

TABLE II

Compd	Bp, °C (mm)	n_D	C, %		H, %	
			Calcd	Found	Calcd	Found
I	...	n_D^{25} 1.4980	90.42	90.08	9.58	9.75
II	52-53 (1)	n_D^{26} 1.5132	90.01	89.87	9.99	10.75
III	57-58 (5)	n_D^{24} 1.5030	90.42	90.11	9.58	9.84
IV	72-73 (5)	n_D^{26} 1.5233	90.42	90.03	9.58	9.94
V ^a	80-82 (1)	n_D^{26} \geq 1.530	91.32	90.98	8.68	8.71

^a 92% pure stereoisomer.

protons of the double bond (a) and that at τ 7.76 (4 H) to the four protons adjacent to it (b). The signals at τ 8.26 (2 H), 8.43 (1 H), 8.75 (2 H), and 9.03-9.19 (3 H) may be attributed to the c, d, and e protons and to those of the cyclopropane ring, respectively. The ir spectrum shows absorption bands at 687, 1665 (*cis* internal double bonds), 785, and 813 cm^{-1} (nortricyclene).

The mass spectrum of the new NBD dimer shows a parent peak at m/e 184. The nmr spectrum of this compound (92% pure,¹⁶ Figure 1e) exhibits a signal at τ 4.03 (2 H) and a multiplet at τ 8.97-9.18 (3 H), which may be assigned respectively to the *cis* internal double bond and to the nortricyclene system. The ir bands (795, 810, 814, 822, 1319, and 1563 cm^{-1}) are in agreement with the presence of norbornene and nortricyclene groups.

The complexity of the nmr spectra of the new compounds precludes an assignment of their stereostructures.

Experimental Section

Reagents.—Ethyl ether and benzene were dried by distillation from LiAlH_4 and stored under nitrogen. Butadiene (Phillips special purity) was drawn from the gaseous phase and used without any further purification. Dimethylallene and norbornadiene (Fluka, purum) and bis(diphenylphosphine)ethane (Strem) were used as supplied. (*i*- C_3H_7) MgCl was prepared according to Grignard technique from 2-chloropropane and Mg turnings. AlEt_2Cl (Fluka, practicum) was used as received.

Oligomerizations.—The reactions were carried out under nitrogen in glass vials.

In a typical run, the reagents were introduced into the vial, cooled to -78° , in the following order: iron compound, bisphosphine (when used), acyclic diene (when used), norbornadiene, and the organometallic compound. A small amount of *n*-decane was also added as internal standard for the subsequent chromatographic analysis.

Oligomerizations with $\text{Fe}(\text{COT})_2^4$ were carried out by dissolving the Fe compound directly in the liquid monomers.

The sealed vial was maintained in a thermostated bath for the time indicated in Table I. The reaction product was diluted with ether, washed with dilute HCl and water, and finely dried over K_2CO_3 .

Characterization of the Compounds.—After the quantitative chromatographic analysis of the crude reaction product (Perkin-Elmer 800, methylsilicone SE 30, programmed temperature, He), fractional distillation and isolation of the pure products were accomplished on the enriched fractions by preparative vpc (*C. Erba P*, tricyanoethoxypropane, 170° , He for I, apiezon, programmed temperature for the others).

Spectroscopic characterizations were: ir spectroscopy (Perkin-Elmer 125, NaCl); nmr spectroscopy (Varian HA, 100 Mcps, room temperature, CCl_4 or C_6D_6 solvents, TMS as internal standard); and mass spectroscopy (72 eV). Table II reports the elemental analysis, boiling points, and n_D values of all new compounds.

(16) The remaining product consists of the known "major" dimer,¹¹ which shows small peaks in the nmr spectrum (Figure 1e) at τ 3.95, 8.08 and 8.74.

Registry No.—NBD, 121-46-0; BD, 106-99-0 DMA, 513-35-9; I, 22158-36-7; II, 22158-37-8; III 22158-38-9; IV, 22158-39-0; V, 7781-74-0.

The Preparation of 2,3,5,6-Tetrakis(methylthio)norbornane by Degradation of a Metal Complex of Norbornadiene with Dimethyl Disulfide

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Iron carbonyl complexes of the type $[\text{RSFe}(\text{CO})_3]_2$ are readily obtained by heating $\text{Fe}_3(\text{CO})_{12}$ with dialkyl disulfides.² In an attempt to prepare a chromium complex of a similar type, the reaction between norbornadienetetracarbonylchromium (I) and dimethyl disulfide in boiling methylcyclohexane was investigated. Instead of the desired chromium carbonyl complex, a white, air-stable, sublimable, metal-free derivative of composition $\text{C}_7\text{H}_8(\text{SCH}_3)_4$ was obtained. Evidently, the dimethyl disulfide removed the norbornadiene ligand from the chromium carbonyl complex I in a manner similar to the bromination of π -cyclobutadiene and π -cyclopentadienyl metal complexes to give 1,2,3,4-tetrabromocyclobutane³ and 1,2,3,4,5-pentabromocyclopentane,⁴ respectively.

The proton nmr spectrum of $\text{C}_7\text{H}_8(\text{SCH}_3)_4$ clearly indicated it to be the substituted norbornane derivative II. The resonances at τ 7.06, 7.62, 7.82, and 8.15 may be assigned to the four *equivalent* protons of the two two-carbon bridges, the two bridgehead protons, the 12 protons of the four equivalent methylthio groups, and the two protons of the one one-carbon bridge, respectively. The singlet resonance from the four equivalent protons of the two two-carbon bridges permits unambiguous identification of the reaction product as the all-*exo* isomer II, since coupling between the *exo* protons and the bridgehead protons of the all-

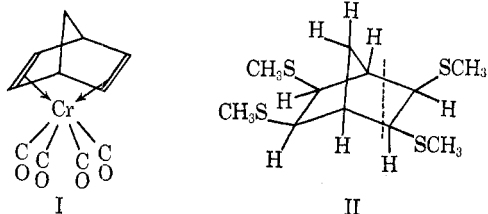
(1) Fellow of the Alfred P. Sloan Foundation, 1967-1969.

(2) R. B. King, *J. Amer. Chem. Soc.*, **84**, 2460 (1962), and references cited therein.

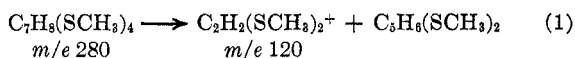
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(4) A. N. Nesmeyanov, E. G. Perevalova, and V. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **100**, 1099 (1955); R. B. King and K. H. Pannell, *J. Amer. Chem. Soc.*, **90**, 3984 (1968).

ternative all-endo isomer is expected to be about 4 cps on the basis of comparison with previously reported nmr data on other norbornane derivatives.⁵



The mass spectrum of II exhibited an intense parent molecular ion at m/e 280. This underwent fragmentation by several parallel pathways, including not only losses of neutral CH_3 and CH_3SH fragments and the formation of $\text{C}_5\text{H}_5(\text{SCH}_3)_2^+$ like other norbornane derivatives⁶ but also the following more unusual process (eq 1). This process appears to involve cleavage of



metastable ion: m/e 51.3 ($120^2/280 = 51.4$)

similar bonds (dotted lines in structure II) to the retro Diels-Alder fragmentations previously reported⁶ in the mass spectra of various derivatives of norbornadiene, norbornene, and benzonorbornene, but not generally in derivatives of norbornane, which cannot be formed by Diels-Alder reactions. This anomalous "pseudo retro Diels-Alder" fragmentation in the mass spectrum of II may occur because of the stabilization of the unsaturated product ion $\text{C}_2\text{H}_2(\text{SCH}_3)_2^+$ by overlap of the filled π orbitals of the C_2H_2 carbon atoms with the empty d orbitals of the sulfur atoms.

The preparation of II from the nonbornadiene complex I described in this note suggests that degradation of norbornadiene-metal carbonyl derivatives in various ways may provide routes to novel norbornane derivatives not readily accessible by more conventional synthetic techniques. Several attempts to prepare II by boiling various mixtures of norbornadiene and dimethyl disulfide failed even when catalytic amounts of iron pentacarbonyl were added.

Experimental Section

Preparation of 2,3,5,6-Tetrakis(methylthio)norbornane (II).—A mixture of 1.0 g (3.9 mmol) of norbornadienetetracarboxylchromium (I),⁷ 2.0 ml (2.1 g, 22.4 mmol) of dimethyl disulfide, and 40 ml of methylcyclohexane was boiled under reflux for 24 hr in a nitrogen atmosphere. The reaction mixture was filtered hot and the filtrate was cooled to room temperature and finally in a -78° bath. The pale yellow crystals which separated were filtered and dried to give 0.438 g (40%) of 2,3,5,6-tetrakis(methylthio)norbornane (II). The pure white, analytical sample, mp $140-144^\circ$, was obtained by sublimation of some of this crude product at 110° (0.1 mm).

Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{S}_4$: C, 47.2; H, 7.1; S, 45.7; mol wt, 280. Found: C, 46.6; S, 46.8; mol wt, 280 (mass spectrum).

The infrared spectrum (KBr) showed absorption at 2950 (w) and 2885 (w) (both CH), 1450 (w), 1435 (m), 1415 (m), 1315 (m), 1300 (w), 1277 (w), 1270 (w), 1248 (w), 1175 (w), 1140 (vw), 1028 (vw), 1008 (vw), 976 (w), 961 (w), 950 (w), 921 (w), and 900 cm^{-1} (w).

(5) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(6) A. Tatematsu, Y. Hafa, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron*, **22**, 2213 (1966).

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The proton nmr spectrum was taken on a Varian A-60 spectrometer in CS_2 solution and showed absorption at τ 7.06 (s, $W_{1/2} \cong 3$ cps), 7.62 (apparent t, $J = 1.5$ cps), 7.82 (s), and 8.15 (br, $W_{1/2} \cong 5$ cps). The approximate relative intensities were 4:2:12:2, respectively.

The mass spectrum was taken on a Perkin-Elmer Hitachi RMU-6 mass spectrometer at 70 eV and a chamber temperature of 210° . It showed peaks at m/e (rel intensity, ion) 280 [100, $\text{C}_7\text{H}_8\text{S}_4(\text{CH}_3)_4^+$], 265 [17, $\text{C}_7\text{H}_8\text{S}_4(\text{CH}_3)_3^+$], 233 [10, $\text{C}_7\text{H}_8\text{S}_3(\text{CH}_3)_3^+$], 232 [13, $\text{C}_7\text{H}_7\text{S}_3(\text{CH}_3)_3^+$], 217 [12, $\text{C}_7\text{H}_7\text{S}_3(\text{CH}_3)_2^+$], 185 [52, $\text{C}_7\text{H}_7\text{S}_2(\text{CH}_3)_2^+$], 169 [11, $\text{C}_7\text{H}_6\text{S}_2\text{CH}_3^+$], 159 [12, $\text{C}_7\text{H}_5\text{S}_2(\text{CH}_3)_2^+$], 146 [13, $\text{C}_4\text{H}_4\text{S}_2(\text{CH}_3)_2^+$], 145 [12, $\text{C}_4\text{H}_3\text{S}_2(\text{CH}_3)_2^+$], 139 [21, $\text{C}_7\text{H}_8\text{SCH}_3^+$], 138 [27, $\text{C}_7\text{H}_7\text{SCH}_3^+$], 137 [94, $\text{C}_7\text{H}_6\text{SCH}_3^+$], 133 [21, $\text{C}_3\text{H}_3\text{S}_2(\text{CH}_3)_2^+$], 125 [23, $\text{C}_7\text{H}_7\text{S}^+$], 123 [48, $\text{C}_7\text{H}_6\text{S}^+$], 122 [99, $\text{C}_7\text{H}_6\text{S}^+$], 121 (ca. 100, $\text{CH}_3\text{SC}_2\text{H}_3\text{SCH}_3^+$), 120 [very intense (off scale), $\text{CH}_3\text{SC}_2\text{H}_2\text{SCH}_3^+$], 113 [52, $\text{C}_6\text{H}_6\text{SCH}_3^+$], 107 (ca. 140, $\text{CH}_3\text{SC}_2\text{H}_3\text{S}^+$), 105 [48, $\text{CH}_3\text{SC}_2\text{H}_2\text{S}^+$], 99 [25, $\text{C}_6\text{H}_7\text{S}^+$], 97 [64, $\text{C}_6\text{H}_6\text{S}^+$], 91 [95, C_7H_7^+], 87 [86, $\text{C}_4\text{H}_7\text{S}^+$], 85 [26, $\text{C}_6\text{H}_5\text{S}^+$], 79 [36, C_6H_7^+], 77 [37, C_6H_5^+], 73 [26, $\text{C}_3\text{H}_5\text{S}^+$], 67 [87, C_5H_7^+], 65 [67, C_5H_5^+], 61 [150, $\text{C}_2\text{H}_5\text{S}^+$], 47 [31, CH_3S^+], 45 [92, CH_3S^+], 41 [33, C_3H_5^+], and 39 [42, C_3H_3^+]. Metastable ions were observed at m/e 250.7 (280 \rightarrow 265), 192.9 (280 \rightarrow 232), 101.8 (185 \rightarrow 137), 51.3 (280 \rightarrow 120), and 39.8 (280 \rightarrow 105).

Registry No.—II, 22003-57-2.

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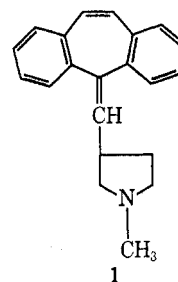
Nuclear Magnetic Resonance Spectra of 5-(1-Methyl-3-pyrrolidinylmethylene)-5H-dibenzo[a,d]cycloheptene

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Recently, Ebnöther, Jucker, and Stoll² showed the presence of atropisomerism in certain 5H-dibenzo[a,d]cycloheptene derivatives. We wish to report a similar observation of nmr spectroscopy studies on 5-(1-methyl-3-pyrrolidinylmethylene)-5H-dibenzo[a,d]cycloheptene.



The nmr spectrum of 1 in chloroform-*d* at room temperature had two N-methyl singlet bands at 2.15 and 2.28 ppm and two olefinic proton doublet absorptions centered at 5.58 and 5.63 ppm ($J = 9.1$ and 10.0 cps, respectively). As the temperature (nitrobenzene and *p*-anisaldehyde solutions) was increased, the nmr spectrum remained fairly constant up to about

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(2) A. Ebnöther, E. Jucker, and A. Stoll, *Helv. Chim. Acta*, **48**, 1237 (1965).