of pure (*p*-bromophenyl)acetylene, mp 64 °C (lit. mp 64–65 °C,[10,11] 63.5–63.7 °C[12]).

Similar results were obtained by using the elimination procedure of Kimura and Regen.[3] ^{1}H NMR ($CDCl_3$): δ 3.12 (s, 1 H), 7.47 (d, 2 H), 7.35 (d, 2 H).[13]

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Synthesis of Hexacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]undecane-8-carboxylic Acid (Homopentaprismane-8-carboxylic Acid)

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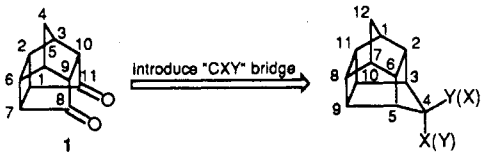
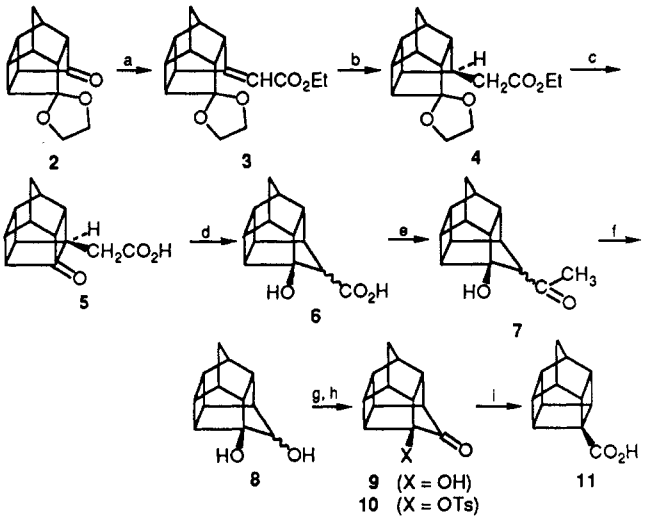
As part of a continuing program concerned with the synthesis and chemistry of novel polycyclic systems,[1] we are seeking new synthetic entries into highly strained cage molecules. In a previous study,[2] a synthesis of 1,3-bishomopentaprismane was developed that involved introduction of a methylene bridge across the 8,11-positions of a readily available[3] cage dione, pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**1**, Scheme I). More recently, another, potentially general method has been developed to introduce a *functionalized* methylene bridge across the 8,11-positions of **1**. We now report the successful application of this strategy for the synthesis of the title compound (**11**). The parent hydrocarbon, homopentaprismane,[3,4] and several substituted homopentaprismanes have been synthesized previously in our laboratory[4] and by other investigators.[5-7]

Our synthesis of **1** is outlined in Scheme II. Wadsworth–Emmons reaction[8,9] of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione monoethylene ketal (**2**)[5a] with ethyl (diethoxyphosphinyl)acetate afforded the corresponding 8-carbethoxymethylene derivative, **3**, in 92% yield. This material was obtained as a mixture of two isomers as judged by the fact that its ^{13}C NMR spectrum contained 34 resonances (i.e., twice the number expected from the formula of **3**). Tandem gas chromatography–mass spectral (GC/MS) analysis revealed that these two isomers were present in ratio 68:32.

Scheme I



Scheme II[a]



[a] (a) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF, reflux 36 h (93%); (b) H_2 (1 atm), Pd–C, EtOAc, room temperature, 2 days (100%); (c) 10% aqueous H_2SO_4, dioxane, reflux 2 days (90%); (d) NaH, DMF–THF, 20 h (91%); (e) MeLi, THF (80%); (f) $(CF_3CO)_2O$, 90% aqueous H_2O_2, 1 day, followed by 5% aqueous NaOH, MeOH, 50 °C, 17 h (60%); (g) NCS, Me_2S, Et_3N, −25 °C (77%) *or* $(COCl)_2$–DMSO, −60 °C → −40 °C (42%); (h) TsCl, py (88%); (i) 20% aqueous KOH, reflux 7 h (94%).

The corresponding *endo*-11-carbethoxymethylene derivative, **4**, was prepared in quantitative yield by catalytic hydrogenation of **3**.[2] Treatment of **4** with aqueous sulfuric acid hydrolyzed both the ester and ketal moieties to produce **5** (90% yield). The ^{13}C NMR spectrum of **5** displays singlet resonances at δ 178.33 and 221.02 that correspond to the CO_2H and ketone carbonyl carbon atoms, respectively, in this compound.

The key step in the synthesis, i.e., the introduction of a functionalized methylene bridge across the 8,11-position, was achieved by treatment of **5** in dimethylformamide–tetrahydrofuran with excess sodium hydride [or, somewhat less conveniently, with excess lithium diethylamide (LDA)]. A substituted 1,3-bishomopentaprismane, **6**, was thereby obtained in 91% yield. This material was obtained as a mixture of two isomers (ratio 69:31 by GC/MS analysis); its ^{13}C NMR spectrum contained 26 resonances.

Some difficulty was experienced when we attempted to decarboxylate **6** oxidatively. Thus, efforts to introduce an SMe group into **6** or into its methyl ester by using the method of Trost and Tamaru[10] resulted only in quantitative recovery of starting material. Our attempts to introduce an α-hydroperoxyl group into **6** by use of LDA–oxygen at −78 °C[11] also were unsuccessful.

Net oxidative decarboxylation of **6** ultimately was performed successfully as follows. Carboxylic acid **6** was

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converted into the corresponding methyl ketone, **7** (80%), by reaction with methyllithium. Surprisingly, we were unable to perform Baeyer–Villiger oxidation of **7** by using *m*-chloroperbenzoic acid, even when the reaction was conducted in refluxing chloroform for an extended time. However, Baeyer–Villiger oxidation of **7** succeeded with trifluoroperacetic acid, which provided diol **8** (60%) after alkaline workup. The ^{13}C NMR spectrum of this material displayed 28 resonances, thereby indicating the presence of two isomers (ratio 62:38 by GC/MS analysis).

Oxidation of the secondary OH group in **8** to give keto alcohol **9** could be accomplished: (i) in 40% yield by using oxalyl chloride–dimethyl sulfoxide at low temperature (Swern oxidation)[12] or (ii) in 77% yield with *N*-chlorosuccinimide–dimethyl sulfide in the presence of triethylamine.[13] The infrared spectrum of **9** displays a strong absorption at 1740 cm^{-1}, which is due to the C=O stretching vibration. The ^{13}C NMR spectrum of this compound contains 12 resonances, one of which, a singlet at δ 214.91, corresponds to absorption due to the ketone carbonyl carbon atom.

Conversion of **9** into the corresponding tosylate, **10**, followed by reaction with aqueous potassium hydroxide solution (semibenzilic acid rearrangement) afforded homopentaprismane-8-carboxylic acid (**11**, 94% overall yield). The ^{13}C NMR spectrum of **11** consists of 12 resonances, including a singlet at δ 180.98 that is due to absorption by the CO_2H carbon atom.

In conclusion, the reaction sequence shown in Scheme II has been used successfully to convert a readily available cage compound (**2**)[5] into the title compound, **11**. This convenient nine-step sequence affords **11** in 23% overall yield.

Experimental Section

Melting points and boiling points are uncorrected. GC/MS analysis was performed by using a Hewlett-Packard Model 5790 GC/MS equipped with a 0.2 mm × 12 m capillary column (5% acetophenone–gum stationary phase). High-resolution mass spectra were obtained at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, NE.

8-(Carbethoxymethylene)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-11-one Ethylene Ketal (3). A stirred suspension of sodium hydride (13.0 g, 0.54 mol) in dry tetrahydrofuran (THF, 300 mL) under argon was cooled externally to 0–5 °C. Ethyl (diethoxyphosphinyl)acetate (111.0 g, 0.49 mol) was added dropwise during 90 min, and stirring was continued at 0–10 °C for an additional 1 h. A solution of **2**[5a] (50.0 g, 0.23 mol) in dry THF (200 mL) was added dropwise to the cold, stirred mixture under argon during 2 h. The mixture was allowed to warm gradually to room temperature, was stirred for 12 h at room temperature, and then was refluxed for 36 h. The resulting mixture was cooled to 10 °C and was quenched with saturated aqueous ammonium chloride solution until the pH reached 5–6 (ca. 150 mL). After extraction with ethyl acetate (3 × 200 mL), the combined organic layers were washed with brine, dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel (10% ethyl acetate–hexane mixed solvent as eluent). Compound **3** (61.5 g, 93%) was thereby obtained as a colorless oil: bp 150–155 °C (0.05 mm); IR (neat) 2960 (s), 2770 (m), 1720 (s), 1700 (s), 1650 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.22 (two overlapping t, J = 6.6 Hz, 3 H), 1.32 (*AB*, J_{AB} = 10.5 Hz, 1 H), 1.73 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.20–2.88 (m, 8 H), 3.63–3.84 (m, 4 H), 4.05 (two overlapping q, J = 6.6 Hz, 3 H), 5.49 and 5.55 (2 s, total 1 H): ^{13}C NMR ($CDCl_3$) δ 14.17 (2 C, q), 35.99 (d), 36.84 (t), 37.01 (t), 39.77 (d), 39.84 (d), 39.87 (d), 40.80 (d), 42.08 (d), 42.44 (d), 42.51 (d), 43.90 (d), 44.51 (d), 44.60 (d), 46.18 (d), 47.29 (d), 50.53 (d), 50.96 (d), 51.44 (d), 59.22 (t), 59.25 (t), 63.21 (t), 63.28 (t), 65.42 (2 C, t), 109.22 (d), 109.31 (d), 112.64 (s), 115.39 (s), 166.36 (s), 166.57 (s), 167.04 (s), 167.11 (s); mass spectrum (70 eV), m/e (relative intensity) 288 (molecular ion, 100). GC/MS analysis of this material (injection port temperature 250 °C, initial column temperature 150 °C, column temperature increased 10 deg min^{-1} to a maximum of 250 °C) indicated that it consisted of two isomers, ratio 68:32.

Anal. Calcd for $C_{17}H_{20}O_4$: M_r 288.1362. Found (high-resolution mass spectrometry): M_r 288.1361.

Catalytic Hydrogenation of 3. A mixture of **3** (51.0 g, 0.18 mol) and 5% palladized charcoal (10.0 g) in ethyl acetate (500 mL) was reduced with stirring under hydrogen atmosphere at ambient conditions for 48 h. The reaction mixture was filtered to remove catalyst, and the filtrate was concentrated in vacuo. Compound **4** (51.2 g, 100%) was thereby obtained as a colorless oil: bp 150–152 °C (0.05 mm); IR (neat) 2940 (s), 2860 (m), 1700 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.15 (*AB*, J_{AB} = 10.5 Hz, 1 H), 1.35 (t, J = 6.6 Hz, 3 H), 1.61 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.05–3.1 (m, 11 H), 3.95 (m, 3 H), 4.20 (q, J = 6.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.41 (q), 33.90 (t), 34.00 (t), 38.22 (d), 38.93 (d), 39.51 (d), 39.69 (d), 41.74 (d), 45.02 (d), 46.36 (d), 46.42 (d), 48.23 (d), 59.91 (t), 52.24 (t), 65.57 (t), 115.68 (s), 175.15 (s); mass spectrum (70 eV), m/e (relative intensity) 290 (molecular ion, 100), 245 (51), 224 (84).

Anal. Calcd for $C_{17}H_{22}O_4$: M_r 290.1518. Found (high-resolution mass spectrometry): M_r 290.1516.

8-Oxo-*endo*-11-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecaneacetic Acid (5). A mixture of **4** (61.2 g, 0.21 mol), 10% aqueous H_2SO_4 (350 mL), and dioxane (200 mL) was refluxed for 48 h. The resulting mixture then was concentrated in vacuo to a volume of ca. 350 mL (to remove most of the dioxane), and the remaining aqueous mixture was extracted with methylene chloride (4 × 75 mL). The combined organic extracts were washed successively with water (3 × 40 mL) and with brine (2 × 30 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo. Recrystallization of the residue from ethyl acetate–hexane mixed solvent afforded pure **5** (41.4 g, 90%) as a colorless microcrystalline solid: mp 121–122 °C; IR (KBr) 3600–2700 (br, s), 1730 (s), 1700 cm^{-1} (s); ^1H NMR (DMSO-d_6) δ 1.35 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.72 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.0–3.1 (m, 11 H), 11.8 (br s, 1 H, peak disappeared upon addition of D_2O); ^{13}C NMR ($CDCl_3$) δ 31.75 (t), 35.81 (t), 37.34 (d), 39.03 (d), 42.00 (d), 42.09 (d), 42.83 (d), 43.41 (d), 48.18 (d), 50.55 (d), 52.24 (d), 178.33 (s), 221.02 (s).

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42. Found: C, 71.21; H, 6.54.

3-Hydroxyhexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane-4-carboxylic Acid (6). A solution of **5** (40.0 g, 0.18 mol) in dry dimethylformamide (DMF, 100 mL) and dry THF (200 mL) under nitrogen was cooled externally to 0–5 °C. Sodium hydride (12.96 g, 0.540 mol) was added with stirring in small portions during 45 min. The reaction mixture was allowed to warm slowly to room temperature and then was stirred for 20 h. The mixture again was cooled to 0 °C and then rendered acidic to litmus by careful addition of 10% aqueous hydrochloric acid solution (ca. 450 mL). THF was removed by heating in vacuo at 35–40 °C, and the remaining aqueous mixture was extracted with ethyl acetate (4 × 100 mL). The combined organic layers were washed successively with water (3 × 70 mL) and with brine (2 × 50 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo. The solid residue was triturated with ether and filtered. The filtrate was concentrated in vacuo to afford essentially pure unreacted **5** (1.8 g). The residue remaining after trituration contained **6** (36.4 g, 91%), which was isolated as a colorless microcrystalline solid: mp 154–155 °C; IR (KBr) 3500–2700 (br, s), 1690 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.55 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.90 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.35–3.05 (m, 10 H), 6.85 (br s, 1 H, peak disappeared upon addition of D_2O); ^{13}C NMR ($CDCl_3$–DMSO-d_6 mixed solvent) δ 40.03 (t), 41.04 (t), 41.97 (d), 43.20 (d), 43.23 (d), 43.30 (d), 43.35 (d), 43.46 (d), 44.48 (d), 45.00 (d), 45.87 (d), 45.98 (d), 46.69 (d), 46.74 (d), 47.55 (d), 46.74 (d), 50.87 (d), 52.23 (d), 55.52 (d), 56.74 (d), 58.47 (d), 59.35 (d), 92.15 (s), 92.52 (s), 174.73 (s), 175.48 (s). Compound **6** was

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converted into its methyl ester; GC/MS analysis of this ester (injection port temperature 250 °C, initial column temperature 100 °C, column temperature increased 10 deg min^{-1} to a maximum of 200 °C) indicated that it consisted of two isomers, ratio 69:31.

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.56; H, 6.32. Found: C, 71.45; H, 6.50.

3-Hydroxy-4-acetylhexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (7). A solution of **6** (2.0 g, 9.2 mmol) in dry THF (20 mL) under argon was cooled externally to 0 °C. Methyllithium (1 M solution in ether, 30 mL, 30 mmol) was added dropwise with vigorous stirring during 15 min, and the resulting solution was stirred at 0–5 °C for 2 h. The reaction mixture was allowed to warm slowly to room temperature and then was stirred for 8 h. The reaction again was cooled to 0–5 °C, was quenched via addition of 2 N aqueous hydrochloric acid solution (20 mL), and then was extracted with ether (3 × 30 mL). The combined extracts were washed successively with 5% aqueous sodium bicarbonate solution (3 × 25 mL), water (2 × 25 mL), and brine (2 × 25 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo. The oily residue was purified by column chromatography on silica gel (1:1 ethyl acetate–hexane mixed solvent as eluent), thereby affording **7** (1.6 g, 80%) as a colorless oil. The material obtained after chromatographic workup was used without additional purification: IR (neat) 3420 (br, s), 2950 (s), 2840 (m), 1700 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.41 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.70 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.00 and 2.05 (2 s, total 3 H), 2.17–2.98 (m, 10 H), 3.5 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.29 (q), 29.71 (q), 40.12 (t), 41.11 (t), 42.38 (d), 43.15 (d), 43.21 (d), 43.27 (d), 43.38 (d), 43.57 (d), 44.43 (d), 44.89 (d), 46.54 (d), 46.59 (d), 46.67 (d), 47.04 (d), 47.63 (d), 48.01 (d), 51.32 (d), 51.87 (d), 55.53 (d), 56.62 (d), 66.03 (d), 66.81 (d), 92.48 (s), 93.04 (s), 212.67 (s), 212.13 (s); mass spectrum (70 eV), *m/e* (relative intensity) 216 (molecular ion, 10.1), 173 (40.1), 155 (56.3), 135 (48.2), 107 (32.8), 95 (32.0), 91 (34.0), 79 (21.1), 77 (36.4), 43 (100.0). GC/MS analysis of this material (injection port temperature 250 °C, initial column temperature 100 °C, column temperature increased 10 deg min^{-1} to a maximum of 200 °C) indicated that it consisted of two isomers, ratio 68:32.

Anal. Calcd for $C_{14}H_{16}O_2$: M_r 216.1150. Found (high-resolution mass spectrometry): M_r 216.1145.

Hexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane-3,4-diol (8). A solution of **7** (10.0 g, 46 mmol) in dichloromethane (100 mL) was cooled externally to 0–5 °C. A mixture of trifluoroacetic anhydride (17.84 g, 85.0 mmol) and 90% aqueous hydrogen peroxide (3.0 g, 88 mmol) was added dropwise with stirring, and stirring was continued for 5 h after all oxidant had been added. The reaction mixture was allowed to warm gradually to room temperature and then was stirred for 24 h. The reaction mixture then was washed with 10% aqueous sodium carbonate solution (3 × 30 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo. Methanol (20 mL) and 10% aqueous sodium hydroxide (10 mL) were added to the residue, and the resulting mixture was heated at 50 °C for 17 h. The resulting basic mixture was cooled to 0–5 °C and then neutralized to pH 6–7 by gradual addition of 10% aqueous hydrochloric acid solution (ca. 20 mL). The resulting mixture was extracted with ethyl acetate (4 × 30 mL), and the combined extracts were washed successively with water (3 × 25 mL) and brine (2 × 20 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford a waxy semisolid. This material was triturated with cold ether, thereby affording **8** (5.3 g, 60%); recrystallization from ethyl acetate–hexane afforded a colorless microcrystalline solid: mp 214–215 °C; IR (KBr) 3540–3100 (br, s), 2930 (s), 2840 (m), 1300 (m), 1280 (m), 1100 (m), 1050 (m), 1030 cm^{-1} (m); ^1H NMR (DMSO-d_6) δ 1.2, (*AB*, J_{AB} = 10.5 Hz, 1 H), 1.6 (*AB*, J_{AB} = 10.5 Hz, 1 H), 1.76–2.8 (m, 9 H), 3.44–3.84 (m, 1 H), 4.32 and 4.54 (2 s, total 1 H), 4.73 and 5.13 (2 d, J = 3.6 Hz, total 1 H); ^{13}C NMR ($CDCl_3$) δ 38.46 (t), 38.48 (d), 40.94 (t), 43.14 (d), 43.17 (d), 43.25 (d), 44.40 (d), 44.52 (d), 44.83 (d), 44.86 (d), 45.11 (d), 45.53 (d), 46.71 (d), 46.73 (d), 47.35 (d), 47.58 (d), 47.98 (d), 52.02 (d), 53.06 (d), 54.48 (d), 82.21 (d), 84.44 (d), 92.77 (s), 93.58 (s); GC/MS analysis of this material (injection port temperature 250 °C, initial column temperature 150 °C, column temperature increased 10 deg min^{-1} to a maximum of 250 °C) indicated that it consisted of two isomers, ratio 62:38.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37. Found: C, 75.58; H, 7.56.

3-Hydroxyhexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecan-4-one (9). Method A. A solution of oxalyl chloride (740 mg, 5.8 mmol) in methylene chloride under argon was cooled externally to ca. −60 °C. A solution of dry DMSO (900 mg, 11.6 mmol) in dry methylene chloride (2 mL) was added dropwise with stirring, and stirring was continued for 5 min after the addition of DMSO–CH_2Cl_2 solution had been completed. The resulting solution was stirred at −60 °C for 5 min. A cold solution of diol **8** (500 mg, 2.63 mmol) in 3:1 methylene chloride–DMSO (3 mL) then was added, and the resulting mixture was stirred at −60 °C for 30 min. Isopropylamine (2.70 g, 26.7 mmol) then was added, and the resulting mixture was stirred at −50 °C for 20 min. The reaction mixture was allowed to warm slowly to room temperature and then was washed successively with cold 1% aqueous hydrochloric acid solution (2 × 5 mL), 5% aqueous sodium carbonate solution (2 × 5 mL), water (2 × 10 mL), and brine (2 × 10 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (20% ethyl acetate–hexane mixed solvent as eluent). Pure **9** (210 mg, 42%) was thereby obtained as a colorless microcrystalline solid: mp 189–190 °C; IR (KBr) 3540–3000 (br, s), 2920 (s), 2840 (m), 1740 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.6 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.92 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.55–3.20 (m, 9 H), 4.76 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 34.89 (t), 38.91 (d), 42.32 (d), 45.10 (d), 46.21 (d), 46.38 (d), 46.81 (d), 46.87 (d), 49.40 (d), 50.93 (d), 85.53 (s), 214.91 (s).

Anal. Calcd for $C_{12}H_{12}O_2$: M_r 188.0837. Found (high-resolution mass spectrometry): M_r 188.0838.

Method B. A suspension of *N*-chlorosuccinimide (NCS, 310 mg, 2.33 mmol) in dry toluene (10 mL) was cooled externally (dry ice–carbon tetrachloride bath) to −25 °C, and dimethyl sulfide (DMS, 180 mg, 2.9 mmol) was added dropwise with stirring. The resulting mixture was allowed to warm slowly to −3 °C to ensure complete formation of a 1:1 NCS–DMS complex. The cold bath then was replaced, and the mixture again was cooled to −25 °C. A suspension of diol **8** (100 mg, 0.53 mmol) in dry toluene (5 mL) was added under argon with stirring during 2 min. The reaction mixture was stirred at −25 °C for 40 min after the addition of **8** had been completed. A solution of triethylamine (480 mg, 4.75 mmol) in pentane (1 mL) then was added, and the resulting mixture was stirred for 35 min. During this time, the temperature of the reaction mixture was maintained between −25 °C and −10 °C. The reaction mixture was allowed to slowly warm to +10 °C and then was stirred at this temperature for 15 min. Ether (50 mL) then was added, and the mixture was filtered. The ethereal filtrate was extracted successively with ice-cold 1% aqueous hydrochloric acid solution (2 × 15 mL), water (3 × 20 mL), and brine (2 × 20 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography by using the procedure described in method A, above. Pure **9** (76 mg, 77%) was thereby obtained: mp 188–190 °C. The infrared, proton NMR, and carbon-13 NMR spectra of the material thereby obtained were identical in all respects with the corresponding spectra of the material synthesized by using method A, above.

3-(Tosyloxy)hexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecan-4-one (10). A mixture of **9** (100 mg, 0.53 mmol), dry pyridine (0.4 mL), and *p*-toluenesulfonyl chloride (150 mg, 0.78 mmol) was heated under argon at 95–98 °C for 1 h. The reaction mixture was allowed to cool slowly to room temperature and then was stored in the freezer compartment of a refrigerator for 15 h. Methylene chloride (30 mL) was added, and the resulting mixture was stirred at room temperature for 10 min. The resulting light brown solution was cooled to 0 °C and then washed successivly with cold 10% aqueous sulfuric acid solution (3 × 10 mL), saturated sodium bicarbonate solution (3 × 10 mL), water (30 mL), and brine (30 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel (20% ethyl acetate–hexane mixed solvent as eluent). Compound **10** (160 mg, 88%) was thereby obtained as a waxy semisolid: IR (KBr) 3100 (w), 2940 (s), 2840 (w), 1740 (s), 1570 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.50 (*AB*, J_{AB} = 10.5 Hz, 1 H), 1.73 (*AB*, J_{AB} = 10.5 Hz, 1 H),

2.39 (s, 3 H), 2.57–3.25 (m, 9 H), 7.27 (d, J = 7.5 Hz, 2 H), 7.93 (d, J = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.41 (q), 34.52 (t), 38.32 (d), 40.81 (d), 44.03 (d), 46.20 (d), 46.54 (d), 47.01 (d), 47.17 (d), 49.42 (d), 50.19 (d), 94.74 (s), 126.67 (d), 127.44 (d), 129.40 (d), 130.12 (d), 134.93 (s), 144.55 (s), 205.93 (s). Compound **10** was used as obtained for the next synthetic step, without further purification.

Hexacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]undecane-8-carboxylic Acid (Homopentaprismane-8-carboxylic Acid, 11). A mixture of **10** (60 mg, 0.18 mmol) and 20% aqueous potassium hydroxide solution (20 mL, excess) was refluxed for 7 h. The resulting mixture was allowed to cool to room temperature and then was washed with methylene chloride (2 × 10 mL) to remove nonacidic impurities. The aqueous layer was cooled to 0 °C, and the pH of the solution was adjusted to 2.0 by dropwise addition of 50% (w/w) aqueous sulfuric acid solution (ca. 7 mL). The resulting turbid mixture was extracted with methylene chloride (3 × 20 mL). The combined organic extracts were washed successively with water (3 × 20 mL) and with brine (3 × 20 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo, thereby affording **11** (31 mg, 94%). Pure **11** was obtained by recrystallization from chloroform–hexane as a colorless microcrystalline solid: mp 133–134 °C; IR (KBr) 3500–2300 (br, s), 1640 (s), 1400 (m), 1300 (m), 1252 (m), 1250 (m), 1230 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 2 H), 2.73–3.34 (m, 9 H), 10.38 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 39.74 (t), 40.39 (d), 44.94 (d), 46.37 (d), 46.83 (d), 48.45 (d), 49.49 (d), 50.66 (d), 50.79 (d), 51.44 (d), 54.37 (s), 180.98 (s).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.36; H, 6.33.

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Registry No. **2**, 58228-93-6; (*E*)-**3**, 120789-84-6; (*Z*)-**3**, 120828-04-8; **4**, 120789-85-7; **5**, 120789-86-8; **6** (isomer 1), 120789-87-9; **6** (isomer 2), 120851-15-2; **6** methyl ester (isomer 1), 120789-91-5; **6** methyl ester (isomer 2), 120851-16-3; **7** (isomer 1), 120789-92-6; **7** (isomer 2), 120851-17-4; **8** (isomer 1), 120789-93-7; **8** (isomer 2), 120851-18-5; **9**, 120789-88-0; **10**, 120789-89-1; **11**, 120789-90-4; $(EtO)_2P(O)CH_2CO_2Et$, 867-13-0.

Reactions of a Semistabilized Arsonium Ylide with Aldehydes: Counterion Effects on Product Selectivity

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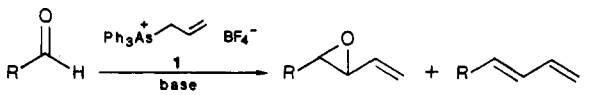
The reaction of arsonium ylides with carbonyl compounds has been described in the literature over the past 30 years following the initial report by Henry and Wittig.[1] The significant contribution in this field was made by Still in 1981, who demonstrated the synthetic utility of unstabilized arsonium ylides to give *trans*-epoxides exclusively.[2] Various other groups have shown that stabilized arsonium ylides give rise to olefin products only.[3-5] The reaction of semistabilized arsonium ylides with carbonyl compounds results in a mixture of olefin and epoxide products.[6] However, various methods to control the reaction pathway of semistabilized (e.g., benzylic and allylic) arsonium ylides have since appeared in the literature.[7-9]

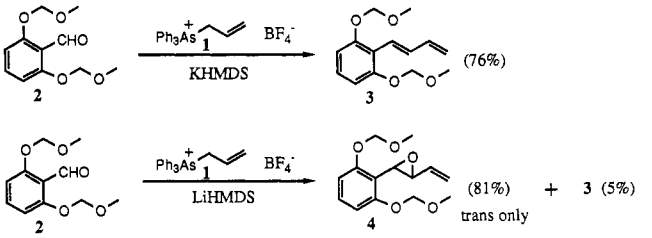
In connection with our synthetic efforts in the aflatoxin area, the reactivity of the ylide generated from allyltriphenylarsonium tetrafluoroborate (**1**) was investigated. We report herein that the selectivity for the formation of either epoxides or olefins is dependent upon the choice of base used for generation of the arsonium ylide. The reaction of arsonium allylides with carbonyl compounds to give epoxides has been reported,[8a] and the counterion dependence of arsonium benzylides on product formation has been discussed;[9] however, this appears to be the first example of counterion-dependent product formation with regard to arsonium allylides.

Table I. Reaction of Allyltriphenylarsonium Ylides with Aldehydes[g]



	R	base	epoxide (%)[a] (trans:cis)[b]	*trans*-diene (%)
1		LiHMDS	**5**[c] (70) (2:1)	**8** (0)
2		LiHMDS	**6**[d] (55) (2:1)	**9** (0)
3	$CH_3(CH_2)_6$	LiHMDS	**7**[c] (71) (2:1)	**10** (0)
4		KHMDS	**5** (0)	**8**[c] (59)
5		KHMDS	**6** (0)	**9**[e] (61)
6	$CH_3(CH_2)_6$	KHMDS	**7** (3) (2:1)	**10**[f] (54)

[a] Isolated yields. [b] As determined by ^{1}H NMR. [c] Reference 16. [d] Reference 17. [e] Reference 18. [f] Reference 19. [g] All compounds gave spectral characteristics consistent with those previously reported.



Deprotonation of allyltriphenylarsonium tetrafluoroborate (**1**)[10] with 1.1 equiv of potassium hexamethyldisilazide (KHMDS) in THF at −65 °C and treatment of the resulting ylide with aldehyde **2** gave diene **3** exclusively

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(10) A modification of the procedure reported by Oesch was used: Oesch, F.; Sparrow, A. J.; Platt, K. L. *J. Labelled Compd. Radiopharm.* **1983**, *20*, 1297. After the reaction mixture was heated for 3 days, the solvent was removed in vacuo and the residue taken up in CH_2Cl_2. This mixture was shaken with a solution (ca. 10 M) of $NaBF_4$ in water. The aqueous layer was washed twice with CH_2Cl_2, and the combined organics were dried through Na_2SO_4. Concentration in vacuo followed by trituration three times with dry THF resulted in allyltriphenylarsonium tetrafluoroborate as a white solid in 90% yield.

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