Experimental Section[7]

4-Dichloromethyl-3,4-dimethyl-2,5-cyclohexadienone (3).— By the reaction of 3,4-dimethylphenol with chloroform and 15% aqueous sodium hydroxide, 3,[4] mp 100–101°, was prepared in 15% yield.

4-Dichloromethyl-3,4-dimethyl-1-keto-1,4-dihydronaphthalene (5).—To a solution of 30.0 g (0.17 mol) of 3,4-dimethyl-1-naphthol[8] in 1 l. of 20% aqueous sodium hydroxide at 65° was added dropwise 200 g of chloroform during 1 hr. The mixture was refluxed for 2 hr, stirred at room temperature overnight, and diluted with an equal volume of water. The usual work-up afforded 8.0 g of a dark oil. Distillation and collection of the cut, bp 167–190° (1 mm), gave 5.5 g (12%) of 5 as colorless needles: mp 87.5–88.5° (from benzene–hexane); ir 6.04 μ (C=O); nmr (CCl₄) 1.81 (s, 3 H), 2.29 (d, 3 H), 6.19 (s, 1 H), 6.48 (m, 1 H), and 7.4–8.2 ppm (4 H).

Anal. Calcd for $C_{13}H_{12}Cl_2O$: C, 61.2; H, 4.7; Cl, 27.8. Found: C, 61.1; H, 5.0; Cl, 27.8.

3-(β,β-Dichloroethyl)-4-methylchlorobenzene (4).—A solution of 15.0 g (0.07 mol) of 3 and 15.2 g (0.07 mol) of phosphorus pentachloride in 160 ml of phosphorus oxychloride was refluxed for 4 hr, and then strip-distilled to remove 75% of the solvent. The remainder was left at room temperature overnight and then poured over 100 g of crushed ice. After the usual work-up, distillation gave 12.1 g (74%) of colorless 4: bp 82.5–83.5° (0.20 mm); n^{25}D 1.5614.

Anal. Calcd for $C_9H_9Cl_3$: C, 48.4; H, 4.1; Cl, 47.6. Found C, 48.2; H, 4.2; Cl, 47.6.

Comparative reactions of 1 and of 3 with phosphorus pentachloride in refluxing methylene chloride showed that the former required 4–6 min for complete reaction (absence of ir band near 6 μ) while the latter required 24–26 min.

Oxidation of 1 g of the above rearrangement product in 15 ml of pyridine with a solution of 1.5 g of potassium permanganate in 25 ml of water containing 15 ml of pyridine for 2 hr at room temperature and 4 hr at 60° gave 0.60 g of recovered material after the usual work-up. Acidification of the aqueous phase gave 0.20 g (66%) of 5-chloro-2-methylbenzoic acid, mp 169–170° (lit.[3a] mp 169.5–171°), identical with an authentic sample.[3a]

4-Dichloromethyl-3,4-dimethyl-1-phenyl-2,5-cyclohexadienol (6).—A solution of 5.0 g (0.024 mol) of 3 in 200 ml of dry ether was added to ca. 0.05 mol of phenylmagnesium bromide in 400 ml of ether. The solution was refluxed for 2 hr, cooled, and poured over 400 g of crushed ice. The organic layer was worked up as usual to give 10.4 g of a semisolid which contained 6. After standing for 20 min, the material was filtered and 6.5 g of clear cubes of 6 (ir 2.73 μ) was obtained. As 6 is unstable at room temperature, no analysis was obtained. If heated rapidly after insertion in a bath at 80°, 6 melts at about 90°. In solution 6 is also unstable, as rearrangement to 8 occurs readily.

3-(β,β-Dichloroethyl)-4-methylbiphenyl (8).—A solution of 7.5 g (0.03 mol) of freshly prepared 6 in 100 ml of methylene chloride was refluxed for 1–2 hr and worked up as usual to give 6.9 g of an orange oil. Distillation gave 5.2 g (73%) of 3-(β,β-dichloroethyl)-4-methylbiphenyl (8): bp 138–140° (0.30 mm); n^{25}b 1.6059.

Anal. Calcd for $C_{15}H_{14}Cl_2$: C, 68.0; H, 5.3; Cl, 26.7. Found: C, 68.0; H, 5.1; Cl, 26.8.

The nmr and infrared spectra were consistent with the structure indicated. A 1.5-g sample of the above rearrangement product was added to a solution of 2.0 g of potassium permanganate in 45 ml of water. After refluxing for 18 hr, the mixture was filtered. Acidification of the filtrate followed by ether extraction and work-up as usual of the organic layer gave 1.05 g (88%) of 2-methyl-5-phenylbenzoic acid, mp 205–206°, identical with an authentic sample.[9]

3-(β,β-Dichloroethyl)-4-methyl-1-phenylnaphthalene (9).—A solution of 3.0 g (0.012 mol) of 5 in 200 ml of ether was added to a solution of phenylmagnesium bromide (prepared from 0.02 mol of bromobenzene in 300 ml of ether). The mixture was stirred overnight at room temperature and poured over 200 g of crushed ice. The organic layer was worked up as usual to give crude carbinol 7, which was heated at 120° for 5 min and cooled. Distillation gave 1.7 g (57%) of recovered 5, bp 149–168° (0.21 mm), and 1.9 g of residue. The latter was chromatographed over silica gel and purified by molecular distillation to give 1.3 g (81%, based on recovered 5) of 9: mp 81–82° (from hexane); nmr (CCl₄) 2.50 (s, 3 H), 3.48 (d, 2 H), 5.69 (t, 1 H), and 6.9–8.0 (1 H, aromatic region). Analysis by mass spectrometry at 70 eV gave the expected parent, parent + 2 and parent + 4 ions at m/e 314, 316, and 318, respectively, in a ratio of 1.0: 0.64:0.13 (calculated ratio on the basis of relative isotopic abundances for the two chlorine atoms present gave 1.0:0.65: 0.11).

Anal. Calcd for $C_{19}H_{16}Cl_2$: C, 72.4; H, 5.1; Cl, 22.5. Found: C, 72.2; H, 5.1; Cl, 22.7.

Trapping of 6-Dichloromethyl-6-methyl-1-methylene-3-phenyl-2,4-cyclohexadiene (10).—The color of a refluxing solution of 1.2 g of 6 and an equimolar amount of tetracyanoethylene in 30 ml of methylene chloride for 30 min changed from yellow to green to red. After the solution had cooled, the solvent was removed under dry nitrogen to give 1.50 g (91%) of a tan 1:1 adduct (11). Recrystallization from chloroform–hexane gave 1.2 g of 11 as colorless plates, mp 184–185° in a sealed tube (bath preheated to 170°). Attempted sublimation led to decomposition. The nmr spectrum (acetone-d_6) showed peaks at 1.52 (s, 3 H), 3.01 (s, 1 H), 3.06 (s, 1 H), 4.18 (d, 1 H, J_{HH} = 3 Hz), 5.00 (d, 1 H, J_{HH} = 3 Hz), 6.59 (s, 1 H), 6.90 (s, 1 H), and 7.4–8.0 (5 H, aromatic region). Analysis by mass spectrometry at 70 eV gave the proper parent, parent + 2 and parent + 4 ions at m/e 392, 394, and 396, respectively, in a ratio of 1.0:0.66:0.14 (calculated ratio on the basis of relative isotopic abundances for two chlorine atoms present gave 1.0:0.65:0.11). Other characteristic ions present were at m/e 357 and 359 (corresponding to loss of a chlorine atom from parent and parent + 2 ions) and at m/e 264 and 266 (corresponding to loss of tetracyanoethylene from parent and parent + 2 ions).

Anal. Calcd for $C_{21}H_{14}Cl_2N_4$: N, 14.3. Found: N, 14.5.

Reaction of 1 with Tri-n-butylphosphine.—A solution of 5.0 g (0.02 mol) of 1 and 5.2 ml(0.02 mol) of tri-n-butylphosphine in 50 ml of benzene was heated at reflux for 6 hr under dry nitrogen. Analysis of an aliquot by nmr and thin layer chromatography showed that one part of 1 and two parts of 3 were present. Addition of 50 ml of absolute ethanol, followed by refluxing for an additional 18 hr, gave no change in the ratio of dienones present.

Catalytic Norbornadiene–Butadiene and Norbornadiene–1,1-Dimethylallene Codimerization

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In previous papers,[1–3] we described the behavior of iron catalysts, and in particular of bis(cyclooctatetraene)iron [Fe(COT)₂] in the cooligomerization of some unsaturated hydrocarbons. After having studied the

(7) Melting points and boiling points are uncorrected. Analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and the Alfred Bernhardt Microanalytical Laboratory at the Max Planck Institute, Mühlheim (Ruhr), West Germany. The nmr spectra were recorded on a Varian Associates A-60 A spectrometer, employing tetramethylsilane as an internal reference. Chemical shifts are reported in parts per million downfield from tetramethylsilane. The phrase "worked up in the usual manner," used throughout this section, refers, with minor variations, to the handling of organic solutions in the following manner. The organic solution was successively washed with water and saturated sodium chloride solution and dried by filtering through a bed of anhydrous magnesium sulfate, and the solvent was removed *in vacuo.*

(8) O. Kruber and W. Schade, *Ber.,* **68B,** 11 (1935).

(9) M. S. Newman and J. A. Eberwein, *J. Org. Chem.,* **29,** 2516 (1964).

(1) A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Lett.,* **22,** 2037 (1967).

(2) A. Carbonaro, A. Greco, and G. Dall'Asta, *J. Org. Chem.,* **33,** 3948 (1968).

(3) A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Lett.,* **49,** 5129 (1968).

TABLE I
NORBORNADIENE-1,3-BUTADIENE AND NORBORNADIENE-1,1-DIMETHYLALLENE CODIMERIZATIONS AND NORBORNADIENE DIMERIZATION CATALYZED BY IRON COMPOUNDS

Monomer			Solvent[a]				Catalyst system[b]		Reacn conditions		Conversion,[c]	Main products[d]			
												1:1 adduct		NBD dimer	
NBD, mmol	BD, mmol	DMA, mmol	BZ, ml	DEE, ml	Fe compd, mmol		Organometallic compd, mmol	BPE, mmol	Temp, °C	Time, hr	%	%[e]	Structure	Structure V, %[e]	Structure VI, %[e]
7.6	7.4			3	Fe(COT)₂	0.19	(i-C₃H₇)MgCl 4.3		22	24	73	18	I	68	13
29.6	24.0			3	FeCl₃	0.79			50	20	48	21	I	74	5
196	222		15		FeA₃	0.5	Al(C₂H₅)₂Cl 10.0	1.40	80	3	41	{40, 20}	IV, III	39	1
29.6		20		3	FeCl₃	0.79	(i-C₃H₇)MgCl 4.3		35	20	62	11	II	46	45
29.6		40	10	3	FeCl₃	0.79	(i-C₃H₇)MgCl 4.3		35	20	43	18	II	69	13
98.0		58			FeA₃	0.25	Al(C₂H₅)₂Cl 5.0	0.57	80	3	39	50	II	48	2
29.0				3	Fe(COT)₂	0.076			35	4	22			50	50
29.0					FeCl₃	0.79	(i-C₃H₇)MgCl 4.3		35	20	35			50	50

[a] BZ = benzene; DEE = diethyl ether. [b] FeA₃ = tris(acetylacetonate)iron; BPE = bis(diphenylphosphine)ethane. [c] Mol of NBD reacted/mol of NBD introduced. [d] By-products mainly consist of acyclic polymers of the acyclic diene when used in excess. [e] g% of indicated product/g of main products = selectivity.

reaction between norbornadiene (NBD) and bisubstituted acetylenic hydrocarbons[3] promoted by the above catalysts, we focused our attention both to the catalyzed reactions between NBD and 1,3-butadiene (BD) or 1,1-dimethylallene (DMA), respectively, and to the catalyzed dimerization of NBD, which always accompanies these reactions.

The most significant results obtained from these investigations are summarized in Table I. The identification of the new compounds was based mainly on spectroscopic measurements (see below).

In the presence of Fe(COT)₂[4] or of the FeCl₃–(i-C₃H₇)MgCl system as catalysts, NBD and BD[5] yielded compound I, and NBD and DMA[6] gave compound II. The selectivity of these reactions is rather low (ca. 20%; see Table I); actually, dimers of NBD are formed as predominant reaction products.
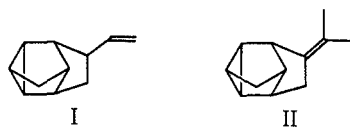
In the presence of the three-component catalyst system tris(acetylacetonate)iron–AlEt₂Cl–bis(diphenylphosphine)ethane,[7] the reaction between NBD and DMA still yields II with higher selectivity (ca. 50%), while the reaction between NBD and BD produces two new 1:1 adducts, corresponding to structures III and IV. The formation of these latter codimers is quite selective: together, they nearly constitute 60% of the total products, the remainder still consisting of NBD dimers (Table I).
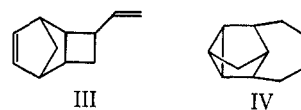
NBD dimers, which always form simultaneously with the above codimers, generally arise from two different kinds of addition. In the presence of BD or DMA, predominantly an isomeric mixture of dimers with the mononortriciclenic structure V is formed; while in the absence of these dienes, almost equal

(4) The preparation of Fe(COT)₂ is reported in a paper by A. Carbonaro, A. Greco, and G. Dall'Asta, J. Organometal. Chem., in press.

(5) Isoprene and 1,3-pentadiene react under the same conditions, forming 1:1 adducts with NBD; in the case of pentadiene the yield is still lower than in that of butadiene. These compounds have not been isolated in the pure state; hence we will not refer to them.

(6) Among the cumulated dienes, allene rapidly yields the known crystalline homopolymer, even in the presence of NBD.

(7) A. Miyake, G. Hata, M. Iwamoto, and S. Yuguchi, 7th World Petroleum Conference, Mexico City, April 1967, P.D. no. 22 (3).

amounts of isomers with structure V and with the bisnorbornenic structure VI result (Table I).[8]

V and VI may exist in different stereoisomeric forms.[9] In the cases examined by us, VI almost exclusively consists of the *exo,trans,exo* stereoisomer. Among the stereoisomers of V, we found two of the three already described in the literature, *i.e.*, those called by Katz and Acton "minor" and "major" dimers.[10] Moreover, using the bis(phosphine) containing iron catalyst, a new stereoisomer of V was formed in prevalence; its nmr spectrum differs from those reported in the literature for the other three stereoisomers.[11,12]

Two oligomerization runs of NBD alone are reported in Table I in order to compare the influence of the diene comonomer on the selectivity of formation of V and VI.

As stated previously,[3,13] zerovalent iron complexes are the parent catalytic centers that promote the oligomerizations of different unsaturated hydrocarbons. However, not all complexes containing zero-valent iron are active; *e.g.*, $Fe(NO)_2(CO)_2$[14] does not oligomerize norbornadiene in the presence of butadiene.

Identification of the New Oligomers.—The above formulas were attributed to the new compounds on the basis of the elemental analysis and of the mass, nmr, and ir spectra.

The mass spectrum of I shows a parent peak at m/e 146. The nmr spectrum of I is given in Figure 1a; the signals at τ 4.25 (1 H) and 5.30 (2 H) are attributed to the vinyl groups, and the very broad peak centered at *ca.* τ 9.25 (3 H) is due to the three protons of the three-membered ring.[15] These attributions are consistent with the presence in the ir spectrum of absorption bands at 900, 989, 1633 (vinyl group), 787, and 816 cm^{-1} (nortricyclene ring system[15]).

The mass spectrum of II exhibits a m/e 160 parent peak. Its nmr spectrum (Figure 1b) shows two multiplets at τ 9.08 and 9.28 (3 H total) assigned to the three cyclopropane protons, whereas in the τ 8.50–8.70 (9 H) region a set of signals attributable to the methyls, to the endomethylenic protons, and to an unassigned proton of the cycle is found. The peaks at τ 7.54 (1 H) and 7.98 (2 H) may be attributed to the three protons adjacent to the double bond. The ir spectrum of II shows absorption bands at 1370 cm^{-1} due to the methyl groups, and at 795 and 818 cm^{-1} due to the nortricyclenic system.

The mass of III was found to be 146. Its nmr spectrum exhibits (Figure 1c) signals attributable to the double bond [τ 4.17 (3 H)] and to the vinyl group [τ 4.17 (3 H) and 5.20 (2 H)]. The ir spectrum is characterized by absorption bands at 908, 990, 1635, 3078 (vinyl group), 702, 1322, 1561, and 3058 cm^{-1} (norbornene system[15]).

(8) The above-described reactions do not occur thermally, at least under moderate conditions. III and VI arise from a four-membered olefin reaction that on the basis of molecular-orbital considerations should be thermally forbidden [R. Hoffman and R. B. Woodward, *J. Amer. Chem. Soc.*, **86**, 2046 (1965)], but catalytically allowed [F. D. Mango and J. H. Schaehtschneider, *ibid.*, **89**, 2484 (1967)].

(9) D. D. Eley, H. Pines, and P. B. Weisz, Ed., "Advances in Catalysis," 1st ed, Academic Press, New York, N. Y., 1968, p 382.

(10) T. J. Katz and N. Acton, *Tetrahedron Lett.*, **27**, 2601 (1967).

(11) J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012 (1966).

(12) T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, **32**, 1301 (1967).

(13) Paper cited in ref 4.

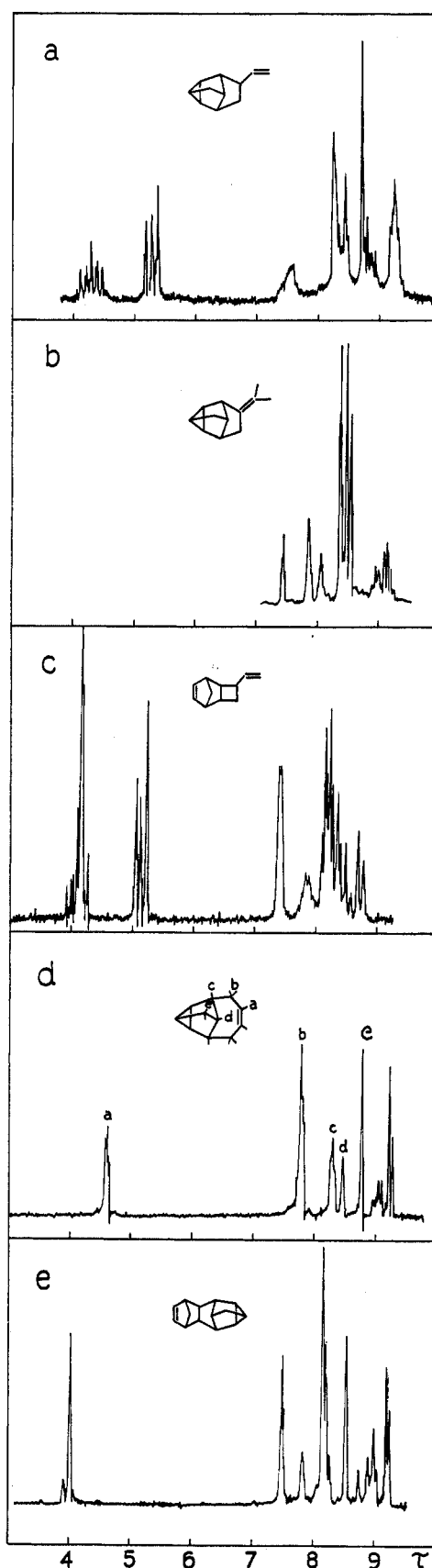(14) J. P. Candlin and W. H. Janes, *J. Chem. Soc., C*, 1856 (1968).

Figure 1.—100-Mcps pmr spectra of the adducts: (a) I in C_6D_6; (b) II in C_6D_6; (c) III in CCl_4; (d) IV in CCl_4; (e) V in CCl_4.

The mass of IV was found to be 146. Figure 1d shows the nmr spectrum of this compound; the peak centered at τ 4.61 (2 H) likely corresponds to the two

(15) *Cf.* Mrowca and Katz,[11] and references cited therein.

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$_3$H$_7$)MgCl was prepared according to Grignard technique from 2-chloropropane and Mg turnings. AlEt$_2$Cl (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 Fe(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$_2$CO$_3$.

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$_6$D$_6$ 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.

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 [RSFe(CO)$_3$]$_2$ are readily obtained by heating Fe$_3$(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 C$_7$H$_8$(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-tetrabromocyclobutane[3] and 1,2,3,4,5-pentabromocyclopentane,[4] respectively.

The proton nmr spectrum of C$_7$H$_8$(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 al-

(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.
(3) D. J. Severn and E. M. Kosower, *Tetrahedron Lett.*, 2119 (1968).
(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).