Syntheses of Some Chloronorbornanes. An Improved Synthesis of 1,4-Dichloronorbornane[1]

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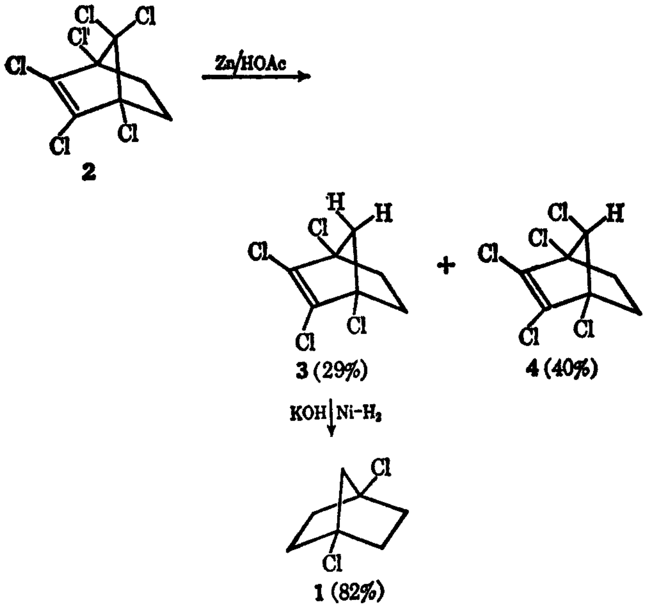
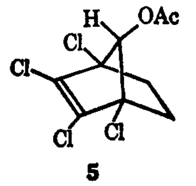
1,4,7,7-Tetrachloronorbornane (**9**), prepared by reduction of 1,2,3,4,7,7-hexachloronorbornene (**2**) with hydrogen over palladized charcoal, is conveniently further reduced to 1,4-dichloronorbornane (**1**) by the action of diphenyltin dihydride in diglyme at 110–120°. This represents an improved synthesis of **1** (54% over-all, compared with 22% over-all yield by Wilcox's published[2] procedure). Partial reduction of **9** to 1,4,7-trichloronorbornane (**10**), uncontaminated by **1**, has been effected by using lithium aluminum hydride–lithium hydride in refluxing tetrahydrofuran and by using tri-*n*-butyltin hydride in refluxing methylcyclohexane. The difference in appearance between the nmr spectrum of **9** in benzene and in pyridine is rationalized in terms of a specific solvation interaction between the substrate and the pyridine-ring nitrogen in the collision complex. The dipole moments of **1**, **9**, and **10** have been measured (1.32, 3.30, and 2.83 D, respectively).

In connection with our current interest in the mechanism of insertion of electrophilic carbenes into carbon–halogen bonds, it became desirable to synthesize 1,4-dichloronorbornane (**1**) in quantity. A three-step synthesis of **1** in over-all yield 22% (Scheme I) has been reported by Wilcox and Zajacek.[2] We speculated that the pentachloronorbornene, **4**, may well be an intermediate in a stepwise reduction of **2**, and, accordingly, we increased the reaction time to allow for reduction of additional **4** to **3**. Although a higher yield of **3** did result, we obtained in addition a third product to which we have assigned the structure **5** on the basis of microanalytical data and nmr spectral evidence (Figure 1). Spin-decoupling experiments (Figure 1, inset A) reveal a long-range coupling ($J_{5n,7} = J_{6n,7} = 1.3$ Hz).

SCHEME I





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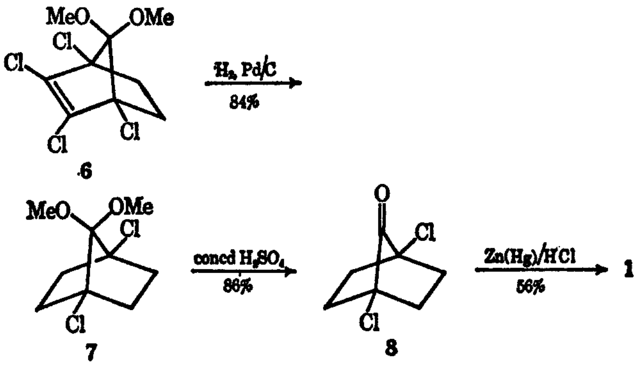
Our observation of finite coupling between the 7 proton and the AA′BB′ multiplet centered at δ 2.1 requires that the configuration about C_7 be such that the 7 proton is *syn* to the double bond.[3,4] Furthermore, the magnitude of the difference frequency utilized in the decoupling experiment ($\Delta\delta = 184$ Hz) suggests that the upfield portion of the AA′BB′ multiplet is due to the *endo* protons (H_{5n}, H_{6n}), the downfield portion being due to the *exo* protons (H_{5x}, H_{6x}).

The observation of **5** and the absence of the corresponding *syn* isomer among the products of the zinc–acetic acid reduction of **2** suggests that the reduction of **2** to **3** occurs in a stepwise fashion, competing with a solvolytic process. This is the first evidence, to our knowledge, of participation by a dihalogenated double bond in solvolysis of a 7-substituted norbornene.

Our first attempt to improve the yield of **1** is summarized in Scheme II. This scheme affords **1** in 41% yield from the readily prepared[5] 1,2,3,4-tetrachloro-7,7-dimethoxynorbornene (**6**); however, the over-all yield of **1** including the preparation of **6** is only 27%.

SCHEME II



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[1] Presented in part at the 23rd Southwest Regional Meeting of the American Chemical Society, Little Rock, Ark., Dec 7–9, 1967, no. 159.

[2] C. F. Wilcox and J. G. Zajacek, *J. Org. Chem.*, **29**, 2209 (1964).

[3] (a) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961); (b) for a review, see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[4] See A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*, **90**, 3724 (1968), and references cited therein.

[5] (a) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); (b) P. G. Gassman and J. L. Marshall, unpublished work. We thank Dr. Gassman for providing us with a detailed experimental procedure for the preparation of **6**.

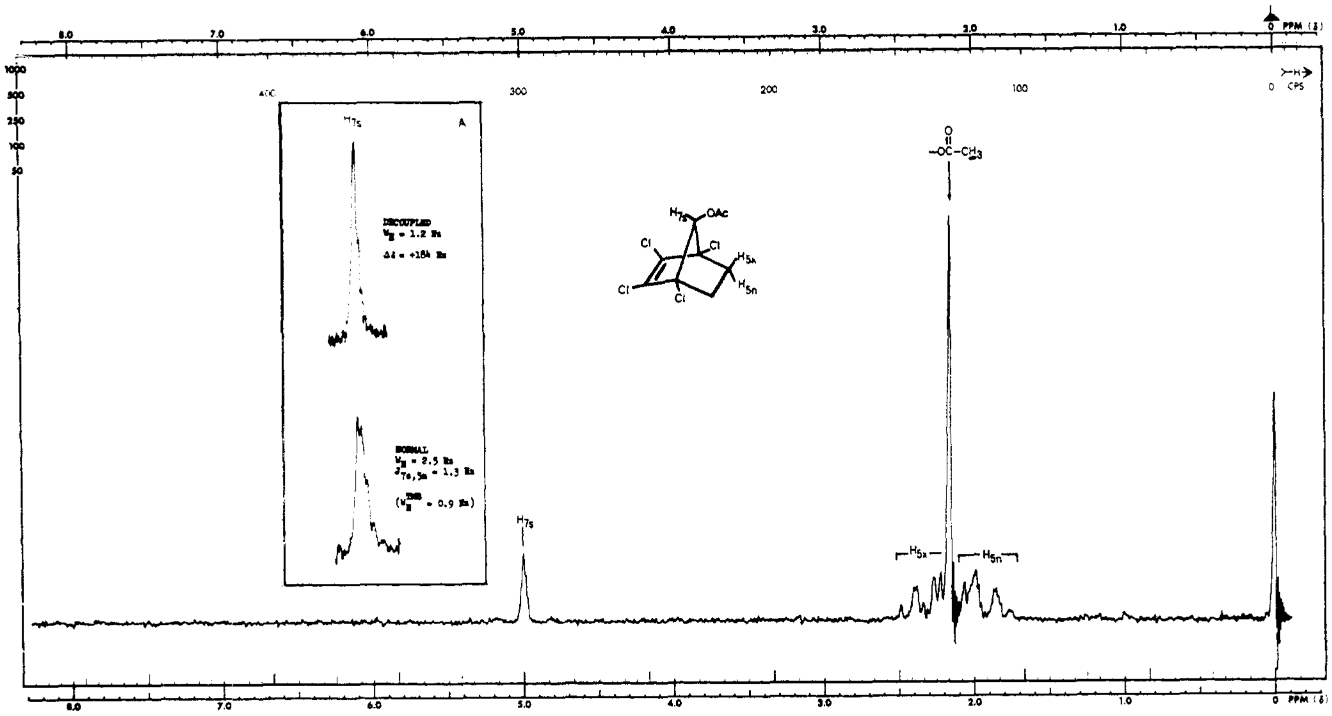
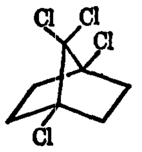


Figure 1.—Nmr spectrum of **5** ($CDCl_3$ solution) at 60 MHz. Inset A: bridge proton (H_7) decoupled from the 5,6-*endo* protons (H_{5n}, H_{6n}), difference frequency 184 Hz.

In a second attempt at an improved synthesis of **1**, we elected first to carry out hydrogenolysis–reduction of the dichlorinated double bond in **2**, followed by reduction of the bridge (7,7) halogens in the resulting 1,4,7,7-tetrachloronorbornane, **9**. Zinc–acetic acid reduction of **9** proved unsuitable for preparing **1** (see Experimental Section). Tri-*n*-butyltin hydride and also lithium hydride–lithium aluminum hydride reduced **9** to 1,4,7-trichloronorbornane, **10**, in fair to good yield, but these reagents proved incapable of further reduction of **10** to **1**. Diphenyltin dihydride,[6] was found effective in reducing **9** to **1**; the over-all yield of **1** in our three-step synthesis starting with hexachlorocyclopentadiene and concluding with the diphenyltin dihydride reduction of **9** was 54%.



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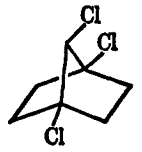

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The nmr spectra of **9** in benzene, pyridine, and chloroform are shown in Figure 2. The spectrum in benzene best reveals the asymmetric pattern that distinguishes AA′A″A‴BB′B″B‴ systems (*e.g.*, **9**) from the simpler, centrosymmetric AA′BB′ systems.[7]

The large apparent difference between the spectrum of **9** in pyridine and in benzene is very likely due to a specific solvation interaction between the substrate and the pyridine-ring nitrogen in the collision complex.[8]

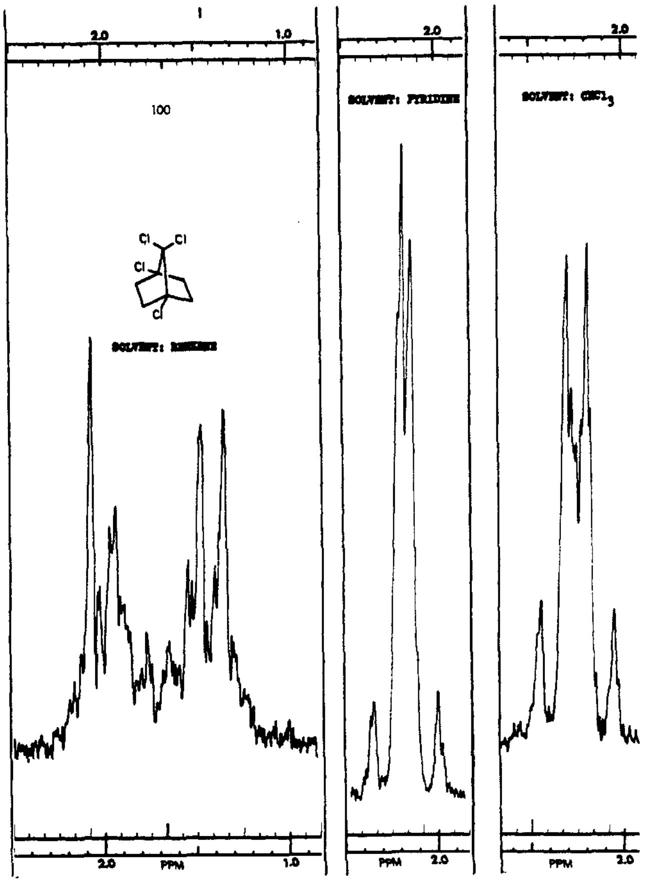

Figure 2.—Nmr spectra of **9** in benzene, pyridine, and $CHCl_3$ solutions (12% w/w) at 60 MHz.

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(6) H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963).

(7) (a) The nmr spectra of several AA′A″A‴BB′B″B‴ systems have been reported; *cf.* Varian High Resolution NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1963, Spectra No. 416, 445, 557, and 619. We thank Professor Norman S. Bhacca for calling these spectra to our attention. (b) See also footnote 13 in C. F. Wilcox, Jr., and G. C. Whitney, *J. Org. Chem.*, **32**, 3348 (1967).

(8) P. V. Demarco, E. Farkas, D. Doddrell, B. Mylari, and E. Wenkert, *J. Amer. Chem. Soc.*, **90**, 5480 (1968).

To check this hypothesis, studies of solvent dilution effects on the nmr spectra of **1**, **9**, and **10** are currently in progress.[9]

Our suggestion of specific heteroatom solvation of **9** in pyridine is supported by dipole moment studies. We would expect such a solvent–substrate interaction to be most important in the event that some demand is placed by the substrate upon the solvating power of the solvent;[9,10] *i.e.*, in the event that **9** possesses a relatively high permanent dipole moment. Measurements of the dipole moments of **1**, **9**, and **10** (Table I) reveal that this is indeed the case.

TABLE I

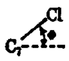
DIPOLE MOMENTS (D) OF CHLORONORBORNANES[a]

		μ_{calcd}	
Compound	μ_{obsd}	Unit vector[b]	Other method
1	1.32[c]	1.58	1.49[d]
10	2.83 ± 0.01	3.27	3.00[e]
9	3.30 ± 0.01	3.96	3.64[f]

[a] Measured in dilute cyclohexane solution at 25.0 ± 0.1°. [b] Reference 11a. [c] Reference 11b; this value was confirmed in the present work. [d] Vector sum, 2 × (1-chloronorbornane)

(θ = 139°).[11b] [e] Vector sum, (1,4-dichloronorbornane) + (7-chloronorbornane)

Φ = 34°30′: B. Franzus, *et al.*, *J. Amer. Chem. Soc.*, **90**, 3721 (1968). [f] Vector sum, (1,4-dichloronorbornane) + 2 × (7-chloronorbornane)



(Φ = 34°30′).

Wilcox has performed extensive investigations involving the determination and correlation of the dipole moments of chloronorbornanes.[11] Values calculated from Wilcox's data are listed in Table I for comparison with our observed values. The values calculated by Wilcox's unit vector model,[11a] shown in column 3, are all significantly higher than the observed values. This result is not surprising. In cases where two bond moments of similar magnitude are juxtaposed (geminal or vicinal substitution), the individual moments may affect one another by induction, which tends to reduce the resultant value of the molecular dipole moment below that which would be anticipated in the absence of this effect.[12] No provision is made in the unit vector model for the phenomenon of induction.

Since the dipole moment of norbornane itself is negligibly small,[11b] the *molecular* dipoles of the appropriate chloronorbornanes, rather than the C–Cl bond dipoles, can to a first approximation be summed vectorially to calculate μ values for **1**, **10**, and **9**. The values thus obtained (column 4, Table I) agree more closely with μ_{obsd} than do the values in column 3, as expected, since the latter calculation tacitly takes into account any induction between the C_1–Cl and C_4–Cl bonds in **1**.

A second possible factor stems from the uncertainty in the values of the angles θ and Φ. A relatively small uncertainty here will produce a large error in μ_{calcd}. For example, in Wilcox's unit vector model, he assigned an *a priori* value of $\theta = 139°$ for compound **1**.[11a] Recent measurements of various bond lengths and bond angles in **1** by electron diffraction[13] permit calculation of the value $\theta = 142 \pm ca.\ 2°$. The range 140–144° for the value of θ leads to the range 1.31–1.45 D for that of μ_{calcd} (unit vector model, $\mu_{C_1-Cl} = 2.12$ D[11b]). Hence, the discrepancy between μ_{calcd} (unit vector model) and μ_{obsd} in **1** may be caused *entirely* by the uncertainty in the value of θ. Lack of the necessary data precludes a corresponding comparison of μ_{obsd} with μ_{calcd} for compounds **9** and **10**. Assessment of the relative importance of induction and structural uncertainty factors in accounting for the discrepancies between μ_{obsd} and μ_{calcd} for any of the compounds **1**, **10**, or **9** is not feasible at present.

Experimental Section

Melting points were determined using a Thomas-Hoover Uni-Melt apparatus and are corrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nmr spectra were obtained on a Varian A-60 instrument equipped with a Varian Model V-6058A spin-spin decoupling apparatus. Coupling constant and chemical-shift values are accurate to within ±0.3 Hz. Dipole moment values were calculated[14] from dielectric constant measurements obtained using a WTW DFL 1-heterodyne beat apparatus (2.0 Mc) at 25.0 ± 0.1°. Mass spectra were obtained through the kind courtesy of Dr. Jordan J. Bloomfield, Monsanto Co., St. Louis, Mo.

Reduction of 1,2,3,4,7,7-Hexachloronorbornane (**2**).—Compound **2** (150.5 g, 0.5 mol) was refluxed and stirred in glacial acetic acid (900 ml) with zinc dust (400 g, 4.5 g-atoms, added in 30-g portions over a 2-hr period) for 27 hr. The mixture was poured into water (4 l.) and extracted with pentane (1 l.). The pentane was washed with 10% aqueous sodium bicarbonate solution (1 l.) and with water (1 l.), filtered, and dried over anhydrous magnesium sulfate, and the solvent was removed by distillation through a 24-in. vacuum-jacketed Vigreux column. Vacuum distillation of the residue afforded two fractions. The first fraction, bp 70–74° (3 mm), contained mainly 1,2,3,4-tetrachloronorbornane (**3**) [lit.[2] bp 70–72° (3 mm), mp 37–38.5°]. The second fraction, bp 90–102° (1.3 mm), was further purified by elution chromatography on Florisil (pentane eluent), affording two products. In order of their appearance in the eluate, these were 1,2,3,4-*syn*-7-pentachloronorbornene (**4**), colorless platelets (from methanol), mp 58–59° (lit.[2] mp 59.2–59.8°), and *anti*-7-acetoxy-1,2,3,4-tetrachloronorbornane (**5**), colorless cubes (from aqueous methanol), mp 123.0–123.8°.

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(9) (a) For a review of solvent effects on nmr spectra, see P. Laszlo in "Progress in NMR Spectroscopy," Vol. 3, J. W. Emsley, J. Feeny, and L. H. Sutcliffe, Ed., Pergamon Press Ltd., London, 1967, p 231; (b) P. Bates, S. Cawley, and S. S. Danyluk, *J. Chem. Phys.*, **40**, 2415 (1964).

(10) (a) For a discussion of collision complex geometries involving substrate interactions with aromatic solvents, see P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964), and references cited therein; (b) see also A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

(11) (a) C. F. Wilcox, *J. Amer. Chem. Soc.*, **82**, 414 (1960); (b) C. F. Wilcox, Jr., J. G. Zajacek, and M. F. Wilcox, *J. Org. Chem.*, **30**, 2621 (1965).

(12) (a) See N. V. Sidgwick, *Chem. Rev.*, **19**, 183 (1936); (b) L. E. Sutton and L. O. Brockway, *J. Amer. Chem. Soc.*, **57**, 473 (1935); (c) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp 235–239; (d) J. W. Smith, "Electric Dipole Moments," Butterworth and Co. (Publishers) Ltd., London, 1955, pp 182–185.

(13) We are grateful to Professor Wilcox for sending us a prepublication copy of his paper describing this work: (J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968).

(14) Dipole moments were calculated with the aid of a computer program using the Halverstadt-Kumler equation. We are grateful to Professor Domenick J. Bertelli, University of California at Santa Barbara, Santa Barbara, Calif., for providing us with a copy of this computer program: D. J. Bertelli and T. G. Andrews, Jr., *Tetrahedron Lett.*, 4467 (1967).

Anal. Calcd for $C_9H_8Cl_4O_2$: C, 37.28; H, 2.78; Cl, 48.91. Found: C, 37.45; H, 2.82; Cl, 48.87.

Integration of the nmr spectrum of the crude product of the zinc–acetic acid reduction of **2** revealed that the ratio of products **3**/**4**/**5** was 44:49:7.

1,4,7,7-Tetrachloronorbornane (**9**).—A solution of **2** (30.1 g, 0.10 mol) in absolute ethanol (250 ml) was reduced over palladized charcoal on a Parr low-pressure hydrogenation apparatus in the presence of triethylamine (25 g, 0.25 mol). After uptake had ceased, the mixture was poured into 10% aqueous hydrochloric acid (1300 ml) and extracted with ether; the ether extract was washed with water, dried (magnesium sulfate), and evaporated. Recrystallization from pentane afforded 1,4,7,7-tetrachloronorbornane (**9**) as colorless platelets, mp 216.0–216.5° (86 ± 1%).

Anal. Calcd for $C_7H_8Cl_4$: C, 35.94; H, 3.45; Cl, 60.62; mol wt, 234. Found: C, 36.26; H, 3.37; Cl, 60.38; mol wt (mass spectroscopy), 232/234/236/238/240, with the intensity profile characteristic of the Cl_4 multiplet.[15]

1,4,7-Trichloronorbornane (**10**). **Method A.**[16]—A solution of **9** (23.4 g, 0.10 mol) in dry tetrahydrofuran (100 ml) was added dropwise over a 1-hr period to a stirred, refluxing solution of lithium aluminum hydride (7.6 g, 0.2 mol) and lithium hydride (0.35 g, 0.05 mol) in dry tetrahydrofuran (200 ml). After 12 hr, the reaction was quenched by dropwise addition of water. The mixture was then poured into water (3 l.) and extracted with pentane (500 ml). The pentane layer was washed with water, dried (magnesium sulfate), and filtered, and the filtrate was concentrated by distillation through a 24-in. vacuum-jacketed Vigreux column. Recrystallization from absolute methanol (−20°) afforded 1,4,7-trichloronorbornane (**10**) as colorless, gummy crystals (13.6 g, 70%); sublimation afforded an analytical sample: mp 69.2–69.8°; nmr spectrum (carbon tetrachloride solution), broad singlet at δ 4.0 (area 2 H), unsymmetrical multiplet (AA′A″A‴BB′B″B‴ pattern) at 1.7–2.6 (area 8 H).

Anal. Calcd for $C_7H_9Cl_3$: C, 42.14; H, 4.55; Cl, 53.31. Found: C, 42.05; H, 4.45; Cl, 53.16.

Method B.[17]—In a three-neck flask equipped with a reflux condenser, mechanical stirrer, and dropping funnel were placed **9** (18.72 g, 0.08 mol) and methylcyclohexane (75 ml). The system was flushed with dry nitrogen and brought to reflux under a dry nitrogen atmosphere. Tri-*n*-butyltin hydride[18] (23.3 g, 0.08 mol) was added dropwise over 30 min. After refluxing for 8 hr, the reaction mixture was poured into warm 10% aqueous sodium hydroxide solution. The mixture was filtered through Celite, and the organic layer was separated and dried (magnesium sulfate). The solution was filtered, and the filtrate was concentrated by careful distillation (120 mm) through a 24-in. vacuum-jacketed Vigreux column. The residue was then distilled; the fraction having bp 80–87° (2.0 mm) consisted mainly of **10** (11.6 g, 72.5%), but some contamination by tin-containing materials was evident.

1,4-Dichloronorbornane (**1**). **Method A.**—Reduction of 1,2,3,4-tetrachloro-7,7-dimethoxynorbornene[5] (**6**, 58.4 g, 0.20 mol) according to Scherer[19] afforded 1,4-dichloro-7,7-dimethoxynorbornane (**7**, 80–90%). Recrystallization from absolute methanol at −20° afforded colorless platelets, mp 95.0–96.0° (lit.[19] mp 95.0–95.6°). The nmr spectrum agreed with that reported by Scherer.[19]

Hydrolysis of **7** (22.5 g, 0.10 mol) in cold, concentrated sulfuric acid (24 hr with stirring) afforded 1,4-dichloro-7-ketonorbornane (**8**, 79%). The ir spectrum of crude **8** displayed significant –OH absorption (3100–3500 cm^{-1}), as well as the expected absorption at 1815 cm^{-1} (C=O). Longer reaction times led to an undesired product which showed strong ir absorption at 1655 cm^{-1}; this material was not examined further.

Ketone **8**, purified by careful drying in an Abderhalden apparatus followed by vacuum sublimation, gave mp 155.5–158.5°. Failure to purify the ketone in this manner before proceeding with the reduction step resulted in impure **1** which resisted further purification by recrystallization.

A solution of **8** (17.9 g, 0.10 mol) in a 3:1 benzene–ethanol solution (40 ml) was added to a mixture of zinc amalgam[20] (50 g, 25% excess), absolute ethanol (30 ml), and concentrated hydrochloric acid (60 ml). The resulting mixture was refluxed with vigorous mechanical stirring for 48 hr during which time five 15-ml portions of concentrated hydrochloric acid were added. Suitable work-up followed by pentane recrystallization at −20° afforded **1** (0.3 g, 56%): mp 78.0–80.0° (lit.[2] mp 78–79°); nmr (CCl_4) singlet at δ 2.0 (area 2 H), superimposed upon an AA′A″A‴BB′B″B‴ multiplet at 1.7–2.5 (area 8 H).

Method B.—To a cooled solution of lithium aluminum hydride (5.5 g, 0.15 mol) in dry diglyme (75 ml) was added a solution of diphenyltin dichloride (1.0 g) in dry diglyme (30 ml). The resulting solution was heated to 110° (oil bath), and a solution of **9** (23.4 g, 0.10 mol) in dry diglyme (50 ml) was added dropwise over a 45-min period (*exothermic*). The resulting mixture was heated with stirring at 110–120° for 24 hr, at which time additional diphenyltin dichloride (1.0 g) was added; heating and stirring were continued for an additional 24 hr. The reaction was then quenched with dilute aqueous hydrochloric acid and extracted twice with 500-ml portions of pentane. The combined pentane layers were washed with water, dried (magnesium sulfate), filtered, and evaporated, affording crude **1** contaminated with 1,4,7-trichloronorbornane (**10**). Integration of the nmr spectrum of the crude product revealed that the ratio of **1**/**10** present was about 93:7.

Recrystallization of crude **1** from methanol at −78° followed by sublimation afforded **1** (10.3 g, 63%), mp 73–76° (lit.[2] mp 77–78°), whose nmr spectrum revealed no trace of the by-product, **10**.

Method C.—Reduction of **9** (11.7 g, 0.050 mol) was effected by dissolving in glacial acetic acid (100 ml), the solution was heated to reflux, and excess zinc powder (50 g) was added in seven equal portions over a 3-hr period. Refluxing and stirring were continued for an additional 36 hr. The nmr spectrum (CCl_4) of the crude product showed **10** and **1** as the sole products, in the ratio 47:53. Column chromatography (silicic acid, pentane eluent) permitted the separation and characterization of the two products. The products could not be conveniently separated by vacuum distillation. No further attempt was made to prepare pure **1** by this method.

Registry No.—**1**, 2941-51-7; **5**, 19202-60-9; **9** 18214-92-1; **10**, 18214-91-0.

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(17) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

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(19) K. V. Scherer, *Tetrahedron Lett.*, 5685 (1966).

(20) E. L. Martin, *Org. Reactions*, **1**, 155 (1942).