Supporting Information

Chloromethanesulfonylethene and Dichloromethanesulfonylethene: New Reagents for Tandem Diels-Alder-Ramberg-Bäcklund Reactions

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β-*Chlorosulfides may be toxic on inhalation, ingestion or skin contact. These compounds should only be handled in a well-ventilated hood using rubber gloves. All glassware used should be rinsed with bleach ("Clorox") immediately after use.*

$ClCH_2SCl$

Chloromethanesulfenyl Chloride (5)[4]. A magnetic stirrer-equipped flask was charged with CH_2Cl_2 (60 mL) and Me_2S_2 (9.16 g, 97 mmole), the mixture was cooled to –78 ^oC and Cl_2 gas was bubbled through slowly using a 9 mm glass tube (a solid was formed plugging smaller bore tubes). The mixture turned red-orange and a colorless solid (CH_3SCl_3) appeared. The mixture turned into a milky, yellow-white slurry, which continued to thicken and lighten until the solution became saturated with chlorine, at which time the mixture took on a yellow-green color. Addition of Cl_2 was stopped and a reflux condenser with drying tube was fitted to the flask. Decomposition of CH_3SCl_3 was promoted by warming the flask to room temperature. An orange liquid formed as HCl was evolved. Concentration in vacuo yielded the title compound as a malodorous, lachrymatory oil (20 g, 88%) which was used without further purification; ^1H NMR (300 MHz, $CDCl_3$) δ 5.12 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 54.8.

$ClCH_2CH_2SCH_2Cl$

1-Chloro-2-chloromethanesulfanylethane (6)[5]**.** Chloromethanesulfenyl chloride (19.2 g, 17.8 mmol) and CH_2Cl_2 (200 mL) were placed in a flask fitted with a gas inlet tube and a drying tube. Ethylene gas was slowly introduced at 0 ^oC until the starting material disappeared as indicated by ^1H NMR analysis. Concentration in vacuo afforded the known title compound as a yellow oil (21.4 g, 90 %) which was used directly for the next step without further purification; bp 99-100 ^oC (15 mm); ^1H NMR (300 MHz, $CDCl_3$) δ 4.75 (s, 2H), 3.76 (t, *J* = 7.8 Hz, 2H), 3.11 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.2, 42.4, 34.0; GC-MS *m/z* (relative intensity) 146 (M^+, ^{37}Cl, 14), 144 (M^+, ^{35}Cl, 20), 111 (23), 109 (63), 95 (51), 45 (100).

$CH_2=CHSO_2CH_2Cl$

Chloromethanesulfonylethene (3a). *m*-Chloroperbenzoic acid (77 %, 107 g, 0.47 mole) was added to a solution of 1-chloro-2-chloromethanesulfanylethane (30.8 g, 0.21 mole) in CH_2Cl_2 (750 mL) over 30 min at room temperature and the mixture was stirred for 16 h. The colorless precipitate was removed by filtration and excess aqueous $NaHCO_3$ was added to the filtrate which was stirred for 16 h. The reaction mixture was washed with H_2O (3 × 200 mL) and brine (3 × 200 mL), and the organic phase was separated, dried (Na_2SO_4) and concentrated in vacuo affording the title compound as a colorless oil (29.4 g, 99 %); see footnote 8 for nmr data; IR ($CHCl_3$) 1149, 1325 (SO_2) cm^{-1}.

$ClCH_2CH_2SCHCl_2$

1-Chloro-2-(dichloromethanesulfanyl)ethane (9). A three-necked round bottom flask was charged with Me_2S_2 (10 mL, 113 mmol) and CH_2Cl_2 (120 mL). The solution was cooled to - 78 ^oC and Cl_2 gas was bubbled through slowly for 3-5 min. The reaction mixture turned reddish orange and a colorless solid precipitated (CH_3SCl_3). The slurry continued to thicken until the solution had been saturated with Cl_2, at which time the mixture took on a yellow-green color and

the addition of Cl_2 was stopped. The reaction mixture was warmed to room temperature and stirred for 1 h to give a bright orange solution with the release of HCl gas, which was absorbed with aqueous NaOH solution. The orange solution was cooled to -78 ^oC and Cl_2 gas was bubbled through again. As before, a colorless solid precipitated. The slurry continued to thicken until the solution had been saturated with Cl_2, at which time the mixture took on a yellow-green color and the addition of Cl_2 was stopped. The reaction mixture was warmed to room temperature, stirred for 1 h, concentrated in vacuo and diluted with CH_2Cl_2 (300 mL). The solution was cooled to 0 ^oC and ethylene gas was bubbled in through a glass tube until the color of the solution lightened. Concentration in vacuo afforded the title compound as a yellow oil (37.2 g; 91%). The product was used directly for the next step without further purification; ^1H NMR (300 MHz, $CDCl_3$) δ 6.83 (s, 1H), 3.84 (t, *J* = 7.3 Hz, 2H), 3.33 (t, *J* = 7.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.1, 42.5, 73.9 (d, *J* = 12.6 Hz).

CH_2=$CHSO_2CHCl_2$

Dichloromethanesulfonylethene (3b). *m*-Chloroperbenzoic acid (77 %, 27 g, 120 mmol) was added to a solution of 1-chloro-2-dichloromethanesulfanylethane (9.0 g, 50 mole) in CH_2Cl_2 (200 mL) over 30 min at 20 °C and the mixture was stirred for 16 h. The colorless precipitate was removed by filtration The filtrate was concentrated and the residue chromatographed (silica gel; 6:1 hexane/EtOAc). The so-purified 1-chloro-2-(dichloromethanesulfonyl)ethane was dissolved in CH_2Cl_2 (200 mL), mixed with 1.1 eq. of aqueous $NaHCO_3$ (excess $NaHCO_3$ is detrimental) and stirred for 16 h. The mixture was washed with H_2O (2 × 100 mL) and brine (2 × 100 mL), dried (Na_2SO_4), concentrated in vacuo, and chromatographed (silica gel; 5:1 hexane/EtOAc) to afford the title compound as a low melting solid, mp 50-51 °C (7.5 g, 86%); see footnote 8 for nmr data; IR ($CHCl_3$) 1145, 1348 cm^{-1} (SO_2), 948, 3020 cm^{-1} (C=C). Anal. Calcd. for $C_3H_4Cl_2O_2S$: C, 20.59; H, 2.30. Found: C, 20.46; H, 2.07.

CH_2=CHSCH_2Cl

Chloromethanesulfanylethene (11). Triisopropylsilanol (0.1 mL, 0.5 mmol) was added to a slurry of pulverized KOH (6.93 g, 0.12 mole) in tetraethyleneglycol dimethyl ether (150 mL) and the mixture was stirred at room temperature for 1 h. 1-Chloro-2-chloromethanesulfanylethane (2.91 g, 59 mmol) was added to the mixture and the color changed from yellow to dark brown. The mixture was stirred at 20 °C until the starting material had disappeared as indicated by TLC (7:1 hexane/EtOAc, ca. 1.5 h). The mixture was then distilled into a liquid nitrogen cooled trap (0.02 Torr). The title compound was separated as a colorless oil from the colorless precipitate using a syringe (4.38 g, 69 %). See footnote 8 for spectroscopic data.

ClCH_2SCHClCH_2SCH_2Cl

1-Chloro-1,2-bis(chloromethanesulfanyl)ethane (12). Chloromethanesulfanylethene (3.03 g, 28 mmol) was added to ClCH_2SCl (3.28 g, 28 mmol) in CH_2Cl_2 (50 mL) at 0 ^oC. The reaction mixture was stirred at room temperature for 1 h and concentrated in vacuo affording the title compound as a yellow oil (5.78 *g*, 96 %). The product was used directly without further purification; ^{1}H NMR δ 5.53 (t, *J* = 6.5 Hz, 1H), 4.98 and 4.80 (AB_q, *J* = 11.2 Hz, 2H), 4.78 (s, 2H), 3.41 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR: δ 64.4, 49.3, 46.7, 38.9; GC-MS *m/z* (rel. inten.), 227 (M^+, ^{37}Cl, 10), 225 (M^+, ^{35}Cl, 29), 108 (94), 97 (43), 95 (100).

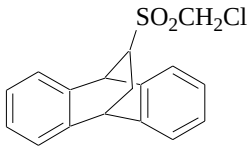
ClCH_2SCH=CHSCH_2Cl

(*E*,*Z*)-1,2-Bis(chloromethanesulfanyl)ethene (13). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 1.66 mL, 11 mmol) was added to a solution of 1,2-bis(chloromethanesulfanyl)-1-chloroethane (1.42 g, 5.5 mmol) in $CHCl_3$ (50 mL) at 0 ^oC and the reaction mixture was heated to reflux for 1 h. The reaction progress was monitored by GC. The organic layer was washed with 0.5 N HCl (2 × 25 mL), $NaHCO_3$ solution (2 × 25 mL), brine (2 × 25 mL), dried (Na_2SO_4) and concentrated in

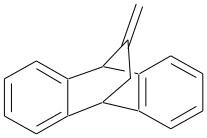
vacuo. Distillation gave the title compound as a light yellow oil (0.61 g, 58 %; *E/Z* 1.3/1). See footnote 8 for spectroscopic data.

$ClCH_2SO_2CH=CHSO_2CH_2Cl$

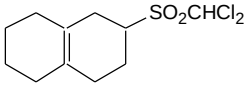
(*E,Z*)-1,2-Bis(chloromethanesulfonyl)ethene ((E,Z)-**4)**. Dimethyldioxirane (100 mL, 0.09 M) was added to a solution of 1,2-bis(chloromethanesulfanyl)ethene (0.4 g, 2.1 mmol) in $CHCl_3$ (5 mL) at room temperature and the reaction mixture was stirred at room temperature overnight. The resulting mixture was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was subjected to column chromatography (hexanes/EtOAc 3/2) affording both the (*E*)-isomer (R_f 0.8, 0.15 g, 28 %) and the (*Z*)-isomer (R_f 0.6, 0.11 g, 20 %) as colorless solids. (*E*)-1,2-bis(chloromethanesulfonyl)ethene: Anal. Calcd. for $C_4H_6Cl_2O_4S_2$: C, 18.98; H, 2.39. Found: C, 19.37; H, 2.06. See footnote 8 for additional physical and spectroscopic data.



3-Chloromethanesulfonyldibenzobicyclo[2.2.2]octadiene. A mixture of anthracene (1.35 g, 7.14 mmol) and chloromethanesulfonylethene (0.5 g, 3.57 mmol) in toluene (1.5 mL) was heated in a sealed tube at 155 ^oC for 7 h. The reaction mixture was taken up in $CHCl_3$ (30 mL), anthracene (0.15 g) was removed by filtration, the filtrate was concentrated in vacuo and the residue chromatographed (1:1 pentane/$CHCl_3$, then $CHCl_3$) gave the title compound as a colorless solid (1.12 g, 96 %), mp 143-145 ^oC; IR (film) 1322 (SO_2), 1146 (SO_2), 1118 (SO_2) cm^{-1}; ^1H NMR δ 7.46-7.16 (m, 8H), 5.00 (d, *J* = 2.1 Hz, 1H), 4.86 (*t*, *J* = 2.7 Hz, 1H), 4.16 (AB_q, *J* = 12.7, 2H), 3.74 (ddd, *J* = 2.4, 6.3, 9.3 Hz, 1H), 2.30-2.26 (m, 2H); ^{13}C NMR δ 143.3, 143.2, 140.9, 137.9, 127.1, 127.1, 126.6, 126.5, 125.6, 124.0, 124.0, 123.6, 59.5, 55.6, 43.5, 43.3, 30.2; Anal. Calcd for $C_{17}H_{15}ClO_2S$: C, 64.04; H, 4.74. Found C, 63.69; H, 4.98.



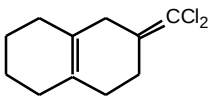
3-Methylenedibenzobicyclo[2.2.2]octadiene. A solution of *t*-BuOK in THF (4.08 mL, 4.08 mmol, 1 M) was added to 3-chloromethanesulfonyldibenzobicyclo[2.2.2]octadiene (0.67 g, 2.04 mmol) in THF (10 mL) at 0 ^{o}C. The reaction mixture was heated at reflux for 1 h, concentrated in vacuo, and the residue was treated with ether (20 mL) and water (20 mL). The aqueous layer was extracted with ether (2 × 20 mL), organic phase washed with water (2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo, affording the known[10b] title compound as colorless crystals (0.39 g, 89 %), mp 104-105 ^{o}C (lit. mp 101-10 2^{o}C[10b]); ^{1}H NMR δ 7.51-7.29 (m, 8H), 5.35 (br s, 1H), 4.94 (d, *J* = 10.2 Hz, 2H), 4.55 (m, 1H), 2.65 (m, 2H); ^{13}C NMR δ 146.5, 143.4, 142.5, 126.2, 123.7, 123.6, 107.4, 107.4, 55.5, 45.0, 35.4; GC *m/z* (rel. inten.) 218 (M^{+}, 28), 178 (100).



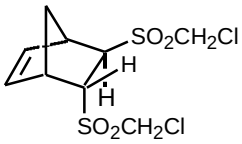
2-Dichloromethanesulfonyl-1,2,3,4,5,6,7,8-octahydronaphthalene. A solution of dichloro-methanesulfonylethene (1.0 g, 5.7 mmol) and 1,2-dimethylenecyclohexane (1.23 g, 11.4 mmol) in toluene (2 mL) was heated to 80-100 ^{o}C in a sealed tube overnight. The mixture was then concentrated in vacuo and chromatographed (silica gel; 5:1 hexane/EtOAc) yielding the title compound (1.52 g, 94%) as colorless crystals, mp 91-93 ^{o}C.; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40- 1.52 (m, 2 H), 1.62-1.75 (m, 2 H), 1.80-1.90 (m, 5 H), 2.03-2.11 (m, 2H), 2.15-2.30 (m, 2 H), 2.42 (t, *J* = 12.6 Hz, 1 H), 3.75-3.85 (m, 1 H), 6.27 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 22.8, 29.1, 29.8, 30.0, 55.5, 124.5, 128.4; IR ($CHCl_3$) 1140, 1322 cm^{-1} (SO_2). Anal. Calcd. for $C_{11}H_{16}Cl_2O_2S$: C, 46.65; H, 5.69. Found: C, 46.81; H, 5.32.

$CH_3SO_2CCl_3$

Methyl Trichloromethyl Sulfone. Dimethyl sulfone (1.5 g, 15.9 mmol) and SO_2Cl_2 (150 mL) were placed in a photoreactor fitted with a Hanovia 450 watt UV lamp, wrapped with nichrome heating wire, and containing at the bottom a gas bubbling tube and topped by a condenser. The mixture was electrically heated to a gentle reflux as Cl_2 was slowly introduced. The refluxing solution was irradiated for 2.5 h while monitoring TLC. The mixture was then concentrated in vacuo, collecting the SO_2Cl_2 for further use. The residue was chromatographed (silica gel; 5:1 hexane/EtOAc) giving the known[11] title compound as colorless crystals (2.86 g, 91 %), mp 163-165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.35 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.4, 103.1.



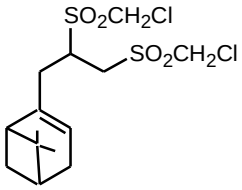
2-Dichloromethylene-1,2,3,4,5,6,7,8-octahydronaphthalene. A solution of 2-dichloromethanesulfonyl-1,2,3,4,5,6,7,8-octahydronaphthalene (566 mg, 2.0 mmol) and trichloromethanesulfonylmethane (742 mg, 4.0 mmol) in THF (15 mL) was cooled to 0 ^{o}C under Ar. A solution of KO*t*Bu in THF (1 M, 4.0 mL, 4.0 mmol) was added dropwise. The reaction mixture was stirred for 1 h at 0 ^{o}C and was quenched with saturated aqueous NH_4Cl. The mixture was extracted with ether (2 × 20 mL), dried ($MgSO_4$), concentrated in vacuo and chromatographed (silica gel; hexane) yielding the title compound (150 mg, 65%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59-1.63 (m, 4 H), 1.83-1.88 (m, 4 H), 2.02 (t, *J* = 6.5 Hz, 2 H), 2.51 (t, *J* = 6.5 Hz, 2 H), 2.79 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 28.5, 29.7, 29.8, 29.9, 30.4, 35.7, 111.6, 125.7, 128.4, 135.5. EIMS: *m/z* 218 (M^+ + 2, 62), 216 (M^+, 93), 181 (100), 145 (80), 117 (30), 91 (55). IR (neat): 715 cm^{-1} (CCl_2), 1643, 1664 cm^{-1} (C=C).



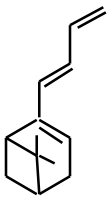
5-*exo*-6-*endo*-Bis(chloromethanesulfonyl)bicyclo[2.2.1]hept-2-ene (15a). Freshly distilled cyclopentadiene (0.21 mL, 2.6 mmol) was added to a suspension of (*E*)-1,2-bis(chloromethanesulfonyl)ethene (0.33 g, 1.3 mmol) in CH_2Cl_2 (4 mL) and the reaction mixture was stirred at room temperature until a colorless clear solution was obtained (ca. 10 min). Concentration in vacuo followed by chromatography of the residue afforded the title compound as a colorless solid (0.35 g, 83 %), mp 144-145 ^oC; IR (film) 1322 (SO_2), 1149 (SO_2), 1121 (SO_2) cm^{-1}; ^1H NMR δ 6.44 (dd, *J* = 3.00, 5.4 Hz, 1H), 6.39 (dd, *J* = 3.00, 5.4 Hz, 1H), 4.75 (d, *J* = 8.4 Hz, 1H), 4.71 (d, *J* = 8.4 Hz, 1H), 4.57 (d, *J* = 12.6 Hz, 1H), 4.44 (dd, *J* = 3.3, 5.1 Hz, 1H), 4.42 (d, *J* = 12.6 Hz, 1H), 3.73 (dd, *J* = 2.1, 5.1 Hz, 1H), 3.52 (m, 2H), 2.03 and 1.71 (AB_q, *J* = 9.6 Hz, 2H); ^{13}C NMR δ 136.8, 136.2, 61.1, 60.5, 56.4, 56.2, 47.6, 46.6, 45.2. Anal. Calcd. for $C_9H_{12}Cl_2O_4S_2$: C, 33.86; H, 3.79. Found: C, 33.51; H, 3.09.

5-*endo*-6-*endo*-Bis(chloromethanesulfonyl)bicyclo[2.2.1]hept-2-ene (15b). Freshly distilled cyclopentadiene (0.1 mL, 1.2 mmol) was added to a suspension of (*Z*)-1,2-bis(chloromethanesulfonyl)ethene (0.15 g, 0.6 mmol) in CH_2Cl_2 (4 mL) and the reaction mixture was stirred at room temperature until a colorless clear solution was obtained (ca. 10 min). This was concentrated in vacuo, and the residue chromatographed (hexanes/EtOAc 5/1) affording the title compound as a colorless solid (0.16 g, 84 %), mp 184-186 ^oC; IR (film) 1331 (SO_2), 1152 (SO_2) cm^{-1}; ^1H NMR (acetone-d_6) δ 6.50 (m, 2H), 5.14 and 4.98 (AB_q, *J* = 12.6 Hz, 4H), 4.79 (m, 2H), 3.82 (m, 2H),

1.76 and 1.65 (AB_q, J = 9.0 Hz, 2H); ^{13}C NMR (acetone-d_6) δ 130.9, 60.3, 53.4, 43.7, 42.8. Anal. Calcd. for $C_9H_{12}Cl_2O_4S_2$: C, 33.86; H, 3.79. Found: C, 33.72; H, 3.48.



2-(1,2-Bis(chloromethanesulfonyl)ethyl-6,6-dimethylbicyclo[3.1.1]hept-2-ene (18) . A mixture of **(***E*)-1,2-bis(chloromethanesulfonyl)ethene (0.57 g, 2.25 mmol) and β-pinene (0.64 g, 4.67 mmol) in toluene (1.5 mL) were placed in a sealed tube and flushed with argon. The white slurry was heated at 135 ^{o}C for 1.5 h, concentrated in vacuo (60 ^{o}C), and the residue chromatographed (hexanes/EtOAc 5/1) yielding the title compound as a colorless solid (0.63 g, 72 %), mp 108-110 ^{o}C; IR (film) 1323 (SO_2), 1122 (SO_2) cm^{-1}; ^{1}H NMR δ 5.09-5.51 (m, 1H), 4.63 and 4.77 (AB_q, J = 12.6 Hz, 2H), 4.45 and 4.77 (AB_q, J = 12.6 Hz, 2H), 4.01-4.13 (m, 2H), 3.29-3.35 (m, 1H), 2.74-2.82 (m, 1H), 2.40-2.50 (m, 2H), 2.26-2.28 (m, 2H), 2.01-2.12 (m, 2H), 1.88 (s, 3H), 1.15 (d, J = 9 Hz, 1H), 0.83 (s, 3H); ^{13}C NMR δ 141.9, 123.1, 57.2, 55.9, 52.0, 47.6, 45.3, 40.3, 38.2, 36.5, 31.7, 31.5, 26.0, 21.1; Anal. Calcd. for $C_9H_{12}Cl_2O_4S_2$: C, 43.29; H, 5.70. Found: C, 43.39; H,5.78.



(*E*)-2-Buta-1,3-dienyl-6,6-dimethyl-bicyclo[3.3.1]hept-2-ene (20) . A solution of *t*-BuOK in THF (3.1 mL, 3.1 mmol, 1 M) was added to β-pinene adduct (0.57 g, 1.46 mmol) in THF (30 mL) at 0 ^{o}C. The reaction mixture was heated to reflux for 1 h. The reaction was quenched with NH_4Cl solution and extracted with $CHCl_3$ (5 × 30 mL). The organic layer was

washed with brine (2 × 30 mL), dried ($MgSO_4$), concentrated in vacuo, and the residue was chromatographed (hexanes) yielding the title compound (30 mg, 12 %) as a colorless oil: ^{1}H NMR δ 6.39 (dd, *J* = 9.9, 16.8 Hz, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 6.01 (d, *J* = 15.6 Hz, 1H), 5.58 (s, 1H), 5.16 (d, *J* = 16.8 Hz, 1H), 5.01 (d, *J* = 9.9 Hz, 1H), 2.56 (m, 1H), 2.45-2.28 (m, 3H), 2.01 (m, 1H), 1.32 (s, 3H), 1.12 (d, *J* = 8.7 Hz, 1H), 0.78 (s, 3H); ^{13}C NMR δ 146.5, 137.7, 134.6, 125.9, 125.5, 115.9, 41.0, 37.8, 32.2, 31.4, 29.7, 26.4, 21.1; GC/MS (relative intensity) *m/z* 174 (M^+, 10), 131 (44), 91 (100), 77 (41); UV (CH_2Cl_2) λ_{max} 278 nm.

Elemental analysis for other Diels-Alder adducts

2-Chloromethanesulfonyl-1,2,3,4,5,6,7,8-octahydronaphthalene (Table 1, entry 4 Diels-Alder adduct). Calcd. for $C_{11}H_{17}ClO_2S$ C, 53.11; H, 6.89. Found, C, 52.78; H, 6.50.

2-Chloromethanesulfonyl-1,2,3,4,5,6,7,8,9,10-decahydroanthracene (Table 1, entry 5 Diels-Alder adduct): Calcd. for $C_{15}H_{21}ClO_2S$: C, 59.88; H, 7.04; Found: C, 60.16; H, 6.65.

4-(Dichloromethanesulfonyl)-1,2-dimethylcyclohexene (Table 1, entry 6 Diels-Alder adduct): Calcd for $C_9H_{14}Cl_2O_2S$: C, 42.03; H, 5.49. Found C, 42.21; H, 5.16.

5-(Dichloromethanesulfonyl)bicyclo[2.2.2]oct-2-ene (Table 1, entry 7 Diels-Alder adduct): Calcd. for $C_9H_{12}Cl_2O_2S$: C, 42.36; H, 4.74. Found: C, 42.41; H, 5.10.

5-*exo*-6-*endo*-Bis(chloromethanesulfonyl)bicyclo[2.2.1]hept-2-ene (**15a**): Calcd. for $C_9H_{12}Cl_2O_4S_2$: C, 33.86; H, 3.79. Found: C, 33.51; H, 3.09.

5-*endo*-6-*endo*-Bis(chloromethanesulfonyl)bicyclo[2.2.1]hept-2-ene (**15b**): Calcd. for $C_9H_{12}Cl_2O_4S_2$: C, 33.86; H, 3.79. Found: C, 33.72; H, 3.48.