0.32 mol) was added as a liquid to 190 g of frozen benzene solution containing 14.5 g of thiocyanogen and 0.8 g of catalyst at −80°. After heating for 2 hr at 40–54°, under a nitrogen pressure of 625 psi, venting, and removal of solvent, the residue was extracted with methylene chloride to provide a 57% overall yield of crystalline FET, mp 35.5–36° (from ethanol).

Anal. Calcd for $C_4H_3FN_2S_2$: C, 29.62; H, 1.86; F, 11.71; N, 17.28; S, 39.53. Found: C, 29.65; H, 1.57; F, 11.4; N, 17.08; S, 39.19.

Spectra.—The three haloalkylene bisthiocyanates had mostly similar ir spectra with the following bands in common: 2900 (s), 2150–2160 (s, sharp),[11] 1415–1425 (s), 1245 (s), 1150 (m), 900 (s), and 408 cm^{-1} (w). Distinctive bands were seen at 1300 (m), 1010 (m), and 632 cm^{-1} (m) for FET, 702 cm^{-1} (m) for CET, and 660 cm^{-1} (m) for BET.

CET had a weak absorption band in the near-ultraviolet region [ϵ_{243} 151 (in methanol)].

The nmr spectra were all consistent with the proposed structures. For BET and CET, the CH_2's were equivalent, giving only a doublet; the CH was a triplet. FET showed an extra coupling from the fluorine, so that the CH was a doubled triplet, and the CH_2 showed a slight nonequivalence. The CH and CH_2 peak positions and $CHCH_2$ couplings (absolute values) were as follows: BET, δ 5.27, 3.79 (J = 7.0 Hz); CET, δ 5.36, 3.70 (J = 6.7 Hz); FET, δ 6.10, ~3.63 (J = 6.0 Hz). In addition, for FET the CHF coupling was 47.2 Hz.

Registry No.—Thiocyanogen, 505-14-6; CET, 24689-89-2; BET, 26799-59-7; FET, 26799-60-0.

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(11) Organic thiocyanates (RSCN) show a medium–strong sharp ir band at 2170–2135 cm^{-1} caused by the C≡N stretch vibration. Organic isothiocyanates (RNCS) have a very strong broader ir band at 2150–2050 cm^{-1} caused by the out-of-phase N=C=S vibration. See N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 201.

Preparation of the Diels–Alder Adducts of Methyl Vinyl Sulfone and Cyclopentadiene and of Their Dihydro Derivatives[1]

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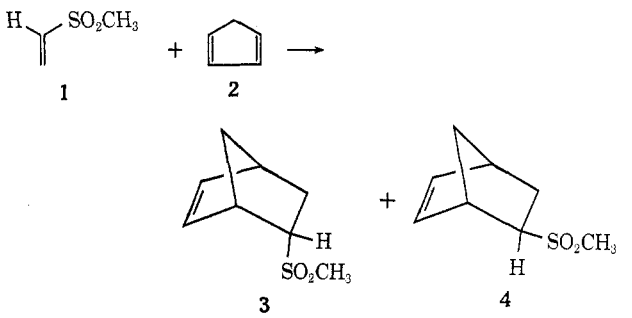
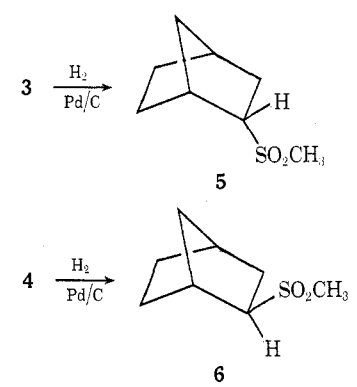
In the course of another problem[2] a need arose for relatively large quantities of the Diels–Alder adducts of methyl vinyl sulfone and cyclopentadiene and the corresponding dihydro derivatives and for a knowledge of the respective stereochemistries in each series. The methyl vinyl sulfone–cyclopentadiene reaction was investigated previously by Snyder,[3] but mention was made only of one adduct isomer, mp 55–56°, and no data or speculation concerning its stereochemistry were reported. Also, the addition of methyl mercaptan to norbornene followed by hydrogen peroxide oxidation has been reported by Davies[4] to afford only *exo*-2-methylsulfonylbicyclo[2.2.1]heptane.

The ambient temperature reaction of methyl vinyl sulfone (**1**)[5] with cyclopentadiene (**2**) was monitored by means of nmr, and the formation of two cycloadducts **3** and **4** was observed. Chromatography on silica gel



afforded pure samples of each isomer. In accord with the endo rule[6] and on the basis of chemical shift data, the structure of the major cycloadduct, mp 55–55.5°, was assigned to the *endo*-methylsulfonyl isomer **3**. The $-SO_2CH_3$ nmr absorption of **3** is observed at a higher field than the corresponding absorption of the minor cycloadduct **4**, mp 41.5–42.5°. The shielding of endo protons or of protons attached to endo functional groups in bicyclo[2.2.1]hept-2-enes and inversely the deshielding of exo protons or of protons attached to exo functional groups are well-recognized phenomena.[7] However, care should be taken to ensure that these effects are due predominantly to the anisotropy of the double bond and not to that of the 5–8 σ bond.[8] Thus, removal of the double bond by hydrogenation should result in a downfield shift for the *endo*-methylsulfonyl hydrogens and an upfield shift for the *exo*-methylsulfonyl hydrogens.[7,8] The expected chemical shifts were indeed observed as can be seen in Table I. Further confirmation of the above structural assignments was obtained by comparison of the *exo*-methylsulfonyl isomer **6** with authentic material.[4] The two sulfones were identical in all respects.



(1) Grants from The Research Corp. and The Petroleum Research Fund, administered by The American Chemical Society, are gratefully acknowledged.

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TABLE I
CHEMICAL SHIFT VALUES

Compd no.	$\delta_{TMS}^{CDCl_3}$ (SO_2CH_3)[a]
3	2.798 ± 0.002
5	2.831 ± 0.002
4	2.897 ± 0.002
6	2.814 ± 0.002

[a] Chemical shifts were obtained from average line frequencies and calibrated by the side-band method with the aid of a Hewlett-Packard Model 4204A audiooscillator and a Model 5216A frequency counter.

It is of interest to note that **6** is reported to fail to undergo potassium *tert*-butoxide induced epimerization.[4] We have confirmed this observation and have noted that **5** may be converted readily into **6** under these conditions. While **6** cannot be epimerized, both its methine and methyl hydrogens α to the sulfone moiety readily undergo deuterium exchange.

Thus pure **6** is available *via* the Davies route[4] or *via* cycloaddition of methyl vinyl sulfone with cyclopentadiene followed by hydrogenation of the mixture of **3** and **4** and subsequent epimerization, and pure **5** may be prepared by hydrogenation of pure **3**.

The ease of epimerization of **5** led us to examine the similar reaction with the unsaturated isomers **3** and **4**. Treatment of either isomer with potassium *tert*-butoxide in *tert*-butyl alcohol afforded the identical mixture containing 79 ± 2% of **4** and 21 ± 2% of **3**. Thus **3**, the major product of the Diels–Alder reaction, may be crystallized from the crude reaction mixture, and the minor isomer **4** may be obtained by direct chromatography of the crude mixture or of an enriched mixture obtained by epimerization.

Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Model 475 spectrometer. Nmr spectra were measured at 60 Mc using tetramethylsilane as an internal standard unless otherwise stated. All microanalyses were determined by MHW Laboratories, Garden City, Mich., except for the deuterium analysis, which was determined by Mr. Josef Nemeth, Department of Chemistry, University of Illinois.

***endo*- and *exo*-5-Methylsulfonylbicyclo[2.2.1]hept-2-ene (3 and 4).**—To a magnetically stirred solution of 1.70 g (25.7 mmol) of cyclopentadiene in 50 ml of carbon tetrachloride was added 2.65 g (25.0 mmol) of methyl vinyl sulfone. The reaction vessel was sealed, and the mixture was stirred for 4 days at ambient temperature. The solvent was removed to yield 4.22 g of a viscous pale yellow oil. The crude adduct was triturated with 20 ml of petroleum ether (bp 30–60°) to give 3.98 g (23.1 mmol, 92.4%) of a semisolid mixture of the two epimers. This mixture was chromatographed on silica gel with increasing percentages of ether–petroleum ether to give 1.06 g (28% of the mixture) of *exo*-5-methylsulfonylbicyclo[2.2.1]hept-2-ene, a colorless viscous oil, bp 94.5° (0.10 mm), which subsequently solidified, mp 40.5–41.5°. Recrystallization from chloroform–*n*-hexane gave white plates: mp 41.5–42.5°; $\nu_{max}^{CCl_4}$ strong 1318 and 1141 cm^{-1} (SO_2); weak 3065 (HC=C), 2985, 1337, and 1296 cm^{-1}; near-ir λ_{max}^{EtOH} 1.657 μ (ϵ 0.637); $\delta_{TMS}^{CDCl_3}$ 1.30–2.30 (m, 4, methylene), 2.65–2.95 (m, 1, $>CHSO_2CH_3$), 2.897 (s, 3, SO_2CH_3), 2.90–3.18 (m, 1, bridgehead), 3.20–3.40 (m, 1, bridgehead), 6.02–6.40 (seven-line pattern, 2, HC=CH).

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.79; H, 7.02; S, 18.61. Found: C, 55.69; H, 6.97; S, 18.50.

Further elution of the column gave 2.79 g (72% of the mixture) of *endo*-5-methylsulfonylbicyclo[2.2.1]hept-2-ene as white crystals, mp 54–55°. Recrystallization from chloroform–*n*-hexane gave white plates: mp 55.0–55.5° (lit.[3] mp 55–56°); $\nu_{max}^{CCl_4}$ strong 1321 (with a shoulder at 1316, SO_2) and 1143 cm^{-1} (SO_2); weak 3065 (HC=C), 1337, 1286, and 1124 cm^{-1}; near-ir λ_{max}^{EtOH} 1.657 μ (ϵ 0.569); $\delta_{TMS}^{CDCl_3}$ 1.17–2.40 (m, 4, methylene), 2.798 (s, 3, SO_2CH_3), 2.90–3.17 (m, 1, bridgehead), 3.20–3.45 (m, 1, bridgehead), 3.40–3.75 (m, 1, $>CHSO_2CH_3$), 5.97–6.40 (eight-line pattern, 2, HC=CH).

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.79; H, 7.02; S, 18.61. Found: C, 55.90; H, 6.99; S, 18.60.

Hydrogenation of *endo*- and *exo*-5-Methylsulfonylbicyclo[2.2.1]hept-2-ene.—A solution of 500 mg (2.91 mmol) of *endo*-5-methylsulfonylbicyclo[2.2.1]hept-2-ene in 30 ml of ethyl acetate was hydrogenated over 10% palladium on powdered charcoal (30 psi) at ambient temperature for 1 hr. The catalyst was removed by filtration, and the solvent was evaporated to afford 490 mg (2.81 mmol, 96.9%) of white crystals, mp 72–74°. Recrystallization from carbon tetrachloride–*n*-hexane gave *endo*-2-methylsulfonylbicyclo[2.2.1]heptane as white plates: mp 73–75°; $\nu_{max}^{CCl_4}$ strong 1328, 1315, and 1148 cm^{-1}; medium 2970 cm^{-1}; weak 2882, 1279, and 1119 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 1.17–2.60 (m, 9, methylene and bridgehead), 2.61–2.90 (m, 1, bridgehead), 2.831 (s, 3, SO_2CH_3), 3.11–3.58 (m, 1, $>CHSO_2CH_3$).

Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10; S, 18.40. Found: C, 55.03; H, 8.10; S, 18.30.

The same procedure was carried out using the *exo*-methylsulfonyl isomer to give 0.5 g (2.87 mmol, 95.3%) of white crystals, mp 71–72°. Recrystallization from carbon tetrachloride–*n*-hexane gave *exo*-2-methylsulfonylbicyclo[2.2.1]heptane as white crystals: mp 75–76.5° (lit.[4] mp 75°); $\nu_{max}^{CCl_4}$ strong 1322, 1316, and 1147 cm^{-1}; medium 2968 and 1332 cm^{-1}; weak 2880, 1277, 1161, and 947 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 1.02–2.29 (m, 8, methylene), 2.29–2.57 (m, 1, bridgehead), 2.814 (s, 3, SO_2CH_3), 2.66–3.11 (m, 2, bridgehead and $>CHSO_2CH_3$).

Deuteration of *exo*-2-Methylsulfonylbicyclo[2.2.1]heptane.—A mixture of 1.00 g (5.74 mmol) of *exo*-2-methylsulfonylbicyclo[2.2.1]heptane, 35 ml of 10% sodium deuterioxide in deuterium oxide, and 10 ml of tetrahydrofuran was refluxed for 6 days under a nitrogen atmosphere. The tetrahydrofuran was evaporated, and the residual solution was extracted with chloroform. The chloroform layer was washed with deuterium oxide and dried over anhydrous magnesium sulfate. Removal of the solvent afforded 0.812 g (4.55 mmol, 79.3%) of pale yellow oil, which subsequently solidified. The crude product, on recrystallization from chloroform–*n*-hexane, afforded 0.742 g (4.16 mmol, 72.5%) of *endo*-2-deuterio-2-trideuteriomethylsulfonylbicyclo[2.2.1]heptane as white plates: mp 79.5–80.5°; $\nu_{max}^{CCl_4}$ strong 1312 and 1146 cm^{-1}; medium 2965, 1158, and 696 cm^{-1}; weak 2878 and 1297 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 1.00–2.26 (m, 8, methylene), 2.30–2.60 (m, 1, bridgehead), 2.67–2.92 (m, 1, bridgehead).

Anal. Calcd for $C_8H_{10}D_4O_2S$: 28.6 atom % excess D. Found: 27.9 atom % excess D.

Base-Catalyzed Epimerization of *endo*- and *exo*-2-Methylsulfonylbicyclo[2.2.1]heptane (5 and 6).—To a solution of 300 mg (1.72 mmol) of *endo*-2-methylsulfonylbicyclo[2.2.1]heptane in 10 ml of dry *tert*-butyl alcohol was added 20 ml of 0.60 *N* potassium *tert*-butoxide in *tert*-butyl alcohol. The solution was refluxed for 24 hr and then quenched with water. After removal of the *tert*-butyl alcohol, the aqueous mixture was extracted with chloroform. Evaporation of the solvent afforded 274 mg (1.57 mmol, 91.4%) of pale yellow crystals. Comparison of nmr and ir spectra and a mixture melting point determination indicated that the product was exclusively the *exo*-methylsulfonyl isomer. The same procedure using 300 mg (1.72 mmol) of the exo isomer gave 282 mg (1.62 mmol, 94.0%) of the starting sulfone.

Base-Catalyzed Epimerization of *endo*- and *exo*-5-Methylsulfonylbicyclo[2.2.1]hept-2-ene (3 and 4).—Under a nitrogen atmosphere a solution of 300 mg (1.74 mmol) of *endo*-5-methylsulfonylbicyclo[2.2.1]hept-2-ene in 10 ml of 0.60 *N* potassium *tert*-butoxide in *tert*-butyl alcohol was refluxed for 7 days and then quenched with water. After removal of the *tert*-butyl alcohol by rotary evaporation, the aqueous mixture was extracted with chloroform. The chloroform layer was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded 214 mg (1.24 mmol, 71.3%) of a pale yellow oil consisting of 79 ± 2% *exo*- and 21 ± 2% *endo*-methylsulfonyl isomers.

Registry No.—**1**, 3680-02-2; **2**, 542-92-7; **3**, 35495-35-3; **4**, 35495-36-4; **5**, 36736-13-7; **6**, 24584-19-8; *endo*-2-deuterio-2-trideuteriomethylsulfonylbicyclo[2.2.1]heptane, 36736-15-9.