J. Org. Chem. **1998,** *63,* 361−365

Lithium−Iodine Exchange Mediated Atom Transfer Cyclization: Catalytic Cycloisomerization of 6-Iodo-1-hexenes

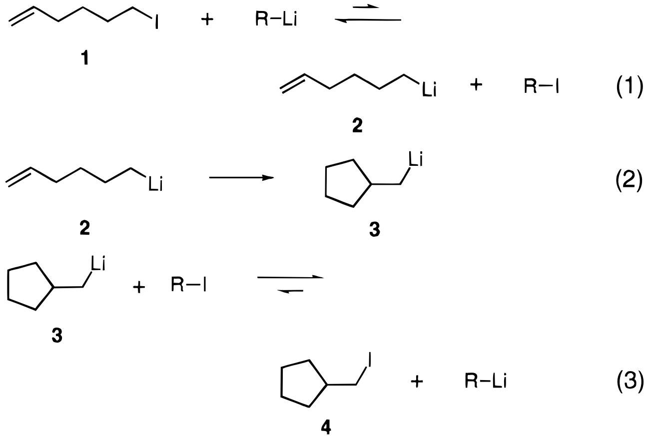
William F. Bailey* and Matthew W. Carson

Department of Chemistry, The University of Connecticut, Storrs, Connecticut 06269-4060

Received October 21, 1997⊗

Treatment of 6-iodo-1-hexene (**1**) in a variety of solvent systems with either MeLi or PhLi at room temperature or above effects clean cycloisomerization of **1** to (iodomethyl)cyclopentane (**4**). This novel transformation, which is mediated by rapid and reversible lithium−iodine exchange processes, most likely involves the following discrete steps: (i) generation of 5-hexenyllithium (**2**) from **1** by exchange with MeLi or PhLi, (ii) irreversible cyclization of **2** to give (cyclopentylmethyl)lithium (**3**) and (iii) virtually complete conversion of **3** to (iodomethyl)cyclopentane (**4**) via a highly favorable lithium−iodine exchange equilibrium. The isomerization sequence **1** → **4** has been found to be effectively catalytic in PhLi when conducted in hydrocarbon−ether solvent mixtures at room temperature.

Low-temperature lithium−iodine exchange between a primary alkyl iodide and 2 molar equiv of *t*-BuLi in a solvent system containing diethyl ether affords the corresponding primary alkyllithium irreversibly and in virtually quantitative yield.[1] When the exchange is conducted using a less reactive organolithium, an equilibrium favoring the more stable organolithium is rapidly established:[2,3] $R{-}I + R'\text{-}Li \rightleftharpoons R{-}Li + R'{-}I$. It occurred to us that it might be possible to exploit the reversible nature of the lithium−iodine exchange reaction to effect isomerization of an alkyl iodide if the initially generated alkyllithium were to undergo an irreversible rearrangement prior to reconversion to the iodide. In an effort to explore this possibility, we have investigated the reversible lithium−iodine exchange reaction of 6-iodo-1-hexene (**1**) with relatively unreactive organolithiums to give 5-hexenyllithium (**2**) under conditions known to result in irreversible cyclization of **2** to (cyclopentylmethyl)lithium (**3**).[4] In principle, as summarized in the scenario presented below (eqs 1−3), treatment of **1** with an appropriate RLi should lead to a net isomerization of **1** to (iodomethyl)cyclopentane (**4**) provided that the organolithium used to initiate the sequence is sufficiently stable to ensure that the equilibrium represented in eq 3 lies far to the right. Herein we disclose the first examples of this anionic atom-transfer isomerization.



Results and Discussion

The potential lithium−iodine exchange mediated isomerization of **1** → **4** was investigated using either MeLi or PhLi to initiate the sequence (eqs 1−3).[5] In light of the fact that the cyclization of **2** to **3** (eq 2) in ethereal solution is fairly rapid only at temperatures above 0 °C ($t_{1/2} \approx 5$ min at 22 °C),[4,6] reactions were conducted at room temperature or above using 0.1 M solutions of **1** under a variety of experimental conditions to survey the effect of solvent, temperature, and reaction time on the isomerization (Table 1). Initial experiments (Table 1, entries 1−8) employed a full molar equivalent of the organolithium initiator due to concern that, at the elevated temperatures needed to effect cyclization of **2** to **3**, such side reactions as coupling, elimination, and proton abstraction from solvent might consume the reactive organometallics.[3] However, as demonstrated by the results

---

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1997.

[1] Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404.

[2] Applequist, D. E.; O'Brien, D. F. *J. Am. Chem. Soc.* **1963**, *85*, 743.

[3] (a) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974. (b) Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, *352*, 1. (c) Gilman, H.; Jones, R. G. *Org. React. (N.Y.)* **1951**, *6*, 339.

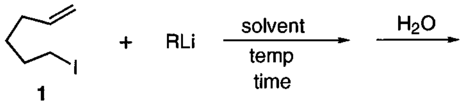
[4] Bailey, W. F.; Patricia, J. J.; DelGobbo, V. C.; Jarret, R. M.; Okarma, P. J. *J. Org. Chem.* **1985**, *50*, 1999. (b) Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K.; Ovaska, T. V.; Rossi, K.; Thiel, Y.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 5720.

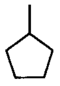
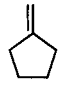
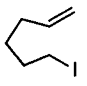
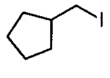
[5] It is important to note that the more reactive alkyllithiums are much less effective than MeLi or PhLi for initiation of the isomerization sequence. Not only is the equilibrium represented in eq 3 less favorable for the production of **4** when a reactive alkyllithium such as *n*-BuLi is employed but, more importantly, the predominant outcome of the reaction of an alkyllithium with **1** at room temperature is coupling. Thus, for example, an equimolar solution of **1** and *n*-BuLi in Et_2O is converted to a mixture of all possible coupling products [octane, 1-decene, pentylcyclopentane, 1,11-dodecadiene, 7-cyclopentyl-1-heptene, and 1,2-dicyclopentylethane] in ∼88% yield on standing at 22 °C for 0.5 h.

[6] It might be noted that the rearrangement of **2** to **3** is significantly more rapid in the presence of a lithiophilic Lewis base such as TMEDA or THF.[4b] Thus, for example, the half-time for cyclization of **2** in the presence of TMEDA is only 6 min at −30 °C.

S0022-3263(97)01939-7 CCC: $15.00

Table 1. Reaction of 6-Iodo-1-hexene (1) with MeLi or PhLi[a]



					products, % yield[b]				
entry	RLi	solvent	temp, °C	time, h			 1	 4	dimers[c]
1	MeLi	Et_2O	22	21	22	3	5	60	3
2		Et_2O	35	3.5	15	2	14	62	3
3		MTBE	55	0.25	7	2	13	67	9
4		n-C_5H_{12}– TMEDA[d]	22	0.5	5	1	20	53	8
5		THF	22	0.25	16	2			62[e]
6	PhLi	Et_2O	22	24	54	2	13	34	2
7		n-C_5H_{12}– Et_2O (9:1 by vol)	22	4	2	1	1	87	2
8		n-C_5H_{12}– Et_2O (50:1 by vol)	22	10	4	1	2	86	1
9		n-C_5H_{12}– Et_2O (9:1 by vol)[f]	22	50	9	1	4	86	
10		c-C_6H_{12}– MTBE (9:1 by vol)[f]	50	0.5	11		34	55	
11		c-C_6H_{12}– MTBE (9:1 by vol)[f]	50	2	12		12	75	

[a] Unless otherwise indicated, reactions were conducted under an argon atmosphere using approximately 0.1 M solutions of 6-iodo-1-hexene in the appropriate solvent to which 1.1 molar equiv of the indicated RLi was added. [b] Yields were determined by capillary GC using internal standards and correction for detector response. [c] Total yield of $C_{12}H_{22}$ compounds [1,11-dodecadiene, 7-cyclopentyl-1-heptene, and 1,2-dicyclopentylethane] produced in the reaction. [d] TMEDA (1.0 molar equiv) was added to a 0.1 M solution of the iodide in pentane prior to the addition of MeLi. [e] The reaction mixture also contained 24% of ethylcyclopentane. [f] Reaction was conducted using 0.25 molar equiv of PhLi.

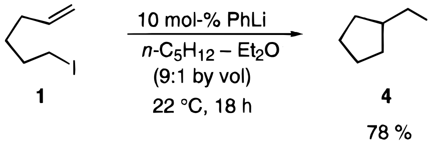
presented below, the isomerization of 6-iodo-1-hexene (**1**) to (iodomethyl)cyclopentane (**4**) may be accomplished cleanly and in high yield using an essentially catalytic quantity of PhLi as initiator.

Cursory inspection of the data summarized in Table 1 reveals that cycloisomerization of 6-iodo-1-hexene (**1**) may indeed be accomplished by treatment of **1** with either MeLi or PhLi. A more detailed examination of the data indicates that the outcome of the reaction depends critically on the choice of solvent used for the isomerization. The use of THF as solvent is to be avoided (Table 1, entry 5); the reaction of **1** with MeLi in THF is quite rapid (15 min) but the bulk of the product (ca. >85%) consists of alkanes derived from coupling of organolithium and alkyl iodide intermediates.[1,3] When conducted in pure diethyl ether, the isomerization of **1** to **4** is accompanied by formation of significant quantities of methylcyclopentane (Table 1, entries 1, 2, and 6). This hydrocarbon is undoubtedly the result of protonation of the intermediate (cyclopentylmethyl)lithium (**3**) by the diethyl ether solvent since the simple expedient of decreasing the proportion of ether in the solvent system serves to remedy the problem (Table 1, cf. entries 6 and 7). It should be noted in this connection that the isomerization of **1** to **4** can also be accomplished cleanly in *tert*-butyl methyl ether (Table 1, entry 3) as well as in hydrocarbon solvent containing as little as 2 vol % of diethyl ether (Table 1, entry 8) or 1 molar equiv of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (Table 1, entry 4).

Not surprisingly, given the fact that the rate of cyclization of 5-hexenyllithium (**2**) to (cyclopentylmethyl)lithium (**3**) is a strong function of temperature,[4] some benefit derives from conducting the isomerization of **1** to **4** at higher temperatures (Table 1, cf. entries 1, 2, and 3). The increase in reaction rate, however, is purchased at the cost of incomplete isomerization: at higher temperatures, proton abstraction from solvent is also accelerated and the RLi initiator is rapidly consumed. Of course, additional RLi may be added to complete the transformation of **1** to **4**.

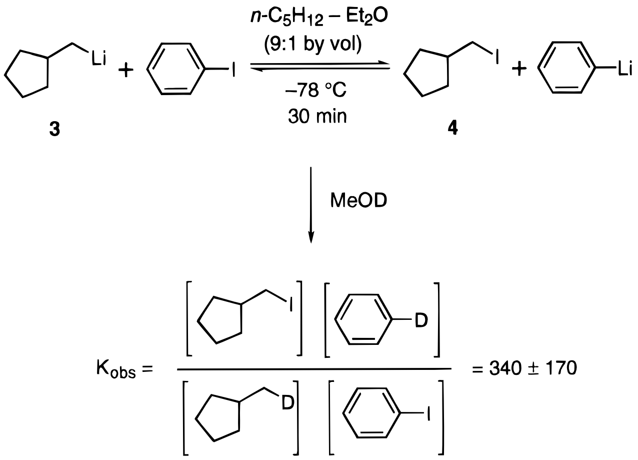
There is an additional feature of the isomerization protocol that is not obvious from the product yields reported in Table 1. Thus, whereas either MeLi or PhLi may be used to effect conversion of **1** to **4**, PhLi is by far the better reagent for this purpose. During the early stages of this research it was noted that reactions conducted in the presence of MeLi failed to proceed to completion unless a large excess (viz., >2 equiv) of the reagent was employed. Indeed, a significant amount of 6-iodo-1-hexene (**1**) remains after prolonged treatment with 1 molar equiv of MeLi (Table 1, entries 1−4). Control experiments revealed that MeLi (but not alkyllithium **2** or **3**) was being removed from solution by fairly rapid reaction with the methyl iodide generated in the initial exchange (eq 1) to give ethane. Indeed, the reaction of 0.1 M CH_3Li with 0.1 M CH_3I in Et_2O at 22 °C cleanly produces ethane with a half-time of approximately 1.5 h. This sequestration of both MeLi and CH_3I over the time period needed for the cycloisomerization of **1** (viz., 21 h at room temperature; Table 1, entry 1), effectively terminates the isomerization sequence (eqs 1 and 3).

There is no such difficulty when PhLi is used as initiator and much less than a full molar equivalent of this reagent serves to convert **1** to **4** in high yield (Table 1, entries 9−11). In fact, as required by the isomerization sequence summarized above (eqs 1−3), *the cycloisomerization reaction is effectively catalytic in PhLi!* Thus, as illustrated below, allowing a 0.3 M solution of **1** in scrupulously dry and deoxygenated pentane−diethyl ether solution (9:1 by vol) to stand in the presence of 10 mol % of PhLi at room temperature for 18 h affords pure (iodomethyl)cyclopentane (**4**) in 78% isolated yield (ca. 88% by GC) following workup and distillation. In principle, a trace of PhLi should lead to complete conversion of **1** to **4**; in practice, it is exceedingly difficult to avoid premature termination of the isomerization sequence via inadvertent quench of organolithiums by proton abstraction from solvent or adventitious moisture when less than ~10 mol % of PhLi is used to initiate the reaction.



The remarkable efficiency of the cycloisomerization cascade (**1** → **4**) initiated by PhLi implies that the final lithium−iodine equilibrium between (cyclopentylmethyl)-lithium (**3**) and iodobenzene to give **4** and PhLi, depicted generically in eq 3, must be quite one-sided. This aspect of the isomerization sequence was investigated, following the method pioneered by Applequist and O'Brien,[2] by determination of the apparent equilibrium constant[7] (K_{obs}) for the rapid lithium−iodine exchange, **3** + PhI ⇌ **4** + PhLi, depicted in Scheme 1. While the highly biased nature of this equilibrium (Scheme 1) precluded precise determination of the apparent equilibrium constant (K_{obs} = 340 ± 170), the result leaves little doubt that the exchange between (cyclopentylmethyl)lithium (**3**) and iodobenzene affords iodomethylcyclopentane (**4**) and PhLi as required for successful operation of the catalytic cycle (eqs 1−3).

Scheme 1



The lithium−iodine exchange mediated isomerization of **1** to **4** discussed above is superficially reminiscent of the radical mediated iodine-transfer cyclization of 6-iodo-1-hexenes that has been documented by Curran's group.[8] Indeed, the radical mediated isomerization of **1** to **4** is a well-characterized process involving a chain mechanism that may be initiated by even trace amounts of an alkyl radical.[8,9] Although a preponderance of evidence indicates that the exchange reaction of an organolithium with a primary alkyl iodide does not involve the generation of radical intermediates,[1,3b,10] it seemed imprudent to rely solely on such precedent to exclude the possibility that the conversion of **1** to **4** in the presence of MeLi or PhLi was the result of a radical-chain process. In an effort to address this issue, we investigated the reaction of MeLi with two different alkyl iodide substrates (Scheme 2) chosen on the basis of their ability to distinguish between a radical-mediated process and one involving an anionic intermediate. As demonstrated by the results presented below, there is no evidence for the intermediacy of radicals in reactions of MeLi (and by inference PhLi) with primary alkyl iodide substrates incorporating the 5-hexenyl iodide moiety.

Reaction of 2-(allyloxy)ethyl iodide (**5**) with 1 equiv of MeLi in Et_2O at room temperature for 5 min results, as shown in Scheme 2, in quantitative β-fragmentation to give the lithium salt of allyl alcohol and ethylene along with a 92% yield of CH_3I. This behavior is characteristic of the generation of (3-oxa-5-hexenyl)lithium via a lithium−iodine exchange;[11] the 3-oxa-5-hexen-1-yl radical, in contrast, is known to cyclize rapidly ($k = 8.5 \times 10^6$ at 25 °C)[12] to give the (3-tetrahydrofuranyl)methyl radical. The reaction of an excess of MeLi with (*E*)-7-iodo-1-methoxy-2-heptene (**6**) in Et_2O at room temperature was also explored: Harms and Stille have previously demonstrated that generation of (8-methoxy-5-heptenyl)-lithium from this substrate by low-temperature ex-

---

[7] Following Applequist and O'Brien,[2] the apparent equilibrium constant (K_{obs}) is derived (Scheme 1) on the assumption that both PhLi and **3** are monomeric even though these organolithiums undoubtedly exist as aggregates in pentane−ether solution;[3] the actual degree of aggregation of PhLi and **3** under the conditions of the equilibration are unknown. The factors affecting the relationship of K_{obs} derived in this way to the true equilibrium constant for a lithium−iodine exchange have been discussed.[2]

[8] (a) Curran, D. P.; Chen, M.-H.; Kim, D. *J. Am. Chem. Soc.* **1986**, *108*, 2489. (b) Curran, D. P.; Kim, D *Tetrahedron Lett.* **1986**, *27*, 5821. (c) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206. (d) Curran, D. P. *Synthesis* **1988**, 417 and 489.

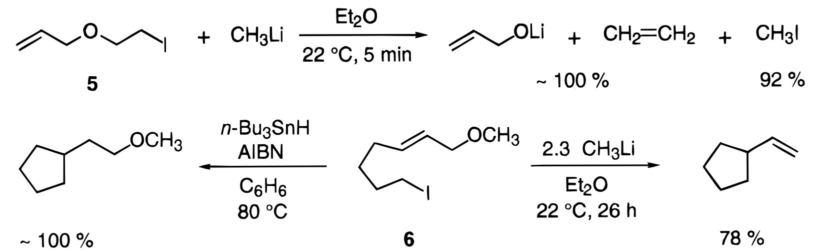
[9] Brace, N. O. *J. Org. Chem.* **1967**, *32*, 2711.

[10] (a) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T.; Wang, W. *Tetrahedron Lett.* **1986**, *27*, 1861. (b) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T. *Tetrahedron Lett.* **1986**, *27*, 1865.

[11] Bailey, W. F.; Punzalan, E. R.; Zarcone, L. M. J. *Heteroat. Chem.* **1992**, *3*, 55.

[12] (a) Smith, T. W.; Butler, G. B. *J. Org. Chem.* **1978**, *43*, 6. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron Lett.* **1985**, *26*, 373.

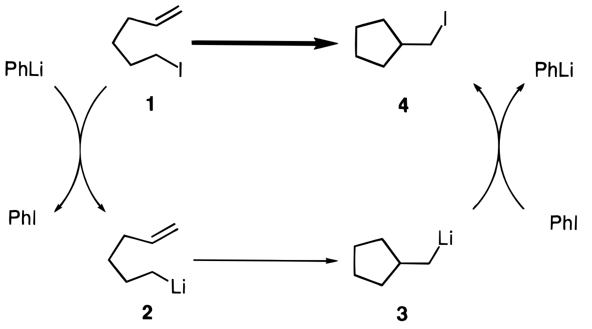
Scheme 2



change with t-BuLi leads in good yield to vinylcyclopentane and CH_3OLi via intramolecular S_N' cyclization.[13] In the event, as illustrated in Scheme 2, prolonged treatment of **6** with 2.3 molar equiv of MeLi afforded vinylcyclopentane in 78% yield as expected from reaction involving reversible formation (eq 1) of (8-methoxy-5-heptenyl)lithium. It might be noted that a large excess of MeLi is required for this transformation since, as noted above, a significant quantity of the reagent is consumed by reaction with the cogenerated methyl iodide and no channel exists, following expulsion of lithium methoxide in the S_N' cyclization, for regeneration of the alkyllithium. The radical-mediated cyclization of **6** (n-Bu_3SnH, AIBN in benzene at 80 °C; Scheme 2), which has not to our knowledge been previously reported, proceeds as expected to give an essentially quantitative yield of (2-methoxyethyl)cyclopentane. In light of these results (Scheme 2) and the data reported above, it seems improbable that the lithium–iodine exchange initiated rearrangement of **1** to **4** is other than an anionic atom transfer process.

Conclusions

Utilization of a reversible lithium–iodine exchange reaction to mediate isomerization of 6-iodo-1-hexene (**1**) to (iodomethyl)cyclopentane (**4**) provides a novel example of a highly atom-economical transformation.[14] The catalytic cycle illustrated below, involving exchange–cyclization–exchange (eqs 1–3), provides an exceedingly simple method for the preparation of cyclopentanes bearing a CH_2I group that is then available for further transformation. We are currently exploring application of this methodology for the construction of polycyclic systems by multiple exchange-initiated cyclization of polyolefinic alkyl iodides.



Experimental Section

General Procedures. Spectroscopic and chromatographic procedures, methods used for the purification of reagents and solvents, and precautions regarding the manipulation of organolithiums have been previously described.[4b] The concentration of commercial solutions (Aldrich) of methyllithium (MeLi) in diethyl ether and phenyllithium (PhLi) in cyclohexane–diethyl ether (7:3 by vol) were determined immediately prior to use by the method of Watson and Eastham.[15] Product mixtures were analyzed by GC on a 25-m × 0.20-mm cross-linked, phenyl methyl (5%) silicone column using temperature programming (30 °C for 16 min, 50 °C/min to 100 °C for 1 min, and then 10 °C/min to 250 °C for 5 min).

Literature procedures, incorporating some minor modifications, were followed for the preparation of 6-iodo-1-hexene (**1**),[16] 2-(allyloxy)ethyl iodide (**5**),[11] and (E)-7-iodo-1-methoxy-2-heptene (**6**).[13]

Exploratory Reactions of 6-Iodo-1-hexene (1) with MeLi or PhLi. Approximately 0.1 M solutions of **1** (typically 0.5–1.0 mmol) containing an accurately weighed quantity of a hydrocarbon internal standard (typically 0.3–0.4 mmol of pure n-decane or cyclohexane) in the appropriate solvent (Table 1) were stirred under an atmosphere of dry, oxygen-free argon with 1.1 molar equiv of either MeLi or PhLi for a period of time at various temperatures: specific conditions of time and temperature are given in Table 1. Reaction mixtures were quenched by cautious addition of water, washed with water, dried ($MgSO_4$), and analyzed by GC and GC/MS using the column and conditions described in the General Procedures to effect base-line separation of each component. Reaction products were identified by comparison of their GC retention times and mass spectra with those of authentic samples; yields reported in Table 1 were corrected for detector response under the conditions of the analysis using accurately weighed samples of pure product and standard.

Isomerization of 6-Iodo-1-hexene (1) to (Iodomethyl)cyclopentane (4) in the Presence of Catalytic PhLi. A flame-dried 50-mL, one-necked, round-bottomed flask, equipped with a Teflon-coated stir bar and capped with a septum, was charged with a solution of 2.21 g (10.5 mmol) of 6-iodo-1-hexene (**1**) in 27 mL of n-pentane and 3 mL of diethyl ether, and 0.63 mL of a 1.72 M solution of PhLi (1.08 mmol) in cyclohexane-diethyl ether (7:3) by volume was added in one portion. The resulting pale-yellow solution was stirred for 18 h at 22 °C under an atmosphere of argon and then quenched with water. The organic layer was washed with brine and dried (Na_2SO_4), and solvent was removed by careful distillation at atmospheric pressure. Kügelrohr distillation of the residue afforded 1.72 g (78%) of (iodomethyl)cyclopentane (**4**): bp (bath temperature) 90–95 °C (38 mm) [lit.[17] bp 75 °C (19 mm)]; ^1H NMR ($CDCl_3$) δ 1.18–1.23 (m, 2 H), 1.55–1.68 (m, 4 H), 1.80–1.84 (m, 2 H), 2.15 (7-line pattern, $J = 7.57$ Hz, 1 H), 3.19 (d, $J = 7.57$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.21, 25.50, 33.38, 42.66.

Evaluation of the Apparent Equilibrium Constant for the Lithium–Iodine Exchange between (Cyclopentylmethyl)lithium (3) and Iodobenzene To Give (Iodomethyl)cyclopentane (4) and PhLi. A solution of 218 mg (1.04 mmol) of 6-iodo-1-hexene (**1**) in 9 mL of n-pentane and 1

---

(13) Harms, A. E.; Stille, J. R. *Organometallics* **1994**, *13*, 1456.

(14) (a) Trost, B. M. *Science* **1991**, *254*, 1471. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.

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

(16) Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098.

(17) Zelinsky, N. D.; Michlina, S. E.; Eventowa, M. S. *Chem. Ber.* **1933**, *66*, 1422.

mL of diethyl ether, containing 79.2 mg (0.558 mmol) of *n*-decane as internal standard, was cooled under an atmosphere of argon to −78 °C and 1.57 mL of a 1.45 M solution of *t*-BuLi (2.28 mmol) in heptane was added dropwise. The reaction mixture was stirred for an additional 5 min at −78 °C, the cooling bath was then removed, and the reaction mixture was stirred at room temperature for 1 h to complete formation of (cyclopentylmethyl)lithium (**3**) and to remove residual *t*-BuLi.[1] The flask was recooled to −78 °C, 194 mg (0.953 mmol) of iodobenzene was added, and the reaction mixture was stirred for 30 min at −78 °C before quench by rapid addition of 1 mL of MeOD. The mixture was allowed to warm to room temperature and was then washed with water and dried ($MgSO_4$). Quantitative analysis of the reaction product by GC, as well as independent GC/MS determination of the d_1-content of methylcyclopentane, indicated that the following compounds were present in the quenched equilibration mixture: methylcyclopentane (0.115 mmol; d_1-content = (15 ± 5)%), benzene (0.859 mmol which was assumed to be 100% monodeuterated; the significant $M^+ - 1$ ion in the mass spectrum of benzene precluded accurate determination of the high d_1-content), iodobenzene (0.121 mmol), and (iodomethyl-)cyclopentane (**4**, 0.825 mmol). The apparent equilibrium constant was evaluated as: $K_{\mathrm{obs}} = [\mathbf{4}][C_6H_5D]/[c\text{-}C_5H_9\text{-}CH_2D][PhI] = 340 \pm 170$.

Reaction of 2-(Allyloxy)ethyl Iodide (5) with MeLi. Neat 2-(allyloxy)ethyl iodide (**5**), 163 mg (0.769 mmol), containing 51.0 mg (0.607 mmol) of cyclohexane as internal standard, was added at 22 °C over a 5 min period to 6.00 mL of a 0.15 M solution of MeLi (0.90 mmol) in ether−pentane (1:5 by vol), and the resulting mixture was stirred at 22 °C for an additional 5 min. Just enough saturated, aqueous ammonium chloride was added to form a clear organic layer, and the organic extract was dried ($MgSO_4$). GC analysis revealed that the reaction had produced allyl alcohol (∼100%) and iodomethane (92%).

Reaction of (*E*)-7-Iodo-1-methoxy-2-heptene (6) with MeLi: Preparation of Vinylcyclopentane. A solution of 231 mg (0.911 mmol) of (*E*)-7-iodo-1-methoxy-2-heptene (**6**) in 10 mL of diethyl ether was treated with 1.14 mL of a 1.83 M solution of MeLi (2.09 mmol) in diethyl ether, and the resulting mixture was stirred under argon at room temperature for 26 h before the addition of 1 mL of water. After drying ($MgSO_4$), GC and GC/MS analysis of the product mixture revealed that the reaction afforded vinylcyclopentane (∼78%) and (2-methoxyethyl)cyclopentane (∼9%) along with approximately 7% of unreacted **6**.

Radical-Mediated Cyclization of (*E*)-7-Iodo-1-methoxy-2-heptene (6): Preparation of (2-Methoxyethyl)cyclopentane. A solution of 99.1 mg (0.389 mmol) of (*E*)-7-iodo-1-methoxy-2-heptene (**6**) in 10 mL of dry benzene was heated to reflux under an atmosphere of argon, and a solution of 1.20 mL (0.446 mmol) of tributyltin hydride and ∼6.6 mg of AIBN in 5 mL of benzene was added via a syringe pump over a 4.5 h period. The resulting mixture was cooled to room temperature and concentrated. GC analysis of the concentrate indicated that the reaction afforded the title ether in virtually quantitative yield. A pure sample of the known ether,[18] free of tin impurities, was isolated by preparative GC on a 10-ft, 10% SE−30 on Anakrom A (60/80 mesh) column at 122 °C: ^1H NMR ($CDCl_3$) δ 1.05−1.10 (m, 2H), 1.48−1.60 (m, 6 H), 1.72−1.85 (m, 3 H), 3.31 (s, 3 H), 3.36 (t, $J = 6.92$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.03, 32.69, 35.82, 36.89, 58.55, 72.37.

Acknowledgment. We are grateful to Mr. Eric DeLeon for the preparation of iodide **6** used in this study. This work was supported by a grant from the Connecticut Department of Economic Development.

JO971939E

---

[18] Tanida, H.; Tsuji, T.; Irie, T. *J. Am. Chem. Soc.* **1966**, *88*, 864.