Heating methyldichlorosilane and Ia to 150° for 3 hr. gave nearly complete conversion to polymer IIIa, but no trace of telomers V or VI by v.p.c. These telomers were the only products when the experiment was duplicated with catalytic amounts of platinum on carbon.

Heating a 2:1 molar ratio of diphenylmethylsilane and Ia with approximately 1% of platinum on carbon for 2 hr. at 100 or 150° gave a nearly quantitative conversion to 1:1 telomer, $\mathrm{Ph_2MeSi(CH_2)_3SiMe_2H}$ [identified by $\mathrm{H^1}$ n.m.r. spectrum showing a singlet for $\mathit{Me}\mathrm{SiPh_2}$ at τ 9.49, a doublet for $\mathit{Me}_2\mathrm{SiH}$ at 10.03, a multiplet for $\mathit{H}\mathrm{Si}$ at 5.94, and the complex patterns for $\mathrm{(CH_2)_3}$, at 8.1–9.5 and Ph at 2.2–3.0]. Heating the above mixture without catalyst for 24 hr. at 100° gave no reaction. Heating for 24 hr. at 150° gave a mixture which contained (by v.p.c. analyses) no Ia, a large amount of unreacted diphenylmethylsilane, and a small amount of 1:1 telomer (approximately 30% of the amount produced in the above platinum-catalyzed reaction).

1-(Dimethylchlorosilyl)-3-(dimethylsilyl)propane.—Heating 36.9 g. (0.39 mole) of dimethylchlorosilane, 20 g. (0.2 mole) of 1,1-dimethyl-1-silacyclobutane, and 0.3 g. of a 0.2 *M* isopropyl alcohol solution of chloroplatinic acid to 55° in a flask fitted with reflux condenser resulted in a vigorously exothermic reaction. Fractional distillation after an additional 8 hr. at 70° afforded 31 g. (0.159 mole, 79.4% yield) of 1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane, b.p. 91° (33 mm.).

2-Methyl-1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane.—Heating 37.8 g. (0.4 mole) of dimethylchlorosilane, 22.8 g. (0.2 mole) of 1,1,3-trimethyl-1-silacyclobutane, and 0.5 g. of platinum on carbon[12] at reflux (45–70°) for 24 hr. gave complete conversion (v.p.c. analysis) of the silacyclobutane to a single higher boiling product. Approximately 60% of the silacyclobutane was consumed during the first 8 hr. at 45–50°. Fractional distillation afforded 35.5 g. (0.17 mole, 85% yield) of 2-methyl-1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane, b.p. 98° (33 mm.).

(Dimethylchlorosilylmethyl)(dimethylsilylmethyl)dimethylsilane.—A mixture of 18.9 g. (0.2 mole) of dimethylchlorosilane, 14.4 g. (0.1 mole) of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, and 0.4 g. of platinum on carbon[12] was heated in a sealed ampoule at 100° for 16 hr. V.p.c. showed complete conversion of disilacyclobutane to a single higher boilint product. Fractional distillation gave 16.2 g. (0.068 mole, 68% yield) of (dimethylchlorosilylmethyl)(dimethylsilylmethyl)dimethylsilane, b.p. 95° (13.5 mm.).

The $\mathrm{H^1}$ n.m.r. spectrum contained the expected doublets for $\mathrm{Si}\mathit{CH}_2\mathrm{Si(CH_3)_2H}$ at τ 10.16 (J = 3.8 c.p.s.) and for $\mathrm{Si}(\mathit{CH}_3)_2\mathrm{H}$ at 9.90 (J = 3.7 c.p.s.), singlets for $\mathrm{CH_2Si}(\mathit{CH}_3)_2\mathrm{CH_2}$ at 9.88, for $\mathrm{Si}\mathit{CH}_2\mathrm{Si(CH_3]_2Cl}$ at 9.84, and for $\mathrm{CH_2Si}(\mathit{CH}_3)_2\mathrm{Cl}$ at 9.58, and a multiplet for $\mathrm{CH_2Si(CH_3)_2}\mathit{H}$ at 6.03. The relative intensities of the absorptions were in accord with these assignments.

Structure Correlations. 1,3-Bis(dimethylchlorosilyl)propane and 1,3-Bis(trimethylsilyl)propane.—Heating 16.02 g. (0.12 mole) of N-chlorosuccinimide and 20.5 g. (0.106 mole) of 1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane in 100 ml. of carbon tetrachloride at reflux for 24 hr. resulted in a quantitative consumption of silicon hydride (v.p.c.). Filtration and distillation gave 20.5 g. (0.0895 mole, 85% yield) of 1,3-bis(dimethylchlorosilyl)propane, b.p. 118° (35 mm.), $n^{25}\mathrm{D}$ 1.4474.

Anal. Calcd. for $\mathrm{C_7H_{18}Cl_2Si}$: $\mathrm{Cl_{hyd}}$, 30.9; Si, 24.5. Found: $\mathrm{Cl_{hyd}}$, 30.0; Si, 24.3.

Treatment of this compound (15 g., 0.0655 mole) with methylmagnesium bromide in tetrahydrofuran gave 10.31 g. (0.0549 mole, 84% yield) of 1,3-bis(trimethylsilyl)propane, b.p. 105 (100 mm.), $n^{25}\mathrm{D}$ 1.4196, lit.[14] $n^{20}\mathrm{D}$ 1.3241. This sample was identical ($\mathrm{H^1}$ n.m.r., infrared) with an authentic sample prepared in 71% yield by adding an equal molar mixture of (3-chloropropyl)-trimethylsilane and trimethylchlorosilane to magnesium in tetrahydrofuran at 40–50°.

2-Methyl-1,3-bis(trimethylsilyl)propane.—A mixture of 0.82 g. of 2-methyl-1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane and 10 ml. of 2.08 *N* methyllithium in ether (Lithium Corp. of America) was heated at reflux for 16 hr. Analysis by v.p.c. showed a quantitative conversion of starting silane to 2-methyl-1,3-bis(trimethylsilyl)propane, $n^{25}\mathrm{D}$ 1.4258, infrared and $\mathrm{H^1}$ n.m.r. spectra identical with authentic standard on the 0.25 g. of product isolated by preparative v.p.c.

The authentic sample of 2-methyl-1,3-bis(trimethylsilyl)-propane, $n^{25}\mathrm{D}$ 1.4258, b.p. 179° (lit.[15] $n^{25}\mathrm{D}$ 1.4285, b.p. 182°), was prepared in 64% yield by adding an equal molar mixture of (3-chloro-2-methylpropyl)trimethylsilane and trimethylchlorosilane to magnesium in tetrahydrofuran at 60–70°.

Acknowledgment.—We are grateful to Dr. A. Lee Smith and Miss Wanda Ratsek for their aid in obtaining and interpreting the $\mathrm{H^1}$ n.m.r. and infrared spectra and to Miss Janet Crane for her assistance with many of the experiments.

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(14) A. V. Topchiev, N. S. Nametkin, T. I. Chernysheva, and S. G. Durgaryan, *Dokl. Akad. Nauk SSSR*, **110**, 97 (1956).

(15) A. D. Petrov, S. I. Sadykh-Zade, and Y. P. Egorov, *Izv. Akad. Nauk Azerb. SSR, Ser. Fiz. Tekhn. i Khim. Nauk*, 122 (1958); *Chem. Abstr.*, **53**, 15954*b* (1959).

Dipole Moments of Norbornane and Chloronorbornanes[1]

CHARLES F. WILCOX, JR., J. G. ZAJACEK,[2] AND M. F. WILCOX

Department of Chemistry, Cornell University, Ithaca, New York

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The dipole moments of norbornane, its four possible monochlorides, and 1,4-dichloronorbornane have been determined in cyclohexane solution. Norbornane has an essentially zero moment. The 7-chloronorbornane shows a significantly smaller moment than the 1-, 2-*exo*-, or 2-*endo*-chlorides. The diminution of the moment is associated with the different hybridization at the C-7 position. From the moment of the 1,4-dichloride and the derived bond moments of the C-1–Cl bond, the intersection angle between the C-1–Cl and C-4–Cl bond vectors is calculated to be 144–145°.

Dipole moment measurements have been used widely in assigning structural configurations and in clarifying even more detailed questions of molecular structure. One complication in such applications to norbornane derivatives is the uncertainty of the dipole moment of the parent hydrocarbon, bicyclo[2.2.1]-heptane **1**. A dipole moment has been measured for this molecule[3]; however the determination was based on a limited set of data and for other reasons to be elucidated later appeared suspect. Another complication of dipole moment studies of norbornyl systems is the possible variation of electronegativity, and hence bond moments, at the three different types of carbon atoms present. Difference in hybridization such as would be expected between C-7 (internal skeletal angle of *ca.* 95°), and C-2 (internal skeletal angle of *ca.* 105°) might be expected to produce measurable differences in the moments of pairs of norbornanes substituted at these positions. While neither of these complications would nullify many of the grosser appli-

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(1) This work was supported by the National Science Foundation.

(2) Taken in part from the dissertation submitted by J. G. Z. to Cornell University for the Ph.D. degree, Sept. 1962.

(3) H. Krieger, *Suomen Kemistilehti*, **B31**, 348 (1958).

TABLE I

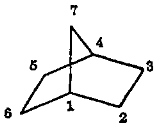
DIPOLE MOMENT DATA

Compd.	α	σ_α	β	σ_β	P_{20}	P_{E_2}	μ	σ_μ
1	0.084	0.018	−0.114	0.004	30.6	30.14	0.15 (0.03[a])	0.07 (0.02[a])
2	1.06	0.034	−0.468	0.024	76.5	39.8	1.32	0.026
3	3.12	0.045	−0.335	0.006	129.6	35.0	2.15	0.015
4	3.01	0.06	−0.342	0.004	125.9	35.0	2.11	0.021
5	3.01	0.06	−0.304	0.009	127.2	35.0	2.13	0.02
6	2.87	0.03	−0.351	0.005	121.2	35.0	2.05	0.01

[a] From comparison of 3 and 4 as described in text.

cations of dipole moment studies, they can become significant when finer structural details are sought.

This paper will present dipole moments for the four possible monochlorides of norbornane as well as norbornane itself. These various moments are used to assign the direction of the moment of norbornane and to calculate this norbornane moment indirectly by vector algebra. The different moments are correlated qualitatively with the geometry of the norbornane skeleton. The norbornane and 1-chloronorbornane moments are employed in calculating the angle of intersection of the extension of the two C–Cl bonds of 1,4-dichlorobicyclo[2.2.1] heptane (2) from its observed dipole moment.



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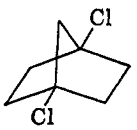

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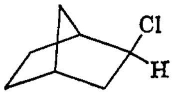

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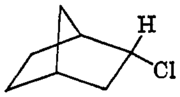

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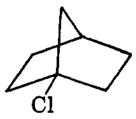

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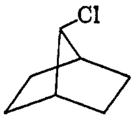

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Results and Discussion

The dipole moments of norbornane (1), 1,4-dichloronorbornane (2), *exo*-2-chloronorbornane (3), *endo*-2-chloronorbornane (4), 1-chloronorbornane (5), and 7-chloronorbornane (6) were determined using cyclohexane as the solvent. Cyclohexane was selected because it was felt that its general similarity to these bicyclic chlorides would minimize deviations due to nonideality of the solutions. An important consideration in rejecting benzene, which had been used earlier in determining the moment of norbornane, was the experience in these laboratories that benzene absorbed water sufficiently rapidly under normal handling conditions to give scattered dielectric constant readings (a referee has noted that this difficulty was probably caused by bubbles rather than moisture).

The dipole moments were determined by the method of Halverstadt and Kumler.[4] This requires the determination of the solute weight fraction dependence of the dielectric constant of solutions of solute ($d\epsilon_{12}/d\omega_2 = \alpha$) and the weight fraction dependence of the specific volume ($dV_{12}/d\omega_2 = \beta$). The slopes α and β are combined with the specific volume of the pure solvent, v_1, its dielectric constant, ϵ_1, and the molecular weight of the solute, M_2, according to eq. 1, to yield the total polarizability of the solute, P_{20}. This quantity was converted into a dipole moment in the standard manner[4] by substraction of the atomic and electronic

$$P_{20} = M_2\left[\frac{3\alpha V_1}{(2 + \epsilon_1)^2} + (V_1 + \beta)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}\right] \qquad (1)$$

polarizations, which in this work were estimated as the sum of atomic refractions.

Halverstadt and Kumler[4] have emphasized that the slope α is constant only for solution of low weight fraction and following their recommendation all dielectric constant measurements employed in this paper were made on solutions of 0.01 weight fraction or less.[5] For the chlorides, measurements were made on five different concentrations of solute. For norbornane, which has a much smaller dipole moment and therefore a smaller α, measurements were made on ten different solutions. The slope α was evaluated by least squares and, as suggested by Smith and Cleverdon,[6] the pure solvent was included in the fit.[7] The slopes, α, and their standard deviations, σ_α, are recorded in Table I.

The slope, β, of the specific volume *vs.* weight fraction plot was determined on solutions that were approximately ten times more concentrated than those used to determine α. Because the calculated dipole moments are not very sensitive to β, the use of higher concentrations does not result in significantly altered accuracy of the final moment.[8] It is, however, considerably easier to determine accurately the change in densities of solutions of weight fraction greater than 0.01.[9] In Table I are recorded the β values and their standard deviations, σ_β.

The last two columns of Table I record the calculated dipole moments and their standard deviations. It should be noted that these standard deviations do not include an error contribution from the electronic and atomic polarizability term P_{E2}. The latter source of error is of unknown magnitude but is undoubtedly largest for norbornane, the molecule with the smallest

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[4] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[5] In a preliminary study,[2] made when only a much less sensitive dielectric constant apparatus was available, measurements were made on solutions of 0.01–0.10 weight fraction. Systematic increases in α with increasing weight fraction were noted for these solutions.

[6] J. W. Smith and D. Cleverdon, *Trans. Faraday Soc.*, **45**, 109 (1949).

[7] Separate evaluation of the α terms without inclusion of the pure solvent gave values essentially identical with those reported in Table I. The concordance of the two procedures indicates that no significant moisture contamination was present.[4]

[8] Exceptional cases occur when α is comparable with β in magnitude and when β is large (*i.e.*, when the specific volume of the solute is large compared with the solvent.)

[9] The equivalence of the β values obtained from the two different concentration ranges was checked for norbornane and 1-chloronorbornane. For both molecules the β values agreed within the experimental error of either method.

moment. As will be brought out in the next paragraph, this norbornane moment agrees well with a value obtained by an indirect but more precise method. The concordance of these two methods of calculating the norboranane moments indicates the polarizability term is not a major source of error within the well-known limits of determining moments by solution measurements.

The dipole moment of norbornane observed directly has a large standard deviation because of its small magnitude. In principle, a more precise value can be obtained by comparing the moments of the 2-*exo*- and 2-*endo*-chlorides. These moments can be written as a vector sum of the moment of norbornane and the "effective" bond moment of a C–Cl bond[10] appropriate to the hybridization of the 2-carbon atom. If the difference of the squares of the vector moments of the 2-*exo*- and 2-*endo*-chlorides is taken, eq. 2 results.

$$(\mu\mathbf{3})^2 - (\mu\mathbf{4})^2 = (\mu\mathbf{1})^2 + 2(\mu\mathbf{1})(\mu_{exo\text{-C-Cl}}) + (\mu_{exo\text{-C-Cl}})^2 - (\mu\mathbf{1})^2 - 2(\mu\mathbf{1})(\mu_{endo\text{-C-Cl}}) - (\mu_{endo\text{-C-Cl}})^2 \quad (2)$$

After cancellation of identical terms[11] eq. 3 is obtained. The bracketed term on the right-hand side

$$(\mu\mathbf{3})^2 - (\mu\mathbf{4})^2 = 2(\mu\mathbf{1})[(\mu_{exo\text{-CCl}}) - (\mu_{endo\text{-CCl}})] \quad (3)$$

can be estimated[12] as (2.15) $(0.957j + 1.341k)$, where the coordinate frame is that of ref. 12. The norbornane vector moment is $|\mu\mathbf{1}|\ k$. When numerical values for $\mu\mathbf{3}$ and $\mu\mathbf{4}$ are substituted in eq. 3 the value calculated for $|\mu\mathbf{1}|$ is 0.03 D.[13] with a standard deviation of 0.02 D. The direction of the norbornane moment can be inferred as pointing up (in the sense of structure **1**) along the principal symmetry axis. It can be calculated from the standard derivations of the various moments that this directional assignment has a probability of 0.93

The lower, indirect norbornane moment of 0.03 D. is favored over the directly determined value of 0.15 D. in spite of the structural assumptions required in its derivation. As noted before, the measured total polarization of norbornane is nearly equal to the molar refraction alone so that a 1.5% increase (atomic polarization correction of 0.5) in the latter would yield a zero moment.[14] Kumler, *et al.*,[15] have estimated the atomic polarization term of norcarane as 0.8. Another related factor in favor of the indirect evaluation is that on the left-hand side of eq. 2 the atomic and electronic polarizability terms formally cancel.

With the estimate of 0.03 D. for the norbornane moment, the effective bond moments of chlorines attached to the 1,2-*exo*-, 2-*endo*-, and 7-positions are 2.12, 2.13, 2.13, and 2.03 D., respectively. These moments are in qualitative accord with the hybridization appropriate to the geometries of the different carbon atoms. The 1-, and 2-carbon atoms have internal skeletal angles of about 105°, whereas the 7-carbon has an internal skeletal angle of about 95°.[12] More s character would be associated with a bond external to the carbon atom with the smaller internal angle[16] which would in turn result in a smaller dipole moment for a chlorine atom attached to this carbon.[16,17]

Krieger[3] has reported a dipole moment for norbornane (**1**) in benzene of 0.58 D. and has assigned its direction opposite to that reported here. Subsequent to the present work, Hirsjarvi and Krieger[18] have revised the norbornane moment downward to 0.24 D. In neither report was an error analysis included. Reanalysis, using a least-squares treatment, of the data in the first report[3] gave a calculated moment of 0.52 D. with a standard deviation of 0.24 D. Reanalysis of the *published* data in the second report[18] gave an imaginary moment. In both reports inadequate attention was given to the value of β, which for norbornane is a more significant term than is α. An alternate treatment of the Krieger data is to note that the sum, $V_1 + \beta$, is for ideal solutions the specific volume of norbornane and might be transferable from one solvent to another. The present measurements with the solvent cyclohexane give this sum a value of 1.178, which compares favorably with the value of 1.183 observed[15] for the structurally similar molecule norcarane. If the 1.178 value is used in place of reported[18] value of 1.159 (σ = 0.028) a moment of 0.16 D. is calculated.

It is of some interest to use the present data to elucidate further the geometry of the norbornane skeleton. With the value of 0.03 D. for norbornane, 2.12 D. for the 1-chloro bond moment, and the observed moment of 1.32 D. for the dichloride **2**, it can be calculated that the angle of intersection of C-1–Cl bond vectors is 145° (σ = 0.4°).[19] This value agrees fairly well with the earlier[12] *a priori* estimation of 139°; however, the agreement may be in part fortuitous because of the simplifying assumptions that were made.

Experimental

Dipole Moment Measurements.—The dielectric constants were measured with a WTW DFL 1-heterodyne beat apparatus (2.0 mc.) at 25.0 ± 0.1°. The cyclohexane solvent (spectral grade) was dried immediately before use by the passage through a 15 × 2 cm. column of 4A Molecular Sieve pellets. The dielectric constant of cyclohexane was taken as 2.015.[20]

Norbornane (**1**) was prepared by hydrogenation of bicycloheptadiene in methanol over platinum oxide and purified by repeated sublimation. Analysis by g.l.c. indicated >99.9% peak purity.

1,4-Dichlorobicyclo[2.2.1]heptane (**2**) was prepared as described previously[21] and purified by repeated sublimation.

exo-**2-Chlorobicyclo[2.2.1]heptane** (**3**) was prepared by passage of hydrogen chloride gas through a solution of 50 g. of norbornane in 120 ml. of petroleum ether (b.p. 30–60°) for 24 hr. at −80°. The solution was washed successively with water, sodium carbon-

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[10] By the effective moment is meant the difference between the bond moment of the C–Cl bond and the bond moment of the corresponding C–H bond. In practice it is usually assumed that the C–H and C–Cl bonds are colinear and that the molecular moment can be written as a sum of bond moments.

[11] The scalar terms $(\mu_{exo\text{-C-Cl}})^2$ and $(\mu_{endo\text{-C-Cl}})^2$ may be cancelled in good approximation because these C–Cl effective moments originate at a common atom.

[12] C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

[13] The error introduced by the assumed geometry is unknown. However, the calculated moment depends largely on the angle between the exterior bonds attached to the 2-carbon atom and is therefore close to 109°. With an exterior angle of 120° and a vertical *endo* bond the derived norbornane moment is reduced by only 0.005 D.

[14] Some workers systematically increase the molecular refractivity term by 5% to correct for the atomic polarization.

[15] W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *J. Am. Chem. Soc.*, **86**, 3126 (1964).

[16] For an independent illustration of this effect, see C. S. Foote, *Tetrahedron Letters*, **No. 9**, 579 (1963).

[17] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

[18] P. Hirsjarvi and H. Krieger, *Suomen Kemistilehti*, **B37**, 140 (1964).

[19] If the norbornane moment is taken to be zero so that $\mu_{\text{C-1-Cl}}$ is 2.13 D., the calculated angle changes to 144°.

[20] National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951, p. 1.

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

ate solution, and water. The solution was dried over calcium chloride and distilled through a 30-cm. glass-helix-packed column to give **3**, b.p. 54–55° (16 mm.), n^{25}_{D} 1.4826 (lit. b.p. 54–55° at 16 mm.,[22] n^{20}_{D} 1.4842,[22] n^{25}_{D} 1.4823[23]).

***endo*-2-Chlorobicyclo[2.2.1]heptane (4)** was prepared according to the procedure of Roberts and Bennett.[24] The crude product after distillation was freed of *exo* contaminant by partial solvolysis at room temperature for 4 hr. in 95% acetone–water containing 60% of the requisite silver nitrate for complete destruction of the chloride. The organic chloride was isolated and resolvolyzed in the same manner. After reisolation, the organic chloride had b.p. 73–73.5° at 40 mm. (lit.[24] b.p. 75° at 41 mm.). Infrared and n.m.r. analysis showed that less than 5% *exo* isomer was present. G.l.c. on several columns failed to separate the *endo* and *exo* isomers.

1-Chlorobicyclo[2.2.1]heptane (5) was prepared according to the procedure of Wiberg[25] and purified by an initial distillation through a 90-cm. tantalum-wire column followed by an additional distillation through a 90-cm. spinning-band column, b.p. 146–148° (lit.[25] b.p. 148–154°). Analysis by g.l.c. indicated *ca.* 98% peak purity.

7-Chlorobicyclo[2.2.1.]heptadiene-2,4 was prepared according to the procedure of Story[26] and purified by distillation through a 90-cm. tantalum-wire column, b.p. 68° at 41 mm. (lit.[26] b.p. 77.5° at 63 mm.). Analysis by g.l.c. showed >99% peak purity.

7-Chlorobicyclo[2.2.1]heptane (6) was prepared by hydrogenation of the above diene in cyclohexane over platinum oxide at room temperature. The catalyst was removed by filtration and the organic chloride was isolated by distillation through a 90-cm. tantalum-wire column to give **6** (81% yield), b.p. 73° at 41 mm., m.p. 41–42°. Analysis by g.l.c. showed >99% peak purity. The infrared spectrum of **6** was in accord with that published by Roberts, *et al.*[27]

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[22] H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **78**, 5010 (1956).

[23] L. Schmerling, *ibid.*, **68**, 195 (1946).

[24] J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

[25] K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961).

[26] P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

[27] J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).

Nuclear Magnetic Resonance Studies of 5,6-Dihalo-2-norbornenes and 2,3-Dihalonorbornanes

P. M. SUBRAMANIAN, MERLE T. EMERSON, AND NORMAN A. LEBEL[1]

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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The n.m.r. spectra of several 5,6-dihalo-2-norbornenes and 2,3-dihalonorbornanes have been examined with the aid of specific deuterium labeling and double resonance. Chemical shifts and many coupling constants have been evaluated. New evidence for long-range coupling between (1) *endo* protons and *anti* 7-protons, (2) vinyl protons and *anti* 7-protons, and (3) the two bridgehead protons has been obtained. Confirmation of the requirements for "virtual coupling" is also presented. Good stereochemical correlations may be made, and the utility of measurements in aromatic solvents is discussed.

Stereochemical assignments in substituted bicyclic systems have been confronted with difficulties despite the rigid geometries involved. The obvious method of dipole moment measurements (where applicable) is often ambiguous primarily because of the lack of precise information of contributions by the basic ring system. For example, in the case of the isomeric 2,3-dibromonorbornanes, the configuration of only the *trans* isomers could be assigned unequivocally by dipole moment data. A distinction between the *endo*- and *exo-cis* compounds was impossible.[2] Of the physical methods available, the most promising approach would seem to be the application of proton magnetic resonance spectral data. Numerous publications have appeared in recent years describing either detailed analyses of the n.m.r. spectra of norbornene (and sometimes norbornane) derivatives[3] or analyses of such spectra for structural and stereochemical assignments. Some ambiguities still remain.

We have accumulated an extensive series of 5,6-dihalo-2-norbornenes and 2,3-dihalonorbornanes and have examined the n.m.r. spectra in detail, utilizing double resonance techniques and deuterium labeling in many cases. The results appear very interesting. Because the structural modifications do not involve large changes in substituent electronegativities, the observed spectra provide data which can be interpreted without recourse to electronegativity differences.

The compounds that were examined are listed in Chart I (p. 2627). Series I consisted of norbornene derivatives; II refers to dihalonorbornanes. Chemical shifts for the various protons of these compounds are given in Tables I and II. Values are recorded in cycles per second downfield from tetramethylsilane. In the case of an unresolvable multiplet, the center is denoted. For those protons where an AB pattern occurs, the resonances for each A and B species have been identified in most cases, and the chemical shifts were calculated from the measured values and coupling constants. Similar calculations were made with the AB portion of a recognizable ABX spectrum.

Many of the various coupling constants were easily recognized and were measured directly from carefully calibrated spectra. With the AB portions of an ABX pattern, only J_{AB} could be obtained by direct measurement; the values of $^1/_2(J_{\mathrm{AX}} + J_{\mathrm{BX}})$ were calculated from measured distances. A combination of measurements including the separation of extreme peaks in a multiplet, the spectra of specific deuterium-labeled analogs, and nuclear magnetic double resonance were applied to extract various coupling constants. The J values thus obtained are tabulated in Table III.

Chemical shifts in aromatic solvents were measured for most of these compounds. Inasmuch as this was a secondary source of information, a comprehensive study was not attempted. The concentration dependence in aromatic solvents is significant. The present limited study has indicated several trends useful for stereo-

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[1] Alfred P. Sloan Foundation Fellow, 1961–1965. To whom communications regarding this article should be directed.

[2] N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 623 (1960); N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *ibid.*, **85**, 3199 (1963).

[3] P. Laszlo and P. v. R. Schleyer, *ibid.*, **86**, 1171 (1964). This article cites a rather extensive list of pertinent references.