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Cyclization Reactions of ω-Tosyloxy-1-alkynyl- and ω-Tosyloxy-1-alkenylborates and Their ω-Halo Analogues

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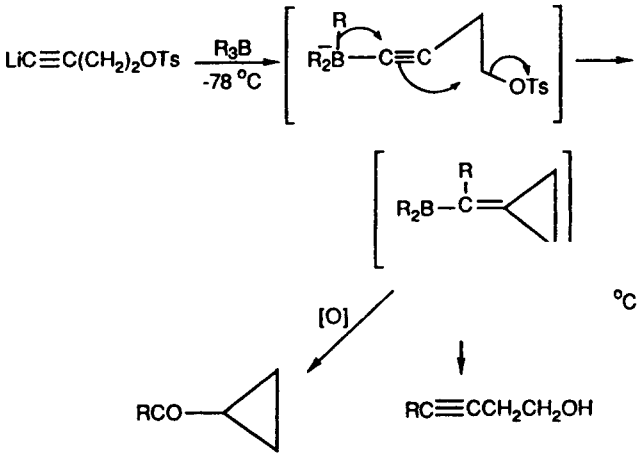
ABSTRACT

The reaction of trialkylboranes with ω-tosyloxy-1-lithio-1-alkynes can induce transfer of an alkyl group from the boron atom to the alkynyl carbon atom with concomitant formation of four- through six-membered carbocycles via intramolecular displacement of the ω-tosyloxy group. The stereoselectivity of the reaction, however, is low (anti/syn=1.6–1.7). The corresponding reaction of ω-halo- or ω-tosyloxy-1-alkenylborates also gives exocyclic alkenes via 1,2-migration-cyclization followed by dehydroboration. In the cases of cyclopropanation, cyclopropylcarbinyl-to-homopropargyl rearrangement rather than dehydroboration takes place. Diphenylzirconocene reacts similarly with 6-lithio-5-hexynyl tosylate to give phenylmethylenecyclopentane in 45% yield. On the other hand, attempts to induce a similar migration with phenyl derivatives of Y, V, Cr, and Mn have led to < 5–10% yields of the same cyclization product.

INTRODUCTION

We have previously reported a cyclization reaction of δ-tosyloxy-1-butynylborates involving 1,2-migration of a carbon group from the boron atom to the alkynyl α-carbon atom (Scheme 1) [1–3]. Its scope beyond cyclopropanation, however, has not been investigated.



SCHEME 1

More recently, we discovered another cyclization reaction of ω-halo-1,1-dimetalloalkenes, especially those containing a 1-silyl group, which can proceed via a similar π-type cyclization, a representative example being that shown in Eq. 1 [4]. Although five-membered ring formation was surprisingly sluggish, the reaction readily provided three-, four-, six-, and seven-membered rings. On the basis of the mechanism shown in Eq. 1, we envisioned that replacement of the aluminum group with a boron group might lead to a 1,2-migration reaction similar to that shown in Scheme 1. Such results would not only be of synthetic interest but also render an additional support for the π-type mechanism shown in Eq. 1. With these considerations in mind, we decided to explore the

*To whom correspondence should be addressed.
This paper is dedicated to Professor Herbert C. Brown of Purdue University on the occasion of his 80th birthday.

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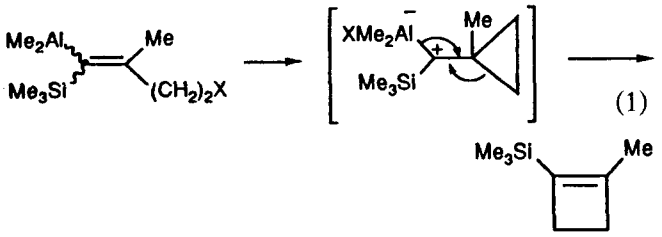
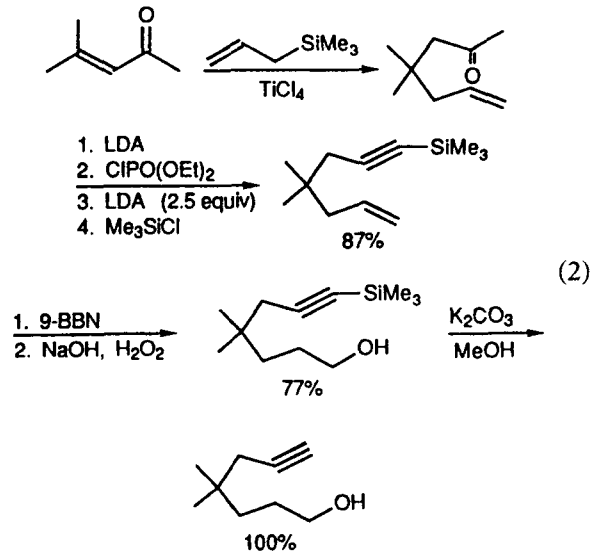
scope of the cyclization of ω-tosyloxy-1-alkynyl- and ω-tosyloxy-1-alkenylboron derivatives and their ω-halo analogues.



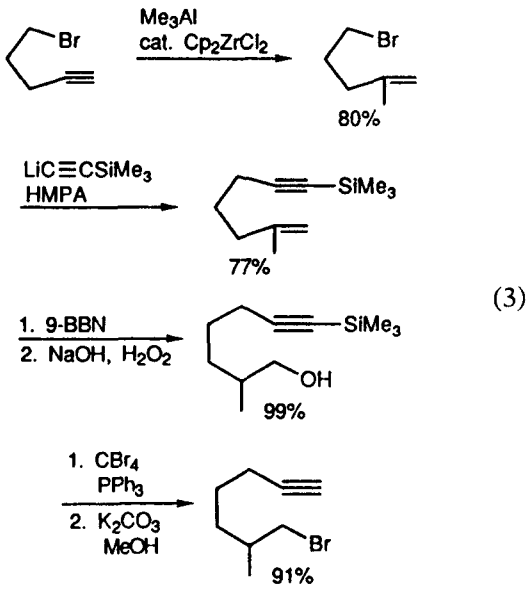
RESULTS AND DISCUSSION

Cyclization of ω-Tosyloxy-1-alkynylborates and ω-Halo-1-alkynylborates

A series of ω-ethynyl-1-alcohols were either purchased from commercial sources or prepared from 1-alkynes via hydroxymethylation and the acetylene zipper reaction [5]. The ω-ethynyl-1-alcohols were converted to ω-tosyloxy-1-alkynes with TsCl (1.5 equiv) and pyridine (2 equiv). The corresponding lithio derivatives **1** were generated in situ by treatment with *n*-BuLi. In some cases, the ω-tosyloxy-1-alkynes were further converted to ω-halo-1-alkynes with the corresponding lithium or sodium halides in acetone. The preparations of ω-ethynyl-1-alcohols corresponding to **2** and **3** were performed as outlined in Eqs. 2 and 3, respectively.

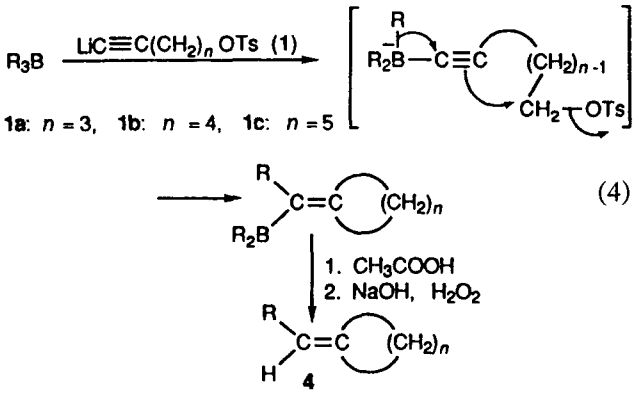


Tricyclopentylborane and tricyclohexylborane were chosen as test organoborane substrates. This choice was in part dictated by our interest in probing the regiochemistry of aspects of the borate cyclization reaction. These organoboranes were mixed with 1-lithio-ω-tosyloxy-1-alkynes or 1-lithio-ω-halo-1-alkynes at −78°C in THF, and the reaction mixtures



were warmed to 25°C. In some cases where the cyclization reaction was slow, the mixtures were eventually heated to 65°C. Upon completion of the reaction, the mixtures were treated with acetic acid and then oxidized with H_2O_2-NaOH.

The reactions involving **1a–1c** proceeded as expected to give the corresponding exocyclic alkenes (Eq. 4), and the experimental results are summarized in Table 1.



To probe the stereochemistry of the reaction, the reaction of tricyclopentylborane with 2 (Eq. 5) and that of tricyclohexylborane with **3** (Eq. 6) were carried out. In each case, that stereoisomer which corresponds to anti addition of the two carbon groups was the major product. However, the stereoisomeric ratio was only 1.6–1.7. The stereochemical assignments were made on the basis of NMR anisotropy and steric compression effects.

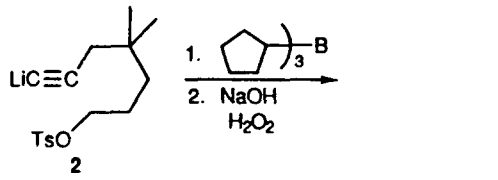
Cyclization of ω-Halo-1-alkenylborates and ω-Tosyloxy-1-alkenylborates

In view of the previously reported results summarized in Scheme 1 [1], we were also interested in

TABLE 1 Reaction of trialkylboranes with ω-tosyloxy-1-lithio-l-alkynes (1).

BR_3	ω-Tosyloxy-l-lithio-l-alkyne	Product	Isolated[a] Yield (%)
	1a	**4a**	61
	1b	**4b**	80
	1c	**4c**	80
	2	**5a** and **5b** (1.7:1)	82
	3[b]	**6a** and **6b** (1.6:1)	62

[a] Based on the ω-tosyloxy-1-alkynes.
[b] A bromo derivative.



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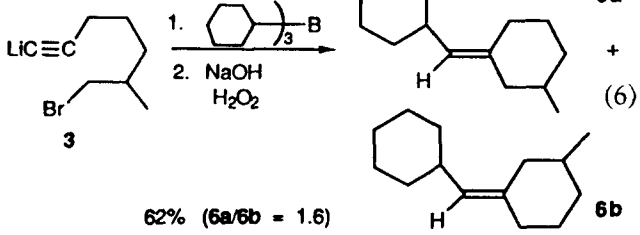
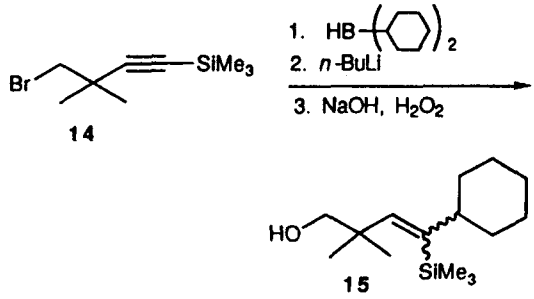


(6)

investigating analogous reactions of ω-halo- or ω-tosyloxy-1-alkenylborates. To this end, we treated 4-bromo-1-(trimethylsilyl)-1-butyne (**7**) successively with dicyclohexylborane (1.1 equiv) in THF and *n*-BuLi (−78 to 25 °C, 1 hour). After oxidation of the reaction mixture with 3N NaOH and 30% H_2O_2, the product isolated in nearly quantitative yield was identified as a 10:1 mixture of the *E* and *Z* isomers of **8** (Scheme 2), indicating that the product before oxidation must be **9**, which could arise *via* **10** and **11** in a manner similar to that shown in Scheme 1.

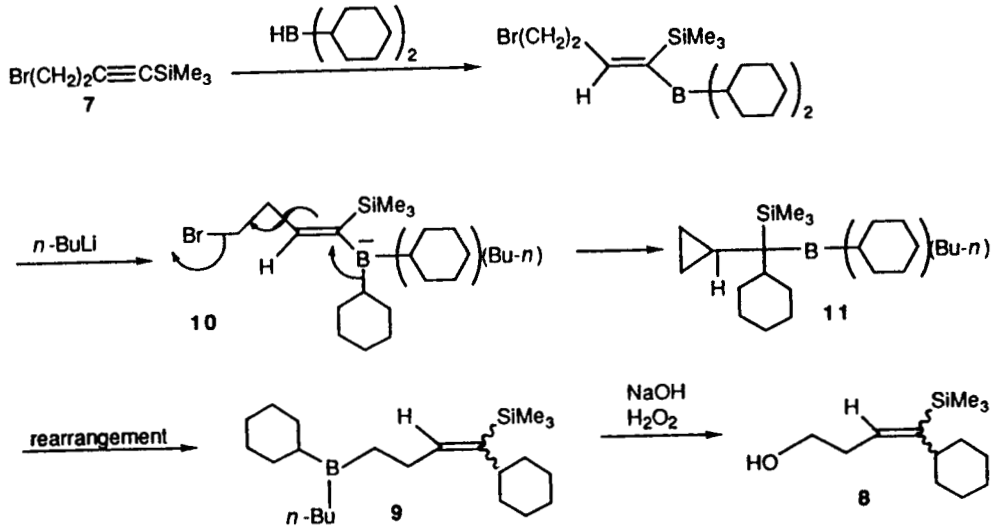
The mechanism shown in Scheme 2 is strongly supported by the results shown in Scheme 3. Clearly, the reaction in these cases is regioselective but not regiospecific. This can be readily explained in terms of a common cyclopropyl intermediate **12**. Presumably, migration of boron to the sterically less hindered γ-carbon atom of the cyclopropyl ring is strongly favored. Protonolysis of the hydroboration products with HOAc prior to cyclization gave **13** and **14**.

A similar cyclization-rearrangement reaction showing > 98% regioselectivity was also observed in the conversion of **15** to **16** (Eq. 7). In this case, the *E/Z* ratio of **16** was 1:2.5.

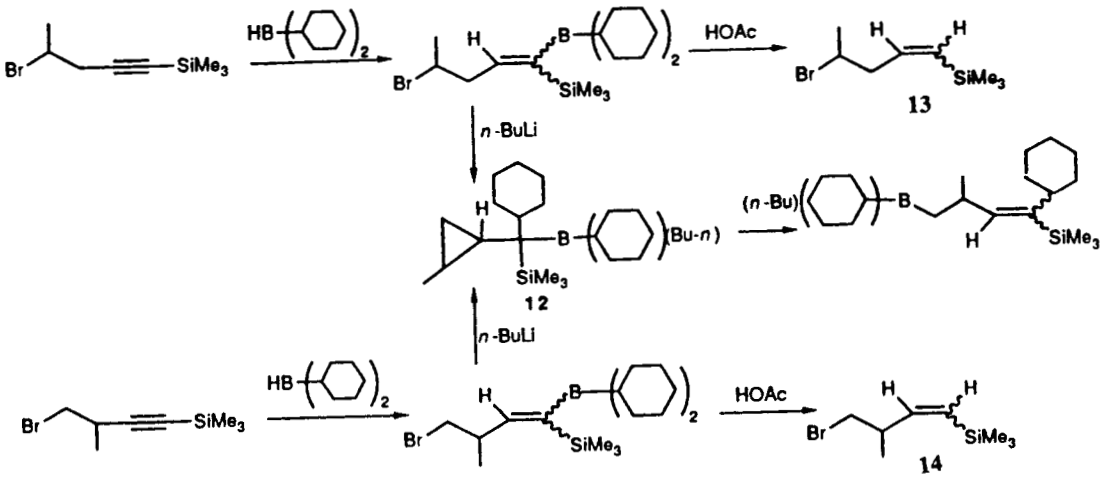


(7)

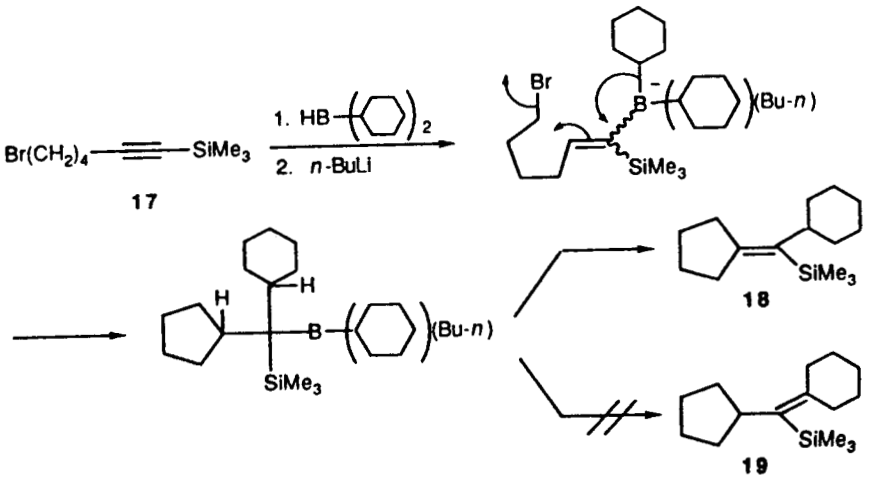
Although interesting, we have so far failed to trap the cyclopropyl derivatives in the alkenylboron reaction discussed above. With the goal of trapping the cyclization product, we treated 6-bromo-1-(trimethylsilyl)-1-hexyne (**17**) with dicyclohexylborane and then with a *n*-BuLi. The reaction provided, after oxidation, **18** as the only cyclization product, although its isolated yield was only 23%. Here again, exclusive migration of a cyclohexyl group took place. Furthermore, the reaction did not give the other possible regioisomer **19** to any detectable extent (Scheme 4). This is in accord with a well-documented generalization by Brown [6] that the five-membered carbocycles favor sp^2 hybridization, while the six-membered homologues favor sp^3 hybridization. Rigorous determination of the regiochemistry by spectroscopic means alone was difficult. So, **18** was independently synthesized as follows. Dibromomethylenecyclopentane, which was prepared in 75% yield by the reaction of cyclopentanone with CBr_4 (2 equiv) and PPh_3 (4 equiv) [7], was treated with *t*-BuLi (1 equiv) at −120°C for 30 min. A THF solution of chloro(cyclohexyl)zirconocene, which was prepared by hydrozirconation of cyclohexene, was then added to the mixture at −120°C. After a few minutes, the reaction temperature was raised to 25°C over a few hours and cooled to −78°C [8]. After addition of I_2 (1.5 equiv), the mixture was warmed to 25°C, and the desired iodide **19** was obtained in 48% yield based on dibromomethylenecyclopentane. The 1,2-migration reaction of an α-haloalkenylzirconium derivative suggested in Scheme 5 appears to be unprecedented. Treatment of **19** with *t*-BuLi (3.2 equiv) at −78°C followed by addition of Me_3SiCl (5 equiv) produced **18** in 76% yield by GLC (40% isolated) (Scheme 5). Its spectral properties are identical to those of a sample of **18** obtained by the alkenylboron migration reaction.



SCHEME 2



SCHEME 3



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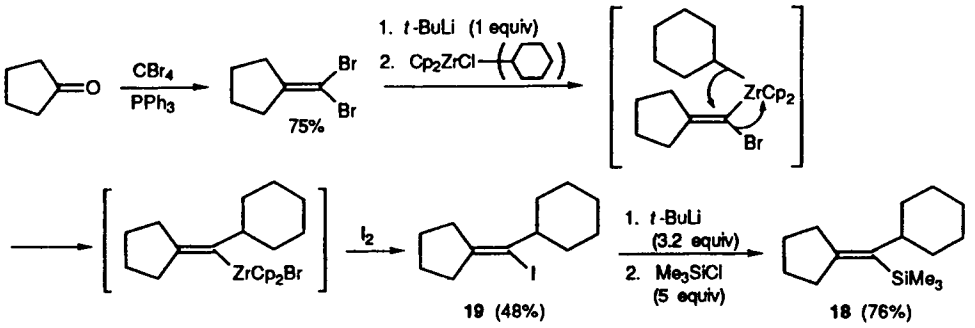
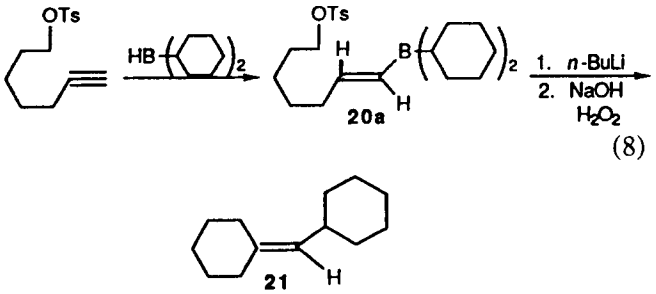


SCHEME 5

In the π-type cyclization reaction of ω-halo-1-alkenylmetals reported earlier, the presence of the second metal, such as Me_3Si, appeared to be essential [4]. In the case of ω-halo- or ω-tosyloxy-1-alkenylboron derivatives, the 1,2-migration process that accompanies the cyclization process presumably provides a driving force, which might make the presence of the second metal group unnecessary. To probe this point, ω-tosyloxy-1-alkenylboranes **20a** and **20b** without a silyl group were generated in situ by hydroboration with dicyclohexylborane of the corresponding alkynes and treated with *n*-BuLi. After oxidation with 3N NaOH and 30% H_2O_2, cyclohexylmethylenecyclohexane **21** was obtained in 60% yield from **20a** (Eq. 8), and an essentially 1: 1 mixture of **22** and **4c** was produced in 45% yield from **20b** (Eq. 9). An authentic sample of **22** was prepared from cyclopentanone as shown in Eq. 10. These results clearly demonstrate that, in the cyclization of ω-tosyloxy-1-alkenylboron derivatives, the second metal group is indeed unnecessary. The lack of regioselectivity in the latter case is puzzling. It suggests that the Me_3Si group may play a crucial role in controlling the regiochemistry of the reaction shown in Scheme 4.



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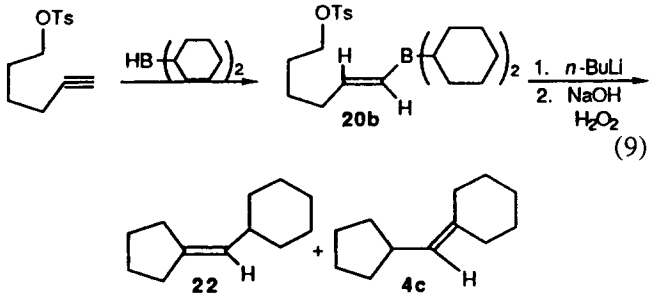
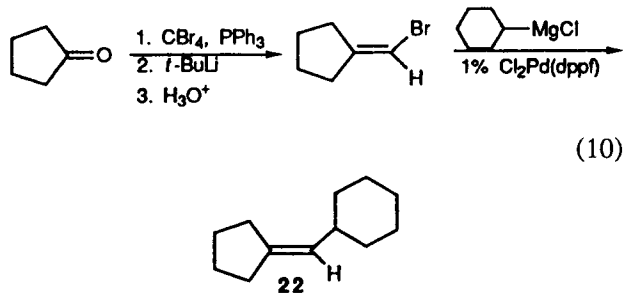


(9)

Reaction of 6-Tosyloxy- and 6-Halo-1-lithio-1-hexynes with Phenyl Derivatives of Transition Metals

The possibility of observing related reactions of organotransition metal complexes was briefly tested. Since a large number of alkyltransition metal species are known to be thermally unstable, phenyl derivatives containing various transition metals were chosen as test substrates. The reaction of **1b** with Cp_2ZrPh_2, where Cp = η^5 -C_5H_5, in THF produced, after hydrolysis, phenylmethylenecyclopentane (**23**) in 45% yield. The use of the corresponding bromide and iodide led to comparable yields of **23** (Eq. 11). The reaction of **1b** with phenyl derivatives of other transition metals that were generated in situ by treating VCl_3, $CrCl_2$, $MnCl_2$, and YCl_3 with PhLi did not yield **23** in any more than 5–10% yield.



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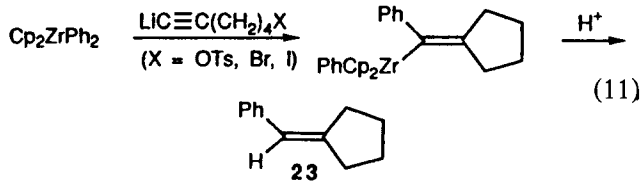
EXPERIMENTAL SECTION

General Procedures

Manipulations involving organometallics were carried out under an atmosphere of N_2 or Ar. Tetra-



(11)

hydrofuran (THF) was distilled from sodium benzophenone ketyl, and the hydrocarbon solvents were distilled from $LiAlH_4$, as needed. Polyhalogenerated hydrocarbons were distilled from P_2O_5. Unless otherwise mentioned, the other chemicals were purchased from commercial sources and used as received.

6-Heptyn-1-ol and Its Tosylate

1-Hexyne was converted to 2-heptyn-1-ol in 81% yield by a literature procedure [9] using *n*-BuLi and paraformaldehyde. Isomerization of 2-heptyn-1-ol into 6-heptyn-1-ol was achieved in 78% yield with $KNH(CH_2)_3NH_2$ in $NH_2(CH_2)_3NH_2$ following a literature procedure [5]. Tosylation of 6-heptyn-1-ol was carried out with TsCl and pyridine (2 equiv) in $CHCl_3$. 4,4-Dimethyl-6-hepten-2-one was prepared in 87% yield by the reaction of 4-methyl-3-penten-2-one with allyltrimethylsilane in CH_2Cl_2 in the presence of $TiCl_4$ [10]. Successive treatment of the ketone obtained above with LDA (1.1 equiv), $ClPO(OEt)_2$ (1.1 equiv), LDA (2.3 equiv), and Me_3SiCl (2.3 equiv) according to a previously reported procedure [11] provided 4,4-dimethyl-7 (trimethylsilyl)-1,6-heptenyne in 87% yield. Its treatment with 9-BBN (1.1 equiv) followed by oxidation with 3N NaOH and 30% H_2O_2 [12] gave 4,4-dimethyl-7-(trimethylsilyl)-6-heptyn-1-ol in 77% yield, which was desilylated with K_2CO_3 in MeOH to give the title compound in quantitative yield. It was then tosylated with TsCl and pyridine in $CHCl_3$.

1-(Trimethylsilyl)-6-methyl-7-bromo-1-heptyne

5-Bromo-1-pentyne was treated with Me_3Al (2 equiv) and Cp_2ZrC1_2 [13] to produce, after hydrolysis, 5-bromo-2-methyl- 1-pentene in 80% yield. Its reaction with 2-(trimethylsilyl)ethynyllithium in HMPA [14] provided 2-methyl-7-(trimethylsilyl)-1,6-heptenyne in 77% yield. Its hydroboration with 1 equiv of 9-BBN followed by oxidation with 3N NaOH and 30% H_2O_2 [12], bromination with CBr_4 and PPh_3, and desilylation with K_2CO_3 in MeOH-ether (4:1) produced the title compound in 86% overall yield.

Reaction of Trialkylboranes with ω-Tosyloxy-1-alkynyllithium

a) Cyclopentylmethylenecyclohexane. Representative Procedure. To a solution of 0.85 g (3 mmol) of 6-heptynyl tosylate in 12 mL of THF was added at −78 °C 1.22 mL of *n*-BuLi in hexane (2.43 M, 3 mmol). To this was added at −78°C tricyclopentylborane (0.38 M in THF, 7.9 mL, 3.0 mmol). The resultant mixture was warmed to 25°C over 1–2 hour, treated with 10 mL of glacial acetic acid at 55–60°C for 5 hour, and then oxidized with 25 mL of 6N NaOH and 10 mL of 30% H_2O_2 at 30–40°C. Extraction with pentane, washing with $NaHCO_3$ and brine, drying over $MgSO_4$, and column chromatography (silica gel, pentane) provided 0.395 g (80%) of the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.05–1.35 (m, 2H), 1.35–1.85 (m, 12H), 1.95–2.2 (m, 4H), 2.5–2.75 (m, 1H), 5.00 (d, J = 9 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.46, 27.18, 28.21, 28.90, 29.34, 34.29, 37.34, 38.30, 127.49, 138.82; IR (neat) 1665 (w), 890 (s), 845 (s) cm^{-1}; High resolution MS Calcd for $C_{12}H_{20}$: 164.1566. Found: 164.1569.

(b) Cyclohexylmethylenecyclobutane. The use of 5-tosyloxy-1-pentynyllithium in THF-hexane (1 mmol, 3 mL) and tricyclohexylborane in THF and eventual heating of the reaction mixture at 65°C overnight gave 0.09 g (61% yield) of the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.9–2.2 (m, 13H), 2.63 (t, J = 7 Hz, 4H), 4.91 (d, J = 2 Hz, 1H); ^{13}C NMR ($CDCl_3$,Me_4Si) δ 17.24, 26.15, 29.46, 31.12, 33.35, 37.34, 126.66, 138.03; IR (neat) 1704 (m), 1448 (s), 1096 (s), 1070 (s), 810 (s) cm^{-1}; High resolution MS Calcd for $C_{11}H_{18}$: 150.1409. Found: 150.1400.

(c) Cyclopentylmethylenecyclopentane. This compound was prepared according to the representative procedure using 6-tosyloxy-l-hexynyllithium, prepared from 5-hexyn-1-yl tosylate (0.25 g, 1 mmol) and *n*-BuLi (1 mmol), and tricyclopentylborane. After the workup, chromatographic separation provided 0.12 g (80% yield) of the title compound [15]: ^1H NMR ($CDCl_3$, Me_4Si) 1.1–1.2 (m, 2H), 1.5–1.8 (m, 10H), 2.21 (t, J = 6 Hz, 4H), 2.4–2.5 (m, 1H), 5.17 (d, J = 9 Hz, 1H); ^{13}C NMR ($CDC1_3$, Me_4Si) δ 22.25, 26.44, 28.63, 33.38, 33.56, 40.81, 125.61, 141.65; IR (neat) 1673 (w), 852 (w) cm^{-1}.

(d) (E)- and (Z)-Cyclopentylmethylene-3,3-dimethylcyclohexane. The use of 7-tosyloxy-4,4-dimethyl-1-heptynyllithium in THF-hexane (1 mmol) and tricyclopentylborane and eventual heating at 65°C for 3 hour gave 0.16 g (81% yield) of the title compound (Z/E = 1.7 by NMR): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.84 (s, 6H), 1.1–1.8 (m, 12H), 1.80 (s, 2H), 2.07 (t, J = 6 Hz, 2H), 2.6–2.7 (m, 1H), 4.95 (d, J = 9 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.52, 25.33, 28.37, 34.42, 36.90, 38.35, 39.83, 42.36, 50.40, 178.76, 136.06; IR (neat) 1670 (w), 1472 (s) cm^{-1}; High resolution MS Calcd for $C_{14}H_{24}$: 192.1878. Found: 192.1870.

(e) (E)- and (Z)-Cyclohexylmethylene-3-methylcyclohexane. The use of 7-bromo-6-methyl-1-heptynyllithium in THF-hexane (1 mmol) and tricyclohexylborane in THF (1 mmol) and eventual heating

at 65°C for 3 hours gave 0.12 g (62% yield) of the title compounds (*E*/*Z* = 1.6): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.88 (d, *J* = 9 Hz, 3H), 0.9–2.2 (m, 19H), 2.46 (d, *J* = 10 Hz, 1H), 4.91 (d, *J* = 9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.78, 26.25, 27.20, 27.64, 34.00, 34.68, 35.46, 36.15, 36.77, 45.67, 128.63, 137.53; IR (neat) 1668 (w), 1446 (s) cm^{-1}. High resolution MS Calcd for $C_{14}H_{24}$: 192.1878. Found: 192.1876.

4-Bromo-3,3-dimethyl-1-(trimethylsilyl)-1-butyne

This compound was prepared by applying a previously reported procedure [16]. To a solution of ethynyltrimethylsilane (5.89 g, 60.0 mmol) in hexane (100 mL) at 0°C was added 2.1 N *n*-BuLi in hexane (28.6 mL, 60.0 mmol) dropwise. After 30 min, $AlCl_3$ (2.67 g, 20.0 mmol) was added, and the reaction mixture was stirred for an additional 30 min at 0°C. Following concentration, the trialkynylalkane was dissolved in 1,2-dichloroethane (50 mL), and a solution of 1,2-dibromo-2-methylpropane (4.32 g, 20.0 mmol) in the same solvent (10 mL) was introduced at 0°C. After 15 min, $AlCl_3$ (2.67 g, 20.0 mmol) was added. The reaction mixture was stirred at 0°C for 1 hour, treated with 3N HCl, extracted with ether, washed with aqueous $NaHCO_3$ and NaCl, and dried ($MgSO_4$). Distillation afforded the title compound (2.25 g, 52%): bp 76–78°C (20 mm): ^{1}H NMR ($CDCl_3$, C_6H_6) δ –0.01 (s, 9H), 1.17 (s, 6H), 3.24 (s, 2H); IR (neat) 2165 (s), 1383 (m), 1365 (m), 1248 (s), 1179 (s), 830 (s), 754 (s) cm^{-1}.

Reaction of 4-Bromo-1-(trimethylsilyl)-1-butyne with Dicyclohexylborane and n-Butyllithium to Produce 4-(Trimethylsilyl)-3-buten-1-ols

(a) (E)- and (Z)-4-Cyclohexyl-4-(trimethylsily1)-3-buten-1-ol. Representative Procedure. Hydroboration of 4-bromo-1-(trimethylsilyl)-1-butyne [4c] was carried out by the addition of a solution of the alkyne (0.41 g, 2.0 mmol) in THF (1 mL) to a slurry of dicyclohexylborane, prepared from cyclohexene (0.45 mL, 0.36 g, 4.4 mmol) and borane-methyl sulfide (0.22 mL, 2.2 mmol) in THF (2 mL). The solution of the resulting alkenylborane was cooled to –78°C, and 2.1 N *n*-butyllithium in hexane (0.95 mL, 2.0 mmol) was added dropwise. The reaction mixture was slowly warmed to 25°C and stirred for 1 hour. Sequential addition of 3N aqueous NaOH (1.0 mL) and 30% aqueous H_2O_2 (1.0 mL) at or below 50°C produced the title compounds in quantitative yield by GLC. The mixture was extracted with ether, washed with aqueous NaCl, dried ($MgSO_4$), and distilled to afford the title alcohols (0.25 g, 55%, *E*/*Z* = 10–20): bp 85°C (0.10 mm, Kugelrohr); ^{1}H NMR for the *E* isomer ($CDCl_3$, C_6H_6) δ –0.04 (s, 9H), 0.9–1.8 (m, 10H), 1.71 (br s, 1H, exchangeable with D_2O), 2.0–2.4 (m, 1H), 2.27 (dt, *J* = 7 and 7 Hz, 2H), 3.51 (t, *J* = 7 Hz, 2H), 5.45 (t, *J* = 7 Hz, lH); ^{13}C NMR for the *E* isomer ($CDC1_3$) δ 0.74, 26.11, 26.86, 32.24, 32.82, 41.71, 62.27, 134.66, 149.71; IR (neat) 3600–3100 (s), 1598 (m), 1245 (s), 1030 (s), 963 (s), 830 (s), 748 (s) cm^{-1}. High resolution MS Calcd for $C_{13}H_{27}OSi$: 227.1831. Found: 227.1807.

(b) (E)- and (Z)-4-Cyclohexyl-2-methyl-4-(trimethyl silyl)-3-buten-1-ol. The use of 4-bromo-1-(trimethylsilyl)-1-pentyne [4c] (0.44 g, 2.0 mmol) in place of 4-bromo-1-(trimethylsilyl)-1-butyne produced the title compounds (0.44 g, 61%) as a 2.5:1 mixture of (*E*)- and (*Z*)-stereoisomers. Application of the same sequence to 4-bromo-3-methyl-1-(trimethylsilyl)-1-butyne [4c] afforded the same products (48% combined) as a 3:1 mixture of (*Z*)- and (*E*)-stereoisomers: bp 80°C (0.04 mm, Kugelrohr): ^{1}H NMR for the *E* isomer ($CDCl_3$, C_6H_6) δ –0.04 (s, 9H), 0.80 (d, *J* = 7 Hz, 3H), 0.9–1.8 (m, 11H), 2.1–2.6 (m, 1H), 2.4–3.0 (m, 1H), 3.25 (d, *J* = 6 Hz, 2H), 5.26 (d, *J* = 10 Hz, 1H); 1H NMR for the Z isomer ($CDCl_3$, C_6H_6) δ 0.02 (s, 9H), 0.79 (d, 7 Hz, 3H), 0.8–2.1 (m, 1H), 2.1–2.9 (m, 2H), 3.27 (d, J = 6 Hz, 2H), 5.51 (d, J = 10 Hz, 1H); ^{13}C NMR for the *E* isomer ($CDCl_3$) δ 0.08, 17.12, 26.08, 26.86 (2C), 33.19, 33.26, 35.72, 41.92, 67.54, 141.53, 148.81; $_{13}$C NMR for the Z isomer ($CDCl_3$) δ 0.83, 17.17, 26.31, 27.10 (2C), 33.87, 34.48, 38.78, 43.30, 67.61, 141.00, 148.16; IR (neat) 3600-3100 (s), 1615 (w), 1246 (s), 1024 (s), 830 (s), 751 (s) cm^{-1}. High resolution MS Calcd for $C_{14}H_{28}$os: 240.1909. Found: 240.1896.

(c) (E)- and (Z)- 4-Cyclohexyl-2,2-dimethyl-4-(trimethylsilyl)-3-buten-1-ol. The use of 4-bromo-3,3-dimethyl-1-(trimethylsilyl)-1-butyne (0.47 g, 2.0 mmol) provided the title compound (0.39 g, 50%) as a 2.5:1 mixture of the *Z*- and *E*-stereoisomers: ^{1}H NMR for the *E* isomer ($CDCl_3$, C_6H_6) δ –0.04 (s, 9H), 0.98 (s, 6H), 0.9–2.4 (m, 12H), 3.27 (s, 2H), 5.46 (s, 1H); ^{1}H NMR for the *Z* isomer ($CDCl_3$, C_6H_6) δ 0.05 (s, 9H), 0.93 (s, 6H), 0.9–2.4 (m, 12H), 3.21 (s, 2H), 5.89 (s, 1H); ^{13}C NMR for the *E* isomer ($CDCl_3$) δ 1.90, 25.95, 26.10, 26.78, 32.86, 39.53, 42.34, 72.46, 143.93 or 145.04, 150.51; ^{13}C NMR for the *Z* isomer ($CDCl_3$) δ 2.28, 25.78, 26.26, 27.29, 34.80, 38.85, 44.47, 72.71, 143.93 or 145.04, 146.89; IR (neat) 3600–3100 (m), 1595 (w), 1248 (s), 1033 (m), 834 (s), 750(m)cm^{-1}. High resolution MS Calcd for $C_{10}H_{15}Si$: 163.0943. Found: 163.0939.

Reaction of 1-(Trimethylsilyl)-6-bromo-1-hexyne with Dicyclohexylborane Followed by Treatment with n-Butyllithiurn to Produce Cyclohexyl(trimethylsilyl)methylenecyclopentane

To a solution of BH_3-Me_2S (10 M, 3.3 mL, 3.3 mmol) in 5 mL of THF was added at 0°C cyclohexene (0.56 g, 0.69 mL, 6.8 mmol), and the mixture was stirred at 0°C for 1 hour. To the resultant white slurry was added at room temperature a solution of 1-(tri-

methylsilyl)-6-bromo-1-hexyne [4c] (0.71 g, 3 mmol) in 5 mL of THF. After stirring the mixture at 25°C for 2 hr, 2.4 M *n*-BuLi (1.38 mL, 3.3 mmol) was added at −78°C, and the mixture was stirred at −78°C for 1 hr, warmed to 25°C, and heated at 65°C for 18 hr. The reaction mixture was oxidized at 50°C with 2.4 mL of 3N NaOH, and 1.8 mL of 30% H_2O_2. After extraction with ether, the organic phase was washed with aqueous NH_4Cl and brine and dried over $MgSO_4$. Concentration followed by distillation provided 0.17 g (23%, 39% by GLC) of cyclohexyl(trimethylsilyl)-methylenecyclopentane along with 0.07 g (10%, 31% by GLC) of (*Z*)-1-(trimethylsilyl)-6-bromo-1-hexene. The physical properties of (*Z*)-1-(trimethylsilyl)-6-bromo-1-hexene are as follows: bp 35–40°C (0.1 mm); IR (neat) 1608 (s), 1243 (s), 824 (s) cm^{-1}, ^1H NMR (CCl_4, C_6H_6) δ 0.06 (s, 9H), 1.3–2.3 (m, 4H), 3.33 (t, J = 6 Hz, 2H), 5.42 (d, J = 14 Hz, 1 H), 6.0–6.4 (m, 1 H), ppm. The physical properties of cyclohexyl-(trimethylsilyl)methylenecyclopentane are as follows: bp 65–66°C (0.05 mm); ^1H NMR (CCl_4, C_6H_6) δ 0.13 (s, 9H), 1.0–1.8 (m, 14H), 2.0–2.5 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 2.41, 25.80, 26.33, 27.03, 27.32, 31.57, 32.17, 34.41, 45.40, 135.04, 153.64; IR (neat) 1590 (m), 1245 (s), 830 (s), 750 (m), 670 (m) cm^{-1}; Anal. Calcd for $C_{15}H_{28}Si$: C, 76.19; H, 11.93. Found: C, 76.02; H, 11.79.

Independent Synthesis of Cyclohexyl(trimethylsilyl)methylenecyclopentane

To a mixture of 0.493 g (0.24 mL, 2.05 mmol) of α, α-(dibromomethylenecyclopentane, prepared in 75% yield by treatment of cyclopentanone with CBr_4 (2 equiv) and PPh_3 (4 equiv) [7], was added at −120°C 2.06 M *t*-BuLi in pentane (1.01 mL, 2.08 mmol). After 30 min a solution of chloro(cyclohexyl)zirconocene, prepared by the reaction of Cp_2ZrCl_2 (0.88 g, 3 mmol) suspended in 6 mL of THF with cyclohexene (0.30 mL, 3 mmol) for 12 hr at 25°C, was added at −120°C. The reaction mixture was slowly warmed to 25°C over a few hours and cooled to −78°C. To this was added a solution of 0.76 g (3 mmol) of iodine in 3 mL of THF. After warming the mixture to 25°C over 1–2 hr, it was hydrolyzed with water, extracted with pentane, washed with aqueous $Na_2S_2O_3$, $NaHCO_3$, and water, and dried over $MgSO_4$. A few crystals of 2,6-di(*t*-butyl)-p-cresol were added, and the mixture was concentrated and column chromatographed (SiO_2, pentane) to give 0.28g (45% yield) of iodo(cyclohexyl)methylenecyclopentane: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.25–1.9 (m, 15H), 2.25–2.4 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.42, 25.74, 25.79, 28.06, 32.21, 33.42, 41.46, 45.48, 107.98, 146.67; IR (neat) 1635 (m), 890 (m), 800 (m) cm^{-1}. To a 0.10 g (0.35 mmol) of iodo(cyclohexyl) methylenecyclopentane in 1 mL of ether was added at −78°C 2.06 M *t*-BuLi in pentane (0.55 mL, 1.13 mmol). After stirring for 3 hr at −78°C, 0.19 g (0.22 mL, 1.75 mmol) of Me_3SiCl and 4 mL of THF were sequentially added at −78°C, and the mixture was warmed to 0°C. Analysis of an aliquot by GLC indicated the formation of the desired product in 76% yield. After recooling to −78°C, it was quenched with 2 mL of water and warmed to 25°C. On the other hand, quenching at 25°C resulted in the formation of a mixture of products that was difficult to purify. The mixture was treated with aqueous NH_4Cl, extracted with pentane, washed with aqueous $NaHCO_3$, and dried over $MgSO_4$. Distillation of the concentrated residue provided 36 mg (40% yield) of the title compound: bp 60–65°C (0.05 mm Hg). Its ^1H and ^{13}C NMR and IR spectra were indistinguishable from those of the sample obtained by the allkenylborate migration reaction.

Reaction of ω-Tosyloxy-1-alkenylboranes with n-Butyllithium to Produce Exocyclic Alkenes

a) Cyclohexylmethylenecyclohexane. Representative Procedure. To a solution of dicyclohexylborane (2 mmol) in THF was added 6-heptynyl tosylate (2 mmol, 0.53 g) at 0°C, and the mixture was stirred for 3 hr. *n*-Butyllithium (2 mmol) was added slowly at −78°C. The reaction mixture was warmed slowly to 25°C and oxidized with 3N NaOH (3 mL) and 30% H_2O_2 (3 mL, 1 hr). It was extracted with ether, washed with water, dried over $MgSO_4$, and chromatographed (99:1 pentane-ether) to give 0.11 g (60% yield) of the title compound [15]: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.0–1.7 (m, 16H), 2.0–2.2 (m, 5H), 4.89 (d, J = 9 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4S) δ 26.42, 27.28, 28.45, 29.05, 29.39, 34.15, 36.32, 37.44, 128.17, 138.09; IR (neat) 3048 (w), 1666 (w), 892 (s), 838 (s) cm^{-1}.

b) Cyclohexylmethylenecyclopentane and Cyclopentylmethylenecyclohexane. The use of 5-hexynyl tosylate (2 mmol, 0.50 g) in place of 6-heptynyl tosylate gave 0.07 g (45% yield) of a 1:1 mixture of the title compounds. These compounds have been identified as a mixture by comparing their spectra with those of their authentic samples prepared as described below.

Cyclohexylmethylenecyclopentane Prepared via Palladium-Catalyzed Cross Coupling

To bromomethylenecyclopentane (0.16 g, 1 mmol), which was prepared by treatment of dibromomethylenecyclopentane with *t*-BuLi followed by hydrolysis at −120°C [17], in ether (5 mL) were added sequentially 7.3 mg (0.01 mmol) of Cl_2Pd (dppf), where dppf = bis(diphenylphosphino)ferrocene, and cyclohexylmagnesium chloride in ether (1.4 M, 1.2 mL, 1.7 mmol) [18]. The reaction mixture was warmed to 25°C, stirred for several hours, and

quenched with aqueous NH_4Cl. Extraction with pentane, washing with aqueous $NaHCO_3$ and water, drying over $MgSO_4$, concentration, and column chromatography (SiO_2, pentane) provided 97 mg (59% yield) of the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.4 (m, 6H), 1.5–1.8 (m, 8H), 1.95–2.1 (m, 1H), 2.1–2.25 (m, 4H), 5.09 (d, J = 9 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 26.20, 26.24, 26.37, 26.46, 28.37, 33.22, 33.58, 36.79, 126.47, 141.12; IR (neat) 1670 (w), 890 (s), 810 (s) cm^{-1}; High resolution MS Calcd for $C_{12}H_{20}$: 164.1566. Found: 164.1552.

Cyclopentlmethylenecyclohexane Prepared via Nickel-Catalyzed Cross Coupling

Chloromethylenecyclohexane was prepared in 46% yield according to a literature procedure [19] by the Wittig reaction of cyclohexanone with a reagent generated in situ by treatment of $[ClCH_2PPh_3]I$ with KOBu-*t* in HOBu-*t*: bp 60–65°C (10 mm Hg); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.56 (m, 6H), 2.12 (m, 2H), 2.36 (m, 2H), 5.76 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 26.29, 26.62, 27.84, 28.41, 34.08, 108.39, 141.97; IR (neat) 3070 (m), 1635 (m), 990 (s), 905 (s), 860 (s), 810 (s), 790 (s), 745 (s), 625 (m) cm^{-1}. To 0.26 g (2.0 mmol) of chloromethylenecyclohexane and 1 mol% of Cl_2Ni(dppp) (11 mg, 0.02 mol) [20] in ether (2 mL) was added at 0°C 1.4 M cyclopentylmagnesium bromide in ether (1.7 mL, 2.4 mmol) [21]. After stirring the mixture overnight at 25°C, it was quenched with aqueous NH_4Cl, extracted with pentane, washed with aqueous $NaHCO_3$ and water, dried over $MgSO_4$, evaporated, and column chromatographed (SiO_2, pentane) to produce 0.264 g (79% yield) of the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.1–1.3 (m, 2H), 1.45–1.85 (m, 12H), 2.0–2.25 (m, 4H), 2.5–2.75 (m, 1H), 4.99 (d, J = 9 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.34, 27.06, 28.09, 28.77, 29.22, 34.15, 37.20, 38.16, 127.08, 138.39; IR (neat) 1665 (w), 940 (m), 845 (m) cm^{-1}.

Reaction of Diphenylzirconocene with 1-Lithio-ω-tosyloxy-1-hexyne to Give Phenylmethylenecyclopentane

To a solution of Cp_2ZrCl_2 (0.292 g, 1.0 mmol) in THF (3 mL) at −78°C was added slowly 2.0 M PhLi in cyclohexane-ether (1.0 mL, 2.0 mmol). After 1 hr at this temperature, a solution of 6-tosyloxy-1-hexynyllithium (1.0 mmol) in THF (3 mL) was added to the reaction mixture. The mixture was warmed to 25°C over 3 hr, quenched with 3N HCl, extracted with ether, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, concentrated, and column chromatographed (silica gel, pentane) to give 0.07 g (45% yield) of the title compound [22]: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.6–1.9 (m, 4H), 2.5–2.7 (m, 4H), 6.40 (br s, 1H), 7.1–7.5 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.65, 27.22, 31.19, 35.95, 120.76, 125.58, 127.92, 128.17, 138.87, 147.21; IR (neat) 3090 (w), 3060 (w), 3040 (m), 1660 (m), 1600 (m), 915 (m), 865 (m), 750 (m), 700 (s) cm^{-1}.

The use of 6-bromo- and 6-iodo-1-hexynes which were prepared by treatment in acetone of 5-hexyn-1-yl tosylate with LiBr and NaI, respectively, led to the formation of phenylmethylenecyclopentane in 30–40% yields, showing no advantage over the use of 5-hexynyl tosylate.

Reaction of Other Organotransition Metals with 6-Tosyloxy-1-hexynyllithium

The use of diphenylchromium [8], diphenylmanganese [8], triphenylvanadium [8], or triphenylyttrium [23] (1.0 mmol) in THF (3 mL) in place of diphenylzirconocene in the experiment described above gave biphenyl as the major product and no more than 5–10%, if any, of the desired phenylmethylenecyclopentane.

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