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.[3-10] 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.

Carbonylation of Ethylmercuric Acetate. Into a 45-mL Parr stainless steel reactor[30] 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 reactor[30] 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 pressured 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 $C_4F_6O_4Hg$: 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 $C_4H_6O_4Hg$: 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.

(25) Baird, W. C., Jr.; Surridge, J. H.; Hartgerink, R. L. U.S. Patent 3792069, 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.
(29) Baird, W. C., Jr.; Hartgerink, R. L.; Surridge, J. H. U.S. Patent 3917670, 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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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]

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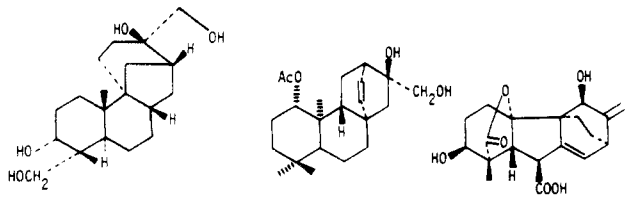
There is a vast amount of data pertaining to bridgehead carbocation stability and solvolysis reactions. An intriguing and synthetically useful feature is that in small to medium-sized ring systems the bridgehead carbocations do not undergo hydride shifts, despite their relative instability compared to the analogous acyclic systems.[2] Another significant feature is that substitution reactions proceed with retention of configuration because of the constraints imposed by the bicyclic system. We became interested in the synthetic utility of bridgehead carbocations as a result of our efforts to synthesize aphidicolin, a terpene that exhibits useful antiviral and anticancer activity. It soon became clear that bridgehead carbocation methodology might be employed to construct several bridged systems common to many families of natural products.[3] Substi-

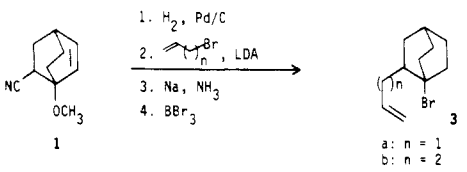


APHIDICOLIN DITERPENOID SC-4 ANTHERIDIOGEN-An

tution chemistry involving synthetically important nucleophiles such as malonates, enol silyl ethers, and allylic silanes had not been reported.[4] This paper details our results with bridgehead carbocations derived from bicyclo[2.2.2]octanes and bicyclo[3.3.1]nonanes.

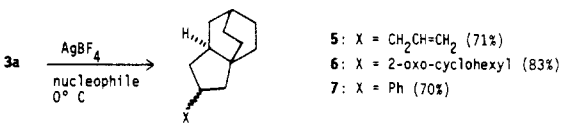
Synthesis of Bicyclic Systems

The starting material for the preparation of bicyclo[2.2.2]octanes was the cyanobicyclo[2.2.2]octene **1**, which was available from Aldrich Chemical Co. This compound was readily alkylated with allyl bromide by using lithium diisopropylamide (LDA) as a base. It was then decyanated by using sodium in liquid ammonia to produce a 1-methoxybicyclo[2.2.2]oct-2-ene which was converted into 1-bromo-6-allylbicyclo[2.2.2]oct-2-ene **2** with boron tribromide in methylene chloride at −78 °C. Catalytic hydrogenation of **1** followed by LDA-mediated alkylation, reductive decyanation, and bromide formation produced the bicyclo[2.2.2]octanes **3a** and **3b** in approximately 30%

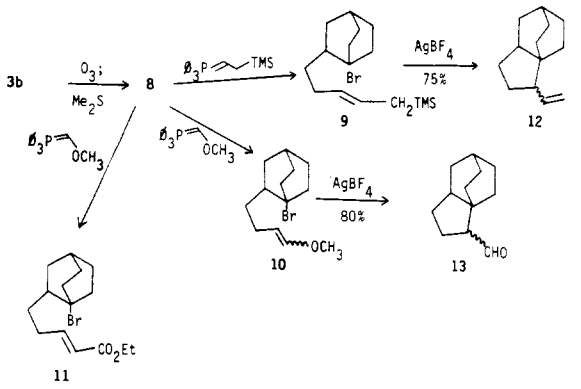


overall yield. The reaction of **2** with several Lewis acids (tin tetrachloride, titanium tetrachloride, and aluminum chloride) in the presence of allyltrimethylsilane afforded only recovered starting material. Surprisingly, even 3 equiv of silver acetate in either acetic acid or methylene chloride did not generate any new products! In contrast, silver trifluoroacetate reacted rapidly with **3a** in methylene chloride at 0 °C to furnish 1-(trifluoroacetoxy)-2-allylbicyclo[2.2.2]octane (**4**). The rationale for the tremendous deactivating influence of the alkene moiety in **2** is not clear. Perhaps the inductive effect of the alkene is destabilizing

Scheme I



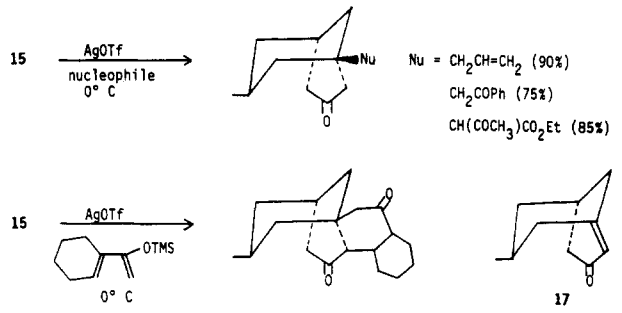
Scheme II



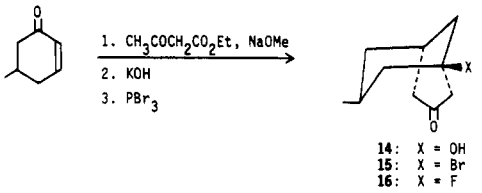
carbocation formation. With this result in hand, bromides **3a** and **3b** were reacted with several representative nucleophiles. The rationale for appending the propenyl and butenyl side chains was to establish a competition between intramolecular and intermolecular trapping of the bridgehead carbocation. The intramolecular trapping process, which had not been achieved prior to the onset of this work, would provide a direct pathway by which to prepare annulated bicyclic ring systems. These systems are subunits in biologically active terpenes such as antheridiogen An.[5] The results of the reaction of **3a** with nucleophiles are illustrated in Scheme I. Intramolecular trapping followed by reaction of the newly formed cyclopentenyl carbocation afforded compounds **5–7** as mixtures of diastereomers. Although the proton NMR of these compounds indicated that the original allyl side chain was no longer present, it was otherwise uninformative. The infrared spectra, exact mass determinations, and analyses supported the assigned structures. Surprisingly, the cyclopentenyl carbocation intermediate could not be converted into either a cyclopentanol or a cyclopentene. This is in contrast with the results in Scheme I and may mean that the cyclopentenyl carbocation is in equilibrium with the bridgehead carbocation and that the site of attack is determined by the size of the nucleophile. The bromide **3b**, when reacted under the conditions that were successful in Scheme I, did not afford any synthetically useful results. It did, however, serve as a key intermediate in the preparation of compounds **9–11** (Scheme II). Bromide **3b** was reacted with ozone followed by reductive workup of the ozonide with excess triphenylphosphine to provide aldehyde **8**. This aldehyde was unstable and was immediately converted into allylic silane **9** by using the Seyferth methodology.[6] Aldehyde **8** was also converted into enol ether **10** and unsaturated ester **11**. Reaction of **9** in methylene chloride with silver tetrafluoroborate gave the tricyclic alkene **12** in 75% yield. Likewise, the enol ether **10** afforded aldehyde **13** (80%). Compounds **12** and **13** were produced as mixtures of diastereomers. Aldehyde **13** could be converted into **12** with methylenetriphenylphosphorane.

(1) Fort, R. C., Jr.; Schleyer, P. v. R. *Adv. Alicyclic Chem.* **1966**, *1*, 283.
(2) Reference 1, p 288.
(3) Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. "The Total Synthesis of Natural Products"; ApSimon, Ed.; Wiley: New York, 1983; Vol. 5, pp 484–488.
(4) Gray, G. W.; Kelly, S. M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 26.
(5) Nakanishi, K.; Endo, M.; Naf, U.; Johnson, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 5579.
(6) Seyferth, D.; Wursthorn, K. R.; Mammarella, R. E. *J. Org. Chem.* **1977**, *42*, 3104.

Scheme III



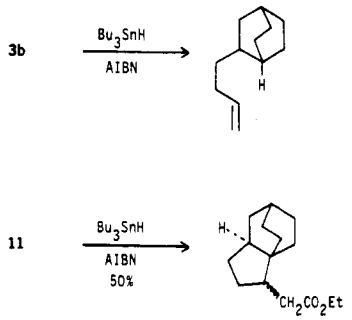
The preparation of the bicyclo[3.3.1]nonane system was accomplished by literature methods.[7] In particular, ketol **14** was synthesized in two steps from ethyl acetoacetate



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 acylic 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

Scheme IV



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

(7) Saito, S.; Yabuki, T.; Moriwake, T.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 529.
(8) Heumann, A. *Synthesis* **1979**, 53.
(9) Bridgehead olefin review: Tetrahedron, **1683**, *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 ($CDCl_3$) 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 $C_{11}H_{17}$ ($M^+ - Br$) requires m/e 149.133 03, measured 149.133 21; ^{13}C NMR ($CDCl_3$) 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 ($CDCl_3$) 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 $C_{12}H_{19}Br$ requires m/e 242.067 01, measured 242.067 60; ^{13}C NMR ($CDCl_3$) 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 ($CDCl_3$) 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 Seyferth[6] was followed to obtain a 72% yield of **9**. **9**: NMR ($CDCl_3$) 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 ($CDCl_3$) 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 ($CDCl_3$) 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 ($CDCl_3$) δ 1.08–2.50 (m, 15 H), 4.90–6.56 (m, 3 H); IR ($CDCl_3$) 1650, 1276, 923, 690 cm^{-1}; mass spectrum, m/z 79, 91, 107, 119, 133, 149, 162, 190; high-resolution mass spectrum for $C_{14}H_{22}$ requires m/e 190.172 15, measured 190.1717. **6**: NMR ($CDCl_3$) 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 ($CDCl_3$) 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 $C_{17}H_{22}$ requires m/e 226.172 15, measured 226.1723.

12: NMR ($CDCl_3$) 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 ($CDCl_3$) 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 $C_{16}H_{20}O$: 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 ($CDCl_3$) 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 ($CDCl_3$) 1695, 1260, 900, 720 cm^{-1}; ^{13}C 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 $C_{16}H_{20}O$ requires m/e 228.151 42, found 228.151 00.

Adduct with Allyltrimethylsilane: 300-MHz NMR ($CDCl_3$) 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}; ^{13}C NMR ($CDCl_3$) 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 $C_{13}H_{20}O$ requires m/e 192.151 42, found 192.151 48.

Adduct with the Enol Silyl Ether of Acetophenone: mp 89–90 °C; 300-MHz NMR ($CDCl_3$) 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 ($CDCl_3$) 1680, 1670 (sh), 1440, 890, 715 cm^{-1}; ^{13}C NMR ($CDCl_3$) 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 $C_{18}H_{22}O_2$ requires m/e 270.161 98, measured 270.161 54.

Adduct of 15 with the Enol Silyl Ether of Methyl Cyclohexenyl Ketone: NMR ($CDCl_3$) δ 0.80 (d, J = 6 Hz, 3 H), 0.80–2.80 (m, 23 H); ^{13}C NMR ($CDCl_3$) 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 $C_{18}H_{26}O_2$: 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 ($CDCl_3$) 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 $C_{15}H_{24}O_2$ requires m/e 236.177 64, 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 = $CH_2CH=CH_2$), 98577-28-7; **15** (Nu = CH_2COPh), 98577-29-8; **15** (Nu = $CH(Ac)CO_2Et$), 98577-30-1; **15** (Nu = Ph), 98577-31-2; **16**, 98577-35-6; $Ph_3P=CHCH_2TMS$, 63922-69-0; $CH_3COCH_2CO_2Et$, 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-(trimethylsilylethenyl)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.