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1-bromobicyclo[2.2.2]octanes and
1-bromobicyclo[3.3.1]nonanes

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Reaction of nucleophiles with bridgehead carbocations derived from 1-bromobicyclo[2.2.2]octanes and 1-bromobicyclo[3.3.1]nonanes

Abstract

Both intramolecular and intermolecular reactions of bridgehead carbocations are described. The carbocations are best generated from the corresponding halide with silver triflate. The carbocations reacted effectively with allyltrimethylsilane, ethyl acetoacetate, benzene, and enol silyl ethers. Bridgehead radicals were also examined.

Disciplines

Chemistry | Environmental Chemistry | Inorganic Chemistry | Organic Chemistry | Other Chemistry | Polymer Chemistry

Comments

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may be substituted for the nitric acid; the true oxidizing agent is nitric oxide, which is regenerated by oxidation with oxygen. The procedure may be modified to produce mercury(II) sulfonates.²⁵

The extent of mercury oxidation in organic acids is dependent on the choice of acid. In acetic acid the nitric oxide catalyzed reaction requires 65 °C, where it proceeds quantitatively to mercury(I) acetate. Attempts to drive the oxidation to completion at high temperatures approaching 100 °C are frustrated by the reaction of mercury(II) acetate with acetic acid to give a polymeric mercury acetoxy species. However, the addition of certain cocatalysts, especially palladium(II) salts, silica gel, or activated carbon (Norite A), allows quantitative conversion to mercury(II) acetate at 65 °C. The role of these agents in promoting the mercury(I) to -(II) oxidation is obscure.

Summary. Good to excellent yields of methyl esters are achieved by the carbonylation of organomercurials in methanol catalyzed by triphenylphosphine complexes of palladium. Ester yields are decreased by hydrogenolysis of the organomercurial to hydrocarbon, a side reaction sensitive to steric and electronic factors. Selectivity to ester is a function of solvent system and catalyst selection; carbonylation to free carboxylic acid is favored by rhodium (and possibly platinum) catalysts and by sterically hindered alcohols. In carboxylic acid and aqueous solvents, carboxylic acids are the exclusive carbonylation products.

Experimental Section

All reagents were purchased from commercial sources and used as received. Organomercury compounds were prepared by published procedures.⁹⁻¹⁰ Group 9 and 10 metal complexes were either purchased from commercial suppliers or synthesized by published procedures.²⁶⁻²⁸ Reaction products were identified by comparison with authentic compounds. Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. NMR spectra were measured on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Vapor-phase chromatography was performed on a Perkin-Elmer Model 226 capillary gas chromatograph equipped with 300 ft × 0.01 in. DC-550 silicone columns.

Representative experimental procedures are given below. For additional examples of these reactions see ref 25 and 29.

(25) Baird, W. C., Jr.; Surridge, J. H.; Hartgerink, R. L. U.S. Patent 3 792 069, 1974.

(26) Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Chem. Commun.* 1965, 131.

(27) (a) Evans, D.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Nature (London)* 1965, 208, 1203. (b) Hallman, P. S.; Evans, D.; Osborn, J. A.; Wilkinson, G. *Chem. Commun.* 1967, 305.

(28) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Wiley: New York, 1973; pp 452-458.

Carbonylation of Ethylmercuric Acetate. Into a 45-mL Parr stainless steel reactor³⁰ were charged 0.29 g (1 mmol) of ethylmercuric acetate, 0.02 g (0.02 mmol) of tris(triphenylphosphine)chlororhodium(I), 10 mL of methanol, and a small magnetic stirrer. The bomb was closed, purged with carbon monoxide, and pressurized to 500 psig. The bomb was suspended in an oil bath at 100 °C and stirred overnight. The bomb was cooled, and its contents were analyzed. A 66% yield of methyl propionate based on ethylmercuric acetate was recovered along with a 75% yield of metallic mercury. Thiocyanate titration of the reaction mixture accounted for 25% of unreacted ethylmercuric acetate.

Carbonylation of Phenylmercuric Trifluoroacetate. To a 1000-mL Parr Series 4500 pressure reactor³⁰ were charged 29.2 g (74 mmol) of phenylmercuric trifluoroacetate, 250 mL of methanol, and 0.007 g (0.01 mmol) of bis(triphenylphosphine)dichloropalladium(II). The reactor was pressurized to 90 psig with carbon monoxide and stirred at 85-90 °C for 1.5 h. The reaction yielded 68% methyl benzoate and gave a 75% yield of mercury.

Synthesis of Mercury(II) Trifluoroacetate. A 50-mL glass pressure tube was charged with 1.02 g (5 mmol) of mercury, 5 mL of trifluoroacetic acid, and 0.04 g (0.45 mmol) of concentrated nitric acid. The tube was pressurized with oxygen to 60 psig and was then shaken at room temperature for 1 h, during which the pressure decreased to 38 psig. Thiocyanate titration of the solution showed 100% conversion to mercury(II). Removal of the solvent gave a 98% yield of crystalline mercury(II) trifluoroacetate.

Anal. Calcd for C₄F₆O₄Hg: C, 11.25; Hg, 47.01. Found: C, 11.87; Hg, 45.90.

The mercury(II) trifluoroacetate was stirred overnight at room temperature with benzene to give a quantitative yield of phenylmercuric trifluoroacetate, which was shown to be identical with an authentic sample.

Synthesis of Mercury(II) Acetate. Into a 50-mL glass pressure tube were charged 20 mL of acetic acid, 1 g (4.8 mmol) of mercury, 0.02 g (0.23 mmol) of concentrated nitric acid, and 0.04 g (0.05 mmol) of bis(triphenylphosphine)dichloropalladium(II). The reaction was pressurized with oxygen to 60 psig and agitated at 65 °C for 24 h. Thiocyanate titration gave a 96% yield of mercury(II) acetate, which was recovered by evaporation of the solvent.

Anal. Calcd for C₄H₆O₄Hg: C, 15.07; H, 1.90; Hg, 62.95. Found: C, 15.42; H, 1.82; Hg, 62.73.

The mercury salt was reacted with benzene in acetic acid to give authentic phenylmercuric acetate.

(29) Baird, W. C., Jr.; Hartgerink, R. L.; Surridge, J. H. U.S. Patent 3 917 670, 1975.

(30) Parr Instrument Co., Moline, IL.

(31) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Reaction of Nucleophiles with Bridgehead Carbocations Derived from 1-Bromobicyclo[2.2.2]octanes and 1-Bromobicyclo[3.3.1]nonanes

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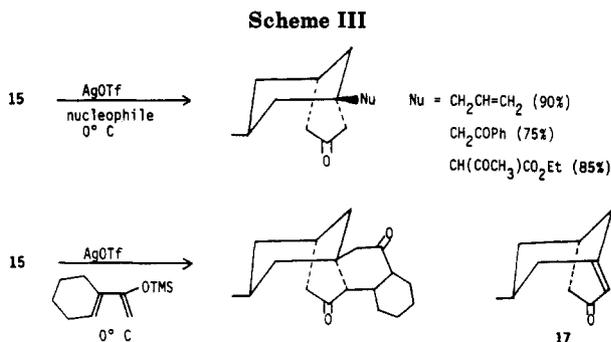
Department of Chemistry, Iowa State University, Ames, Iowa 50011

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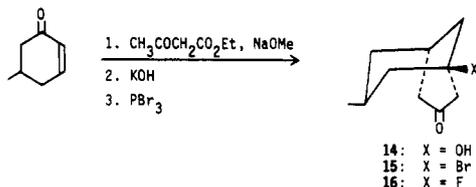
Both intramolecular and intermolecular reactions of bridgehead carbocations are described. The carbocations are best generated from the corresponding halide with silver triflate. The carbocations reacted effectively with allyltrimethylsilane, ethyl acetoacetate, benzene, and enol silyl ethers. Bridgehead radicals were also examined.

While many synthetic chemists have studied the applications of aliphatic and alicyclic carbocations, the area

of bridgehead carbocations has been studied primarily by physical organic chemists.¹

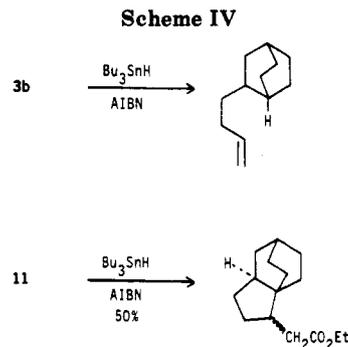


The preparation of the bicyclo[3.3.1]nonane system was accomplished by literature methods.⁷ In particular, ketol 14 was synthesized in two steps from ethyl acetoacetate



and 5-methylcyclohexenone. The bromo ketone 15 was isolated in 80% yield from the reaction of 14 with phosphorus tribromide. While a few reactions of 15 with silver salts such as silver acetate and silver fluoride had been reported, there were no literature examples of the use of allylic silanes or enol silyl ethers.⁸ The bromide 15 was treated with allyltrimethylsilane, ethyl acetoacetate, and the enol silyl ether of methyl cyclohexenyl ketone. Modest yields of substitution products were obtained. Each product was contaminated with 1-fluorobicyclo[3.3.1]nonan-3-one (16), presumably derived by the interaction of the carbocation with the fluoroborate counterion. In the case of the reaction with allyltrimethylsilane, 16 was the major product. This complication was readily solved by using silver triflate to generate the bridgehead triflate. The substitution reactions then proceeded in excellent yield as illustrated in Scheme III. Of particular interest was the reaction of 15 with the enol silyl ether of methyl cyclohexenyl ketone. While the product of this reaction could be produced via the trapping of the bridgehead carbocation followed by an intramolecular Michael addition, it could also arise from an intermolecular Diels–Alder with the bridgehead enone 17. House has studied the chemistry of several bridgehead enones.⁹ He has demonstrated that while bridgehead enones react in good to excellent yields with nucleophiles, intermolecular Diels–Alder reactions proceed in only modest yields. The possibility that some of the product is formed via the bridgehead enone cannot be ruled out.

The bridgehead radical chemistry was also examined. In contrast to the bridgehead carbocation situation, bridgehead radicals are reported to be only 10 times more reactive than their acyclic counterparts. The 5-hexenyl radical cyclizations are usually facile and have been extensively studied.¹⁰ A 5-hexenyl subunit exists in bromide 3b. It was subjected to tributyltin hydride, excess ethyl acrylate, and a catalytic amount of AIBN in boiling



benzene. The result, depicted in Scheme IV, was reduction to 2-butenylbicyclo[2.2.2]octane. There are examples in the literature in which an activating group such as a carbomethoxyl group is essential for a successful radical cyclization.¹¹ The bromoester 11 was therefore a logical candidate and was next tried. A 50% yield of tricyclic product was obtained. Only one other example of an intramolecular bridgehead radical cyclization has been reported. This example, which appeared prior to the onset of this work, involved an oxabicyclo[3.2.1]octane ring system and resulted in the total synthesis of agarofuran.¹²

The inter- and intramolecular reactions of bridgehead carbocations reported herein establish the feasibility of employing these intermediates in synthesis. Bridged systems such as the bicyclo[2.2.2]octanes and the bicyclo[3.3.1]nonanes can be directly functionalized at the bridgehead position. This strategy offers a unique alternative to existing methodology and suggests new and exciting synthetic pathways to a variety of natural products.

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. Dichloromethane was distilled from phosphorus pentoxide.

Synthesis of Bromoalkenes 3a and 3b. To a suspension of 5% platinum on carbon (0.423 g) in 10 mL of ethanol under a hydrogen atmosphere was added alkene 1 (2.12 g, 12.9 mmol) in 20 mL of ethanol. The suspension was stirred at room temperature for 18 h. The suspension was filtered through Celite and concentrated to provide the crude product. It was chromatographed on silica gel by using 10:1 hexanes/ethyl acetate to provide 1.948 g (91% yield) of pure product.

To a solution of 12.5 mmol of lithium diisopropylamide (LDA) in 20 mL of tetrahydrofuran (THF) containing 1.5 mL of hexamethylphosphoric triamide (HMPA) at -78°C was added the product of the hydrogenation reaction (1.80 g, 10.9 mmol) in 10 mL of THF over 10 min. The reaction was stirred at -78°C for 1 h. The appropriate alkenyl halide (14 mmol) was then added and the reaction was stirred at -78°C for 30 min and then allowed to warm to room temperature. The reaction was partitioned twice between water and ether. The organic layer was dried and concentrated. The crude product was obtained in approximately 75% yield and was taken on to the next step without purification.

To a solution of sodium (1.8 g, 78 mmol) in 120 mL of liquid ammonia was added the alkylated nitrile (11.2 mmol) in 10 mL of THF. The solution was stirred for 1 h. Solid ammonium chloride was then carefully added to quench the excess sodium. The ammonia was then allowed to evaporate, water was added, and the aqueous layer was extracted with ether. The organic layer was dried and concentrated. The crude product was sufficiently pure to be taken on to the next step. To a solution of the decyanated product (6.79 mmol) in 10 mL of methylene chloride at -78°C was added dropwise a 1 M solution of boron tribromide in hexane (8.1 mL, 8.1 mmol). The solution was stirred at -78°C

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(8) Heumann, A. *Synthesis* 1979, 53.

(9) Bridgehead olefin review: *Tetrahedron*, 1983, 36. See also House et al. (House, H. O.; Sieloff, R. F.; Lee, T. V.; DeTar, M. B. *J. Org. Chem.* 1980, 45, 1800) for a paper on the addition of nucleophiles to bridgehead enones.

(10) Beckwith, A. L. *J. Tetrahedron* 1981, 37, 3073.

(11) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* 1983, 105, 3741.

(12) Buchi, G.; Wuest, H. *J. Org. Chem.* 1979, 546.

°C for 40 min. Aqueous sodium bicarbonate solution was then added. The aqueous layer was extracted twice with ether, dried, and concentrated to afford the crude product. The product was purified by passage through a silica gel column using hexanes as the eluent. The yield of **3a** or **3b** was approximately 80%. The overall yield from **1** varied from 30% to 38%.

Bromide 3a: NMR (CDCl₃) δ 1.1–2.85 (m, 14 H), 4.75–6.1 (m, 3 H); IR (film) 1645, 1450, 975, 910 cm⁻¹; high-resolution mass spectrum for C₁₁H₁₇(M⁺ - Br) requires *m/e* 149.13303, measured 149.13321; ¹³C NMR (CDCl₃) δ 23.81, 28.85, 29.01, 31.17, 32.75, 34.21, 35.78, 39.90, 43.47, 72.40, 114.60, 138.60.

Bromide 3b: NMR (CDCl₃) δ 1.1–2.45 (m, 16 H), 4.75–6.25 (m, 3 H); IR (film) 1640, 1450, 975, 907 cm⁻¹; high-resolution mass spectrum for C₁₂H₁₉Br requires *m/e* 242.06701, measured 242.06760; ¹³C NMR (CDCl₃) δ 23.86, 28.85, 29.01, 31.17, 32.75, 34.21, 35.78, 39.90, 43.47, 72.40, 114.60, 138.60.

3-(1-Bromo-2-bicyclo[2.2.2]octyl)propanal (8). Through a solution of **3b** (2.31 g, 9.51 mmol) in 15 mL of methylene chloride at -78 °C was passed ozone until the solution turned blue. The solution was flushed with nitrogen to remove the excess ozone. Triphenylphosphine (2.62 g, 10 mmol) was then added and the solution was allowed to warm to room temperature. A 35% yield of aldehyde **8** was obtained. **8:** NMR (CDCl₃) δ 1.22–2.65 (m, 16 H), 9.84 (t, *J* = 1 Hz, 1 H); IR (film) 1721, 1451, 902, 725 cm⁻¹.

5-(1-Bromo-2-bicyclo[2.2.2]octyl)-1-(trimethylsilyl)-2-pentene (9). The procedure of Seyferth⁶ was followed to obtain a 72% yield of **9**. **9:** NMR (CDCl₃) δ 0.14 (s, 9 H), 1.27–2.50 (m, 18 H), 5.24–5.58 (m, 2 H).

Ethyl 5-(1-Bromo-2-bicyclo[2.2.2]octyl)-2-pentenoate (11). A solution of aldehyde **8** (0.367 g, 1.50 mmol) and (carboethoxymethylene)triphenylphosphorane (0.547 g, 1.57 mmol) in 10 mL of methylene chloride was heated to boiling for 10 h. The solution was concentrated and then diluted with hexanes. The suspension was filtered through Celite to obtain 0.361 g (77% yield) of **11**. **11:** NMR (CDCl₃) δ 1.30 (t, *J* = 7 Hz, 3 H), 1.22–2.55 (m, 16 H), 4.20 (q, *J* = 7 Hz, 2 H), 5.82 (d, *J* = 15 Hz, 1 H), 6.68–7.30 (m, 1 H); IR (film) 1720, 1652, 1264, 976 cm⁻¹.

4-(1-Bromo-2-bicyclo[2.2.2]octyl)-1-methoxy-1-butene (10). The ylide was formed by the reaction of LDA (2.72 mmol) with methoxymethyltriphenylphosphonium bromide (0.932 g, 2.72 mmol) in 9 mL of toluene at 0 °C for 5 min. To this solution was added a solution of **8** (0.222 g, 0.91 mmol) in 8 mL of toluene. The resulting solution was stirred in an ice bath for 1 h. The reaction was partitioned twice between ether and water. The organic layer was dried and concentrated. The product was a 60:40 mixture of stereoisomeric enol ethers.

10: NMR (CDCl₃) δ 1.18–2.50 (m, 16 H), 3.52 and 3.60 (s, 3 H), 5.92 (d, *J* = 6 Hz, 4 H), 6.35 (d, *J* = 13 Hz, 6 H); IR (film) 1652, 1204, 1102, 927 cm⁻¹.

General Procedure for Bridgehead Carbocation Reactions.

To a solution of the bromide (0.5 M in methylene chloride at 0 °C) was added a 10% excess of the requisite silver salt. The suspension was stirred for 1 h. The reaction was partitioned between aqueous NaCl and methylene chloride. The organic layer was then dried, concentrated, and purified by passage through silica gel. **5:** NMR (CDCl₃) δ 1.08–2.50 (m, 15 H), 4.90–6.56 (m, 3 H); IR (CDCl₃) 1650, 1276, 923, 690 cm⁻¹; mass spectrum, *m/z* 79, 91, 107, 119, 133, 149, 162, 190; high-resolution mass spectrum for C₁₄H₂₂ requires *m/e* 190.17215, measured 190.1717. **6:** NMR (CDCl₃) δ 1.1–2.75 (m, 26 H); IR (film) 1702, 1258, 895, 725 cm⁻¹; mass spectrum, *m/z* 231, 246 (M⁺).

7: NMR (CDCl₃) δ 1.1–2.8 (m, 17 H), 7.00–7.50 (m, 5 H); IR (film) 1685, 1445, 890, 715 cm⁻¹; mass spectrum, *m/z* 141, 155, 197, 211, 226 (M⁺); high-resolution mass spectrum for C₁₇H₂₂ requires *m/e* 226.17215, measured 226.1723.

12: NMR (CDCl₃) δ 1.05–2.40 (m, 17 H), 4.85–6.10 (m, 3 H); IR (film) 1450, 924, 710 cm⁻¹; mass spectrum, *m/e* 91, 105, 119, 133, 147, 161, 176. **13:** NMR (CDCl₃) δ 1.10–2.10 (m, 16 H), 2.45 (br s, 1 H), 9.78 (d, *J* = 1 Hz, 1 H); IR (film) 1730, 1455, 1170, 710 cm⁻¹; mass spectrum; *m/e* 67, 79, 97, 135, 149, 178. Anal. Calcd for C₁₆H₂₀O: C, 84.16; H, 8.83. Found: C, 83.93; H, 8.73.

Adduct with 15 and Benzene: mp 107–108 °C; 300-MHz NMR (CDCl₃) δ 0.87 (d, *J* = 6 Hz, 3 H), 1.19–1.30 (m, 2 H), 1.56

(s, 1 H), 1.62–1.78 (m, 2 H), 1.93–2.20 (m, 3 H), 2.43–2.52 (m, 2 H), 2.55–2.63 (m, 1 H), 2.75–2.85 (m, 1 H), 7.18 (s, 5 H); IR (CDCl₃) 1695, 1260, 900, 720 cm⁻¹; ¹³C NMR δ 22.81, 25.61, 31.08, 37.56, 40.44, 40.99, 46.60, 48.62, 53.62, 124.60, 126.27, 128.50, 149.30, 211.49; high-resolution mass spectrum for C₁₆H₂₀O requires *m/e* 228.15142, found 228.15100.

Adduct with Allyltrimethylsilane: 300-MHz NMR (CDCl₃) δ 0.82 (d, *J* = 6 Hz, 3 H), 0.90–1.00 (t, *J* = 12 Hz, 1 H), 1.10–1.21 (br t, *J* = 12 Hz, 1 H), 1.44–1.60 (m, 3 H), 1.63–1.85 (m, 3 H), 1.93–2.10 (m, 1 H), 2.17–2.24 (m, 1 H), 2.33–2.48 (m, 3 H), 4.98–5.13 (m, 2 H), 5.73–5.84 (m, 1 H); IR (film) 1700, 1260, 905, 720 cm⁻¹; ¹³C NMR (CDCl₃) δ 22.79, 25.18, 30.98, 37.40, 37.91, 40.76, 46.73, 48.54, 51.98, 118.08, 133.43, 212.30; high-resolution mass spectrum for C₁₅H₂₀O requires *m/e* 192.15142, found 192.15148.

Adduct with the Enol Silyl Ether of Acetophenone: mp 89–90 °C; 300-MHz NMR (CDCl₃) δ 0.83 (d, *J* = 6 Hz, 3 H), 1.04–1.25 (m, 2 H), 1.50–1.70 (m, 5 H), 1.70–2.04 (m, 2 H), 2.35–2.60 (m, 4 H), 2.92 (q, *J* = 12 Hz, 2 H), 7.42–7.62 (m, 3 H), 7.93 (br d, *J* = 8 Hz, 2 H); IR (CDCl₃) 1680, 1670 (sh), 1440, 890, 715 cm⁻¹; ¹³C NMR (CDCl₃) δ 22.75, 25.10, 30.86, 37.72, 37.98, 40.56, 46.66, 47.52, 50.13, 51.93, 128.14, 128.65, 133.03, 138.55, 198.87, 211.59; high-resolution mass spectrum for C₁₈H₂₂O₂ requires *m/e* 270.16198, measured 270.16154.

Adduct of 15 with the Enol Silyl Ether of Methyl Cyclohexenyl Ketone: NMR (CDCl₃) δ 0.80 (d, *J* = 6 Hz, 3 H), 0.80–2.80 (m, 23 H); ¹³C NMR (CDCl₃) δ 20.15, 21.77, 21.87, 22.50, 23.90, 24.73, 25.40, 25.53, 25.58, 26.27, 26.69, 27.01, 27.27, 28.21, 28.53, 29.99, 32.23, 37.66, 40.57, 40.67, 42.42, 45.00, 45.10, 47.70, 48.00, 49.24, 53.41, 54.59, 55.80, 60.06, 210.63, 210.94, 211.26, 213.72; IR (film) 2920, 2870, 1710, 1690, 1440, 1340, 1210, 800 cm⁻¹. Elemental anal. Calcd for C₁₈H₂₆O₂: C, 78.79; H, 9.55. Found: C, 78.54; H, 9.50.

General Procedure for Bridgehead Radical Reactions. A solution of the bromide, tributyltin hydride, and AIBN (10 mol %) in benzene (0.1 M with respect to the bromide) was heated at 80 °C for 8 h. The solution was concentrated and ether was added. Aqueous KF was added and the mixture was stirred for 30 min. The ether extract was dried and concentrated. The crude product was chromatographed on silica gel using 10:1 hexanes/ethyl acetate to afford the pure product.

Product from 11: NMR (CDCl₃) δ 1.05–2.05 (m, 20 H), 2.25–2.35 (m, 2 H), 4.10–4.20 (q, *J* = 7 Hz, 2 H); IR (film) 1720, 1442, 895, 720 cm⁻¹; mass spectrum, *m/z* 119, 149, 162, 236; high-resolution mass spectrum for C₁₅H₂₄O₂ requires *m/e* 236.17764, measured 236.1779.

Registry No. **1**, 38258-92-3; **1** (dihydro), 98577-05-0; **3a**, 98585-80-9; **3b**, 98577-10-7; **4**, 98577-34-5; (*cis*)-**5**, 98577-18-5; (*trans*)-**5**, 98577-19-6; (*cis*)-**6**, 98577-20-9; (*trans*)-**6**, 98577-21-0; (*cis*)-**7**, 98577-22-1; (*trans*)-**7**, 98577-23-2; **8**, 98577-13-0; **9**, 98577-14-1; (*E*)-**10**, 98577-16-3; (*Z*)-**10**, 98577-17-4; **11**, 98577-15-2; (*cis*)-**12**, 98577-24-3; (*trans*)-**12**, 98577-25-4; (*cis*)-**13**, 98577-26-5; (*trans*)-**13**, 98577-27-6; **14**, 66318-40-9; **15**, 66318-41-0; **15** (Nu = CH₂CH = CH₂), 98577-28-7; **15** (Nu = CH₂COPh), 98577-29-8; **15** (Nu = CH(Ac)CO₂Et), 98577-30-1; **15** (Nu = Ph), 98577-31-2; **16**, 98577-35-6; Ph₃P = CHCH₂TMS, 63922-69-0; CH₃COCH₂CO₂Et, 141-97-9; 1-methoxy-6-allyl-6-cyanobicyclo[2.2.2]oct-2-ene, 98577-11-8; 1-methoxybicyclo[2.2.2]oct-2-ene, 73301-32-3; 1-bromo-6-allylbicyclo[2.2.2]oct-2-ene, 98577-12-9; 5-methylcyclohexenone, 7214-50-8; allyl bromide, 106-95-6; 1-bromo-3-butene, 5162-44-7; 1-methoxy-2-allyl-2-cyanobicyclo[2.2.2]octane, 98577-06-1; 1-methoxy-2-cyano-2-(1-buten-4-yl)bicyclo[2.2.2]octane, 98577-07-2; 1-methoxy-2-allylbicyclo[2.2.2]octane, 98577-08-3; 1-methoxy-2-(1-buten-4-yl)bicyclo[2.2.2]octane, 98577-09-4; (carboethoxymethylene)triphenylphosphorane, 1099-45-2; **15** (1-(trimethylsilyl)ethenyl)cyclohexene adduct, 96791-76-3; methoxymethyltriphenylphosphonium bromide, 33670-32-5; acetophenone (TMS enol ether), 13735-81-4; methyl cyclohexenyl ketone (TMS enol ether), 54781-35-0; allyltrimethylsilane, 762-72-1; benzene, 71-43-2; 1-cyclohexene (TMS ether), 6651-36-1; 2-(1-buten-4-yl)bicyclo[2.2.2]octane, 98577-32-3; ethyl (decahydro-3a,6-etheno-3aH-inden-2-yl)ethanoate, 98577-33-4.