titions approximately equally between the water and benzene. This conclusion is in contrast to that of Starks and Liotta[4] who propose that the better catalysts are those that more strongly favor the organic layer.

Preparative-scale reaction with the alkyl ethers is effective; reaction of 0.69 g of 1-octene with C18-6000-C18 as catalyst gave 0.47 g of isolated hepatanoic acid. Catalyst recovery by precipitation with ethyl ether from benzene solution was complete. Similarly, reaction with the water–methylene chloride system is also preparatively useful with unsubstituted PEG-6000 as the PTA.[2b] Yields of 70% are easily achieved, and again PTA recovery by precipitation makes product isolation trivial.

In summary, we can conclude that the PEG ethers can be designed to provide effective, recoverable PTA's for water–benzene systems. The parent PEG can be used similarly in a water–methylene chloride system.

Experimental Section

Unless otherwise noted, all reagents were obtained from either Aldrich Chemical Co. or Fisher Scientific Co. and are used without further purification. GC work was performed on a Varian 4600 GC with an FID detector and a 5% SE-30 Chromosorb 60/80 column (9 ft × 0.125 in.). HPLC work was performed on a Perkin-Elmer Series 2 liquid chromatograph with an LDC Model 1107 Refracto-Monitor detector and a Water's µBondapak C18 column (30 cm × 3.9 mm). Both the GC and the HPLC were connected with a Varian Vista 401 Data Station. Proton NMR spectra were determined on a Varian EM-360 60-MHz NMR spectrometer.

Synthesis of PEG Ethers. The following preparation is typical: PEG 6000 (10.0 g, 0.00167 mol) was dissolved in 40 mL of dry benzene and added dropwise to a suspension of potassium *tert*-butoxide (10% excess; 0.4 g, 0.00367 mol) in 20 mL of dry benzene under a nitrogen atmosphere. The mixture was allowed to stir at room temperature for 1 h. Octadecyl bromide (2× excess; 2.2 g, 0.00668 mol) was dissolved in 15 mL of dry benzene and added dropwise to the mixture, which was then stirred at room temperature for 72 h. After filtration to remove insoluble salts, the benzene was removed by rotoevaporation. The product was redissolved in methylene chloride and eluted down a short silica gel column (1 in. × 5 in.) with methylene chloride. This removed dissolved salts and some of the unreacted PEG. The eluent was concentrated by rotoevaporation and the PEG ether precipitated by dropwise addition to diethyl ether. Product isolated by precipitation was gummy and difficult to filter. This step served only to remove a portion of the hydrocarbons present. On the basis of the method of Van Alstine,[5] the product was further purified by chromatography on Sephadex LH-20 gel (Pharmacia) with 5:1 methanol–water as eluent (1 g dissolved in 30 mL of eluent on a 1 × 12 in. column with a flow rate of 0.5 mL/min). The eluent was concentrated by rotoevaporation and dried several hours in vacuo. Product thus isolated was 75–90% substituted with 0.2% (w/w) alkyl bromide contaminant remaining.

Characterization of PEG Ethers. The amount of alkyl bromide remaining in the product was determined by GC by comparing with nonane internal standard. Substitution was determined by NMR (in $CDCl_3$) by measuring the ratio of alkyl hydrogens (δ 1.30) to ether hydrogens (δ 3.75). Substitution was also determined for C18 ethers by HPLC (C18 column). Eluent was 65:35 acetonitrile–methanol except for PEG-6000-$(C18)_2$, where 35:65 acetonitrile–methanol was used. Flow was 2.0 mL/min; 5-10 µL of 5% sample was injected.

Kinetics of PEG Ether Synthesis. PEG-1900 monomethyl ether (1.00 g, 0.000526 mol) in 4 mL of dry benzene was added to a suspension of KO-*t*-Bu (10% excess; 0.065 g, 0.00058 mol) in 2 mL of dry benzene. This mixture was stirred at 35 °C for 1 h. One-fifth of the molar equivalent of octyl bromide (0.020 g, 0.000105 mol) in 1.5 mL of dry benzene was added. Samples were periodically withdrawn, and the disappearance of octyl bromide was followed by GC.

Partitioning of PEG Ethers between Benzene and Water. Typically, 1 mL of a 5% (w/w) solution of PEG ether in benzene was quantitatively prepared in a 1-dram vial. An equal volume of water was added and the vial inverted several times to mix the phases. After settling overnight, a weighed portion of the benzene phase was placed in a second vial. Most of the benzene was evaporated under a stream of nitrogen. The samples were dried in vacuo for several hours and the weight of the PEG ether partitioned into benzene determined. This procedure was complicated by emulsification with C18 ethers.

Kinetic Study of Phase-Transfer-Catalyzed Oxidation of Octene. Reactions were conducted in jacketed reaction vials with stirring at 35 °C. The vial was charged with 7.2 mL of 0.4 M $KMnO_4$ in 0.5% acetic acid. After the solution was stirred for 10 min, 2.0 mL of 0.36 M octene in benzene containing 0.7 mmol of nonane (internal standard) and 0.08 g of PTA was added. Aliquots were withdrawn, diluted with acetonitrile, and injected on the GC.

Preparative-Scale Oxidation of Octene. A 250-mL reaction flask was charged with 61 mL of 0.4 M $KMnO_4$ (24.4 mmol) in 0.5% acetic acid. A chilled water bath was used to maintain the temperature below 40 °C as 17 mL of 0.36 M octene in benzene with 0.68 g of PEG-6000-$(C18)_2$ slowly added. Stirring was continued for 5 h, 50% sulfuric acid was added until the solution was acidic, and sodium bisulfite was added to reduce MnO_2. The phases were separated, and the product was removed by extraction into aqueous base. Neutralization, drying, and rotoevaporation gave heptanoic acid (GC, 59%). A second reaction in methylene chloride with PEG gave a 70% yield.

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Registry No. $C_4O(CH_2CH_2O)_nC_4$, 31885-97-9; $C_4O(CH_2CH_2O)_nMe$, 80730-57-0; $C_{18}O(CH_2CH_2O)_nC_{18}$, 36493-26-2; $C_{18}O(CH_2CH_2O)_nMe$, 27252-82-0; $C_8O(CH_2CH_2O)_nMe$, 27252-82-0; $HO(CH_2CH_2O)_nH$, 25322-68-3; $C_6O(CH_2CH_2O)_nC_6$, 27900-79-4; $KMnO_4$, 7722-64-7; 1-octene, 111-66-0; octadecyl bromide, 112-89-0.

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Synthesis of Alkene-Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes. An Improved Synthesis of 8,11-Dimethylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane

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Substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes recently have received considerable attention as intermediates in the synthesis of tricyclopentanoid natural products.[1-3] In our studies of the synthesis and chemistry of new substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes,[4-9]

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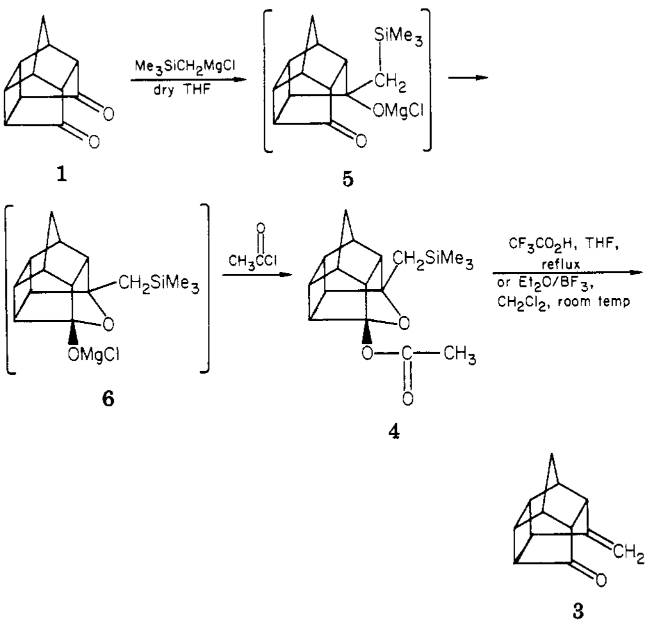
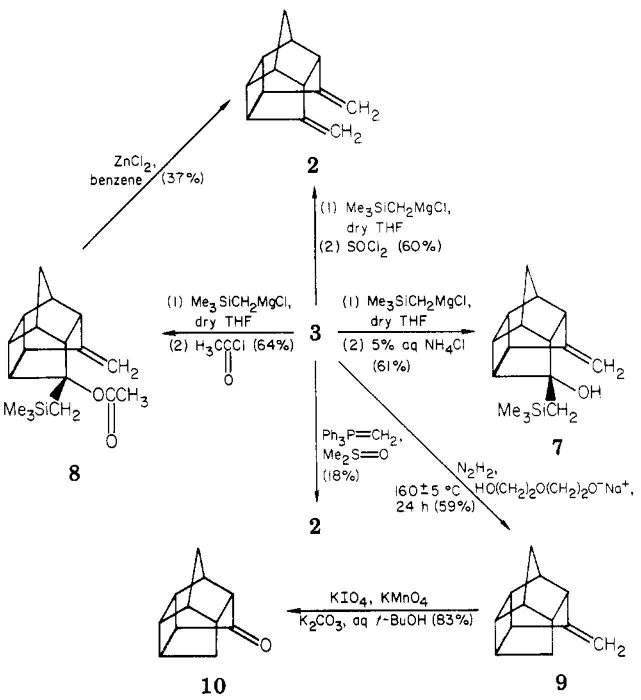
Scheme I



Scheme II



we have sought to synthesize novel cage alkenes by utilizing petacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (**1**) as substrate. Shen and Kuebler[10] have reported the synthesis of 8,11-dimethylenepentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**2**) in 50% yield via reaction of **1** with methylene triphenylphosphorane. However, in our hands, attempts to transform **1** to **2** by a classical Wittig reaction[10,11] afforded only mixtures of alkenes in low yield (ca. 10%). 8-Methylenepentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-11-one (**3**) was also isolated from this reaction, along with an unidentified alkene.

For the introduction of *exo*-methylene groups, the Peterson reaction[12,13] is complementary to the Wittig reaction, and, in some cases,[14] it has been found to be superior to the Wittig reaction for this purpose. A convenient modification of the Peterson reaction was introduced by Chan and Chang,[15] who reacted magnesium alkoxides of β-hydroxy silanes with acetyl chloride (or thionyl chloride) in situ to form alkenes directly. In the case of the reaction with acetyl chloride, the proposed intermediate β-acetoxy silane was not isolated.[15]

In the present study, compound **1** was allowed to react with 1 equiv of [(trimethylsilyl)methyl]magnesium chloride, and the resulting product was quenched with acetyl chloride. Instead of the expected enone (**3**), compound **4** was thereby produced in excellent yield (Scheme I). This result suggests that the intermediate magnesium alkoxide, **5**, undergoes an intramolecular nucleophilic addition to the remaining carbonyl group to afford a hexacyclic intermediate magnesium alkoxide, **6**. Trapping of **6** by addition of acetyl chloride then affords compound **4**. It should be noted that intramolecular ether (or hemiacetal) formation via similar nucleophilic addition of *endo*-11-oxygen to a neighboring 8-carbonyl group in suitably 8,11-disubstituted pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes is a characteristic reaction of this polycyclic ring system.[4,6,16]

Compound **4** could be transformed cleanly to **3** by either of two routes. Thus, refluxing **4** in THF with trifluoroacetic acid (1.2 equiv) for 60 h afforded **3** in excellent yield. A more convenient procedure involves stirring **4** in methylene chloride with boron trifluoride etherate at room temperature for 24 h. An interesting feature of this reaction sequence is the selective conversion of only one of the two identical carbonyl groups in symmetrical dione **1** to an unsymmetrical enone system (**3**).

Attempted conversion of **3** to diene **2** by a Wittig reaction[11] afforded **2** in only 18% yield. Alternatively, **3** was allowed to react with 1 equiv of [(trimethylsilyl)methyl]magnesium chloride in dry THF, and the resulting intermediate was quenched with 5% aqueous ammonium chloride solution. Compound **7** was thereby obtained in 61% yield (Scheme II).

When the adduct of [(trimethylsilyl)methyl]magnesium chloride with **3** was quenched instead with acetyl chloride, the corresponding acetate (**8**) was isolated in 64% yield. This result was unexpected, since β-silylacetates normally are not isolated; instead, they usually undergo spontaneous elimination of trimethylsilyl acetate to afford the corresponding alkene directly.[15] Interestingly, acetate **8** was found to be stable to refluxing toluene (24 h), refluxing trifluoroacetic acid (1.1 equiv) in THF (58 h), refluxing trifluoroacetic acid (1 equiv) in 2:1 THF–HMPA, and refluxing triethylamine (1 equiv, 15 h). However, **8** could be converted to **2** by stirring with zinc chloride in benzene. The highest overall yield of **2** from **3** was obtained by quenching the adduct formed via reaction of [(trimethylsilyl)methyl]magnesium chloride with **3** using thionyl chloride (Scheme II).[17]

Compound **3** also could be converted to the corresponding monoene, **9**, via Wolff–Kishner reduction

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[17] Compound **2** was found to be unstable to atmospheric oxygen. When O_2 was bubbled through a sample of **2**, the viscosity of the sample slowly increased, and a glassy solid formed. Compound **2** has been reported to freeze at ca. 0 °C.[10] However, in our hands, **2** failed to solidify even after storing overnight at −20 °C.

(Scheme II). A small amount of an unidentified alkene was obtained along with **9** in this reaction. Purification of **9** was effected via column chromatography on silica gel impregnated with 20% (w/w) silver nitrate.[18] Attempts to synthesize **9** alternatively via reduction of the tosylhydrazone of **3** with, for example, lithium aluminum hydride,[19] with sodium borohydride,[20] or with sodium cyanoborohydride[21] all failed. Characterization of **9** was completed conveniently via oxidation of its 9-methylene functionality with $KMnO_4$–KIO_4, thereby affording the corresponding monoketone (**10**)[22,23] in excellent yield.

Experimental Section

Melting points and boiling points are uncorrected. Proton NMR spectra (60 MHz) were obtained with either a Varian EM-360 or a Hitachi Perkin-Elmer Model R-24B NMR spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX-90-Q NMR spectrometer. In all cases, signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer Model 1330 infrared spectrophotometer. Mass spectra were obtained with a Hewlett-Packard Model 5985B mass spectrometer (70 eV). Tetrahydrofuran (THF) was purified via distillation from Na-K alloy under inert atmosphere. All commercial reagents were purified prior to use by either distillation or recrystallization, as appropriate. Elemental microanalyses were performed by Midwest Microlab Ltd., Indianapolis, IN.

1-Acetoxy-12-oxa-6-[(trimethylsilyl)methyl]hexacyclo[5.4.1.0^{2,5}.0^{3,10}.0^{4,8}.0^{7,11}]dodecane (4). To a precooled (ice bath) 1 M solution of [(trimethylsilyl)methyl]magnesium chloride (0.15 mol) in dry THF was added diketone **1** (26.2 g, 0.15 mol) dissolved in dry THF (100 mL) during 5 min. The resulting solution was refluxed (3 h) and then cooled to 0 °C. A solution of acetyl chloride (11.8 g, 0.15 mol) in dry THF (15 mL) was then added during 15 min. The resulting reaction mixture was stirred at 50 °C (2 h). Stirring was then continued at room temperature overnight. The reaction mixture was cooled (ice bath), hydrolyzed via the dropwise addition of saturated aqueous NH_4Cl solution, and stirred at room temperature (30 min). The resulting coagulated solid precipitate was filtered and washed with ether. The layers in the filtrate were separated, and the aqueous layer was extracted with ether. The combined ethereal extracts were dried (anhydrous $MgSO_4$) and filtered, and the filtrate was concentrated in vacuo to afford crude **4** (42.8 g, 96%). The crude product was distilled,[24] affording pure **4** (39.8 g, 87%) as a colorless liquid: bp 136 °C (0.02 mm); ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.21 (s, 2 H), 1.48 (d, J = 11 Hz, 1 H), 1.82 (d, J = 11 Hz, 1 H), 2.07 (s, 3 H), 2.35–3.30 (m, 8 H); IR (film) 2963 (s), 2869 (m), 1748 (vs), 1332 (m), 1304 (m), 1253 (s), 1204 (s), 864 (s), 842 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 304 (M^+, 0.4), 155 (31.7), 144 (14.5), 128 (20.1), 116.9 (25.0), 75.1 (32.4), 73 (100.0).

Anal. Calcd for $C_{17}H_{24}O_3Si$: C, 67.07; H, 7.95. Found: C, 67.36; H, 7.93.

8-Methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-11-one (3). Method A. To a solution of **4** (11 g, 0.036 mol) in dry THF (36 mL) was added trifluoroacetic acid (4.94 g, 0.043 mol), and the resulting solution was refluxed (60 h). The reaction mixture was allowed to cool to room temperature at the conclusion of the reflux period. Ether (50 mL) was then added to this solution. After stirring (3 min), the reaction mixture was poured slowly into 5% aqueous $NaHCO_3$ solution (150 mL). The resulting mixture was stirred (10 min), and the layers were then separated. The aqueous layer was extracted with ether, the combined organic layers were dried (anhydrous $MgSO_4$) and filtered, and the filtrate was concentrated in vacuo to afford crude **3** in essentially quantitative yield. Recrystallization from hexane afforded pure **3** (5.25 g, 85%) as a colorless microcrystalline solid: mp 71–72 °C; ^1H NMR ($CDCl_3$) AB pattern, J_{AB} = 11 Hz, δ_A 1.54 (1 H), δ_B 1.88 (1 H), 2.12–3.39 (m, 8 H), 4.52 (d, 2 H); IR (film) 2980 (vs), 2882 (m), 1740 (s), 1668 (m), 907 (vs) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 172.2 (M^+, 73), 144.1 (20.8), 143.1 (21.7), 129.1 (100), 128.2 (52.8), 116.2 (21.7), 115.2 (34.2), 91.2 (29.7), 78.1 (21.5).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.88; H, 7.20.

Method B. To a solution of **4** (1.52 g, 0.005 mol) in methylene chloride (5 mL) was added boron trifluorate etherate (3 drops). The resulting reaction mixture was stirred under argon at room temperature (24 h), at which time the reaction mixture was poured into 5% aqueous $NaHCO_3$ solution (10 mL). After the solution was stirred (15 min), the layers were separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried (anhydrous $MgSO_4$) and filtered, and the filtrate was concentrated in vacuo to afford **3** in essentially quantitative yield (>95% by NMR), mp 71–72 °C.

The tosylhydrazone of **3** was prepared as follows: A solution of **3** (5.167 g, 0.03 mol) and *p*-toluenesulfonylhydrazine (5.587 g, 0.03 mol) in methanol (60 mL) was stirred at room temperature for 24 h. The resulting solution was concentrated in vacuo to ca. 15 mL, cooled to −20 °C, and then maintained at that temperature for 4 h. The reaction mixture was then filtered, and the residue was air-dried to afford the tosylhydrazone of **3** (8.375 g, 82%) as a colorless microcrystalline solid. An analytical sample, mp 148–149 °C, was obtained via recrystallization from carbon tetrachloride solution: ^1H NMR ($CDCl_3$) AB pattern, J_{AB} = 11 Hz, δ_A 1.41 (1 H), δ_B 1.75 (1 H), 2.12–3.52 (m, 11 H), 4.30–4.48 (m, 2 H), AA′BB′ pattern, $\delta_{A,A'}$ 7.24 (2 H), $\delta_{B,B'}$ 7.80 (2 H), 8.36 and 8.55 (2 s, corresponding to NH absorptions in syn and anti isomers, total 1 H); IR (KBr) 3210 (s), 3062 (w), 2962 (s), 2862 (m), 1658 (m), 1593 (m), 1397 (s), 1329 (s), 1160 (vs), 1086 (s), 1010 (s), 912 (m), 888 (m), 808 (s), 790 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) (no M^+), 263.1 (12.6), 262.1 (57.6), 174.1 (69.9), 172.1 (12.0), 171.1 (10.3), 156.2 (13.6), 155.1 (82.3), 146.1 (32.8), 144.1 (27.6), 131.0 (18.4), 129.0 (40.3), 128.2 (17.7), 118.1 (25.0), 117.1 (100), 115.1 (29.1), 91.1 (23.9), 75.1 (10.1), 73.0 (25.5).

Anal. Calcd for $C_{19}H_{20}N_2O_2S$: C, 67.03; H, 5.92. Found: C, 67.00; H, 6.07.

8-Hydroxy-8-[(trimethylsilyl)methyl]-11-methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (7). To a cooled (2 °C) 2 M solution of [(trimethylsilyl)methyl]magnesium chloride (0.02 mol) in dry THF was added **3** (3.44 g, 0.02 mol) in dry THF (5 mL) during 5 min. The resulting mixture was refluxed (7 h); a white solid precipitated 1 h after reflux had been initiated. The reaction mixture was then allowed to cool to room temperature, and ether (100 mL) was added. After stirring (5 min), the reaction mixture was poured into 5% aqueous NH_4Cl solution (200 mL). The layers were separated, and the aqueous layers were extracted with ether. The combined organic layers were dried (anhydrous $MgSO_4$) and filtered, and the filtrate was concentrated in vacuo to afford a yellow oil (5.2 g). This material was chromatographed on silica gel (pentane eluent). After removal of solvent, the product was distilled, affording **7** as a colorless oil (3.2 g, 61%): bp 83–85 °C (0.15 mm); ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 0.75 (s, 2 H), AB pattern, J_{AB} = 11 Hz, δ_A 1.27 (1 H), δ_B 1.71 (1 H), 2.01–3.10 (m, 8 H), 3.31 (s, 1 H), 4.68 (d, 2 H); IR (film) 3526 (s, sharp), 3060 (w), 2954 (s), 2862 (s), 1652 (m), 1348 (s), 1243 (s), 1116 (m), 1104 (m), 845 (vs) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 260.2 (M^+, 3.2), 245.2 (30.7), 227.2 (7.3), 194.1 (14.2), 182.2 (13.0), 181.1 (53.9), 180.1 (22.7), 169.1 (5.6), 168.1 (8.3), 141.0 (5.5), 129.1 (7.4), 128.1 (6.1), 115.1 (16.9), 107.1 (5.0), 105.1 (6.9), 93.1 (6.1), 92.1 (6.0), 91.1 (22.2), 79.1 (11.7), 77.1 (13.8), 75.0 (60.8), 74.1 (10.1), 73.0 (100).

Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.60; H, 9.43.

8-Acetoxy-8-[(trimethylsilyl)methyl]-11-methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (8). To a 1 M solution of [(trimethylsilyl)methyl]magnesium chloride (0.015 mol) in dry THF at room temperature was added **3** (2.6 g, 0.015 mol) in dry

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(18) Compound **9** proved to be exceedingly sensitive to atmospheric oxygen.

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(24) In some cases, small amounts of unreacted starting material (**1**) accompanied **4** in the distillate. Unreacted **1** can easily be removed from **4** by dissolving the distillate in pentane and filtering off precipitated **1**.

THF (10 mL) during 5 min. The resulting mixture was refluxed (7 h). The reaction mixture was then cooled (2 °C, ice bath), and a solution of freshly distilled acetyl chloride (1.18 g, 0.015 mol) in dry THF (3 mL) was added dropwise to the cooled reaction mixture during 5 min. The resulting mixture was stirred at 2 °C (30 min) and then refluxed (15 h). The reaction mixture was then cooled to room temperature, at which time ether (50 mL) was added. After stirring (5 min), the resulting mixture was poured into 5% aqueous $NaHCO_3$ solution (100 mL). The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were dried (anhydrous $MgSO_4$) and filtered, and the filtrate was concentrated in vacuo to afford crude **8** (4.3 g). The crude product was chromatographed on silica gel (pentane eluent) to afford pure **8** (2.92 g, 64%) as a colorless oil: bp 89–93 °C (0.02 mm); ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 1.05 (s, 1 H), 1.11 (s, 1 H), 1.35–1.65 (AB pattern, 2 H), 1.78 (s, 3 H), 2.01–3.29 (m, 8 H), 4.45 (d, J = 2 Hz, 2 H); IR (film) 2944 (vs), 2848 (w), 1708 (vs), 1642 (w), 1348 (m), 1246 (vs), 1236 (vs), 852 (vs), 832 (s) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 302.2 (M^+, 1.5), 260.1 (5.4), 245.1 (6.6), 181.1 (15.3), 170.1 (5.7), 169.1 (13.8), 168.1 (24.2), 167.0 (5.4), 165.1 (12.0), 155.0 (8.8), 153.1 (5.5), 141.0 (6.2), 79.1 (9.5), 78.1 (7.3), 77.0 (10.5), 75.0 (42.0), 74.1 (9.2), 73.0 (100), 66.1 (7.0), 65.0 (5.7).

Anal. Calcd for $C_{18}H_{26}O_2Si$: C, 71.47; H, 8.66. Found: C, 71.58; H, 8.86.

8,11-Dimethylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (2). Method A. To a 2 M solution of [(trimethylsilyl)methyl]magnesium chloride (0.01 mol) in dry THF was added **3** (1.77 g, 0.01 mol) dissolved in dry THF (5 mL). The resulting mixture was refluxed (7 h). The mixture was then cooled (ice bath), and thionyl chloride (1.20 g, 0.01 mol) was added to the cooled reaction mixture. The resulting solution was stirred at 2 °C (30 min) and then at room temperature (1 h). Saturated aqueous NH_4Cl solution (50 mL) was then added dropwise, and the resulting mixture was stirred at room temperature (1 h). The layers were then separated, and the aqueous layer was extracted with ether. The combined organic layers were dried (anhydrous $MgSO_4$) and filtered, and the filtrate was concentrated in vacuo to afford crude **2**. The crude product was chromatographed on a short silica gel column (pentane eluent) to afford pure **2** (1.02 g, 60%) as a colorless oil, bp 109 °C (22 mm). The ^1H NMR and IR spectral data are in accord with literature values:[10] ^{13}C NMR ($CDCl_3$) δ 36.47 (t), 42.38 (d), 44.50 (d), 47.04 (d), 52.35 (d), 102.73 (t), 153.44 (s); mass spectrum (70 eV) m/e (relative intensity), 170.1 (M^+, 26.4), 169.1 (11.2), 155.1 (35.3), 154.1 (10.4), 153.1 (11.6), 142.1 (21.9), 141.1 (22.9), 129.0 (26.1), 128.2 (20.6), 115.1 (27.0), 105.1 (22.2), 104.2 (16.0), 103.2 (11.9), 92.1 (36.1), 91.2 (100).

Method B. To a cooled (ice bath) solution of **8** (2.1 g, 7 mmol) in dry benzene (10 mL) was added anhydrous zinc chloride (0.25 g, 1.9 mmol). The resulting mixture was stirred at ca. 0 °C (15 min) and then allowed to warm to room temperature. Stirring was continued at room temperature for an additional 3 h. The reaction mixture was then poured into water (100 mL), and the layers were separated. The aqueous layer was extracted with benzene. The combined organic layers were washed with saturated aqueous sodium chloride solution, dried (anhydrous $MgSO_4$), and filtered, and the filtrate was concentrated in vacuo to afford **2** (0.44 g, 37%).

8-Methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (9). To diethylene glycol (250 mL) at 10 °C under argon was added small pieces of sodium metal (8.05 g, 0.35 mol). The mixture was stirred until all of the sodium had reacted. The temperature of the resulting solution was raised to 75 °C and stirred at this temperature for 30 min, whereupon anhydrous hydrazine (12 mL, 0.40 mol) was added. The reaction mixture was then heated to 160 ± 5 °C and stirred at this temperature for 24 h. The mixture was allowed to cool to room temperature and then poured into water (500 mL). The layers were separated, and the aqueous layer was extracted with ether. The combined ethereal extracts were washed with brine, dried (anhydrous $MgSO_4$), and filtered, and the filtrate was concentrated in vacuo to afford crude **9** (8.5 g, 77%). The crude product was chromatographed on silica gel that had been impregnated with 20% (w/w) silver nitrate (97:3 hexane–ethyl acetate eluent) to afford pure **9** (6.5 g, 59%) as a colorless oil: bp 32–34 °C (0.05 mm); ^1H NMR ($CDCl_3$) δ 0.97–1.9 (m, 4 H), 1.92–3.32 (m, 8 H), AB pattern, J_{AB} = 1.8 Hz, δ_A 4.52 (1 H), δ_B 4.62 (1 H); ^{13}C NMR ($CDCl_3$) δ 29.60 (t), 35.18 (d), 38.38 (d), 42.66 (d), 42.76 (d), 42.93 (d), 45.15 (d), 46.55 (d), 46.99 (d), 50.29 (d), 103.00 (t), 154.79 (s); IR (film) 3070 (m), 2960 (s), 2865 (m), 1662 (m), 1440 (m), 1305 (m), 1298 (m), 878 (m) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 158.1 (M^+, 47.4), 143.1 (19.3), 128.1 (14.4), 115.1 (15.2), 93.1 (100), 92.1 (40.7), 91.1 (57.5), 80.1 (20.3), 79.1 (27.6), 77.0 (24.7).

Anal. Calcd for $C_{12}H_{14}$: M_r 158.1096. Found (high-resolution mass spectrometry) M_r 158.1099.

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (10). Compound **1** (4.3 g, 0.027 mol) was dissolved in *tert*-butyl alcohol (20 mL), and the resulting solution was added to a solution of potassium periodate (36.8 g, 0.16 mol) and potassium carbonate (33.16 g, 0.24 mol) in 25% aqueous *tert*-butyl alcohol (2 L) at 50 °C. Potassium permanganate (1.0 g, 0.0063 mol) was then added to the reaction mixture, and the resulting solution was stirred vigorously at 50 °C for 25 h. The reaction mixture was then extracted several times with ether. The combined ethereal extracts were washed with brine and then with water, dried (anhydrous $MgSO_4$), and filtered, and the filtrate was concentrated in vacuo to afford **10** (3.6 g, 83%) as a colorless microcrystalline solid. An analytical sample, mp 205–206 °C (sealded tube) [lit. mp 191–192 °C (with sublimation),[22] mp 194–195 °C[23]] was obtained via recrystallization from hot hexane. ^1H NMR, ^{13}C NMR, and IR spectral data are in accord with literature values:[22,23] mass spectrum (70 eV) m/e (relative intensity), 160.1 (M^+, 44.9), 145.1 (18.6), 132.1 (12.2), 117.1 (22.7), 115.1 (20.1), 95.1 (100), 94.1 (38.1), 91.1 (35.7), 82.1 (43.9), 79.1 (44.9), 78.1 (21.7), 77.1 (31.7), 67.1 (12.9), 66.1 (41.1), 65.1 (23.4), 51.1 (14.0).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.15; H, 7.61.

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