pentane at 0 °C (Table IV and Figure 2). In this case, the ratio of 7a to 7b changed from 95/5 after 7 min to 90/10 after 9 h. We judge that the latter represents the equilibrium ratio under these conditions. One peculiar aspect of this particular reaction is that, as 6a disappeared, its isomer 6b was formed in as much as 41% yield. Evidently, the isomerization reaction between 6a and 6b is faster than the overall rate of Li–I exchange, and in contrast with the relative stability of 5a and 5b, 6b is more stable than 6a even in hexane–pentane.

The most noteworthy finding in the experiments presented in the preceding paragraph is that the rate of configurational isomerization of 5 is rapid and is almost comparable to that in ether. If the mechanism of isomerization does not significantly change
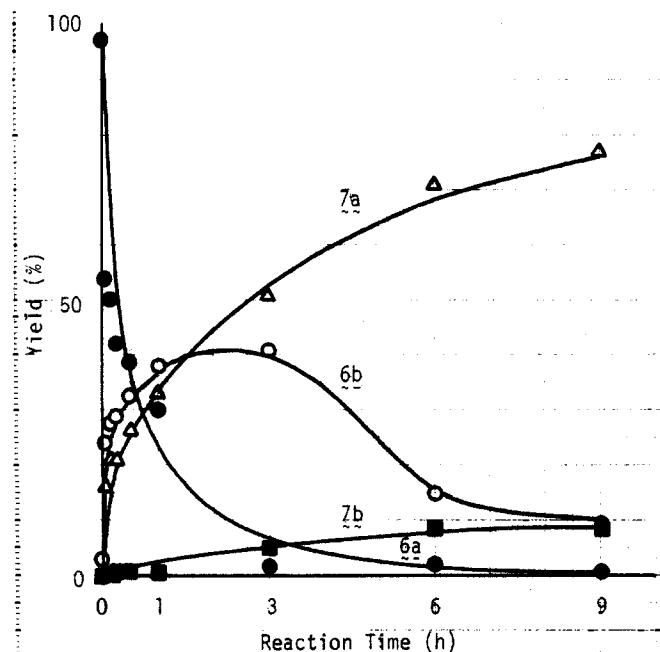
(13) (a) Panek, E. J.; Neff, B. L.; Chu, H.; Panek, M. G. *Ibid.* 1975, *97*, 3996. (b) Knorr, R.; Lattke, E. *Tetrahedron Lett.* 1977, 3969 and pertinent earlier references cited therein.

Figure 2. Reaction of (*E*)-1-iodo-1-(trimethylsilyl)-1-octene (6a) with *tert*-butyllithium in hexane–pentane at 0 °C. The results were obtained by GLC analysis after hydrolysis.

in going from ether to hexane, the above finding would strongly favor mechanism VII over mechanism V. However, the facts that the stereochemistry of the major isomer changes from *E* to *Z* in going from ether to hexane and that the Li–I exchange process is slower than the isomerization process in hydrocarbons do not permit us to make a clear choice between the two most plausible mechanisms for the reaction in ether. A future investigation of the reaction must take into consideration the effect of aggregation and some additional mechanisms, especially one-electron transfer mechanisms in cases where Li–I exchange is slower than isomerization.[14]

Experimental Section

General. All organometallic reactions were run under an inert atmosphere of nitrogen. Unless otherwise stated, chemicals were used as received. Tetrahydrofuran (THF) and ether were dried with sodium and benzophenone. Zinc chloride was flame-dried in vacuo. Diethylzinc and diisobutylaluminum hydride (DIBAH) were obtained in metal cylinders from Ethyl Corp. Diethylaluminum chloride was obtained from Alfa Chemicals Co. Gas–liquid chromatographic analyses (GLC) were performed on SE-30 columns with appropriate linear and saturated hydrocarbons as internal standards. The GLC response factor of a compound against an internal standard was measured and used to calculate its amount in a reaction mixture.

(*E*)- and (*Z*)-1-Iodo-1-(trialkylsilyl)-1-alkenes. These compounds were prepared by a literature method.[8]

(*E*)-1-Iodo-1-(trimethylsilyl)-1-octene (6a) was prepared in 54% yield (37 g) by treatment of 40 g (222 mmol) of 1-octynyltrimethylsilane in 200 mL of ether with 41 mL (230 mmol) of DIBAH at 40 °C for 3 h, followed by addition of 70 g (276 mmol) of iodine in THF at −78 °C: bp 80–81 °C (0.35 mm); ¹H NMR (CCl₄) δ 0.18 (s, 9 H), 0.65–0.95 (m, 3 H), 1.0–1.5 (m, 8 H), 1.85–2.15 (m, 2 H), 7.06 (t, *J* = 8 Hz, 1 H). The *E*/*Z* ratio was 97/3.

(*E*)-1-Iodo-1-(triethylsilyl)-1-hexene (8a) was prepared in a similar manner: bp 95–96 °C (0.3 mm); ¹H NMR (CCl₄) δ 0.4–1.5 (m, 22 H), 1.85–2.2 (m, 2 H), 7.18 (t, *J* = 8 Hz, 1 H). The *E*/*Z* ratio was 91/9.

(*Z*)-1-Iodo-1-(trimethylsilyl)-1-octene (6b) was prepared by a literature method[1a] using 6.2 g (20 mmol) of (*E*)-1-iodo-1-(trimethylsilyl)-1-octene, 50 mL of ether, 23.5 mL (1.7 M, 40 mmol) of *tert*-butyllithium, and 6 g (24 mmol) of iodine: yield 4.7 g (76%); bp 70–72 °C (0.3 mm); ¹H NMR (CCl₄) δ 0.09 (s, 9 H), 0.6–1.0 (m, 3 H), 1.05–1.6 (m, 8 H), 1.9–2.3 (m, 2 H), 6.03 (t, *J* = 6 Hz, 1 H). The *E*/*Z* ratio was 9/91.

(14) The Li–I exchange reaction in etherial solvents, e.g., THF, involving aryl iodides appears to be a polar process proceeding via hypervalent iodine "ate" complexes [Reich, H. J.; Phillips, N. H.; Reich, I. L. *J. Am. Chem. Soc.* 1985, *107*, 4101]. The possibility that the Li–I exchange process in hydrocarbons may involve radical species cannot be ruled out.

(Z)-1-Iodo-1-(triethylsilyl)-1-hexene (8b) was prepared in a similar manner: ¹H NMR (CCl₄) δ 0.4–1.5 (m, 22 ᵢ₁), 1.9–2.25 (m, 2 H), 6.04 (t, J = 7 Hz, 1 H). The E/Z ratio was 8/92.

Protonolysis of (Z)-1-Lithio-1-(trimethylsilyl)-1-octene.[1a] To 0.31 g (1 mmol) of (E)-1-iodo-1-(trimethylsilyl)-1-octene (6a) in 2 mL of ether was slowly added at –78 °C 1.18 mL (1.7 M, 2 mmol) of *tert*-butyllithium. After the mixture had been stirred for 30 min, 1 mL of methanol was added at –78 °C. Analysis of an aliquot by GLC indicated that (Z)-1-(trimethylsilyl)-1-octene, which was isomerically ca. 97% pure, was formed in essentially 100% yield.

Reaction of a 1:1 Mixture of (E)-1-Iodo-1-(trimethylsilyl)-1-octene and (E)-1-Iodo-1-(triethylsilyl)-1-hexene with tert-Butyllithium. To a mixture of 0.22 g (0.7 mmol) of (E)-1-iodo-1-(trimethylsilyl)-1-octene and 0.23 g (0.7 mmol) of (E)-iodo-1-(triethylsilyl)-1-hexene in 5 mL of ether was added 1.6 mL (2.8 mmol, 1.76 M) of a pentane solution of *tert*-butyllithium at –78 °C. The reaction mixture was stirred for 2 h at –78 °C, warmed to 22 °C, and stirred for 1 h. To the resulting mixture was added 460 mg (1.8 mmol) of iodine in THF at –78 °C. The mixture was stirred for 2 h at –78 °C, warmed to 0 °C, and then quenched with aqueous NH₄Cl solution. The organic layer was analyzed by GLC. 1-Iodo-1-(trimethylsilyl)-1-octene and 1-iodo-1-(triethylsilyl)-1-hexene were present in 88% (Z/E = 91/9) and 83% (Z/E = 92/8) yields, respectively, in the stereoisomeric ratios indicated in parentheses. No crossover products were present.

Reaction of (E)-1-Iodo-1-(trimethylsilyl)-1-octene with a Deficient Amount of tert-Butyllithium. To 0.31 g (1 mmol) of (E)-1-iodo-1-(trimethylsilyl)-1-octene in 2 mL of ether was added 0.94 mL (1.7 M, 1.6 mmol) of *tert*-butyllithium at –78 °C. After stirring for 1 h at –78 °C, the mixture was warmed to room temperature and then quenched with aqueous NH₄Cl solution. The organic layer was analyzed by GLC with *n*-nonane as an internal standard. (E)-1-(Trimethylsilyl)-1-octene, (Z)-1-(trimethylsilyl)-1-octene, and (Z)-1-iodo-1-(trimethylsilyl)-1-octene were obtained in 56%, 15%, and 29% yields, respectively. Only a trace amount of (E)-1-iodo-1-(trimethylsilyl)-1-octene remained unreacted.

Reaction of (Z)-1-Lithio-1-(trimethylsilyl)-1-octene with tert-Butyllithium. *tert*-Butyllithium (1.76 mL, 1.7 M, 3 mmol) was added at –78 °C to 0.31 g (1 mmol) of (E)-1-iodo-1-(trimethylsilyl)-1-octene in 2 mL of ether. The mixture was stirred for 1 h at –78 °C and warmed to room temperature. After stirring for 1 h at room temperature, the reaction mixture was quenched with aqueous NH₄Cl solution. The organic layer was analyzed by GLC. (E)-1-(Trimethylsilyl)-1-octene and (Z)-1-(trimethylsilyl)-1-octene were obtained in 69% and 16% yields, respectively. 1-(Trimethylsilyl)octane (11) was not detected. One unidentified product was present in a minor amount (≤5% of 7 in GLC peak area). Its amount did not increase by increasing either the reaction time or the amount of *t*-BuLi. Its retention time is longer than that of 7 but distinctly shorter than that of (2-*tert*-butyloctyl)trimethylsilane [IR (neat) 2960 (s), 2930 (s), 2860 (s), 1245 (s), 860 (s), 835 (s) cm⁻¹; ¹H NMR (CCl₄, C₆H₆) δ –0.04 (s, 9 H), 0.8–0.95 (m with a singlet at 0.80, 12 H), 1.1–1.4 (m, 13 H)] obtained in ca. 40% yield by treating 7 with 1 equiv of *t*-BuLi for 12 h at room temperature followed by protonolysis.

Determination of the Rates of Isomerization of (Z)-1-Lithio-1-(trimethylsilyl)-1-octene. To 2.46 g (7.9 mmol) of (E)-1-iodo-1-(trimethylsilyl)-1-octene in 10 mL of ether was slowly added 9.0 mL (1.76 M, 15.8 mmol) of a pentane solution of *t*-BuLi at –78 °C. The mixture was stirred for 2 h at –78 °C. A 5-mm NMR sample tube was immersed in a dry ice bath. The reaction mixture was transferred into the cold NMR sample tube by using a short double ended needle cooled with dry ice. The NMR tube was inserted into a probe of the NMR instrument at –50 °C and kept at –50 °C for 2–3 min. The sample was then warmed to –40, –20, –10, or 0 °C. The isomerization reactions at these temperatures were followed by ¹H NMR analysis performed every minute. The amounts of (E)- and (Z)-1-lithio-1-(trimethylsilyl)-1-octenes were determined on the basis of the integrations of the signals for their trimethylsilyl protons [–0.09 ppm (E) and –0.03 ppm (Z)]. The final E/Z ratios at these temperatures were 92/8–88/12. The isomerization reaction obeys the first-order rate law. The reaction rates obtained at –40, –20, –10, and 0 °C were 2.9 × 10⁻², 1.5 × 10⁻¹, 2.2 × 10⁻¹, and 5.0 × 10⁻¹ min⁻¹, respectively. The half-lives were 24, 4.7, 3.2, and 1.4 min, respectively. The enthalpy and entropy of activation calculated from these results were ΔH‡ = 8.4 ± 1.0 kcal/mol and ΔS‡ = 37 ± 3 cal/(mol·K).

Determination of the Rates of Isomerization of (Z)-1-Lithio-1-(trimethylsilyl)-1-octene in the Presence of 1 or 2 equiv of tert-Butyllithium. The rates of isomerization were determined at –10 °C as described above by using 1.23 g (3.95 mmol) of (E)-1-iodo-1-(trimethylsilyl)-1-octene, 6.75 mL (1.76 M, 11.88 mmol) or 9.0 mL (1.76 M, 15.84 mmol) of *t*-BuLi, and 2.75 mL of ether. The rates of isomerization of (Z)-1-lithio-1-(trimethylsilyl)-1-octene in the presence of 1 or 2 equiv of *t*-BuLi

determined at –10 °C were both 0.18 ± 0.02 min⁻¹.

Determination of the Countercation Effects in the Isomerization Reactions of 1-Metallo-1-(trimethylsilyl)-1-octenes Containing Potassium, Magnesium, Zinc, and Aluminum. (a) Isomerization of (Z)-1-Lithio-1-(trimethylsilyl)-1-octene (5a) in the Presence of 3 equiv of Potassium tert-Butoxide. To a mixture of 0.31 g (1 mmol) of (E)-1-iodo-1-(trimethylsilyl)-1-octene (6a) and 1 mL of ether was slowly added 1.2 mL (1.7 M, 2 mmol) of *tert*-butyllithium in pentane at –78 °C. The mixture was stirred for 1 h. To this was added slowly 0.33 g (3 mmol) of potassium *tert*-butoxide in 4 mL of THF at –78 °C. After stirring for 3 h, it was quenched with 2 mL of methanol at –78 °C and washed with water. The organic layer was analyzed by GLC. (E)-1-(Trimethylsilyl)-1-octene (7b) and (Z)-1-(trimethylsilyl)-1-octene (7a) were obtained in 70% and 30% yields, respectively. The reaction of 5a in the absence of potassium *tert*-butoxide was carried out under the same conditions except that 4 mL of THF was added instead of a mixture of potassium *tert*-butoxide and 4 mL of THF. GLC analysis indicated that 7b and 7a were obtained in 13% and 87% yields, respectively.

(b) Isomerization of (E)-1-(Ethylzinco)-1-(trimethylsilyl)-1-octene. An ether–pentane solution of 5a was prepared as above from 1 mmol of 6a. To this was slowly added at –78 °C ethylzinc chloride prepared by treating 62 mg (0.5 mmol) of diethylzinc with 68 mg (0.5 mmol) of zinc chloride in 4 mL of THF. The mixture was stirred for 1 h at –78 °C and warmed to room temperature. Hydrolysis of an aliquot gave 7a and 7b in 68% and 20% yields, respectively. Another aliquot was heated to 50 °C for 1 h. GLC analysis of the hydrolysis products indicated the formation of 7a and 7b in 18% and 73% yields, respectively. The Z/E ratio did not change, even after the reaction mixture, before quenching, was heated for an additional 2 h at 50 °C.

(c) Isomerization of (E)-1-(Ethylmagnesio)-1-(trimethylsilyl)-1-octene. This reaction was carried out in a manner similar to that for the isomerization reaction of (E)-1-(ethylzinco)-1-(trimethylsilyl)-1-octene using 0.47 mL (2.15 M, 1 mmol) of ethylmagnesium bromide in THF and 3.53 mL of THF instead of ethylzinc chloride in THF. After the reaction mixture was warmed to room temperature, GLC analysis of a hydrolyzed aliquot indicated the presence of 7a and 7b in 77% and 17% yields, respectively. Another aliquot was heated for 18 h at 50 °C. After hydrolysis, GLC analysis indicated the presence of 7a and 7b in 53% and 41% yields, respectively.

(d) Isomerization of (E)-1-(Diethylalumino)-1-(trimethylsilyl)-1-octene. The title compound was generated in situ by treating 1 mmol of 6a with 0.12 g (1 mmol) of diethylaluminum chloride in 4 mL of THF in a similar manner as described above. The mixture was stirred at –78 °C for 1 h and then warmed to room temperature. An aliquot was quenched and analyzed by GLC, which indicated the 7a to 7b ratio was 74/26. Even after the reaction mixture was heated at 50 °C for 1 and 12 h, the 7a to 7b ratio remained constant at 72/28.

In a separate experiment, a ca. 90/10 mixture of (Z)-1-lithio-1-(trimethylsilyl)-1-octene (5a) in hexane was prepared from 1 mmol of 6a in the same manner as described for the reaction of 6a with *tert*-butyllithium in hexane. To this ether-free solution of 5a was added 0.36 g (3 mmol) of diethylaluminum chloride at –78 °C for 1 h; the reaction mixture was then warmed to room temperature. An aliquot was quenched and analyzed by GLC, which indicated the 7a to 7b ratio was 80/20. This ratio did not change even after the heating of the mixture for 24 h at 50 °C.

The results of the experiments (a)–(d) are summarized in Table II.

Determination of the Rates of Isomerization of (Z)-β-Lithio-β-(trimethylsilyl)styrenes. (E)-β-Iodo-β-(trimethylsilyl)styrene and its para-substituted derivatives (13) were prepared by treating the corresponding (trimethylsilyl)phenylacetylenes (12) (13.9 g, 80 mmol) with DIBAH (11.4 g, 80 mmol) and *N*-methylpyrrolidine (6.8 g, 80 mmol) in 50 mL of heptane[15] followed by iodinolysis with iodine (25.4 g, 100 mmol) in THF. The starting acetylenes (12) prepared by reaction of (2-(trimethylsilyl)ethynyl)zinc chloride with the corresponding aryl iodides in the presence of 5 mol % of Pd(PPh₃)₄[10] were available in our laboratories.[16] (E)-β-Iodo-β-(trimethylsilyl)styrenes yielded the following data.

(a) (E)-β-Iodo-β-(trimethylsilyl)styrene: bp 86–90 °C (0.3 mm); IR (neat) 3055 (m), 3022 (m), 2978 (s), 2895 (m), 1600 (m), 1563 (m), 1488 (s), 1442 (s), 1405 (m), 1245 (s), 830–870 (br s) cm⁻¹; ¹H NMR (CCl₄, Me₄Si) δ –0.04 (s, 9 H), 7.1–7.4 (m, 5 H), 8.43 (s, 1 H); ¹³C NMR (CDCl₃) 0.89, 112.75, 127.96, 128.41, 140.37, 144.23, 154.92. High-resolution MS calcd for C₁₁H₁₅ISi: 301.9989. Found: 301.9986.

(b) (E)-β-Iodo-β-(trimethylsilyl)-*p*-methoxystyrene: bp 129–132 °C (0.35 mm); IR (neat) 3000 (w), 2960 (s), 2838 (m), 1605 (s), 1510 (s), 1245 (s), 1173 (s), 1032 (s), 888 (s), 836 (s) cm⁻¹; ¹H NMR (CCl₄,

(15) Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520.
(16) The experimental details will be published elsewhere.

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Me₄Si) σ -0.11 (s, 9 H), 3.61 (s, 3 H), 6.6-7.1 (m, 4 H), 8.15 (s, 1 H); ^{13}C NMR (CDCl₃) δ -1.25, 55.22, 113.37, 130.04, 131.29, 143.42, 159.60.

High-resolution MS calcd for C₁₂H₁₇IOSi: 332.0094. Found: 332.0083.

(c) (*E*)-β-Iodo-β-(trimethylsilyl)-*p*-methylstyrene: bp 90-92 °C (0.35 mm); IR (neat) 3020 (w), 2958 (m), 1506 (m), 1246 (s), 840 (s) cm⁻¹; ^{1}H NMR (CCl₄, Me₄Si) δ -0.05 (s, 9 H), 2.22 (s, 3 H), 6.96 (s, 4 H), 8.19 (s, 1 H); ^{13}C NMR (CDCl₃) δ 1.01, 21.29, 127.82, 128.64, 137.56, 137.67, 155.14.

High-resolution MS calcd for C₁₂H₁₇ISi: 316.0145. Found: 316.0137.

(d) (*E*)-β-Iodo-β-(trimethylsilyl)-*p*-chlorostyrene: bp 104-106 °C (0.35 mm); IR (neat) 2955 (s), 2900 (m), 1593 (m), 1483 (s), 1395 (m), 1246 (s), 1090 (s), 1013 (s), 825-865 (br s) cm⁻¹; ^{1}H NMR (CCl₄, Me₄Si) δ -0.09 (s, 9 H), 6.9-72 (m, 4 H), 8.09 (s, 1 H); ^{13}C NMR (CDCl₃) δ 0.96, 113.67, 128.22, 129.20, 133.84, 138.78, 153.49.

High-resolution MS calcd for C₁₁H₁₄ClISi: 335.9599. Found: 335.9596.

The rates of isomerization of **13** were determined as described earlier in this section by measuring the integrations of the ^{1}H NMR signals for the alkenyl protons of the *E* and *Z* isomers at appropriate time intervals at -20 °C. The ^{1}H NMR chemical shifts for the alkenyl protons of the lithiated derivatives were as follows: *p*-H (*Z* = 8.66, *E* = 8.44), *p*-MeO (*Z* = 8.58, *E* = 8.40), *p*-Me (*Z* = 8.59, *E* = 8.39), and *p*-Cl (*Z* = 8.62, *E* = 8.41). The first-order rate constants were 0.200 ± 0.010 (*p*-H), 0.220 ± 0.010 (*p*-MeO), 0.205 ± 0.015 (*p*-Me), and 0.185 ± 0.015 (*p*-Cl) min⁻¹.

Reaction of a Mixture of (*E*)-1-(Trimethylsilyl)-1-octene and Ethyl Vinyl Ether with *tert*-Butyllithium. To a mxiture of 0.18 g (1 mmol) of (*E*)-1-(trimethylsilyl)-1-octene (**7b**), 0.07 g (1 mmol) of ethyl vinyl ether, and 2 mL of THF was added 0.59 mL (1.7 M, 1 mmol) of *tert*-butyl-lithium in pentane at -78 °C. After stirring for 30 min at -78 °C, the mixture was warmed to room temperature and stirred for 30 min. The ^{1}H NMR spectrum of the reaction mixture indicated that 1-lithio-1-ethoxyethylene was formed in ca. 50% yield, with the other 50% remaining unreacted. Essentially 100% of **7b** remained unreacted without showing any sign of its reaction with *tert*-butyllithium.

Reaction of (*Z*)-1-Iodo-1-(trimethylsilyl)-1-octene (6b) with 1-Lithio-1-ethoxyethylene (14). 1-Lithio-1-ethoxyethylene (**14**) was prepared by a literature method[11] using 0.23 g (3.2 mmol) of ethyl vinyl ether, 2 mL of THF, and 1.18 mL (1.7 M, 2 mmol) of *tert*-butyllithium. To this was added 0.31 g (1 mmol) of **6b** at room temperature. After the mixture stirred for 1 h, examination of the reaction mixture by ^{1}H NMR spectroscopy and GLC indicated no reaction had taken place.

Reaction of (*E*)-1-Lithio-1-(trimethylsilyl)-1-octene (5b) with 1-Iodo-1-ethoxyethylene. 1-Lithio-1-ethoxyethylene was prepared as in the preceding experiment. To this was added slowly 0.51 g (2 mmol) of iodine in 2 mL of THF at -78 °C. After stirring for 1 h at -78 °C, the

reaction mixture was warmed to room temperature. Its ^{1}H NMR spectrum showed that the peak at 4.8 ppm for the vinyl protons of 1-lithio-1-ethoxyethylene had disappeared and that two doublets had appeared at 4.6 and 5.1 ppm. To this solution was added at room temperature **5b** prepared by treatment of 0.62 g (2 mmol) of **6b** in 2 mL of ether with 2.35 mL (1.7 M, 4 mmol) of *tert*-butyllithium at -78 °C. After the mixture was stirred for 1 h at room temperature, ^{1}H NMR analysis indicated that (*Z*)-1-iodo-1-(trimethylsilyl)-1-octene (**6b**) and 1-lithio-1-ethoxyethylene were obtained in 86% and 84% yields, respectively.

Reaction of (*E*)- and (*Z*)-1-Iodo-1-(trimethylsilyl)-1-octenes (6) with *tert*-Butyllithium in Hexane-Pentane. To 0.93 g (3 mmol) of (*E*)- or (*Z*)-1-iodo-1-(trimethylsilyl)-1-octene (**6**) dissolved in 3 mL of hexane was added 3.53 mL (1.7 M, 6 mmol) of *tert*-butyllithium in pentane at 0 °C. The mixture was stirred at 0 °C and analyzed by GLC after hydrolysis. The experimental results are summarized in Tables III and IV as well as in Figures 1 and 2. Treatment of the reaction mixture derived from the *Z* isomer of **6** with D₂O after 9 h gave (*Z*)-1-deuterio-1-(trimethylsilyl)-1-octene, whose ^{1}H NMR spectrum showed the β-alkenyl proton signal at 6.2 ppm (J_{H-H} = 8 Hz, J_{H-D} = 2 Hz). When an excess of ether or THF (10 equiv) was added after 9 h at 0 °C to the reaction mixture derived from the *Z* isomer of **6**, the *E/Z* ratio of **7**, obtained after hydrolysis, changed from ca. 10/90 to ca. 80/20 within 10-15 min after the addition of ether or THF.