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Effect of Solvent and Temperature on the Lithium−Bromine Exchange of Vinyl Bromides: Reactions of *n*-Butyllithium and *t*-Butyllithium with (*E*)-5-Bromo-5-decene

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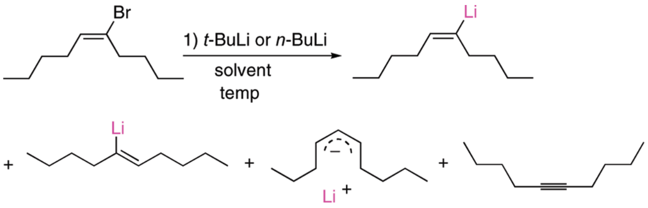

The outcome of reactions of (*E*)-5-bromo-5-decene (**1**), a representative vinyl bromide, with *t*-BuLi or *n*-BuLi at 0 °C and room temperature, respectively, in a variety of solvent systems has been investigated. Vinyl bromide **1** does not react with *t*-BuLi in pure heptane; however, the presence of even small quantities of an ether in a predominantly heptane medium resulted in virtually complete consumption of **1** at 0 °C, resulting in nearly the same distribution of products, including 60−80% of (*Z*)-5-decenyllithium, regardless of the solvent composition. Vinyl bromide **1** reacts slowly with *n*-BuLi at room temperature in a variety of ether and heptane-ether mixtures to afford a mixture of products including significant quantities of recovered starting material. The results of these experiments demonstrate that lithium−bromine exchange between a vinyl bromide and either *t*-BuLi or *n*-BuLi at temperatures significantly above −78 °C is not an efficient method for the generation of a vinyllithium.

Introduction

We have been interested for some time in the effects of solvent and temperature on the outcome of lithium−halogen exchange reactions of organohalides with *n*-butyllithium (*n*-BuLi) or *t*-butyllithium (*t*-BuLi).[1] Several years ago, we reported the results of a study of the reactions of a representative aryl bromide, 1-bromo-4-*t*-butylbenzene, with *n*-BuLi or *t*-BuLi at 0 °C in a variety of solvent systems.[2] The products of reactions of the aryl bromide with *n*-BuLi varied considerably with changes in solvent composition: there was no reaction with *n*-BuLi in pure heptane; the slow exchange reaction in diethyl ether was virtually quantitative in heptane containing a small quantity of THF; and the reaction with *n*-BuLi in THF resulted in considerable coupling. On the other hand, lithium−bromine exchange was found to be the exclusive outcome of reactions of the aryl bromide with *t*-BuLi at 0 °C in every solvent studied except pure hydrocarbons.[2]

Prompted by the results of this study, we have extended the investigation to assess the effect of solvent and temperature on the outcome of the reactions of a representative vinyl bromide, (*E*)-5-bromo-5-decene (**1**), with *t*-BuLi and *n*-BuLi. As detailed below, the behavior of the vinyl bromide when treated with an alkyllithium at temperatures near ambient is considerably more complex than is the behavior of an aryl bromide. The results of this study imply that a vinyllithium can not be generated cleanly from a vinyl bromide by lithium−bromine exchange at temperatures significantly above −78 °C.

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(1) (a) Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098. (b) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T.; Wang, W. *Tetrahedron Lett.* **1986**, *27*, 1861. (c) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T. *Tetrahedron Lett.* **1986**, *27*, 1865. (d) Bailey, W. F.; Ovaska, T. V. Mechanisms of Importance in Synthesis. In *Advances in Detailed Reaction Mechanisms*; Coxon, J. M., Ed.; JAI Press: Greenwich, CT; Vol. 3, 1994, p 251. (e) Wiberg, K. B.; Sklenak, S.; Bailey, W. F. *J. Org. Chem.* **2000**, *65*, 2014. (f) Bailey, W. F.; Brubaker, J. D.; Jordan, K. P. *J. Organomet. Chem.* **2003**, *681*, 210. (g) Bailey, W. F.; Rathman, T. L. In *Process Chemistry in the Pharmaceutical Industry: Challenges in an Ever Changing Climate*; Gadamasetti, K., Braish, T., Eds.; CRC Press: Boca Raton, FL, 2008; Vol. 2, p 205. (h) Rathman, T. L.; Bailey, W. F. *Org. Process Res. Dev.* **2009**, *13*, 144.

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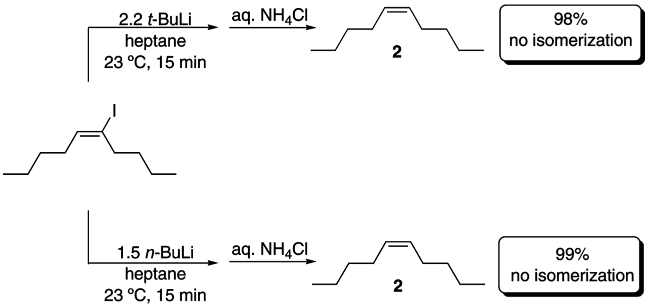
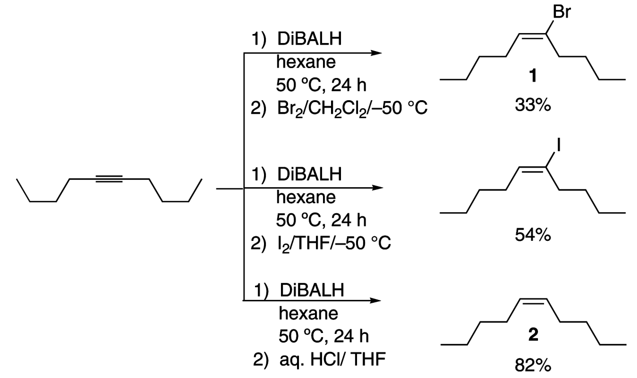
Results and Discussion

Isomerically pure (*E*)-5-bromo-5-decene (**1**) was obtained by DIBALH reduction of 5-decyne and quench with bromine, as illustrated in Scheme 1;[3] (*E*)-5-iodo-5-decene and (*Z*)-5-decene (**2**) were prepared in analogous fashion.[3] At the outset it should be noted that (*E*)-5-bromo-5-decene (**1**) was observed to isomerize slowly to an approximately 90:10 mixture of the *E*- and *Z*-isomers on standing in ambient light at room temperature or upon distillation. This slow loss of stereochemical integrity was not unexpected; some time ago, Dreiding and Pratt noted that isomerically pure samples of vinyl bromides isomerize to an equilibrium mixture upon exposure to ambient light.[4] Consequently, samples of **1** are best stored in a dark refrigerator. Nonetheless, the isomeric composition of the 5-bromo-5-decene used in this study ranged from E/Z = 99:1 to 89:11, and the results of the experiments discussed below were corrected, where appropriate, to reflect the differing isomeric compositions of the vinyl bromide substrate.

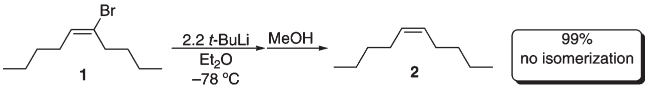
Several procedures have been developed for the preparation of vinyllithiums by lithium−halogen exchange. Peterson and Polt,[5] as well as Utimoto and co-workers,[6] have reported that vinyllithiums may be generated stereospecifically and in high yield at room temperature by lithium−iodine exchange between a vinyl iodide and either *t*-BuLi or *n*-BuLi in a hydrocarbon solvent. Indeed, this is an excellent, experimentally straightforward method for the preparation of vinyllithiums with retention of configuration: isomerically pure (*Z*)-5-decene (**2**) was obtained in virtually quantitative yield, as shown below, upon treatment of (*E*)-5-iodo-5-decene with either *t*-BuLi or *n*-BuLi in heptane at +23 °C followed by quenching of the vinyllithium with aqueous acid. In this connection, it might be noted that Utimoto and co-workers observed that vinyl bromides afforded low yields of vinyllithium when treated with *n*-BuLi at room temperature in hydrocarbon solution but the products of such reactions were not reported (vide infra).[6]



SCHEME 1



A widely used method for the preparation of vinyllithiums, developed by Seebach and Neumann,[7] involves low-temperature lithium-halogen exchange between a vinyl bromide or iodide using 2 mol equiv of *t*-BuLi in an ethereal solvent. Following a slightly modified Seebach-Newman protocol, depicted below,[8] (*E*)-5-bromo-5-decene (**1**) was converted to pure (*Z*)-5-decene in essentially quantitative yield upon treatment with 2.2 equiv of *t*-BuLi in diethyl ether at −78 °C followed by quench with methanol.



In short, lithium−bromine exchange between a vinyl bromide and an alkyllithium is a rapid and clean reaction when conducted at low temperature ($\leq$78 C) in an ethereal solvent, but it is a slow and ineffective process when conducted at room temperature in a hydrocarbon solvent. It occurred to us that it might be possible to prepare vinyllithiums at temperatures significantly higher than −78 °C by conducting the lithium−bromine exchange in a hydrocarbon−ether solvent system. To this end, the effect of solvent variation on the course of reactions of (*E*)-5-bromo-5-decene (**1**) with *t*-BuLi and with *n*-BuLi were explored at 0 °C and at room temperature, respectively.

Reactions with *t*-BuLi. Experiments were conducted at 0 °C in solvent systems composed of heptane-dialkyl ethers in various proportions.[9] As detailed in the Experimental Section, 2.2 mol equiv of *t*-BuLi in heptane was added dropwise at 0 °C to solutions of **1** in the appropriate solvent, and the resulting 0.1 M reaction mixtures were allowed to stand under argon at 0 °C for an additional 15 min before quench with MeOH. Control experiments involving an "inverse addition" demonstrated that adding solutions of **1** in heptane−dialkyl ethers to *t*-BuLi in heptane afforded identical results. Thus, the mode of addition of *t*-BuLi and vinyl bromide is inconsequential to the outcome of reactions. Crude product mixtures were analyzed by capillary GC and by GC-MS, affording baseline separation of the five products (**2**−**6**), illustrated in Scheme 2, that accounted for essentially the total material balance.[10] The (*Z*)-5-decene (**2**), (*E*)-5-decene (**3**), 5-decyne (**5**), and 5-*t*-butyl-5-decanol (**6**) were identified by comparison of their retention times and

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(3) (a) Zweifel, G.; Whitney, C. *J. Am. Chem. Soc.* **1967**, *89*, 2753. (b) Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 2754.

(4) Dreiding, A. S.; Pratt, R. J. *J. Am. Chem. Soc.* **1954**, *76*, 1902.

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(6) (a) Shinokubo, H.; Miki, H.; Yokoo, T.; Oshima, K.; Utimoto, K. *Tetrahedron* **1995**, *51*, 11681. (b) Yokoo, T.; Shinokubo, H.; Oshima, K.; Utimoto, K. *Synlett* **1994**, 645.

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(8) Bailey, W. F.; Wachter-Jurcsak, N. M.; Pineau, M. R.; Ovaska, T. V.; Warren, R. R.; Lewis, C. E. *J. Org. Chem.* **1996**, *61*, 8216–8228.

(9) Given the fairly rapid consumption of *t*-BuLi by proton abstraction from various ethers at 0 °C, the exchange reaction between **1** and *t*-BuLi in solvent containing more than 10% by vol of an ether was not investigated. The half-life of *t*-BuLi in various solvents has been reported: see Stanetty, P.; Mihovilovic, M. *J. Org. Chem.* **1997**, *62*, 1514.

(10) The second equivalent of *t*-BuLi used in these reactions consumes the *t*-BuBr cogenerated in the exchange to give isobutane, isobutylene, and LiBr; no attempt was made to quantitate these products: see (a) Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404. (b) Seebach, D.; Neumann, H. *Chem. Ber.* **1974**, *107*, 847.

SCHEME 2

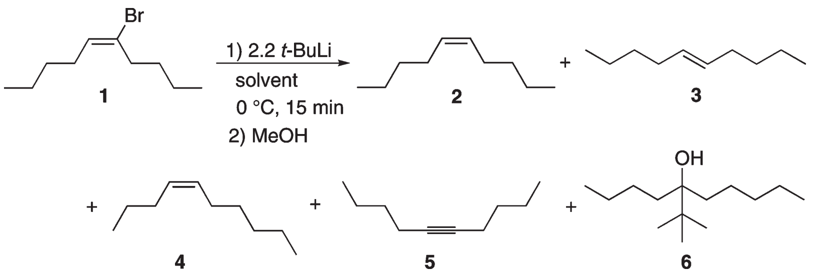

TABLE 1. Reactions of (*E*)-5-Bromo-5-decene (1) with *t*-BuLi at 0 °C in Various Solvents (Scheme 2)

		products,[a] %					
entry	solvent	**2**	**3**	**4**	**5**	**6**	**1**
1	heptane	2.3	tr		1.3	0.5	95.1
2	heptane−Et_2O (99:1 by vol)	72.9	16.0	8.0	1.8	1.3	
3	heptane−Et_2O (19:1 by vol)	71.3	17.0	6.3	2.2	2.8	tr
4	heptane−Et_2O (9:1 by vol)	66.8	17.5	8.3	1.7	1.4	
5	heptane−THF (99:1 by vol)	72.7	17.2	6.7	1.6	2.0	
6	heptane−THF (19:1 by vol)	69.0	17.5	6.9	1.5	1.5	
7	heptane−THF (9:1 by vol)	66.0	20.2	7.6	1.9	3.2	
8	heptane−MeTHF[b] (99:1 by vol)	83.8	10.6	2.5	1.3	0.8	tr
9	heptane−MeTHF[b] (19:1 by vol)	80.8	8.0	6.9	1.5	1.8	tr
10	heptane−MeTHF[b] (9:1 by vol)	77.4	9.6	7.4	1.7	2.2	tr
11	heptane−MTBE (99:1 by vol)	71.1	16.5	6.6	1.6	tr	2.4
12	heptane−MTBE (19:1 by vol)	67.7	21.9	4.9	2.6	1.3	tr
13	heptane−MTBE (9:1 by vol)	62.0	27.2	4.6	2.6	3.4	

[a] Yields were determined by capillary GC; tr indicates that a trace (viz. < 0.2%) of material was detected. [b] 2-Methyltetrahydrofuran.

mass spectra to those of authentic samples; (*Z*)-4-decene (**4**) was identified on the basis of its reported GC retention time and EI mass spectrum.[11] It might be noted that the allene, 4,5-decadiene, whose mass spectra has been reported,[12] was not observed as a product of any of the reactions. The results of these experiments are summarized in Table 1.

Inspection of the data presented in Table 1 reveals that *t*-BuLi in heptane is, for all intents and purposes, unreactive; 95% of the starting bromide (**1**) is recovered (Table 1, entry 1). Given that *t*-BuLi is known to exist as a tetrameric aggregate in hydrocarbon solvent,[13] it would appear that the tetrameric species does not participate effectively in the lithium−bromine exchange. However, the presence of even small quantities (viz, 1% by vol) of an ether (Et_2O, THF, 2-methyltetrahydrofuran,[14] or MTBE) in a predominantly heptane medium resulted in virtually complete consumption of the vinyl bromide (Table 1, entries 2, 5, 8, and 11). Moreover, and somewhat surprisingly, addition of any of the ethers used in this study, in any proportion from 1 to 10% by volume, led to nearly the same product distribution. The yield of (*Z*)-5-decenyllithium, assayed as (*Z*)-5-decene (**2**), is a rather modest 60−80% for all of the reactions studied (Table 1). Clearly, lithium−bromine exchange is not an efficient process in hydrocarbon−ether mixtures at 0 °C.

The rather high proportion of (*E*)-5-decene (**3**) in the product mixtures was unanticipated. Were the lithium−bromine exchange to proceed with retention of configuration, via a 10-Br-2-ate intermediate or transition state,[15] (*Z*)-5-decenyllithium would result and the product, following quench with MeOH, would be (*Z*)-5-decene (**2**). Given that a vinyllithium generated under the conditions used for the reactions summarized in Table 1 (15 min at 0 °C) is expected to be configurationally stable,[16] it would seem that lithium−bromine exchange with retention of configuration is not the exclusive route followed in these reactions. The results are consistent with an exchange that proceeds, at least in part, via single-electron transfer (SET) from the *t*-BuLi to the vinyl bromide substrate to give a vinyl radical intermediate[17] (Scheme 3). Vinyl radicals are known to invert rapidly[18] and, for this reason, an exchange proceeding by SET would be expected to result in at least partial isomerization of the vinyllithium product. The fact that the relative proportions of (*Z*)-5-decene (**2**) and (*E*)-5-decene (**3**) are roughly constant (viz. **2**/**3** ~ 4) for all reactions except for those conducted in a medium containing significant amounts of 2-methyltetrahydrofuran (Table 1, entries 9 and 10; **2**/**3** ~ 9) is consistent with this rationale.

The formation of small quantities of alkyne **5** in these reactions is almost certainly the result of an elimination of HBr from the vinyl bromide substrate. The observation of minor but non-negligible quantities of (*Z*)-4-decene (**4**) as a product of these reactions is more problematic. The fact that only the *Z*- isomer is observed (a control experiment, using a commercial sample containing both (*Z*)-4-decene and (*E*)-4-decene, demonstrated that both isomers could be detected by the GC method used for analysis of reaction mixtures) suggests, as illustrated in Scheme 4, that (*Z*)-4-decene (**4**) was generated by protonation of an allyllithium intermediate: the U-shaped geometry of the 1,3-dialkylallyl anion depicted in Scheme 4 is

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[11] *National Institute of Standards and Technology Chemistry WebBook, Standard Reference Database No. 69*. http://webbook.nist.gov/chemistry (accessed December **2009**).

[12] Back, T. G.; Krishna, M. V.; Muralidharan, K. R. *J. Org. Chem.* **1989**, *54*, 4146.

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[14] 2-Methyltetrahydrofuran, which is only partially soluble in water, has been used as a solvent for a variety of organometallic reactions; it reacts more slowly with organolithium reagents than does THF: see (a) Aycock, D. F. *Org. Process Res. Dev.* **2007**, *11*, 156. (b) Bates, R. *J. Org. Chem.* **1972**, *37*, 560.

[15] Wiberg, K. B.; Sklenak, S.; Bailey, W. F. *Organometallics* **2001**, *20*, 771.

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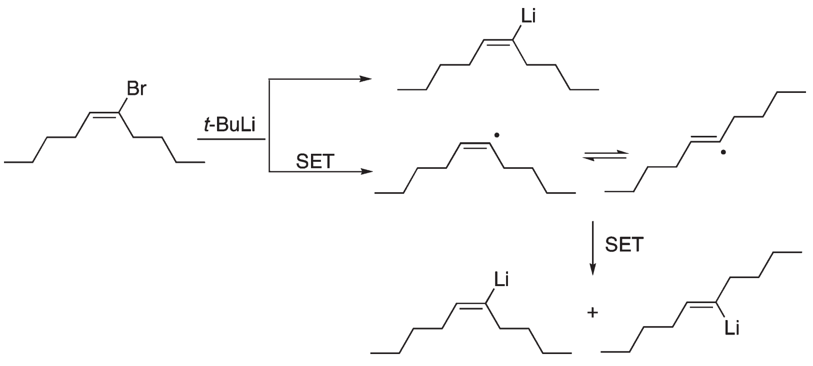
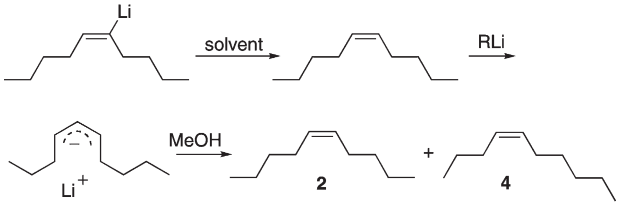
SCHEME 3

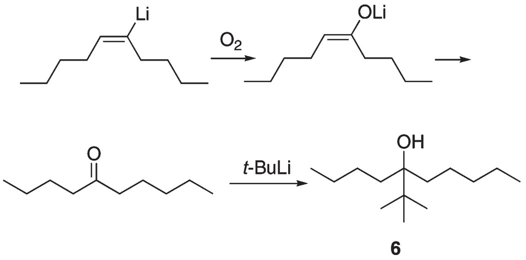


SCHEME 4



consistent with the well-established preference for allylic anions to adopt the *Z*-geometry.[19] Such an allyllithium would be formed upon proton abstraction (either by *t*-BuLi or a vinyllithium) from (*Z*)-5-decene (**2**) generated by inadvertent quench of (*Z*)-5-decenyllithium by solvent or adventitious moisture.

The presence of minor amounts of alcohol **6** in some of the reaction product mixtures has a more prosaic origin: dissolved molecular oxygen. Typically, an organohalide substrate should be rendered oxygen-free by freeze–thaw cycles or by sparging with argon before conducting a lithium-halogen exchange reaction; however, due to concerns about the potential configurational photolability of (*E*)-5-bromo-5-decene noted above, the vinyl bromide was not deoxygenated before use in these experiments. Consequently, the vinyllithium product is apparently trapped by reaction with dissolved molecular oxygen present in the reaction mixtures to give a lithium enolate.[20] As illustrated below, addition of residual *t*-BuLi to the ketone generated upon quench of reaction mixtures accounts for the formation of small quantities of tertiary alcohol **6**.



Reactions with *n*-BuLi. Experiments with *n*-BuLi in hexane were conducted at room temperature (reactions of *n*-BuLi with vinyl bromide **1** were very slow at 0 °C) in solvent systems composed of pure heptane, Et_2O, THF, 2-methyltetrahydrofuran, or MTBE as well as in various heptane–ether mixtures. As detailed in the Experimental Section, 1.2 mol equiv of *n*-BuLi in hexane was added dropwise at room temperature to solutions of **1**, and the resulting 0.1 M solutions were stirred at room temperature for 30 min before quenching with MeOH. Crude product mixtures were analyzed as described above. The results of these experiments are summarized in Table 2.

With the exception of reactions run in THF-rich solvent (Table 2, entries 6 and 7), the six products depicted in Scheme 5 accounted for virtually the entire material balance: 5-butyl-5-decene (**7**) was identified by comparison of its mass spectrum to that reported for this alkene;[21] and 5-butyl-5-decanol (**8**) was identified by comparison of its retention time and mass spectrum to that of an authentic sample.[22] Reactions conducted in heptane–THF (1:1 by vol) or in pure THF (Table 2, entries 6 and 7) afforded, in addition to the products illustrated in Scheme 5, a number of extraneous, unidentified compounds likely derived from reactions of organolithiums with THF or the products generated from fragmentation of the THF upon reaction with *n*-BuLi.[23]

It is apparent that *n*-BuLi reacts more slowly with vinyl bromide **1** than does *t*-BuLi; indeed, recovered starting material is, by far, the major component in all reactions except those run in THF or 1:1 by vol heptane–THF (Table 2, entries 6 and 7). Use of THF-rich solvent systems resulted in significant amounts (ca. 15%) of 5-butyl-5-decene (**7**) from coupling of the vinyllithium product with 1-bromobutane cogenerated in the lithium–bromine exchange reaction.[24] The other products observed in these reactions are entirely analogous to those observed in the *t*-BuLi initiated exchanges discussed above. Plainly, as noted by Utimoto and co-workers,[6] lithium–bromine exchange between *n*-BuLi and **1** is not a practical route to a vinyllithium.

Conclusions

Vinyllithiums may be prepared stereospecifically and in virtually quantitative yield by two methods: (1) lithium–iodine

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[19] (a) Wilson, K. W.; Roberts, J. D.; Young, W. G. *J. Am. Chem. Soc.* **1950**, *72*, 215. (b) Felkin, H.; Frajerman, C.; Gault, Y. *J. Chem. Soc., Chem. Commun.* **1966**, 75. (c) Schlosser, M.; Hartmann, J.; David, V. *Helv. Chim. Acta* **1974**, *57*, 1567. (d) Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674. (e) Bywater, S.; Worsfold, D. J. *J. Organomet. Chem.* **1978**, *159*, 229. (f) Brownstein, S.; Bywater, S.; Worsfold, D. J. *J. Organomet. Chem.* **1980**, *199*, 1.

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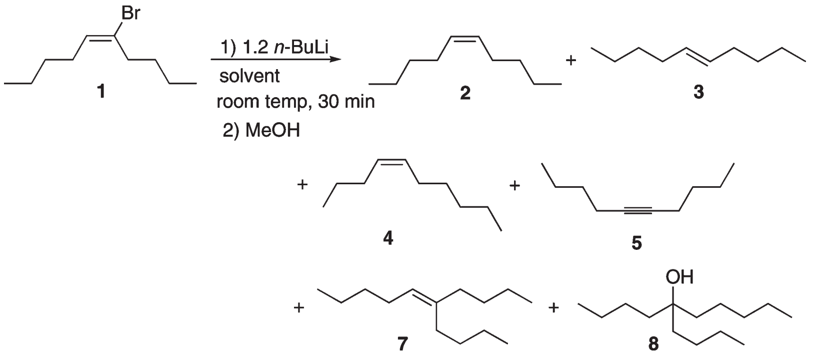
[24] No attempt was made to quantitate the amounts of butane, 1-bromobutane, 1-butene, or octane that may have been produced by extraneous reactions of *n*-BuLi.

TABLE 2. Reactions of (*E*)-5-Bromo-5-decene (1) with *n*-BuLi at Room Temperature in Various Solvents (Scheme 5)

		product,[a] %						
entry	solvent	**2**	**3**	**4**	**5**	**7**	**8**	**1**
1	heptane							~100
2	heptane−Et_2O (9:1 by vol)	tr	tr	tr	tr		tr	98.0
3	heptane−Et_2O (1:1 by vol)	2.5	tr	0.5	2.4	0.5	2.0	88.0
4	Et_2O	4.3	tr	0.7	2.7	0.7	1.7	86.0
5	heptane−THF (9:1 by vol)	5.7	tr	0.6	0.5	tr	2.2	84.0
6	heptane−THF (1:1 by vol)	56.7	0.7	5.2	5.9	15.3	2.6	
7	THF	56.8	0.6	5.1	6.0	16.1	2.3	
8	heptane−MeTHF (9:1 by vol)[b]	2.8	tr	tr	1.8	0.8	1.0	86.0
9	heptane−MeTHF (1:1 by vol)[b]	26.3	0.6	2.4	13.7	1.2	1.2	48.8
10	MeTHF[b]	29.9	0.6	2.2	13.0	1.6	1.7	42.5
11	heptane−MTBE (9:1 by vol)	8.0	tr	0.9	0.8	0.7	1.1	87.1
12	heptane−MTBE (1:1 by vol)	11.2	tr	1.2	3.5	0.8	4.1	77.3
13	MTBE	25.9	0.7	2.4	4.0	0.8	2.0	61.2

[a] Yields were determined by capillary GC; tr indicates that a trace (viz. < 0.2%) of material was detected. [b] 2-Methyltetrahydrofuran.

SCHEME 5



exchange between a vinyl iodide and either *t*-BuLi or *n*-BuLi at room temperature in a hydrocarbon solvent;[5,6] or (2) low-temperature (viz. ≤ 78 C) lithium−bromine exchange between a vinyl bromide and two molar equivalents of *t*-BuLi in diethyl ether.[7,8] The results presented above (Tables 1 and 2) demonstrate that, to the extent (*E*)-5-bromo-5-decene (**1**) is representative of its class, lithium−bromine exchange at temperatures significantly higher than −78 °C using either *t*-BuLi or *n*-BuLi in hydrocarbon solution or in hydrocarbon−ether mixtures is not an efficient process for the generation of vinyllithiums.

Experimental Section

The concentrations of *t*-BuLi in heptane (FMC) and *n*-BuLi in hexane (FMC) were determined prior to use by the method of Watson and Eastham.[25] Anhydrous heptane was freshly distilled from sodium; anhydrous diethyl ether, THF, 2-methyltetrahydrofuran, and MTBE were freshly distilled from a dark-purple solution of sodium and benzophenone. A sample of 5-butyl-5-decanol (**8**) was prepared as described by Whitmore and co-workers;[22] (*E*)-5-decene (**3**) was a commercial sample.

(*E*)-5-Bromo-5-decene (1). A solution of 45 mL of a 1.0 M solution of DIBALH in hexane (45 mmol) and 6.10 g (44.2 mmol) of 5-decyne was stirred at 50 °C under argon for 24 h. The hexane was removed by rotary evaporation under nitrogen, 20 mL of dry THF was added, the resulting solution was cooled to −50 °C, and 37.5 mL of a 1.2 M solution of bromine in dichloromethane (45 mmol) was added via syringe pump at a rate of 1 mL/h. Upon complete addition, the solution was allowed to warm and stir at room temperature for 1 h before addition of 50 mL of 10% aq HCl. The aqueous phase was discarded and the organic layer was washed with 10% aq sodium bisulfite, saturated, aq $NaHCO_3$, water, and brine, dried ($MgSO_4$), and concentrated by rotary evaporation. Distillation (Kugelrohr; bath temp. 35 °C (5 mm)) removed residual alkyne and alkene; distillation (Kugelrohr) at a bath temp. of 75 °C (5 mm; lit.[26] bp 64−66 °C (0.9 mm)) gave 3.20 g (33%) of the title compound. Significant decomposition was observed during each distillation. GC analysis revealed that the isolated product was a 98:2 mixture of *E*/*Z* isomers, respectively. Upon standing at room temperature in ambient light, the mixture slowly isomerized to give an *E*/*Z* ratio of 90:10; if stored at −2 °C or below in the absence of light, no isomerization occurred. The title compound displayed the following spectroscopic properties: ^{1}H NMR ($CDCl_3$) δ 0.88−0.96 (m, 6H), 1.21−1.44 (m, 6H), 1.47−1.61 (five-line pattern, $J = 7.9$ Hz, 2H), 2.01 (q, $J = 7.4$ Hz, 2H), 2.42 (t, $J = 7.4$ Hz, 2H), 5.84 (t, $J = 7.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.2, 21.97, 22.4, 29.5, 30.5, 31.7, 35.4, 126.2, 132.6.

(*E*)-5-Iodo-5-decene. A solution of 45 mL of a 1.0 M solution of DIBALH in hexane (45 mmol) and 6.00 g (43.4 mmol) of 5-decyne was stirred at 50 °C under argon for 24 h. The hexane was removed by rotary evaporation, 22 mL of THF was added, the resulting solution was cooled to −50 °C, and 28.4 mL of a 1.55 M solution of iodide in THF (44.0 mmol) was added via syringe pump at a rate of 1 mL/h. The reaction mixture was worked up as described above for the preparation of **1**. Distillation of the residue afforded 6.20 g (54%) of the title compound as a 99:1 mixture of *E*/*Z* isomers: bp 85 °C (6 mm; lit.[27] bp 96 °C (18 mm)); ^{1}H NMR ($CDCl_3$) δ 0.90−0.96 (m, 6H), 1.24−1.35 (m, 6H),

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(25) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(26) Brown, H. C.; Bhat, N. G.; Rajagopalan, S. *Synthesis* **1986**, *6*, 480.

(27) Tamao, K.; Akita, M.; Maeda, K.; Kumada, M. *J. Org. Chem.* **1987**, *52*, 1100.

1.38−1.51 (five-line pattern, $J = 7.8$ Hz, 2H), 2.03 (q, $J = 7.2$ Hz, 2H), 2.37 (t, $J = 7.3$ Hz, 2H), 6.17 (t, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.2, 21.8, 22.4, 30.8, 31.5, 31.6, 38.4, 103.7, 141.6.

(*Z*)-5-Decene (2). A solution of 36 mL of a 1.0 M solution of DIBALH in hexane (36 mmol) and 4.70 g (34.0 mmol) of 5-decyne was stirred at 50 °C under argon for 24 h. The hexane was removed by rotary evaporation, 18 mL of THF was added, and the resulting solution was cooled to −50 °C before dropwise addition of 25 mL of 10% aq HCl. The reaction mixture was worked up as described above for the preparation of **1** and concentrated by rotary evaporation to yield 3.90 g (82%) of isomerically pure title compound:[28] ^{1}H NMR ($CDCl_3$) δ 0.92 (t, $J = 7.2$ Hz, 6H), 1.30−1.41 (m, 8H), 2.00−2.05 (m, 4H), 5.35 (dt, $J = 3.3$, $J = 1.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.6, 27.1, 32.2, 130.1.

5-*tert*-Butyl-5-decanol (6). A solution of 3.25 g (20.8 mmol) of 5-decanone in 40 mL of diethyl ether was cooled to 0 °C and 14.6 mL of 1.50 *M* solution of *t*-BuLi in pentane (21.8 mmol) was added dropwise. After complete addition, the solution was allowed to stir for 1 h at 0 °C before addition of 10 mL of saturated, aq NH_4Cl. The aqueous phase was discarded and the organic phase was washed with water and brine, dried ($MgSO_4$), and concentrated by rotary evaporation. The residue was distilled to afford 1.83 g (41%) of the title alcohol as a clear oil: bp 89−90 °C (6 mm); ^{1}H NMR ($CDCl_3$) δ 0.85−0.99 [overlapping patterns, i.e., 0.94 (s, 9H), 0.85−0.99 (m, 6H)], 1.05−1.20 (bs, 1H), 1.27−1.37 (m, 10H), 1.45−1.58 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.3, 14.4, 22.9, 24.0, 24.8, 26.8, 27.4, 33.2, 35.3, 35.5, 38.9, 77.6; HRMS-EI (*m*/*z*): $[M - H_2O]^+$ calcd for $C_{14}H_{28}$, 196.2211; found, 196.2191.

Reactions of (*E*)-5-Bromo-5-decene with *t*-BuLi or *n*-BuLi. A flame-dried, septum-capped, 25-mL flask was charged under a positive pressure of argon with an accurately weighed quantity (ca. 0.5−1.0 mmol) of (*E*)-5-bromo-5-decene (**1**) and the appropriate quantity of heptane and ether needed to make a 0.1 M solution of **1** in the desired solvent ratio. The solution was cooled to 0 °C for reactions with *t*-BuLi or left at room temperature for reactions with *n*-BuLi and then either 1.2 mol equiv of *n*-BuLi in hexanes or 2.2 mol equiv of *t*-BuLi in heptane was added dropwise. Upon completion of the addition, the mixture was allowed to stir at 0 °C or room temperature for an additional 15 or 30 min, respectively, and then quenched with MeOH. The organic layer was washed with water, dried ($MgSO_4$), and the crude products were analyzed by GC on a 30 m × 0.25 mm × 0.25 μm Chiraldex B-DM column and by GC-MS on a 25 m × 0.2 mm × 0.33 μm DB-5 cross-linked 5% phenyl methyl silicone capillary column. The results are summarized in Tables 1 and 2.

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Supporting Information Available: NMR and mass spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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[28] Campbell, E. *J. Am. Chem. Soc.* **1941**, *63*, 2684.