Radical-Mediated Synthesis of Bridgehead-Substituted Bicycloalkanes. A Convenient Route to the Bicyclo[3.2.1]octyl System

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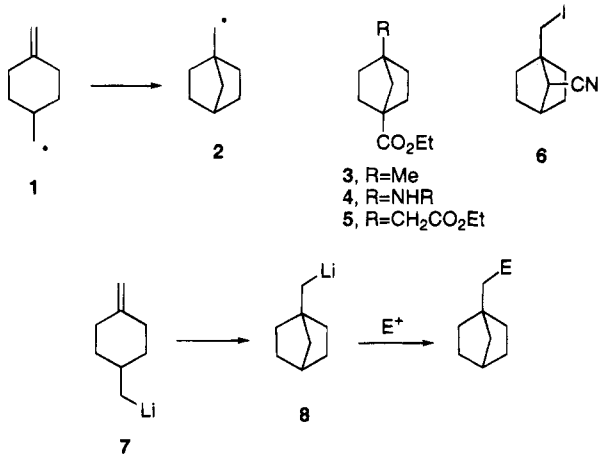
Cyclization of the (3-methylenecyclohexyl)ethyl radical (**9**) to the isomeric 1-bicyclo[3.2.1]octylmethyl radical (**10**) occurs with an activation energy of 11.6 kcal mol^{-1}, a barrier which compares favorably with the calculated value of 12.6 kcal mol^{-1} determined by force field calculations. It is shown that the facility for ring closure of **9** can be exploited for high-yield synthesis of bicyclo[3.2.1]octanes with useful functionality at the bridgehead including the preparation of models of the bicyclo-[3.2.1]octyl moiety in the gibberellin sytem.

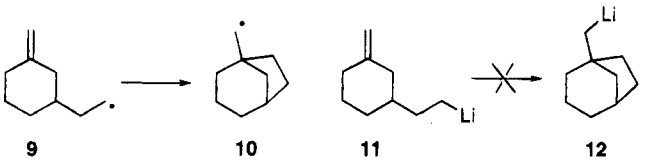
Introduction

We have recently shown[1] that, despite the fact that it is characterized by a relatively high activation energy (12.7 kcal mol^{-1}), 5-*exo* trig cyclization of the 4-methylenecyclohexyl radical **1** to give the strained bicyclo[2.2.1]-heptyl system **2** is a thermodynamically favorable process. Accordingly, ring closure of derivatives of **1** has been found[1,2] to provide an attractive entry into bicyclo[2.2.1]-heptanes with useful functionality at the bridgehead; the esters **3**–**5** as well as the nitrile **6** were all prepared in yields >75% in this way.

One of the interesting aspects of the radical interconversion **1** → **2**, aside from its intrinsic synthetic utility, is that it has an analogy in "carbanion" chemistry. Thus, Bailey and Khanolkar[3] have demonstrated that low-temperature cyclization of [(4-methylenecyclohexyl)-methyl]lithium (**7**) yields the isomeric bicyclo[2.2.1]heptyl species **8** which can be trapped subsequently by appropriate electrophiles. The two cyclization processes **1** → **2** and **7** → **8**, therefore, represent complementary procedures for the synthesis of bridgehead-substituted bicyclo[2.2.1]heptanes.



In view of the importance of the bicyclo[3.2.1]octyl ring moiety in naturally-occurring compounds[4] such as the gibberellins and kaurenes, the search for versatile synthetic pathways to this bicyclic ring system continues to attract attention, and in this context we recently initiated a study of the behavior of the (3-methylenecyclohexyl)-ethyl radical (**9**); cyclization of **9** to give **10** along similar lines to the rearrangement observed for radical **1** would provide an alternative route to bicyclo[3.2.1]octanes. An additional impetus for this work was the knowledge that Bailey and his associates[5] have made the surprising observation that, in contrast to [(4-methylenecyclohexyl)-methyl]lithium (**7**), the corresponding alkyllithium **11** could not be induced to cyclize to the isomer **12**. We now wish to report the results of our investigation.



Results and Discussion

In order to provide a theoretical test of the feasibility of the rearrangement **9** → **10**, we adopted the molecular mechanics approach described by Beckwith and Schiesser[6] for the cyclization of a series of 5-hexenyl radicals, a technique we had previously found[1] to provide a reliable assessment for the potential for cyclization of the (4-methylenecyclohexyl)methyl radical (**1**). The transition state (Figure 1) for the process **9** → **10** was located by MNDO modeling and its existence established by standard force constant calculations. The parameters specified in the figure were then employed as constants in the usual MM2 procedure of energy minimization for the transition state. The theoretical value of the activation energy, E_a, for the interconversion **9** → **10** was thus determined using the procedure described[6] and found to be 12.6 kcal mol^{-1}. This barrier is somewhat lower than

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(4) See: Hadjiarapoglu, L.; de Meijere, A.; Seitz, H.-J.; Klein, I.; Spitzer, D. *Tetrahedron Lett.* **1994**, *35*, 3269 and references 1–6 therein. See also: Sagawa, S.; Nagaoka, H.; Yamada, Y. *Tetrahedron Lett.*, **1994**, *35*, 603. Barker, A. J.; Begley, M. J.; Mellor, M.; Otieno, D. A.; Pattenden, G. *J. Chem. Soc., Perkin Trans. I* **1983**, 1893.
(5) Bailey, W. F.; Nurmi, T. T.; Patricia, J. J.; Wang, W. *J. Am. Chem. Soc.* **1987**, *109*, 2442.
(6) Beckwith, A. L. J.; Cliff, M. D.; Schiesser, C. H. *Tetrahedron* **1992**, *48*, 4641. Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1995**, *41*, 3925.

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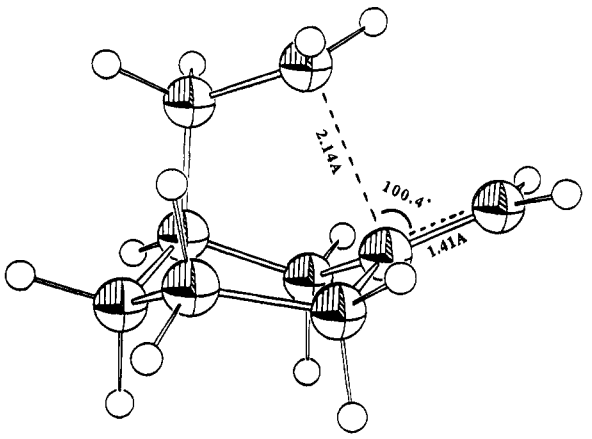

Figure 1. Calculated transition state structure for the ring closure of the (3-methylenecyclohexyl)ethyl radical (**9**).

the calculated value for the ring closure **1** → **2** (13.5 kcal mol^{-1}), suggesting that cyclization of radical **9** to give the bicyclo[3.2.1]octyl ring system should be energetically more favorable. By analogy with the homolog **1**, cyclization of which is also under stereoelectronic control, products arising from 6-*endo* cyclization of **9** are not expected because of geometrical constraints in the associated transition state.

For an experimental determination of the activation energy associated with ring closure of radical **9**, we employed (3-methylenecyclohexyl)ethyl bromide (**13**) as an obvious precursor. Authentic specimens of the possible products **16** and **17** were also required; a sample of the hydrocarbon **16** was available from an earlier investigation,[7] and **17** was prepared by low-temperature reduction of the bromide **13** in neat tributyltin hydride.

A preliminary assessment of the potential for cyclization of the radical **9** was made by dropwise treatment of a 0.025M solution of the parent bromide **13** in boiling toluene with 1.1 equiv of Bu_3SnH in the presence of a catalytic amount of AIBN. GC analysis of the product showed it to consist of a 9:1 mixture of the hydrocarbons **16** and **17**, the identities of which were established by comparison of their retention times with those of the authentic specimens. This observation augured well for subsequent experiments devised to synthesize more highly functionalized bicycloalkane derivatives; it also confirmed the prediction from the calculations that the rearrangement **9** → **10** should occur with relative ease.

An experimental estimate of the activation energy of cyclization of radical **9** was obtained by application of standard procedures employed for these reactions in which kinetic measurements are performed using pseudo-first-order conditions (10 equiv of Bu_3SnH) (Scheme 1). The GC-determined ratios of the isomeric products **16** and **17** led to the kinetic data displayed in Table 1. The integrated rate equation (eq 1) corresponding to Scheme 1, where [Bu_3SnH] ≫ [**13**], follows:

$$\frac{16}{17} = \frac{k_c}{k_H}\frac{1}{Bu_3SnH} \qquad (1)$$

in which k_c is the rate constant for the cyclization process **9** → **10** and k_H is the rate constant for abstraction of a

Scheme 1

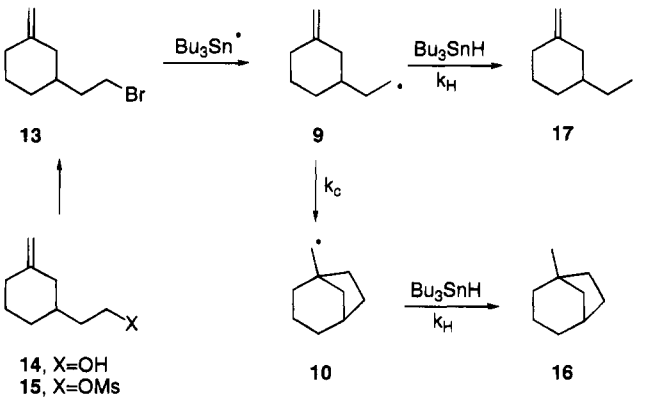

Table 1. Kinetic Data for Cyclization of the (3-Methylenecyclohexyl)ethyl Radical (9) in *tert*-Butylbenzene

		product ratios		
temp, °C	[Bu_3SnH], M	**16**	**17**	log k_c/k_H
80	0.025	3.5	96.5	−3.05
100	0.025	5.9	94.2	−2.81
120	0.025	10.2	89.8	−2.55
140	0.025	15.5	84.5	−2.34

hydrogen atom from Bu_3SnH by the radical **9**. Hence, it follows that

$$\log\frac{k_c}{k_H} = \Delta \log A - \frac{E_a}{2.303RT} \qquad (2)$$

The Arrhenius parameters for the cyclization **9** → **10** were derived by a standard single-variable regressional analysis of the data displayed in Table 1. This leads to the following expression (eq 3).

$$\log\frac{k_c}{k_H} = (1.87 \pm 0.275) - \frac{(7.93 \pm 0.47)}{2.303RT} \qquad (3)$$

Using the typical rate of H-abstraction from Bu_3SnH by primary radicals:[8]

$$\log k_H = (9.07 \pm 0.24) - \frac{(3.69 \pm 0.32)}{2.303RT}$$

as the value of k_H leads to expression 4

$$\log k_c = (10.94 \pm 0.36) - \frac{(11.6 \pm 0.57)}{2.303RT} \qquad (4)$$

from which the value of k_c at 25 °C is calculated to be 2.6 × 10^2 s^{-1}.

The value of the pre-exponential term is 10.9, which is in the range of logA values commonly observed for cyclizations of this kind.[9] The activation barrier to cyclization is found to be 11.6 kcal mol^{-1}, and this is seen to be in very good agreement with the calculated value (12.6 kcal mol^{-1}) obtained above. As predicted, the barrier for isomerization **9** → **10** is lower than the value for cyclization of the isomeric species **1**. This is consistent with the requirement that the ring adopt a boat-like conformation in the transition state in the rearrangement

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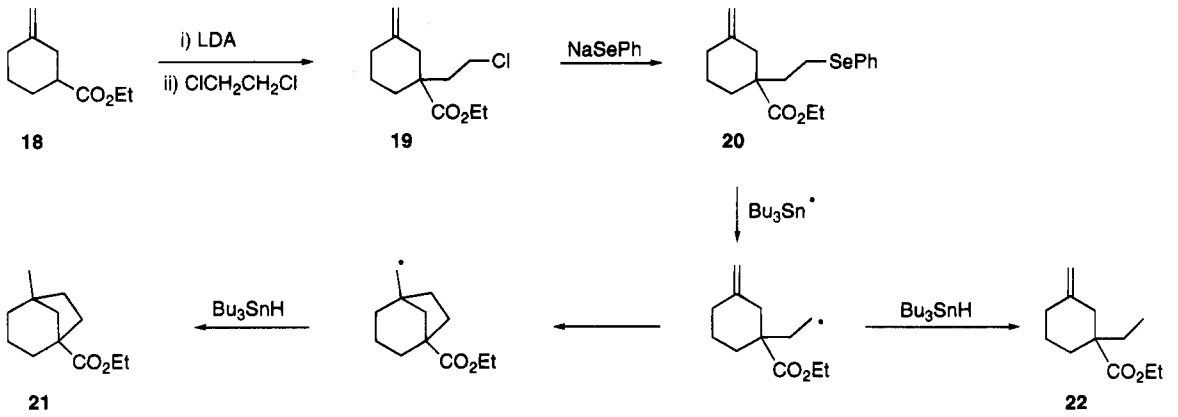
Scheme 2



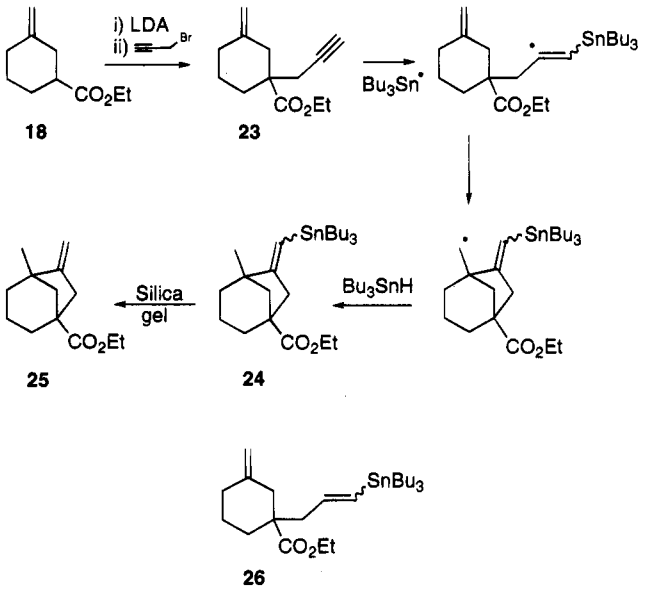
leading to **2** which is more demanding energetically than the necessity for a pseudoaxial arrangement of the side chain during cyclization of radical **9** to give **10**. Interestingly, however, the rate of the cyclization **9** → **10** is marginally less than that of **1** → **2**.[1] We attribute this to the operation of an unfavorable entropy effect associated with essentially free rotation of the side chain during isomerization of **9**. Presumably this is reflected in the lower value of the log *A* term observed in the case of the ring closure **9** → **10**.

An investigation into possible synthetic applications of the interconversion **9** → **10** was then undertaken with the specific goal of generating bicyclo[3.2.1]octanes with versatile functional groups at the bridgehead. For expediency, we selected selenide **20** as the modified radical precursor in the expectation that cyclization would yield a bicycloalkane with an ester group at the bridgehead. Scheme 2 illustrates that the synthesis of **20** can be accomplished readily from ethyl 3-ketocyclohexane-1-carboxylate by standard methodology. By way of interest, it was found convenient in performing the interconversion **18** → **19**, the precursor to the phenylselenide **20**, to introduce the the chloroethyl side chain using 1,2-dichloroethane as alkylating agent because it was found to minimize competing side reactions compared with the use of 1-bromo-2-chloroethane.[10]

The selenide **20** was then exposed to the conditions we had earlier found to be especially conducive to optimum cyclization[1] in related systems, viz., syringe-pump-controlled slow addition of a solution of Bu_3SnH in toluene containing a catalytic amount of AIBN over 3 h to a solution of the substrate in boiling toluene. To our delight, this process gave an excellent yield of a product consisting of a 92:8 mixture of the cyclized to unrearranged isomers **21** and **22**. Removal of the unsaturated contaminant was performed by treating a solution of the mixture in dichloromethane with bromine followed by evaporation of solvent and then distillation of the residue. The route depicted in Scheme 2 therefore represents an attractive route to the bicyclo[3.2.1]octyl bridgehead ester **21**, an unknown compound, which was obtained in 36% overall yield in four relatively easy steps from ethyl 3-ketocyclohexane-1-carboxylate.

With the aim of developing a procedure to bicyclo[3.2.1]-octane containing an exocyclic double bond, thus mimicking the type of moiety present in gibberellins,[11] we chose

Scheme 3



to exploit the novel discovery by Stork and Moor[12] that alkene cyclization can be promoted by β-trialkylstannyl radicals. The latter are generated conveniently by addition of tributyltin radicals to a terminal alkyne. The ester **18** was therefore converted into the propynyl derivative **23** via its enolate anion using standard manipulations (Scheme 3), and the latter, dissolved in boiling toluene, was exposed to the conditions described above involving slow addition of tributyltin hydride. This yielded a product which appeared to be homogeneous and whose NMR properties were consistent with the structure **24**. The vinylstannane underwent protiodestannylation when stirred in methylene chloride with silica gel for 5 days, and the derived product was found to consist of the unsaturated bicyclo[3.2.1]octyl ester **25** in excellent yield (80% from **18**). None of the uncyclized isomer **26** was detected in the product, and accordingly, cyclization of the alkyne **23** under these conditions represents a viable additional entry into this ring system which is obtained without isomeric contamination.[13]

In summary, this study demonstrates that the application of radical-mediated processes to readily-available (3-methylenecyclohexyl)ethyl derivatives leads to suitably-substituted bicyclo[3.2.1]octanes in excellent yield and

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(12) Stork, G.; Moor, R. M.; *Tetrahedron Lett.*, **1986**, *27*, 4529.
(13) For a related radical-induced ring closure, see: Marinovic, N. N.; Ramanathan, H. *Tetrahedron Lett.* **1983**, *18*, 1871.

under relatively mild conditions. One of the unexpected observations to emerge from the work is that whereas these radical interconversions are favorable and give bicycloalkanes almost quantitatively, the corresponding cyclic material is not produced from the related lithiated derivatives **11** of the (3-methylenecyclohexyl)ethyl system.

We have recently initiated an investigation to assess whether this process is applicable to the synthesis of hetereocyclic analogs of both the bicyclo[2.2.1]heptyl and bicyclo[3.2.1]octyl systems.

Experimental Section

Molecular mechanics calculations[14] were carried out on a Macintosh IIvx using PCMODEL. Kinetic experiments[15] and general experimental procedures[16] were performed as described. 2-(3-Methylenecyclohexyl)ethanol (**14**) was prepared from 2-cyclohexen-1-one as described.[5] Ethyl 3-ketocyclohexane-1-carboxylate was prepared from the diastereomeric mixture of ethyl 3-hydroxycyclohexane-1-carboxylate[17] as described[17] for the analogous 4-keto ester.[1]

3-(2-Bromoethyl)-1-methylenecyclohexane (13). The mesylate of 2-(3-methylenecyclohexyl)ethanol (**14**) was prepared by the method of Crossland and Servis[18] (yield: 90%) and used without further purification. Lithium bromide (2.17 g, 0.025 mmol) was added to a stirred solution of the crude mesylate **15** (1.36 g, 6.24 mmol) in dry DME (15 mL) and the mixture allowed to stir at room temperature for 24 h. The mixture was poured into water and extracted with pentane (3×). The combined extracts were washed successively with water and saturated NaCl and then dried ($MgSO_4$). Removal of the solvent and distillation of the residue (Kugelrohr: 110 °C (20 mmHg)) afforded the bromide **13** (1.09 g, 86%) as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 4.6 (s, 2H), 3.51 (t, 2H), 2.45−1.05 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 148.2, 107.7, 40.92, 39.45, 37.50, 34.99, 31.80, 31.55, 26.70. Anal. Calcd for $C_9H_{15}Br$: C, 53.22; H, 7.44. Found: C, 53.29; H, 7.55.

3-Ethyl-1-Methylenecyclohexane (17). The bromide **13** (0.3 g) and a few crystals of AIBN were added to deoxygenated tributyltin hydride (3 mL) under nitrogen, and the mixture was subjected to irradiation with a 300 W tungsten lamp for 60 min. The volatile component which was removed from the reaction mixture under reduced pressure (1 mmHg) and condensed in a liquid nitrogen/acetone trap (~−100 °C) proved to be the hydrocarbon **17**: ^{1}H NMR ($CDCl_3$) δ 4.6 (s, 2H), 2.40−0.75 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 149.7, 106.7, 41.46, 40.99, 35.25, 32.27, 29.48, 27.17, 11.42; HRMS calcd for C_9H_{16}, 124.1252; found, 124.1250.

Ethyl 3-Methylenecyclohexanecarboxylate (18). Sodium hydride (2.96 g, 0.123 mol) was stirred in dry dimethyl sulfoxide (130 mL) at 70 °C for 1 h. Methyltriphenylphosphonium iodide (49.8 g, 0.123 mol) was added to the cooled mixture and stirred for a further 1 h at room temperature, after which the solution was treated with ethyl 3-ketocyclohexanecarboxylate (15 g, 0.088 mol) in dry DMSO (20 mL). After being stirred at 50 °C for 45 min, the reaction mixture was cooled, poured into water, and extracted with pentane (3×). The combined extracts were washed successively with water and saturated NaCl and then dried ($MgSO_4$). Removal of the solvent and distillation of the residue (Kugelrohr: 75 °C (1 mmHg)) yielded the title compound **18** as a clear oil (12.0 g, 81%): ^{1}H NMR ($CDCl_3$) δ 4.66 (s, 2H), 4.15 (q, 2H), 2.65−1.4 (m, 9H), 1.21 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 175.1, 146.9, 108.6, 60.16, 44.32, 37.22, 34.36, 28.64, 26.54, 14.19. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.16; H, 9.61.

Ethyl 1-(2-Chloroethyl)-3-methylenecyclohexanecarboxylate (19). A solution of diisopropylamine (4.17 mL, 29.5 mmol) in dry THF (75 mL) was treated with a solution of 2 M solution of BuLi in cyclohexane (14.8 mL, 29.5 mmol) followed by HMPA (12 mL) at −40 °C under a nitrogen atmosphere. The mixture was cooled to −80 °C and a solution of ethyl 3-methylenecyclohexanecarboxylate (**18**) (4.5 g, 26.8 mmol) in THF (15 mL) was added with the tempreature maintained below −70 °C throughout the addition. After 15 min, 1,2-dichloroethane (10 g, 0.11 mol) was added and the mixture was allowed to warm to room temperature. The mixture was poured into water (50 mL) and extracted with pentane (3×). The combined extracts were washed successively with with saturated NH_4Cl and water (4×), before being dried ($MgSO_4$). Evaporation of the solvent and distillation of the residual oil (Kugelrohr: 80 °C, (0.3 mmHg)) yielded the title compound **19** as a clear liquid (4.23 g, 68%): ^{1}H NMR ($CDCl_3$) δ 4.66 (s, 2H), 4.17 (q, 2H), 3.6−3.28 (m, 2H), 2.73−1.37 (m, 10H), 1.24 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 175.1, 144.7, 110.3, 60.56, 47.70, 42.27, 40.15, 40.14, 34.24, 32.59, 23.52, 14.18. Anal. Calcd for $C_{12}H_{19}O_2Cl$: C, 62.47; H, 8.30. Found: C, 62.53; H, 8.39.

Ethyl 3-Methylene-1-[2-(selenophenyl)ethyl]cyclohexanecarboxylate (20). Sodium borohydride (0.12 g) was added to a solution of diphenyl diselenide (0.47 g, 1.52 mmol) in absolute ethanol (10 mL). After the bright yellow solution turned colorless, ethyl 1-(2-chloroethyl)-3-methylenecyclohexanecarboxylate (**19**) (0.5 g, 2.17 mmol) in ethanol (1 mL) was added and the combined mixture was heated under reflux for 3 h. The cooled solution was diluted with water (10 mL) and extracted with CH_2Cl_2 (3×). The combined extracts were washed with water (2×) and then saturated NaCl solution before being dried ($MgSO_4$). After removal of the solvent, the light yellow residue was distilled (Kugelrohr: 130 °C (0.1 mmHg)) to give the title compound **20** as a clear oil (0.61 g, 81%): ^{1}H NMR ($CDCl_3$) δ 7.6−7.1 (m, 5H), 4.68 (s, 2H), 4.10 (q, 2H), 2.94−1.35 (m, 12H), 1.17 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 175.4, 145.2, 132.3, 130.2, 129.1, 126.8, 110.1, 60.42, 49.20, 42.14, 38.55, 34.41, 32.67, 23.72, 22.08, 14.31. Anal. Calcd for $C_{18}H_{24}O_2Se$: C, 61.58; H, 6.88. Found: C, 61.55; H, 6.68.

Ethyl 5-Methylbicyclo[3.2.1]octane-1-carboxylate (21). Tributyltin hydride (0.52 g, 1.79 mmol) in dry toluene (15 mL) containing a few crystals of AIBN was added slowly over a period of 3 h to a solution of ethyl 1-[2-(selenophenyl)ethyl]-3-methylenecyclohexanecarboxylate (**20**) (0.6 g, 1.71 mmol) in refluxing toluene (55 mL). After the reaction had gone to completion (GC analysis), the mixture was cooled and a few drops of bromine were added. The solvent was removed *in vacuo* leaving a yellow liquid which upon careful distillation (Kugelrohr: 100 °C (1 mmHg)) afforded the title compound **21** (0.271 g, 81%) as a clear oil: ^{1}H NMR ($CDCl_3$) δ 4.11 (q, 2H), 2.10−1.24 (m, 12H), 1.22 (t, 3H), 1.05 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 177.5, 60.07, 50.89, 48.87, 40.84, 38.98, 36.02, 34.00, 33.10, 27.16, 20.18, 14.24. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.09; H, 10.24.

Ethyl 1-Ethyl-3-methylenecyclohexanecarboxylate (22). A solution of LDA was prepared by the addition of a 1.6 M solution of BuLi in hexane (4.03 mL, 6.54 mmol) followed by HMPA (4 mL) to a solution of diiosopropylamine (0.66 g, 6.54 mmol) in dry THF (15 mL) at −50 °C under a nitrogen atmosphere. The mixture was cooled to −80 °C, and ethyl 3-methylenecyclohexanecarboxylate (**18**) (1 g, 5.95 mmol) in THF (5 mL) was added with the temperature maintained below −70 °C throughout the addition. After 15 min, bromoethane (2.13 mL, 29.7 mmol) was added and the mixture was allowed to warm to room temperature. The mixture was poured into water (10 mL) and extracted with pentane (3×). The combined extracts were washed successively with water (4×), before being dried ($MgSO_4$). Evaporation of the solvent and distillation of the residue (Kugelrohr: 105 °C (20 mmHg)) yielded the title compound **22** as a clear liquid (0.92 g, 79%): ^{1}H NMR ($CDCl_3$) δ 4.64 (s, 2H), 4.12 (q, 2H), 2.71−1.35 (m, 10H), 1.22 (t, 3H), 0.78 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 176.2, 145.9, 109.3, 59.99, 48.73, 42.06, 34.52, 32.50, 30.86, 23.85, 14.24, 8.52. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.03; H, 10.14.

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Ethyl 3-Methylene-1-(2-propynyl)cyclohexanecarboxylate (23). A solution of LDA was prepared by the addition of a 1.8 M solution of BuLi in hexane (3.5 mL, 6.22 mmol) followed by HMPA (4 mL) to a solution of diisopropylamine (0.63 g, 6.22 mmol) in dry THF (12 mL) at −40 °C under a nitrogen atmosphere. The mixture was cooled to −80 °C, and ethyl 3-methylenecyclohexanecarboxylate (**18**) (0.95 g, 5.65 mmol) in THF (4 mL) was added with the temperature maintained below −70 °C throughout the addition. After 15 min, propargyl bromide (2.67 mL, 22.6 mmol) was added and the mixture was allowed to warm to room temperature. The mixture was poured into water and extracted with pentane (3×). The combined extracts were washed successively with saturated NH_4Cl and water (4×), before being dried ($MgSO_4$) after which the solvent was evaporated. The resultant light yellow liquid was distilled (Kugelrohr: 85 °C (1.5 mmHg)) to yield the title compound **23** as a clear liquid (1.13 g, 96%): IR (neat) 3295 (s), 2120 (w), and 1732 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.70 (s, 2H), 4.14 (q, 2H), 2.5−1.4 (m, 11H), 1.25 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 175.0, 144.9, 110.3, 80.31, 70.78, 60.62, 47.86, 41.41, 34.20, 31.86, 26.49, 23.46, 14.22. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.70; H, 8.80. Found: C, 76.20; H, 9.21.

Ethyl 5-Methyl-6-methylenebicyclo[3.2.1]octane-1-carboxylate (25). Tributyltin hydride (1.16 g, 4.0 mmol) in dry toluene (30 mL) containing a few crystals of AIBN was slowly added over a period of 3 h to a solution of ethyl 1-(2-propynyl)-3-methylenecyclohexanecarboxylate (**23**) (0.75 g, 3.64 mmol) in refluxing toluene (150 mL). After the addition was complete, heating was continued for another 2 h after which the mixture was cooled and the solvent removed *in vacuo* leaving a yellow liquid. The residue was then stirred in the presence of silica gel (4 g) in CH_2Cl_2 (15 mL) at room temperature for 5 days. Carefull distillation (Kugelrohr: 80 °C (1.5 mmHg)) afforded the title compound **25** (0.63 g, 83%) as a clear oil: ^1H NMR ($CDCl_3$) δ 4.90−4.66 (m, 2H), 4.15 (q, 2H), 2.77−1.3 (m, 10H), 1.24 (t, 3H), 1.11 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 177.0, 157.0, 103.0, 60.29, 49.00, 47.51, 44.89, 40.97, 40.76, 33.31, 24.02, 20.14, 14.25. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.74; H, 9.78.

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Supplementary Material Available: ^{13}C NMR spectrum of **17** (1 page). 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.

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