Facile Preparation of Alkenylidenecycloalkanes by Cyclization of Acetylenic Alkyllithiums Bearing a Propargylic Leaving Group

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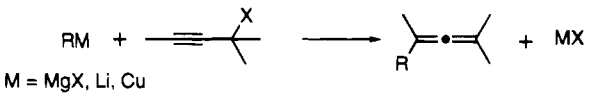
Received August 11, 1994

The intermolecular addition of various organometallic reagents to acetylenes bearing a good leaving group at the propargylic position is a classical route to allenes.[1] Much less information is available on the intramolecular variant of this S_N2' reaction.

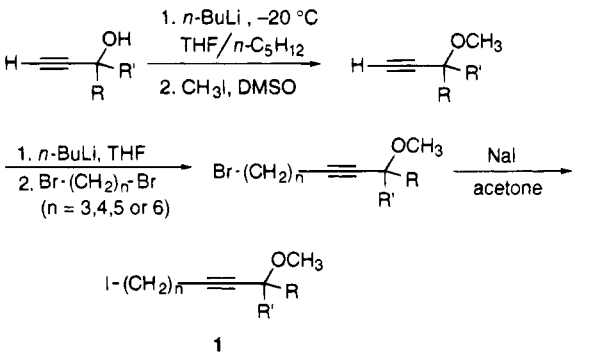


The facile exo-dig ring closure of acetylenic alkyllithiums,[2] coupled with the ease with which these organometallics may be prepared by lithium–iodine exchange,[3] suggested that cyclization of an acetylenic alkyllithium bearing a leaving group at the distal propargylic position would provide a convenient route to exocyclic allenes.[4] As demonstrated by the results detailed below, the intramolecular S_N2' ring-closure of acetylenic alkyllithiums derived from ω-iodoalkyl propargylic methyl ethers delivers alkenylidenecycloalkanes in high yield.

Results and Discussion

The requisite ω-iodoalkyl propargylic methyl ethers **1** were prepared in a straightforward fashion as depicted in Scheme 1. Treatment of approximately 0.1 M solutions of **1** in *n*-pentane–diethyl ether at −78 °C with 2.0–2.2 molar equiv of *t*-BuLi serves to generate the corresponding acetylenic alkyllithiums (**2**) in virtually quantitative yield.[3] The unsaturated alkyllithiums are stable at low temperature; quenching reaction mixtures generated by lithium–iodine exchange with MeOH at −78 °C affords pure methyl propargylic ethers. However, when solutions of **2** bearing a 3-, 4-, or 5-carbon tether are allowed to warm and stand at room-temperature for 1 h, a clean intramolecular S_N2' ring-closure ensues to give the exocyclic allene (Scheme 2; **2** → **3** → **4**). Although the cyclization of **2** → **4** is formulated in Scheme 2 as involving the intermediacy of **3**, allene formation may well be a concerted if not entirely synchronous process.

Scheme 1



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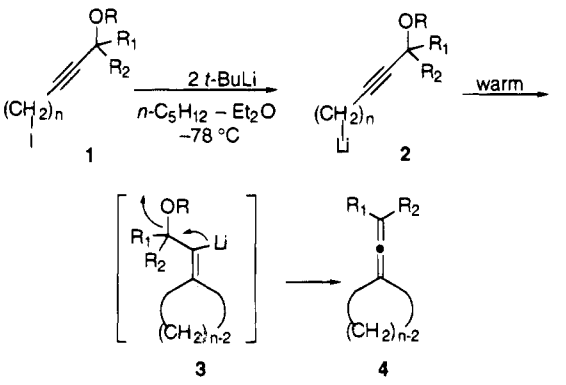
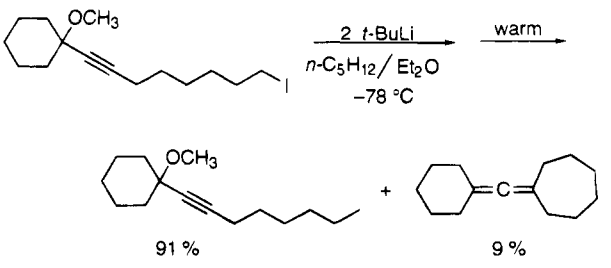
Scheme 2



1 **2** **3** **4**

Be that as it may, the results summarized in Table 1 demonstrate that cyclization of **2** provides an experimentally simple, high yield, direct route to four-, five-, and six-membered alkenylidenecycloalkanes. It should be noted that isolation of pure allene **4** is a simple matter: silica gel chromatography using a hydrocarbon eluent serves to remove the small amount of uncyclized methyl propargylic ether that is produced as a byproduct in the lithium–iodine exchange used to generate **2**.[3]

Allene formation by intramolecular S_N2' ring-closure of ω-lithio methyl propargylic ethers is less facile when the tether length exceeds five carbon atoms. Thus, as shown below, the acetylenic alkyllithium derived from 1-(8-iodo-1-octynyl)-1-methoxycyclohexane cyclizes to the extent of only ~9% when allowed to stand at room temperature for 1 h. The remaining 91% of the reaction mixture was the uncyclized, methyl propargylic ether (79% isolated yield).



In summary, acetylenic alkyllithiums bearing a methoxy group at the distal propargylic position cleanly cyclize to give four-, five-, and six-membered alkenylidenecycloalkanes in good to excellent yield (Table 1).

(1) (a) Landor, S. R. *The Chemistry of Allenes*; Academic Press: New York, 1982; Vol. 1. (b) Rutledge, T. F. *Acetylenes and Allenes*; Reinhold: New York, 1969. (c) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes, A Laboratory Manual;* Elsevier: Amsterdam, 1981. (d) Pattenden, G. In *Comprehensive Organic Chemistry*; Barton D., Ollis W. D., Eds.; Pergamon Press: New York, 1979; Vol. 1, Ch. 2. (e) Taylor, D. R. *Chem Rev.* **1967**, *67*, 317.

(2) (a) 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, 1994; Vol. 3, pp 251–273. (b) Bailey, W. F.; Ovaska, T. V. *J. Am. Chem. Soc.* **1993**, *115*, 3080. (c) Wu, G.; Cederbaum, F. E.; Negishi, E. *Tetrahedron Lett.* **1990**, *31*, 493. (d) Bailey, W. F.; Ovaska, T. V. *Tetrahedron Lett.* **1990**, *31*, 627. (e) Bailey, W. F.; Ovaska, T. V. *Organometallics* **1990**, *9*, 1694. (f) Bailey, W. F.; Ovaska, T. V.; Leipert, T. K. *Tetrahedron Lett.* **1989**, *30*, 3901.

(3) Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404.

(4) This approach to exocyclic allenes finds precedent in the work of Broka and co-workers on the preparation of vinyl-substituted tetrahydrofurans via cyclization of α-oxa-5-hexenyllithiums bearing an allylic OCH_3 group. See: (a) Broka, C. A.; Lee, W. J.; Shen,T. *J. Org. Chem.* **1988**, *53*, 1338. (b) Broka, C. A.; Shen, T. *J. Am. Chem. Soc.* **1989**, *111*, 2981.

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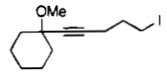
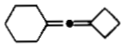
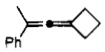
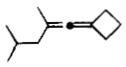
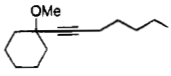
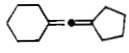
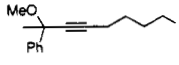
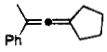
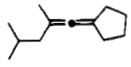
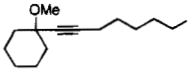
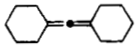
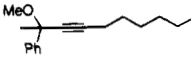
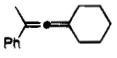
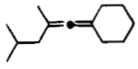
Table 1. Preparation of Exocyclic Allenes (Scheme 2)[a]

entry	iodide	allene	yield,[b] %
1			72
2			88
3			88
4			86
5			90
6			84
7			85
8			74
9			62

[a] Acetylenic alkyllithiums **2** were generated at −78 °C by addition of 2.0−2.2 equiv of *t*-BuLi to a solution of the appropriate iodide **1** in *n*-pentane−diethyl ether (3:2 by vol), the cooling bath was then removed, and the mixture was allowed to warm and stand at room temperature for 1 h prior to quench with an excess of methanol. [b] Isolated yield of chromatographically pure product.

Experimental Section

General. General spectroscopic and chromatographic procedures, methods used for the purification of reagents and solvents, and precautions regarding the manipulation of organolithiums have been previously described.[5]

Literature procedures, incorporating some minor modifications, were followed for the preparation of 1-ethynyl-1-methoxycyclohexane,[6] 3-methoxy-3,5-dimethyl-1-hexyne,[7] and 3-methoxy-3-phenyl-1-butyne.[8]

Preparation of Acetylenic Alkyl Bromides. This procedure represents a modification of that described by Crandall and Michaely.[9] The propargylic methyl ether, diluted with dry THF (~80 mL THF for a 0.1 mol scale reaction), was added dropwise to a solution of *n*-BuLi in hexanes (1.03 mol of *n*-BuLi per 1 mol of alkyne), and the resulting solution was heated at gentle reflux for 2.5 h. The contents of the flask were then cooled to room temperature, the appropriate dihalide was added in one portion (1.56 mol dihalide per 1 mol of alkyne), and the reaction mixture was heated at reflux overnight. The cooled reaction mixture was partitioned between brine and diethyl ether, the aqueous layer was extracted with diethyl ether, and the combined organic layers were dried ($MgSO_4$) and concentrated by rotary evaporation. Distillation of the residue or elution from a short column of silica gel afforded pure products whose structures were established on the basis of the following spectroscopic data.

1-(5-Bromo-1-pentynyl)-1-methoxycyclohexane: 63% yield; bp 101−105 °C (0.3 mm); ^{1}H NMR ($CDCl_3$) δ 1.24−1.85 [m, 10 H (complex pattern)], 1.98−2.07 (m, 2 H), 2.42 (t, J = 6.72 Hz, 2 H), 3.34 (s, 3 H), 3.51 (t, J = 6.48 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.44, 22.86, 25.50, 31.64, 32.27, 36.95, 50.48, 73.95, 81.82, 84.00. Anal. Calcd for $C_{12}H_{19}OBr$: C, 55.61; H, 7.39. Found: C, 55.95; H, 7.39.

1-(6-Bromo-1-hexynyl)-1-methoxycyclohexane: 78% yield; bp 108−115 °C (0.05 mm); ^{1}H NMR ($CDCl_3$) δ 1.25−1.85 (m, 10 H), 1.85−1.88 (m, 2 H), 1.94−2.05 (m, 2 H), 2.29 (t, J = 6.89 Hz, 2 H), 3.34 (s, 3 H), 3.44 (t, J = 6.56 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.84, 22.85, 25.49, 27.19, 31.68, 33.13, 36.95, 50.44, 73.92, 81.85, 85.21; IR (neat) 2960, 2880, 2130, 1420, 1270, 1240, 1060, 1000 cm^{-1}. Anal. Calcd for $C_{13}H_{21}BrO$: C, 57.15; H, 7.75. Found: C, 57.18; H, 7.69.

1-(7-Bromo-1-heptynyl)-1-methoxycyclohexane: 75% yield; bp 123−128 °C (0.07 mm); ^{1}H NMR δ 1.25 −1.91(complex overlapping patterns,16 H), 2.26 (t, J = 6.54 Hz, 2 H), 3.34 (s, 3 H), 3.42 (t, J = 6.74 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.49, 22.87, 25.52, 27.30, 27.96, 32.23, 33.52, 36.99, 50.41, 73.95, 81.48, 85.71; IR (neat) 2950, 2870, 2200, 1420, 1320, 1240, 1150, 1120, 1060, 900 cm^{-1}. Anal. Calcd for $C_{14}H_{23}BrO$: C, 58.54; H, 8.07. Found: C, 58.70; H, 8.33.

1-(8-Bromo-1-octynyl)-1-methoxycyclohexane: 76% yield; bp 130−135 °C (0.03 mm); ^{1}H NMR δ 1.26−1.63 (complex pattern, 12 H), 1.83−1.93 (m, 6 H), 2.25 (t, J = 6.70 Hz, 2 H), 3.34 (s, 3 H), 3.42 (t, J = 6.71 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.52, 22.87, 25.52, 27.59, 27.84, 28.59, 32.63, 33.66, 37.01, 50.38, 73.96, 81.27, 86.01; IR (neat) 2920, 2890, 2230, 1440, 1340, 1300, 1270, 1090, 930 cm^{-1}. HRMS calcd for $C_{15}H_{25}OBr$ 300.1089, found 300.1084.

7-Bromo-2-methoxy-2-phenyl-3-heptyne: 46% yield; R_f = 0.35 (2% Et_2O−hexanes); ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 3 H), 2.07−2.17 (m, 2 H), 2.55 (t, J = 6.79 Hz, 2 H), 3.18 (s, 3 H), 3.56 (t, J = 6.42 Hz, 2 H), 7.25−7.60 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.52, 31.50, 32.21, 32.77, 52.26, 76.53, 81.39, 85.76, 125.99, 127.63, 128.19, 143.08; IR (neat) 3020, 2950, 2220, 1430, 1080, 750, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{17}BrO$: C, 59.80; H, 6.09. Found: C, 59.59; H, 5.83.

8-Bromo-2-methoxy-2-phenyl-3-octyne: 45% yield; bp 125 °C (0.25 mm); ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 3 H), 1.73−1.81 (m, 2 H), 1.98−2.06 (m, 2 H), 2.40 (t, J = 6.92, 2 H), 3.18 (s, 3 H), 3.46 (t, J = 6.58, 2 H), 7.28−7.38 (m, 3 H), 7.56−7.60 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.95, 27.11, 31.73, 32.76, 33.02, 52.21, 76.53, 80.83, 86.96, 125.9, 127.5, 128.1, 143.08; IR (neat) 3020, 2960, 2250, 1450, 1240, 1100, 870, 770, 710 cm^{-1}. Anal. Calcd for $C_{15}H_{19}OBr$: C, 61.03; H, 6.49. Found: C, 61.25; H, 6.77.

9-Bromo-2-methoxy-2-phenyl-3-nonyne: 75% yield; R_f = 0.59 (2% Et_2O−hexanes); ^{1}H NMR ($CDCl_3$) δ 1.59−1.64 (m, 4H), 1.69 (s, 3 H), 1.85−1.95 (m, 2 H), 2.37 (t, J = 6.49 Hz, 2 H), 3.18 (s, 3 H), 3.41 (t, J = 6.66 Hz, 2 H), 7.27−7.38 (m, 3 H), 7.57−7.60 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.59, 27.38, 27.86, 32.22, 32.76, 33.43, 52.18, 76.49, 80.52, 87.43, 126.02, 127.5, 128.1, 143.2; IR (neat) 3020, 2940, 2860, 2200, 1430, 1220, 1080, 850, 750, 690 cm^{-1}. Anal. Calcd for $C_{16}H_{21}BrO$: C, 62.14; H, 6.84. Found: C, 62.42; H, 7.05.

1-Bromo-6-methoxy-6,8-dimethyl-4-nonyne: 45% yield; R_f = 0.47 (2% Et_2O−hexanes); ^{1}NMR ($CDCl_3$) δ 0.97 (d, J = 6.67 Hz, 6 H), 1.37 (s, 3 H), 1.53−1.62 (m, 2 H), 1.83−1.90 (m, 1 H), 1.98−2.08 (m, 2 H), 2.42 (t, J = 6.74 Hz, 2 H), 3.31 (s, 3 H), 3.52 (t, J = 6.47 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.41, 24.17, 24.26, 24.81, 26.49, 31.56, 32.23, 49.84, 50.98, 73.60, 82.81, 83.53; IR (neat) 2950, 2290, 1420, 1150, 1070 cm^{-1}. Anal. Calcd for $C_{12}H_{21}BrO$: C, 55.18; H, 8.10. Found: C, 54.94; H, 7.82.

10-Bromo-4-methoxy-2,4-dimethyl-5-decyne: 58% yield; bp 135−140 °C (Kugelrohr, 2 mm); ^{1}H NMR ($CDCl_3$) δ 0.94 (d, J = 6.61 Hz, 6 H), 1.34 (s, 3 H), 1.51 (m, 2 H), 1.59−1.66 (m, 2 H), 1.85−1.97 (overlapping multiplets, 3 H), 2.24 (t, J = 6.91 Hz, 2 H), 3.27 (s, 3 H), 3.45 (t, J = 7.05 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.83, 24.18, 24.27, 24.79, 26.52, 27.13, 31.71, 33.05, 49.88, 50.95, 73.63, 82.33, 84.67; IR (neat) 2950, 2270, 1470, 1150, 1090 cm^{-1}. Anal. Calcd for $C_{13}H_{23}BrO$: C, 56.73; H, 8.42. Found: C, 56.72; H, 8.70.

11-Bromo-4-methoxy-2,4-dimethyl-5-undecyne: 32% yield of approximately 90% pure material; bp 110 °C (0.5 mm); ^{1}H NMR ($CDCl_3$) δ 0.97 (d, J = 6.62 Hz, 6 H), 1.37 (s, 3 H), 1.46−1.62 (overlapping patterns, 6 H), 1.85−1.92 (m, complex pattern, 3 H), 2.24 (t, J = 6.66 Hz, 2 H), 3.31 (s, 3 H), 3.41 (t, J = 6.77 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.48, 24.18, 24.27, 24.79, 26.55, 27.33, 27.87, 32.25, 33.51, 49.88, 50.94, 73.64, 81.95, 85.17; IR

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(7) Hennion, G. F.; Boisselle, A. P. *J. Org. Chem.* **1961**, *26*, 2677.
(8) Hennion, G. F.; Fleck, B. R. *J. Am. Chem. Soc.* **1955**, *77*, 3253.
(9) Crandall, J. K.; Michaely, W. J. *J. Org. Chem.* **1984**, *49*, 4244.

(neat) 3000, 2280, 1490, 1420, 1330, 1220, 1100 cm^{-1}. HRMS calcd for $C_{13}H_{22}OBr$ ($M^+ - CH_3$) 273.0854, found 273.0849.

Preparation of Acetylenic Alkyl Iodides 1. The freshly distilled acetylenic alkyl bromide was added to an approximately 0.66 M solution of anhydrous sodium iodide in dry acetone (2.2 equiv of sodium iodide per mol of bromide). The mixture was stirred at room temperature under nitrogen for 5–10 h and then heated at reflux for an additional 1 h. The solution was cooled and filtered by suction, the solid residue was washed with acetone, and the combined filtrate and washings were concentrated by rotary evaporation. The residue was partitioned between water and diethyl ether and the organic layer was washed with 10% sodium thiosulfate and water. Drying over $MgSO_4$ and solvent removal afforded 90–97% product. The iodides were purified by passage through a short column of silica gel eluting with pentane and the structures were established on the basis of the following spectroscopic properties.

1-(5-Iodo-1-pentynyl)-1-methoxycyclohexane: 93% yield; ^1H NMR ($CDCl_3$) δ 1.22–1.64 (complex patterns, 10 H), 1.77–2.00 (m, 2 H), 2.36 (t, J = 6.68 Hz, 2 H), 3.28 (t, J = 6.88 Hz, 2 H), 3.31 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 5.20, 19.74, 22.86, 25.49, 32.17, 36.94, 50.48, 73.93, 82.48, 83.82; IR (neat) 2980, 2890, 2230, 1440, 1350, 1300, 1270, 1230, 1180, 1090, 930 cm^{-1}. Anal. Calcd for $C_{12}H_{19}OI$: C, 47.07; H, 6.25. Found: C, 47.31; H, 6.46.

1-(6-Iodo-1-hexynyl)-1-methoxycyclohexane: 96% yield; ^1H NMR ($CDCl_3$) δ 1.21–1.97 (complex patterns, 14 H), 2.24 (t, J = 6.87 Hz, 2 H), 3.17 (t, J = 6.85 Hz, 2 H), 3.29 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 5.94, 17.60, 22.83, 25.48, 29.42, 32.39, 36.94, 50.42, 73.88, 81.88, 85.15; IR (neat) 2970, 2890, 2240, 1440, 1340, 1290, 1240, 1090, 930 cm^{-1}. HRMS calcd for $C_{13}H_{21}OI$ 320.0637, found 320.0633.

1-(7-Iodo-1-heptynyl)-1-methoxycyclohexane: 97% yield; ^1H NMR ($CDCl_3$) δ 1.20–1.61 (m, complex pattern, 12 H), 1.78–1.84 (m, 4 H), 2.23 (t, J = 6.47 Hz, 2 H), 3.16 (t, J = 6.93 Hz, 2 H), 3.32 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 6.50, 18.47, 22.86, 25.52, 27.73, 29.61, 32.94, 36.98, 50.41, 73.91, 81.52, 85.67; IR (neat) 2960, 2890, 2220, 1440, 1340, 1210, 1090, 930 cm^{-1}. Anal. Calcd for $C_{14}H_{23}OI$: C, 50.31; H, 6.94. Found: C, 49.98; H, 6.98.

1-(8-Iodo-1-octynyl)-1-methoxycyclohexane: 97% yield; ^1H NMR ($CDCl_3$) δ 1.22- 1.60 (m, complex pattern, 14 H), 1.77–1.83 (m, 4 H), 2.21 (t, J = 6.74 Hz, 2 H), 3.15 (t, J = 6.98 Hz, 2 H), 3.31 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 6.81, 18.54, 22.89, 25.54, 27.63, 28.59, 29.92, 33.36, 37.02, 50.41, 73.97, 81.30, 86.02; IR (neat) 2900, 2880, 2200, 1410, 1310, 1160, 1060, 900 cm^{-1}; HRMS calcd for $C_{15}H_{25}OI$ 348.0950, found 348.0948.

10-Iodo-4-methoxy-2,4-dimethyl-5-decyne: 93% yield; ^1H NMR ($CDCl_3$) δ 0.97 (d, J = 6.58 Hz, 6 H), 1.37 (s, 3 H), 1.50–1.67 (m, 5 H), 1.85–1.97 (m, 2 H), 2.26 (t, J = 6.90 Hz, 2 H), 3.21 (t, J = 6.86 Hz, 2 H), 3.31 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 5.91, 17.62, 24.20, 24.24, 24.80, 26.55, 29.39, 32.44, 49.89, 50.97, 73.63, 82.35, 84.66; IR (neat) 2970, 2200, 1430, 1350, 1270, 1200, 1150, 1070 cm^{-1}. Anal. Calcd for $C_{13}H_{23}IO$: C, 48.46; H, 7.19. Found: C, 48.82; H, 7.27.

11-Iodo-4-methoxy-2,4-dimethyl-5-undecyne: 91% yield; ^1H NMR ($CDCl_3$) δ 0.97 (d, J = 6.00 Hz, 6 H), 1.37 (s, 3 H), 1.48–1.59 (m, 7 H), 1.82–1.89 (m, 2 H), 2.24 (t, J = 6.58 Hz, 2 H), 3.19 (t, J = 6.95 Hz, 2 H), 3.31 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 6.52, 18.48, 24.19, 24.28, 24.79, 26.57, 27.66, 29.66, 32.99, 49.90, 50.97, 73.65, 81.98, 85.17; IR (neat) 2960, 2210, 1390, 1350, 1260, 1160, 1070 cm^{-1}. Anal. Calcd for $C_{14}H_{25}IO$: C, 50.01; H, 7.49. Found: C, 50.34; H, 7.75.

7-Iodo-2-methoxy-2-phenyl-3-heptyne: 97% yield; ^1H NMR ($CDCl_3$) δ 1.69 (s, 3 H), 2.02–2.11 (m, 2 H), 2.51 (t, J = 6.73 Hz, 2 H), 3.18 (s, 3 H), 3.34 (t, J = 6.67 Hz, 2 H), 7.25–7.59 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 5.19, 19.85, 32.04, 32.79, 52.29, 76.53, 81.43, 85.61, 125.99, 127.63, 128.19, 142.96. HRMS calcd for $C_{13}H_{14}OI$ ($M^+ - CH_3$) 313.0089, found 313.0081.

8-Iodo-2-methoxy-2-phenyl-3-octyne: 97% yield; ^1H NMR ($CDCl_3$) δ 1.69 (s, 3 H), 1.66–1.77 (m, 2 H), 1.95–2.03 (m, 2 H), 2.39 (t, J = 6.91 Hz, 2 H), 3.18 (s, 3 H), 3.23 (t, J = 6.83 Hz, 2 H), 7.28–7.39 (m, 3 H), 7.56–7.59 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 5.89, 17.76, 29.39, 32.48, 32.78, 52.25, 76.52, 80.88, 86.95, 126.01, 127.56, 128.15, 143.7. Anal. Calcd for $C_{15}H_{19}OI$: C, 52.62; H, 5.60. Found: C, 52.92; H, 5.93.

9-Iodo-2-methoxy-2-phenyl-3-nonyne: 97% yield; ^1H NMR ($CDCl_3$) δ 1.55–1.66 (m, 4 H), 1.69 (s, 3 H), 1.83–1.92 (m, 2 H), 2.37 (t, J = 6.62 Hz, 2 H), 3.19 (s, 3 H), 3.20 (t, J = 6.90 Hz, 2 H), 7.25–7.38 (m, 3 H), 7.57–7.60 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 6.49, 18.63, 27.68, 29.75, 32.81, 32.98, 52.25, 76.53, 80.55, 87.47, 126.06, 127.54, 128.14, 143.7; IR (neat) 3040, 2900, 2840, 2210, 1430, 1220, 1070, 850, 750, 690 cm^{-1}. Anal. Calcd for $C_{16}H_{21}OI$: C, 53.96; H, 5.94. Found: C, 54.40; H, 6.30.

1-Iodo-6-methoxy-6,8-dimethyl-4-nonyne: 96% yield; ^1H NMR ($CDCl_3$) δ 0.97 (d, J = 6.63 Hz, 6 H), 1.37 (s, 3 H), 1.53–1.57 (m, 2 H), 1.83–1.92 (m, 1 H), 1.96–2.03 (m, 2 H), 2.37 (t, J = 6.70 Hz, 2 H), 3.30 (t, J = 6.71 Hz, 2 H), 3.31 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 5.18, 19.69, 24.17, 24.26, 24.79, 26.46, 32.10, 49.79, 50.98, 73.59, 82.85, 83.29; IR (neat) 2950, 2200, 1430, 1340, 1250, 11150, 1060 cm^{-1}. HRMS calcd for $C_{11}H_{18}OI$ ($M^+ - CH_3$) 293.0403, found 293.0389.

General Procedure for the Preparation of Alkenylidenecycloalkanes 4. The acetylenic alkyl iodide was transferred under an atmosphere of either dry argon or dry nitrogen into a flame-dried, round-bottomed flask, fitted with a rubber septum and an inert-gas inlet. Enough dry *n*-pentane–ether (3:2 by volume) was added so that the final concentration of the iodide was ~0.1 M. The flask was cooled to −78 °C (dry ice–acetone bath) and a solution of *t*-BuLi in pentane (2.0–2.2 equiv of *t*-BuLi per mol of iodide) was slowly added to the stirred iodide solution. After the addition was completed, the reaction mixture was allowed to stand at −78 °C for an additional 5 min. The cooling bath was then removed, and the mixture was allowed to warm and stand at room temperature for 1 h under a blanket of argon or nitrogen. The mixture was quenched by addition of an excess of methanol, washed with water, dried ($MgSO_4$), and concentrated by rotary evaporation. Elution of the residue from silica gel using pentane or hexanes as eluent afforded pure product in the yields given in Table 1. (Cyclohexylidenemethylidene)cyclohexane (Table 1, entry 7) is a known compound[10] whose physical and spectroscopic properties were fully in accord with the assigned structure. The structures of the remaining allenes were established on the basis of the data presented below; product yields are given in Table 1.

(Cyclobutylidenemethylidene)cyclohexane (Table 1, entry 1): ^1H NMR ($CDCl_3$) δ 1.49–1.60 (m, 6 H), 1.85 (quintet, J = 2 H), 2.09 (t, J = , 4 H), 2.82 (t, J = 7.95 Hz, 4 H), 7.17–7.43 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.38, 26.25, 27.65, 30.61, 32.38, 98.33, 105.31, 189.93; IR (neat) 2910, 1960, 1410, 1350, 1210 cm^{-1}. Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.79; H, 10.66.

(2-Phenyl-1-propenylidene)cyclobutane (Table 1, entry 2): ^1H NMR ($CDCl_3$) δ 1.98–2.06 (m, 2 H), 2.08 (s, 3 H), 2.97 (t, J = 7.93 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 17.53, 17.58, 30.03, 102.34, 102.53, 125.81, 126.34, 128.17, 138.44, 195.62; IR (neat) 3020, 2890, 1940, 1430, 750, 680 cm^{-1}. Mass spectroscopic molecular weight calcd for $C_{13}H_{14}$ 170.1096, found 170.1090.

(2,4-Dimethyl-1-pentenylidene)cyclobutane (Table 1, entry 3): ^1H NMR ($CDCl_3$) δ 0.89 (d, J = 6.44 Hz, 6 H), 1.65 (s, 3 H), 1.65–1.96 (overlapping multiplets, 5 H), 2.81 (t, J = 7.85 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 17.36, 20.02, 22.53, 26.39, 30.24, 44.47, 99.26, 101.01, 194.06; IR (neat) 2890, 1940, 1420, 1350, 1150 cm^{-1}; HRMS calcd for $C_{11}H_{18}$ 150.1409, found 150.1406.

(Cyclopentylidenemethylidene)cyclohexane (Table 1, entry 4): ^1H NMR ($CDCl_3$) δ 1.49–1.69 (bm, 10 H), 2.05–2.12 (m, 4 H), 2.27 (apparent t, J = 7.23 Hz 4 H); ^{13}C NMR ($CDCl_3$) δ 26.38., 27.05, 27.80, 31.44, 32.23, 101.04, 102.85, 191.28; IR (neat) 2910, 2860, 1950, 1410, 1060 cm^{-1}. Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.02; H, 10.89.

(2-Phenyl-1-propenylidene)cyclopentane (Table 1, entry 5): ^1H NMR ($CDCl_3$) δ 1.69–1.78 (m, 4 H), 2.06 (s, 3 H), 2.41–2.50 (m, 4 H), 7.05–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.28, 27.16, 30.93, 100.49, 105.42, 125.67, 125.97, 128.15, 138.80, 197.69; IR (neat) 3020, 1900, 1980, 1580, 1420, 1240, 740, 680 cm^{-1}. Anal. Calcd for $C_{14}H_{16}$: C, 90.97; H, 8.75. Found: C, 91.07; H, 8.99.

(2,4-Dimethyl-1-pentenylidene)cyclopentane (Table 1, entry 6): ^1H NMR ($CDCl_3$) δ 0.89 (d, J = 6.36 Hz, 6 H), 1.50–1.75 (m, 5 H), 1.61 (s, 3 H), 1.77 (m, 2 H), 2.02–2.08 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.95, 22.57, 26.36, 27.85, 32.11, 44.39, 95.48, 100.85, 196.00; IR (neat) 2820, 1950, 1420, 1350 cm^{-1}. Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 88.02; H, 12.33.

(10) Bestmann, H. J.; Denzel, T.; Salbaum, H. *Tetrahedron Lett.* **1974**, 1275.

(2-Phenyl-1-propenylidene)cyclohexane (Table 1, entry 8): ^{1}H NMR ($CDCl_3$) δ 1.50–1.62 (m, 6 H), 1.98 (s, 3 H), 2.09–2.14 (m, 4 H), 7.05–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.54, 26.28, 27.88, 31.54, 97.81, 104.33, 125.58, 125.92, 128.16, 138.85, 198.49; IR (neat) 3020, 2900, 2880, 1940, 1540, 1420, 980, 740, 670 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.56; H, 8.96.

(2,4-Dimethyl-1-pentenylidene)cyclohexane (Table 1, entry 9): ^{1}H NMR ($CDCl_3$) δ 0.89 (d, J = 6.35 Hz, 6 H),1.49–1.62 (m, 7 H), 1.61 (s, 3 H), 1.71–1.80 (m, 2 H), 2.00–2.08 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 19.95, 22.57, 22.83, 26.40, 27.86, 32.12, 44.40, 95.48, 100.85, 196.00; IR (neat) 2820, 1950, 1430, 1360 cm^{-1}. Anal. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found: C, 87.79; H, 12.55.

1-Methoxy-1-(1-octynyl)cyclohexane. The general procedure outlined above was followed. Thus, 0.219 g (0.628 mmol) of 1-(8-iodo-1-octynyl)-1-methoxycyclohexane in 6.28 mL of *n*-pentane–diethyl ether (3:2 by vol) was treated with 0.47 mL of 2.96 M *t*-BuLi (1.4 mmol) in pentane. Quench of the reaction mixture with methanol and analysis of the crude product by GC on a 25-m × 0.20-mm cross-linked methyl silicone fused-silica capillary column using temperature programming (initial temperature 100 °C for 5 min, 20 °C/min to 250 °C) revealed the presence of two products in a ratio of 91:9. Preparative GC on an 8-ft, 10% SE-30 on Anakrom A column afforded 110 mg (79%) of the major product which was identified as the title compound on the basis of the following spectroscopic properties: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.76 Hz, 3 H), 1.25–1.88 (complex patterns, 18 H), 2.23 (t, J = 6.85 Hz, 2 H), 3.34 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 13.97, 18.64, 22.53, 22.91, 25.57, 28.46, 28.85, 31.28, 37.06, 50.38, 74.03, 81.01, 86.48; IR (neat) 2850, 2210, 1430, 1060 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.23; H, 11.94. The minor product was tentatively identified as (cyclohexylidenemethylidene)cycloheptane on the basis of its mass spectrum: MS m/z (rel intensity) 190 (M^+, 35), 105 (45), 91 (100), 79 (81), 67 (62).

Acknowledgment. This work was supported by the Connecticut Department of Economic Development.

Supplementary Material Available: Copies of the ^{1}H and ^{13}C NMR spectra for all new compounds for which combustion analytical data are not available (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9413956