1450 cm^{-1}; MS for $C_{11}H_{18}O$ m/z (relative intensity) 166 (M^+, 11), 137 (0.5), 124 (0.5), 111 (64), 83 (100), 55 (81). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.55; H, 11.08. Data for **8b**: ^{1}H NMR ($CDCl_3$) δ 1.10-1.50 (m, 10 H), 1.51-1.95 (m, 10 H), 2.18-2.69 (m, 10 H), 4.96 (m, 2 H, =CH), 5.07 (m, 2 H, =CH); ^{13}C NMR ($CDCl_3$) ppm 213.3, 146.2, 112.5, 50.9, 39.7, 28.5, 28.0, 25.9, 25.7; IR (mineral oil mull) 1703, 1590, 1445, 1395, 1389 cm^{-1}; MS for $C_{22}H_{34}O_2$ m/z (relative intensity) 330 (M^+, 7), 315 (1), 312 (2), 247 (3), 229 (2), 219 (14), 202 (8), 191 (9), 111 (33), 83 (100), 55 (30). Anal. Calcd for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37. Found: C, 79.59; H, 10.66.

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Preparation of 1-Substituted Bicyclo[2.2.1]heptanes by Anionic Cyclization of a 5-Hexen-1-yllithium

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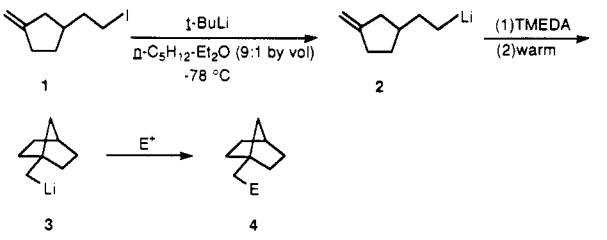
The facile regiospecific isomerization of a 5-hexen-1-yllithium to a (cyclopentyl)methyllithium at room temperature[1] provides a convenient route to functionalized cyclopentylmethyl-containing products.[2-4] As shown below, the precursor olefinic alkyllithiums may be easily prepared in high yield by low-temperature lithium-iodine exchange between an olefinic alkyl iodide and *tert*-butyllithium (*t*-BuLi)[5,6] and the organometallic formed upon 5-*exo*-*trig* cyclization may be functionalized by reaction with any of a variety of electrophiles. Herein we report that this methodology may be used to advantage for the preparation of 1-substituted bicyclo[2.2.1]heptanes via cyclization of the olefinic alkyllithium derived from readily available 3-(2-iodoethyl)-1-methylenecyclopentane (**1**). The two-step, one-pot synthetic sequence is summarized in Scheme I.

The synthesis of the requisite iodide, **1**, which is easily accomplished in straightforward fashion (Scheme II) from 2-cyclopenten-1-one,[7] is detailed in the Experimental Section.

Treatment of a 0.1 M solution of **1** in *n*-pentane-diethyl ether (3:2 by volume) at -78 °C with 2.2 equiv of *t*-BuLi following our general protocol for low-temperature lithium-iodine interchange[5] serves to generate cleanly the corresponding olefinic alkyllithium (**2**) as demonstrated by the fact that quench of such a reaction mixture with methanol at -78 °C affords 3-ethyl-1-methylenecyclopentane in virtually quantitative yield.

Scheme I



Scheme II

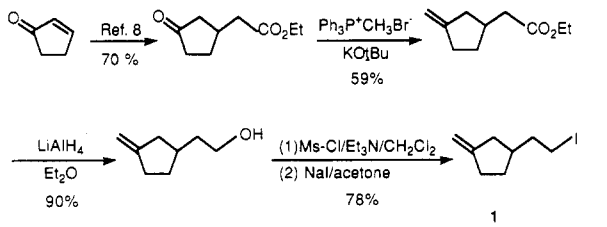
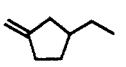
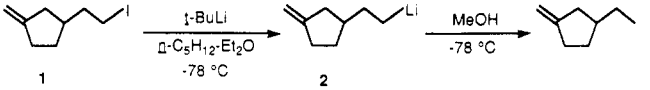


Table I. Exploratory Cyclizations of Organolithium 2[a]

entry	solvent system[b]	time, min	products, % relative yield (% d)[c]	
				
1	2:3	6	96	4 (100)
2	2:3	11	76	24 (88)
3	2:3	20	37	63 (80)
4	2:3	60	18	82 (55)
5	9:1	20	40	60
6	9:1	30	29	71
7	9:1	40	18	82 (86)
8	9:1	60	17	83 (70)

[a] TMEDA (2.2 equiv) was added at -78 °C to a solution of olefinic alkyllithium **2**, generated by lithium-iodine exchange between **1** and *t*-BuLi, the mixture was stirred for 5 min at -78 °C and then allowed to warm for the specified period of time before addition of MeOH (or MeOD). [b] Relative proportions by volume of *n*-pentane-diethyl ether used for the exchange reaction. [c] Percent incorporation of deuterium upon quench with MeOD.



Although the isomerization of **2** to (1-norbornylmethyl)lithium (**3**) is a thermodynamically favorable process, since it produces a C-C σ-bond (bond energy ca. 88 kcal/mol) at the expense of a C=C π-bond (π-bond energy *ca.* 60 kcal/mol), the reaction is, not surprisingly, much slower than the conversion of 5-hexen-1-yllithium to (cyclopentylmethyl)lithium.[1] Indeed, at the inception of this study it was not clear that the cyclization of **2** to **3**, which involves both the generation of a quaternary center and the introduction of additional ring strain, would be competitive with reactions that consume anions such as proton abstraction from solvent and oxidation with adventitious oxygen. In fact, **2** does not cyclize to an appreciable extent when allowed to stand at room temperature in pentane-ether solution and the addition of 2.2 equiv of dry, deoxygenated *N,N,N',N'*-tetramethylethylenediamine (TMEDA) is required to facilitate the isomerization.[2] Optimal conditions for the cyclization of **2** to **3** were established in a series of experiments, summarized in Table I, that involved quenching the reaction

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0022-3263/90/1955-6058$02.50/0

Table II. Preparation of 1-Substituted Bicyclo[2.2.1]heptanes (See Scheme I)[a]

entry	E^+	E	yield,[b] %
1	CH_3OH	H	80
2	CH_3OD	D	72[c]
3	CO_2	CO_2H	55
4	$(CH_2O)_n$	CH_2OH	68
5	CH_3CHO	$CH_3CH(OH)$	64
6	$CH_3(CH_2)_2CHO$	$CH_3(CH_2)_2CH(OH)$	57
7	$(CH_3)_2NCHO$	CHO	65
8	CH_3SSCH_3	SCH_3	70
9	$(CH_3)_3SiCl$	$Si(CH_3)_3$	61

[a] The olefinic alkyllithium was generated at −78 °C by addition of 2.2 equiv of *t*-BuLi to a 0.1 M solution of 1 in *n*-pentane–diethyl ether (9:1 by vol), 2.2 equiv of TMEDA were added, the cooling bath was removed, and the mixture was allowed to warm for 40 min before the addition of an excess of the electrophile. [b] Isolated yields of chromatographically pure product unless otherwise noted. [c] Determined by GC/MS analysis of crude product.

mixture with dry, deoxygenated methanol (or CH_3OD) to give variable amounts of 3-ethyl-1-methylenecyclopentane and 1-methylbicyclo[2.2.1]heptane. The data in Table I reveal that trapping of the product alkyllithium, **3**, by proton abstraction from the solvent is a potentially serious problem when the reaction mixture is allowed to stand for extended periods of time at room temperature.[9] Fortunately, the extent of unwanted protonation can be reduced, albeit not eliminated, by reducing the amount of diethyl ether in the solvent system used for the preparation of **2**. Since, as noted elsewhere,[5,6] it is necessary to conduct the lithium–iodine exchange reaction in a solvent mixture that contains diethyl ether, it is not possible to prepare **2** in pure pentane. The use of a 9:1 (v/v) mixture of *n*-pentane–diethyl ether allows for the rapid generation of **2** at low temperature and also serves to minimize the trapping of both **2** and the cyclized product through protonation (Table I).

Preparative-scale cyclizations of **2** to **3** were conducted as illustrated in Scheme I. The olefinic alkyllithium, **2**, was generated at −78 °C by addition of 2.2 molar equiv of commercial *t*-BuLi in pentane to a 0.1 M solution of **1** in *n*-pentane–diethyl ether (9:1 by volume). Dry, deoxygenated TMEDA (2.2 molar equiv) was added to the −78 °C solution, the cooling bath was removed, and the reaction mixture was allowed to warm under an atmosphere of dry argon for 40 min. As illustrated by the results presented in Table II, (1-norbornylmethyl)lithium, **3**, may be trapped by the addition of any of a variety of electrophiles (Scheme I, **3** → **4**) to give 60–70% isolated yields of functionalized product. It is to be noted that the only contaminants present in the products resulting from these anionic cyclizations are the *unfunctionalized* hydrocarbons, 3-ethyl-1-methylenecyclopentane and 1-methylnorbornane, generated, as noted above, by proton abstraction from the medium.[9,10] Thus, it is a simple matter to purify the functionalized product by chromatography or bulb-to-bulb distillation.

In summary, anionic cyclization of (2-(3-methylenecyclopentyl)ethyl)lithium, **2**, provides a convenient, general route to 1-substituted bicyclo[2.2.1]heptanes. The fact that the cyclization produces (1-norbornylmethyl)lithium, **3**, that may be functionalized at will by addition of an electrophile, coupled with the ease of isolation of product, suggests that this route is the method of choice for the preparation of bicyclo[2.2.1]heptanes bearing a CH_2X moiety.

Experimental Section

^1H and ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ on an IBM AF-270 NMR instrument. The purity of starting materials and products was assessed by analytical gas–liquid chromatography (GC) using either a chromatograph equipped with a flame-ionization detector and a 25-m × 0.20-mm cross-linked methyl silicone (0.33-μm film thickness) fused-silica capillary column or a GC/MSD system operating at 70 eV and fitted with a 12.5-m × 0.20-mm cross-linked dimethyl silicone fused-silica capillary column. High-resolution mass spectra were obtained by EI at 70 eV. Thin-layer chromatography (TLC) was performed on E. Merck precoated (0.2-mm) silica gel 60 F_{254} plates: visualization was accomplished by spraying with 10% ethanolic phosphomolybdic acid and heating. Reaction products were purified by flash chromatography, conducted as described by Still,[11] using Universal Scientific 32–60 μm silica gel.

All reactions involving alkyllithiums were performed in glassware that had been flame-dried under an atmosphere of dry argon, and all manipulations of organolithiums were conducted using standard syringe/cannula techniques[12] under an atmosphere of dry, oxygen-free argon that had been passed through a 5-cm × 50-cm glass column containing an activated BASF R3-11 copper catalyst. Diethyl ether was freshly distilled from dark-purple solutions of sodium/benzophenone. Dry, olefin-free *n*-pentane was obtained as previously described.[2] *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled (bp 120–122 °C) under nitrogen from calcium hydride. Methylene chloride was distilled under nitrogen from calcium hydride. Acetone (Baker, analytical grade) was dried over calcium sulfate and distilled. Sodium iodide was dried at 100 °C (ca. 5 mm) for 8–10 h in a vacuum oven. Paraformaldehyde was dried over phosphorus pentoxide for 8 h in a vacuum desiccator. Brine, used in the extractions, refers to saturated aqueous NaCl solutions. The concentrations of commercial solutions of *t*-BuLi in *n*-pentane (Aldrich) were determined immediately prior to use by titration with *sec*-butyl alcohol in xylene using 1,10-phenanthroline as indicator.[13]

Ethyl 2-(3-Methylenecyclopentyl)acetate. A suspension of 7.32 g (65.2 mmol) of potassium *tert*-butoxide and 23.3 g (65.2 mmol) of methyltriphenylphosphonium bromide in 65 mL of dry diethyl ether was stirred at 0 °C for 1 h under an atmosphere of nitrogen. A solution of 10.1 g (59.3 mmol) of ethyl 2-(3-oxocyclopentyl)acetate, prepared from 2-cyclopenten-1-one[7] by the method of McMurry and co-workers,[8] in 30 mL of dry diethyl ether was then added to the ylide solution. The reaction mixture was stirred at 0 °C for 2 h and then at room temperature for 15 h. Cold water (150 mL) was then added, the organic layer was separated, and the aqueous layer was extracted with 50 mL of fresh diethyl ether. The combined ethereal extracts were dried ($MgSO_4$), and the ether was removed by rotary evaporation to give a yellow oil to which 50 mL of hexanes was added and the flask was cooled in an ice-bath to complete precipitation of triphenylphosphine oxide. The mixture was then filtered, the filtrate was concentrated at reduced pressure, and the residue was purified by flash chromatography on silica gel (5% ethyl acetate–hexanes) to afford 5.90 g (59%) of pure ethyl 2-(3-methylenecyclopentyl)acetate: R_f 0.50 (15% ethyl acetate–hexanes); IR (neat) 3072, 1731, 1655, 1179, and 873 cm^{-1}; ^1H NMR δ 4.84 (apparent s, 2 H), 4.17 (q, J = 7.11 Hz, 2 H), 2.63–2.21 (m, 7 H), 2.08–1.89 (m, 2 H), 1.33 (t, J = 7.11 Hz, 3 H); ^{13}C NMR δ 172.46, 151.42, 105.45, 60.04, 39.62, 39.39, 36.48, 32.40, 31.82, 14.13; HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1144.

(9) At elevated temperatures, organolithiums readily abstract protons from both diethyl ether (Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974) and TMEDA (Kohler, F. H.; Hertkorn, N.; Blumel, J. *Chem. Ber.* **1987**, *120*, 2081).

(10) As noted elsewhere,[2,5,6] lithium–iodine exchange between a primary alkyl iodide and *t*-BuLi invariably results in the formation of a small amount of hydrocarbon, formally derived by reduction of the iodide, via reaction of the alkyllithium produced in the exchange with the cogenerated *tert*-butyl iodide. Thus, a nonnegligible quantity (typically 2–10%)[5,6] of 3-ethyl-1-methylenecyclopentane is produced in the course of the lithium–iodine exchange reaction between **1** and *t*-BuLi.

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2-(3-Methylenecyclopentyl)ethanol. A solution of 5.90 g (35.1 mmol) of ethyl 2-(3-methylenecyclopentyl)acetate in 50 mL of dry diethyl ether was added in a dropwise manner to an ice-cold suspension of 1.30 g (35.1 mmol) of lithium aluminum hydride in 18 mL of dry diethyl ether. The resulting suspension was stirred at room temperature for 1 h and then hydrolyzed by sequential dropwise addition of 1.30 mL of water, 1.30 mL of 15% aqueous sodium hydroxide, and 3.90 mL of water. The mixture was filtered, the solids were washed with fresh diethyl ether, and the combined filtrate and washings were concentrated by rotary evaporation to give an oil. Purification by flash chromatography on silica gel (15% ethyl acetate–hexanes) gave 4.00 g (90%) of the title alcohol: R_f 0.13 (15% ethyl acetate–hexanes); IR (neat) 3342, 3060, 1655, 1049, and 873 cm^{-1}; ^1H NMR δ 4.82 (tightly coupled apparent s, 2 H), 3.62 (t, J = 6.91 Hz, 2 H), 3.13 (br s, 1 H), 2.60–2.17 (m, 3 H), 2.08–1.83 (m, 3 H), 1.71–1.50 (m, 2 H), 1.29 (m, 1 H); ^{13}C NMR δ 152.21, 104.89, 61.49, 39.64, 38.08, 36.71, 32.66, 32.01; HRMS calcd for $C_8H_{15}O$ (CI, MH^+) 127.1123, found 127.1126.

3-(2-Iodoethyl)-1-methylenecyclopentane (1). Following the general procedure of Crossland and Servis,[14] 3.20 g (25.4 mmol) of 2-(3-methylenecyclopentyl)ethanol was converted to its mesylate. The crude mesylate was added to a solution of 4.76 g (31.8 mmol, 1.25 equiv) of anhydrous sodium iodide in 50 mL of dry acetone, and the resulting mixture was stirred under a nitrogen atmosphere at room temperature for 8 h. Inorganic salts were removed by filtration, and the filtrate was concentrated at reduced pressure. The residue was taken up in 50 mL of pentane and washed successively with 10% aqueous sodium thiosulfate, water, and brine. After drying ($MgSO_4$), the solution was concentrated by rotary evaporation to give an oil which was purified by flash chromatography on silica gel using pentane as the eluent to afford 4.68 g (78%) of the title iodide: R_f 0.5 (pentane); IR (neat) 3060, 1649, 1425, 879, and 497 cm^{-1}; ^1H NMR δ 4.85 (tightly coupled m, 2 H), 3.21 (t, J = 7.23 Hz, 2 H), 2.58–1.75 (m, 8 H), 1.29 (m, 1 H); ^{13}C NMR δ 151.68, 105.44, 40.98, 39.28, 38.88, 32.02, 31.91, 5.23. Anal. Calcd for $C_8H_{13}I$: C, 40.68; H, 5.55. Found: C, 40.50; H, 5.66.

General Procedure for the Preparation and Trapping of (1-Bicyclo[2.2.1]heptylmethyl)lithium (3). A 0.1 M solution of 3-(2-iodoethyl)-1-methylenecyclopentane (1) in n-pentane–diethyl ether (9:1 by volume) was cooled to −78 °C under an atmosphere of dry, oxygen-free argon, and 2.2 equiv of a solution of t-BuLi in pentane was added dropwise over a period of 5 min. The reaction mixture was stirred at −78 °C for 10 min, and 2.2 equiv of dry, deoxygenated TMEDA was then added dropwise via syringe. The addition of TMEDA resulted in the formation of a thick, pale-yellow precipitate. The mixture was stirred for 5 min −78 °C, the cooling bath was then removed, and the solution was allowed to warm and stand at room temperature (ca. +22 °C) under argon to effect isomerization of the (2-(3-methylenecyclopentyl)ethyl)lithium (2) to (1-norbornylmethyl)lithium (3) [total time from removal of cooling bath 40 min; it required approx 15 min for the reaction mixture to reach +22 °C]. Functionalization of 3 was accomplished, as detailed below, by recooling the alkyllithium solution to −78 °C, adding an excess (typically 2 equiv) of electrophile, and allowing the mixture to warm to room temperature (Table II).

1-Methylbicyclo[2.2.1]heptane. A solution of 3, prepared as described above, was recooled to −78 °C, 1 mL of dry, deoxygenated methanol was added, and the reaction mixture was allowed to warm to room temperature. The product mixture was washed with water and dried ($MgSO_4$). Analysis of the crude reaction mixture by GC revealed that the title hydrocarbon had been formed in 80% yield. An analytical sample of the product was obtained by washing the crude reaction mixture with several portions of concentrated sulfuric acid to remove alkene and diethyl ether, followed by sequential washing of the pentane extract with saturated aqueous sodium bicarbonate and water. The organic extract was dried ($MgSO_4$) and solvent was carefully removed by rotary evaporation to give pure 1-methylbicyclo[2.2.1]heptane: ^{13}C NMR δ 45.23 (C(7)), 43.33 (C(1)), 37.75 (C(4)), 36.75 (C(2,6)), 31.22 (C(3,5)), 20.91 (CH_3) [lit.[15] ^{13}C NMR δ 45.23, 43.72, 37.76, 36.74, 31.22, 21.00]. The methyl-d_1 compound, prepared in an analogous fashion by quench of 3 with MeOD and isolated in 81% yield, was found by GC/MS analysis to have a d_1 content of 88.5%.

1-Bicyclo[2.2.1]heptylacetic Acid. A solution of 3, prepared as described above from 110.4 mg (0.47 mmol) of 1, was recooled to −78 °C and added via cannula under an atmosphere of argon to a flask containing excess of powdered dry ice covered with dry n-pentane. The reaction mixture was allowed to warm to room temperature with stirring and was then added to 10 mL of a 1.0 M solution of aqueous hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with 3 mL of fresh ether. The combined organic extracts were dried ($MgSO_4$) and concentrated to give 39.7 mg (55%) of the known[16] title acid: IR (neat) 3300–2500, 1702, 1406, 1292, and 928 cm^{-1}; ^1H NMR δ 11.40 (br s, 1 H), 2.57 (s, 2 H), 2.44–2.19 (m, 1 H), 1.75–1.25 (m, 10 H): ^{13}C NMR δ 179.47 (C=O), 45.01 (C(1)), 43.61 (C(7)), 40.30 (C-H_2CO_2H), 36.86 (C(4)), 34.52 (C(2,6)), 30.59 (C(3,5)).

1-Bicyclo[2.2.1]heptylacetaldehyde. A solution of 3, prepared from 224.6 mg (0.95 mmol) of 1 as described above, was recooled to −78 °C, and 0.15 mL (1.90 mmol) of dry dimethylformamide was added via syringe. The solution was allowed to warm to room temperature and was then added rapidly to 10 mL of saturated, aqueous sodium bicarbonate. The organic layer was separated, washed with 5 mL of water, and dried ($MgSO_4$), and volatile components were removed by rotary evaporation to afford 85.3 mg (65%) of the product aldehyde: IR (neat) 2866, 1705, 1444, 1406, and 1254 cm^{-1}: ^1H NMR δ 9.84 (t, J = 2.98 Hz, 1 H), 2.60 (d, J = 2.98 Hz, 2 H), 2.29–2.21 (m, 1 H), 1.79–1.25 (m, 10 H); ^{13}C NMR δ 203.64 (CHO), 49.36 (CH_2CHO), 44.55 (C(1)), 43.33 (C(7)), 36.64 (C(4)), 34.69 (C(2,6)), 30.48 (C(3,5)); HRMS calcd for $C_9H_{14}O$ 138.1045, found 138.1046.

2-(1-Bicyclo[2.2.1]heptyl)ethanol. A solution of 3, prepared from 236.0 mg (1.00 mmol) of 1 via the general procedure outlined above, was cooled to −78 °C, and a suspension of ca. 60 mg (~2 mmol) of dry paraformaldehyde in 0.5 mL of dry n-pentane was added via syringe. The cooling bath was removed, and the reaction mixture was stirred for 0.5 h at room temperature. Brine (10 mL) was added, the organic layer was separated and dried ($MgSO_4$), and the solvent was removed by rotary evaporation to give an oil. Flash chromatography of the crude product on silica gel (15% ethyl acetate–hexanes) gave 95.2 mg (68%) of pure title alcohol: R_f 0.18 (15% ethyl acetate–hexanes); IR neat 3335, 1447, 1049, and 1033 cm^{-1}; ^1H NMR δ 3.73 (t, J = 7.45 Hz, 2 H), 2.17 (m, 1 H), 1.64 (t, J = 7.45 Hz, 2 H), 1.61–1.18 (complex m, 11 H); ^{13}C NMR δ 60.99 (CH_2OH), 45.13 (C(1)), 43.69 (C(7)), 38.59 (CH_2-CH_2OH), 36.71 (C(4)), 34.50 (C(2,6)), 30.59 (C(3,5)); HRMS calcd for $C_9H_{17}O$ (CI, MH^+) 141.1279, found 141.1292.

1-(1-Bicyclo[2.2.1]heptyl)propan-2-ol. A solution of 3, prepared as described above from 117.4 mg (0.50 mmol) of 1, was cooled to −78 °C, and 0.06 mL (0.99 mmol) of freshly distilled, dry acetaldehyde was added dropwise via syringe. The cooling bath was removed, the mixture was allowed to warm to room temperature, and 10 mL of brine was added in one portion. The organic layer was separated, dried ($MgSO_4$), and concentrated by rotary evaporation. The residual oil was purified by flash chromatography on silica gel (15% ethyl acetate–hexanes) to afford 49.0 mg (64%) of pure alcohol: R_f 0.16 (15% ethyl acetate–hexanes); IR (neat) 3335, 1447, 1049, and 1033 cm^{-1}; ^1H NMR δ 3.96 (apparent sextet, J = 6.04 Hz, 1 H), 2.18 (m, 1 H), 1.72 (d, J = 6.04 Hz, 2 H), 1.69–1.27 (complex m, 11 H), 1.23 (d, J = 6.04 Hz, 3 H); ^{13}C NMR δ 66.87 (CHOH), 46.25 (C(1)), 45.40 (CH_2C-HOH), 44.35 (C(7)), 36.59 (C(4)), 35.01 (C(2 or 4)), 34.75 (C(4 or 2)), 30.87 (C(3 or 5)), 30.57 (C(5 or 3)), 25.16 (CH_3); HRMS calcd for $C_{10}H_{19}O$ (CI, MH^+) 155.1436, found 155.1448.

1-(1-Bicyclo[2.2.1]heptyl)pentan-2-ol. A solution of 3, prepared from 110.6 mg (0.47 mmol) of 1 via the general procedure, was cooled to −78 °C, and 0.085 mL (0.96 mmol) of freshly distilled, dry n-butyraldehyde was added dropwise by syringe. The cooling bath was removed, the mixture was allowed to warm to room temperature, and 10 mL of brine was added. The organic phase was separated, dried ($MgSO_4$), and concentrated to give an oil. Purification by flash chromatography on silica gel (15% ethyl

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acetate–hexanes) gave 48.7 mg (57%) of pure alcohol: R_f 0.15 (15% ethyl acetate–hexanes); IR (neat) 3330, 1439, 1049, and 1035 cm^{-1}; ^1H NMR δ 3.75 (m, 1 H), 2.16 (m, 1 H), 1.82–1.13 (complex pattern, 17 H), 0.94 (t, J = 6.90 Hz, 3 H); ^{13}C NMR δ 70.44 (*C*HOH), 46.66 (C(1)), 44.36 (C(7)), 43.57 (CH_2CHOH), 41.22 (CH(OH)CH_2), 36.68 (C(4)), 35.20 (C(2 or 6)), 34.83 (C(4 or 2)), 30.99 (C(3 or 5)), 30.56 (C(5 or 3)), 18.84 (CH_2CH_3), 14.09 (CH_3); HRMS calcd for $C_{12}H_{23}O$ (CI, MH^+) 183.1749, found 183.1745.

1-[(Methylthio)methyl]bicyclo[2.2.1]heptane. A solution of **3**, prepared from 109.6 mg (0.46 mmol) of **1**, was cooled to −78 °C, and 0.085 mL (0.93 mmol) of dimethyl disulfide was added in one portion. The reaction mixture was allowed to warm to room temperature and was then poured into 10 mL of brine. The organic phase was separated, the aqueous phase was extracted with fresh pentane, and the combined organic layers were dried ($MgSO_4$). Volatile components were removed by rotary evaporation to give 50.8 mg (70%) of pure product: ^1H NMR δ 2.76 (s, 2 H), 2.20–2.11 [overlapping patterns, i.e., 2.20–2.11 (m, 1 H), 2.15 (s, 3 H)], 1.75–1.17 (complex m, 10 H); ^{13}C NMR δ 48.64 (C(1)), 43.16 (C(7)), 41.74 (C(8)), 37.22 (C(4)), 34.42 (C(2,6)), 30.74 (C(3,5)), 17.78 (CH_3); HRMS calcd for $C_9H_{16}S$ 156.0973, found 156.0981.

1-[(Trimethylsilyl)methyl]bicyclo[2.2.1]heptane. A solution of **3**, prepared from 203.2 mg (0.86 mmol) of **1** via the general procedure described above, was cooled to −78 °C, and 0.22 mL (1.7 mmol) of freshly distilled chlorotrimethylsilane was added via syringe. The solution was allowed to warm to room temperature and worked up in the usual manner to afford the TMS derivative as an oil. Purification by chromatography on silica gel (*n*-pentane as eluent) gave 95.2 mg (61%) of the title compound: R_f 0.51 (pentane); IR (neat) 1451, 1413, 1239, and 837 cm^{-1}; ^1H NMR δ 2.10 (m, 1 H), 1.38–1.11 (m, 10 H), 0.89 (s, 2 H), 0.01 (s, 9 H); ^{13}C NMR δ 47.17 (C(7)), 46.01 (C(1)), 37.11 (C(2,6)), 36.80 (C(4)), 31.29 (C(3,5)), 24.52 (CH_2-TMS), 0.54 (CH_3); HRMS calcd for $C_{11}H_{22}Si$ 182.1492, found 182.1501.

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Registry No. **1**, 129917-14-2; 1-methylbicyclo[3.3.1]heptane, 10052-18-3; (1-bicyclo[2.2.1]heptyl)acetic acid, 93980-80-4; ethyl 2-(3-oxocyclopentyl)acetate, 62457-60-7; ethyl 2-(3-methylenecyclopentyl)acetate, 129917-15-3; 2-(3-methylenecyclopentyl)-ethanol, 113616-12-9; 1-[(2-mesyloxy)ethyl]-3-methylenecyclopentane, 129917-16-4; 1-bicyclo[2.2.1]heptylacetaldehyde, 129917-17-5; 2-(1-bicyclo[2.2.1]heptyl)ethanol, 129917-18-6; 1-(1-bicyclo[2.2.1]heptyl)propan-2-ol, 34298-82-3; 1-(1-bicyclo-[2.2.1]heptyl)pentan-2-ol, 129917-19-7; 1-[(methylthio)methyl]-bicyclo[2.2.1]heptane, 129917-20-0; 1-[(trimethylsilyl)methyl]-bicyclo[2.2.1]heptane, 129917-21-1; acetaldehyde, 75-07-0; *n*-butyraldehyde, 123-72-8.

Supplementary Material Available: ^1H and ^{13}C spectra for all new compounds (16 pages). Ordering information is given on any current masthead.

^{13}C NMR Spectroscopic Study of γ-Substituted Tris(ethynyl)methyl Cations[1]

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Introduction

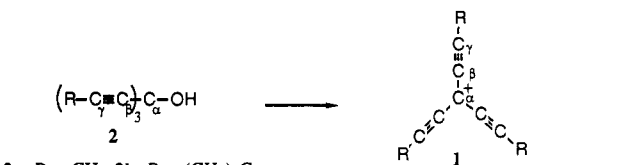
Over the years there has been considerable interst in the study of alkynylcarbocations (propargyl cations) (A)[2]. The positive charge in these cationic systems can be delocalized over the ethynyl system, thus giving rise to mesomeric allenyl cations (B). Such allenyl cations are of significant interest because they are structurally related to the elusive vinyl cations. We[2b] have earlier utilized ^{13}C NMR spectroscopy to study a number of alkylethynylmethyl cations. By choosing appropriate reference compounds, the relative contribution of the two mesomeric structures was estimated. In contrast to the mono(alkylethynyl)methyl cations, however, little is known about the bis- and tris-(alkylethynyl)methyl cations.[3] Miller and co-workers[4] previously studied the tris(*tert*-butylethynyl)methyl cation by ^1H NMR spectroscopy. No ^{13}C data were, however, reported. Komatsu et al.[3b] prepared tris(phenylethynyl)methyl cation and studied its ^{13}C NMR parameters. They found that the degree of positive charge delocalization to C_γ apparently increases as the number of ethynyl groups increases. However, no study, to date, has been reported in which the extent of charge delocalization in a series of γ-substituted tris(alkylethynyl)methyl cations was examined with regard to the C_γ-substituent.

A B

Results and Discussion

In our continued interest in persistent ethynylmethyl cations, we undertook a study of a series of γ-substituted tris(ethynyl)methyl cations.[2]

Ion **1a–d** were prepared by ionization of the corresponding γ-substituted tris(alkyl)methyl alcohols **2a–d** in FSO_3H–SO_2ClF solution at −78 °C.



2

2a: R = CH_3; **2b**: R = $(CH_3)_3C$; **2c**: R = $(CH_3)_3Si$; **2d**: R = Ph; **2e**: R = H

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1a: R = CH_3; **1b**: R = $(CH_3)_3C$; **1c**: R = $(CH_3)_3Si$; **1d**: R = Ph; **1e**: R = H

Tris(propynyl)methyl alcohol **2a** was prepared by the reaction of propynyllithium (generated from 1-propyne and methyllithium) with diethyl carbonate. Similar, γ-(trimethylsilyl)propynyllithium and γ-phenylpropynyllithium were generated from the corresponding acetylene and treated with diethyl carbonate to afford **2c** and **2d**, respectively. Tris(3,3-dimethylbutynyl)methyl alcohol (**2b**) was prepared by the literature procedure.[4]

Carbon-13 NMR spectroscopy was used for the study of ions **1a–d** as carbon-13 chemical shifts give an indication of the charge densities at carbon atoms of similar hybridization and substitution.[2b,5] The ^{13}C NMR parameters

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