justified since the effects of iodobenzene on the reaction rates probably are reflected to the same degree in the rate constant for the forward and reverse reactions.

The Effects of Medium Polarity on Dichloride Dissociation.—If photochemical processes are omitted from consideration, it now seems clear that the dissociation of iodobenzene dichloride in a non-polar medium requires a polar catalyst. The arguments outlined in the introduction which suggest that the dichloride does not liberate free chlorine as an intermediate when it reacts with unsaturates to form their dihalides are thus strongly supported. It is particularly significant that not only Barton and Miller[4] but also Cristol, Stermitz and Ramey[1] found that when moisture was included in the medium in such reactions, the geometric configuration of the addition product shifted toward that obtained when free chlorine rather than the dichloride was used as the halogen source. Although the results of the present investigation indicate that water alone will not promote dichloride dissociation, it is entirely conceivable that traces of hydrogen chloride were present in the chloroform solvent used in these reactions. It is also possible that water functions without a cocatalyst in chloroform.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Proton Magnetic Shieldings in the Haloalkanes

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The failure of the classical theory to account quantitatively for the dependence of proton magnetic resonance line position on sample bulk susceptibility is explained in terms of induced molecular magnetic anisotropy in the medium. Methods for obtaining relative intramolecular shielding constants are discussed. Relative shielding constants for protons in a number of haloalkanes are presented. Some of the factors contributing to shielding in the haloalkanes are discussed, and a correlation with molecular electric dipole moment is noted.

Introduction.—Nuclear magnetic resonance (hereinafter n.m.r.) spectroscopy has shown itself to be a powerful tool in the solution of qualitative analytical problems in organic chemistry, as in diverse other fields. One of the pressing problems in the application of this technque is the elaboration of a method for dissecting the intramolecular chemical shielding (as it would be measured in a single molecule) from the other influences affecting n.m.r. line position, such as volume susceptibility, sample shape and orientation, solvent magnetic anisotropy and chemical association. A theory permitting the complete separation of these effects would be of great value in the application of n.m.r. as an analytical tool. It would also facilitate further development of the theory of proton shielding in organic molecules.[1–3]

Previous measurements on haloalkanes have indicated the existence of important correlations between structure and line position. The pioneering work of Meyer and Gutowsky[4] established a trend toward less proton shielding as the number of halogens on the carbon bearing the proton is increased. Measurements made by Shoolery and Dailey[5] indicate that the protons of methyl halides as well as the protons in the α-position of the ethyl halides are progressively less shielded in the series iodide–bromide–chloride. These findings suggested a close connection between electronegativity and proton shielding,[5] which if preserved throughout the range of organic compounds would greatly simplify the interpretation of proton magnetic resonance spectra.

Binary mixtures of alkyl halides and/or saturated hydrocarbons show quite "regular" solution behavior with respect to solvent susceptibility corrections.[6] This "regular" behavior makes possible a reasonably accurate estimation of true intramocular shielding constants. Even in this case solvent interaction is not negligible; however, the uncertainties in the shieldings are small compared to the shielding differences themselves so that a true order of shieldings may be obtained.

Interaction in Solution and Standardization of Spectra.—In the absence of chemical association, binary mixtures of simple aliphatic compounds exhibit proton magnetic resonance lines, the positions of which are predictable on the basis of the expression[7]

$$\mathcal{H} = (1 - \sigma_i)\mathcal{H}_i^0(1 - \alpha\kappa) \qquad (1)$$

where $\mathcal{H}$ is the resonant field for protons at the frequency employed, σ_i is the intramolecular shielding factor for the ith proton, $\mathcal{H}_i^0$ is the field which must be applied externally to the sample in order to excite resonance in the ith proton, α is a constant dependent on the sample shape, and κ is the volume susceptibility of the liquid. The constant α has values ranging from 2.3 to 3.0 for a variety of binary mixtures of non-polar liquids in cylindrical sample tubes oriented transversely to the field.[6] The classically calculated value of α for this geometry is

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(1) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **86**, 243 (1956).

(2) J. A. Pople, *J. Chem. Phys.*, **26**, 1111 (1956); *Proc. Roy. Soc. (London)*, **A236**, 515 (1956); **A239**, 541, 550 (1957).

(3) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(4) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

(5) J. N. Shoolery and B. P. Dailey, THIS JOURNAL, **77**, 3977 (1955).

(6) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1647 (1957), and unpublished work.

(7) E. R. Andrew, "Nuclear Magnetic Resonance," Cambridge University Press, 1956, p. 78.

$2\pi/3$ or 2.09. The discrepancy between α and $2\pi/3$, which may be called β, represents a correction term for the failure of the Lorentz cavity model. One of the ways in which this discrepancy may be interpreted is in terms of an induced molecular magnetic anisotropy in solvent molecules in the vicinity of a solute molecule.[8]

For example, assume that the approach of a solvent molecule (s) to a distance r from the solute molecule (m) results in an induced magnetic anistropy in the solvent molecule,[9] such that the molecular susceptibility in the direction of the intermolecular axis is χ_A and perpendicular to it χ_B (Fig. 1). The applied field induces a moment in the solvent molecule which produces a secondary magnetic field at the subject molecule. The component of this field in the direction of the static applied field is given by

$$\mathcal{H}_{loc} = \mathcal{H}^0(2\chi_A \cos^2\theta - \chi_B \sin^2\theta)r^{-3} \qquad (2)$$

where θ is the angle between the direction of the applied field and the intermolecular axis.[10] Averaging for all orientations of the intermolecular axis, there is obtained for the average local field

$$<\mathcal{H}_{loc}> = \frac{2}{3}\mathcal{H}^0(\chi_A - \chi_B)r^{-3} \qquad (3)$$

Setting the number of molecules at a distance between r and $r + dr$ from the subject molecule, equal to $\phi(r)dr$ and summing for all the molecules in solution, results in the expression

$$<\mathcal{H}_{loc}> = 2\mathcal{H}^0\chi \int \phi(r)Z(r)r^{-3}dr \qquad (4)$$

where $Z(r)$, the anisotropy function is defined by

$$\chi_A - \chi_B = 3Z(r)\chi \qquad (5)$$

χ being the molecular susceptibility of the solvent as calculated from the macroscopically observed volume susceptibility.

As a crude test for the magnitude of the effect expected on such a basis, the lattice model for liquids is applied. It is assumed that only the nearest neighbors in solution are effective in shifting a resonance. For a face-centered cubic or hexagonal lattice, there are twelve nearest neighbors, and their average distance from the central molecule may be calculated from the relation

$$r^3 = \sqrt{2}M/dN \qquad (6)$$

where M is the molecular weight, d the density and N = Avogadro's number. Equation 4 then takes the form

$$<\mathcal{H}_{loc}> = 12\sqrt{2}Z(r)\mathcal{H}^0\kappa = \beta\mathcal{H}^0\kappa \qquad (7)$$

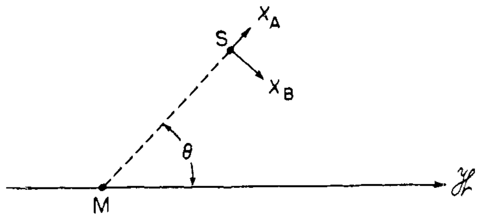

Fig. 1.—Induced magnetic anisotropy.

The range of values for β then reflects the range of values for $Z(r)$, the anisotropy function. It is not surprising that the range of values for non-polar solvents and solutes is not too large.

From previous measurements a mean value of 0.5 may be calculated for β. The corresponding value of the anistropy function $Z(r)$, according to equation 7, is 0.03.

An interesting aspect of the "regular" behavior of binary mixtures is that for both components β is the same and essentially constant over the composition range. There is thus an interesting reciprocal relationship connecting the anisotropy functions for component A in solvent B and *vice versa*. There is a definite difference between β's for one compound in several solvents, however. This can be shown by considering the results for the three possible binary mixtures of three substances. For example, the following separations are observed in the corresponding mixtures

dioxane–cyclohexane	−212
methyl iodide–dioxane	+141
cyclohexane methyl iodide	+ 76

The non-zero algebraic sum can arise only if β varies in this series. Numerous other similar cases could be cited.

With compounds behaving regularly, standardization by the use of the capillary method[11] and extrapolation to infinite dilution in a solvent, or by the use of the same solvent as an internal standard in binary mixture with the haloalkanes give the same result. The use of a different solvent, however, will give a slightly different set of relative shielding values as a result of variations in β for the various binary pairs. In the present study, cyclohexane has been used as the reference in binary mixtures with the haloalkanes. We also have used *t*-butyl chloride and methyl iodide and frequently checked our results by direct inter-comparison between the two haloalkanes themselves in liquid mixture. Though anomalies of the kind noted above with dioxane, methyl iodide and cyclohexane were noted, they were small enough to permit the estimation of true relative shieldings for the protons in haloalkanes to within five parts in one hundred million.

Experimental.—Materials used were the best commercially available though not especially purified. Spectra were taken of liquids in 5-mm. glass tubes using the spinning sample assembly in a Varian model V 4300 B nuclear magnetic resonance spectrometer with a 12-inch Varian electromagnet equipped with a flux stabilizer. Separations of resonance lines were measured by the side-band method or the wiggle-beat method. Under favorable conditions, line separations could be obtained by the side-band method to within half a cycle. The wiggle-beat method gave separa-

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(8) N. Bloembergen and W. C. Dickinson, *Phys. Rev.*, **79**, 179 (1950). Other possibilities include an effect on the intramolecular shielding tensor by solvent molecules and anomalous shieldings by permanent magnetic anisotropy in neighboring solvent molecules with preferred orientations in the vicinity of the solute molecule. The first explanation seems inadequate because there is no apparent reason for the total "extra" shift to be roughly proportional to the solvent bulk susceptibility, as observed, while the second explanation suffers from the disadvantage that one would predict the occurrence of negative as well as positive values.

(9) Such an anisotropy could arise through the deformation of the electronic orbitals by dispersion forces between molecules in a liquid. The main contribution would presumably be through the diamagnetic part of the molecular susceptibility tensor. The paramagnetic part would be expected to be changed only slightly, considering the relative insensitivity of the electronic absorption spectra of non-polar molecules to changes in non-polar solvents; *cf.* H. C. Longuet-Higgins and J. A. Pople, *J. Chem. Phys.*, **27**, 192 (1957).

(10) This derivation is based on the point-dipole approximation, assuming r and θ to be unambiguously assignable. A more rigorous but less easily applicable expression may be obtained from the complete shielding theory of Ramsey; *cf.* ref. 3.

(11) A. A. Bothner-By and R. E. Glick, THIS JOURNAL, **78**, 1071 (1956).

tions to one-tenth of a cycle for closely spaced lines. Samples were not de-gassed.

Discussion

Results.—The estimated proton shieldings for a number of haloalkanes are given in Table I. The relative shielding numbers are obtained from the arbitrarily chosen equation

$$\text{shielding} = (\sigma_{\mathrm{Rx}} - \sigma_{\mathrm{CH}}) \times 10^8 \qquad (8)$$

where σ_{Rx} and σ_{CH} represent the factors for haloalkane protons and cyclohexane protons in liquid mixtures of the two.

TABLE I

PROTON MAGNETIC RESONANCE SHIELDING[a] IN HALOALKANES RELATIVE TO CYCLOHEXANE

Compound	$(\sigma_{\mathrm{Rx}} - \sigma_{\mathrm{CH}}) \times 10^8$			
	α-H's	β-H's	γ-H's	ω-H's
CH_3I	− 74			
CH_3Br	−122			
CH_3Cl	−159			
C_2H_5I	−177	−42		
C_2H_5Br	−197	−20		
C_2H_5Cl	−214	0		
n-C_3H_7I	−177	−37	+48	
n-C_3H_7Br	−195	−42	+45	
n-C_3H_7Cl	−212	−35	+53	
i-C_3H_7I	−288	−43		
i-C_3H_7Br	−278	−23		
i-C_3H_7Cl	−273	− 2		
n-C_4H_9I	−177	Not resolved		+53
n-C_4H_9Br	−197			+53
n-C_4H_9Cl	−210			+53
t-C_4H_9I	...	−50		
t-C_4H_9Br	...	−33		
t-C_4H_9Cl	...	−13		
n-$C_5H_{11}Br$	−192	Diffuse peak moves toward +15 as chain is lengthened		+53
n-$C_6H_{13}Br$	−192			+53
n-$C_7H_{15}Br$	−195			+58
Cyclopentyl I	−290	(−45) one peak		
Cyclopentyl Br	−297	(−47) one peak		
Cyclopentyl Cl	−287	(−40) one peak		
Cyclohexyl I	−290	(−12, −62)		
Cyclohexyl Br	−272	(− 5, −55)		
Cyclohexyl Cl	−252	(0, −32)		
Cyclopropyl Cl	−154	+74		
CH_2I_2	−245			
CH_2Br_2	−354			
CH_2BrCl	−381			
CH_2Cl_2	−390			
CHI_3	−348			
$CHBr_3$	−545			
$CHBr_2Cl$	−567			
$CHBrCl_2$	−580			
$CHCl_3$	−587			
CH_3CHBr_2	−452	−106		
$ClCH_2CH_2Cl$	−226			
$BrCH_2CH_2Cl$	−225			
	−233			
$BrCH_2CH_2Br$	−223			
$BrCH_2CH_2CH_2Cl$	−227	−81		
	−211			
n-C_5H_{12}	+ 56	+19		
n-C_6H_{14}	+ 54	+17		
n-C_9H_{20}	+ 54	+16		
$(CH_3)_2CHCH(CH_3)_2$	+ 58	..		
$(CH_3)_4C$	+ 53			
Cyclopropane	+127			
Cyclopentane	− 6.5			
(Cyclohexane)	0			

[a] As measured from the centers of spin-spin multiplets. No corrections were applied for interactions of J and σ.

Sources of Shielding.—Attempts to apply the complete shielding theory of Ramsey[1] to organic molecules of such complexity as the haloalkanes are faced with insuperable difficulties. It is possible from a general consideration of the theory to discern certain aspects which lend themselves to qualitative estimation, and to consider these separately as possible contributors to the shieldings. Following McConnell,[3] we may further break down the diamagnetic and paramagnetic terms in the shielding expression[1] into contributions from local and remote electron groups in the molecule. A local group may be defined as a group which is involved directly in the binding of the proton; a remote group of electrons is separated by at least one bond from the proton in question.

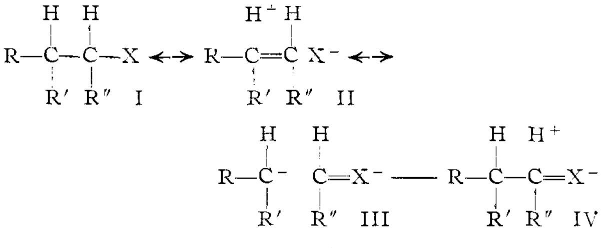
The local diamagnetic contribution to the shielding presumably is proportional to the electron density in the vicinity of the proton, and is expected to be affected by the proximity of electron-withdrawing or -releasing groups in the molecule. Excited electronic states involving the electrons "belonging" to the proton could contribute to a local temperature independent paramagnetism, but it is assumed here that the excitation energies of C–H bonds are all large and of about equal magnitude, so that the effect is roughly constant.

Diamagnetic and paramagnetic contributions to the shielding from remote electron groups are nonzero only if the particular group susceptibility is anisotropic. The influence of electron-withdrawing substituents in the molecule and magnetic anisotropy in remote electron groups will be considered in turn.

(1) **Proximity of Electron-releasing or Withdrawing Groups.**—Electron-releasing or -withdrawing groups may act by an *inductive* mechanism or an *electromeric* mechanism. If the pure inductive effect is operative one expects most effective electron withdrawal (less shielding) by the most electronegative element. It already has been pointed out by Dailey and Shoolery[5] that the shieldings in the methyl halides are consistent with this idea, and that if it is assumed that the inductive effect is largely attenuated by the C–C bond in the ethyl derivatives, then the relative shieldings of the α- and β-protons in ethyl halides also fall into line. This effect cannot by itself account for the relative proton shieldings as measured in the present study; for example, it is noted that the shieldings for the β-protons of the ethyl derivatives (as well as of the *i*-propyl and *t*-butyl derivatives) increase as the electronegativities of the halogens increase. The α-proton shieldings in the ethyl derivatives thus show a smaller dependence on the electronegativity of the halogen than one would infer from the data on the methylene–methyl separation. A more important objection to the idea of direct dependence on electronegativity is the observation that the shieldings of the *α-protons* in isopropyl halides show a slight

increase as the electronegativity of the halogen increases, an inversion of order relative to the methyl series, which is even more marked with the cyclohexyl halides.

Consideration of possible electromeric shifts ameliorates the situation slightly. Some of the conceivable resonance contributors for an alkyl halide are



Forms, II, III and IV are all expected to contribute to a greater extent for halides with higher atomic numbers. These forms indicate a lowered electron density in the neighborhood of the α- and β-protons, and their increasing contribution would therefore lead to the reverse trend in shieldings observed with the protons of the *i*-propyl and cyclohexyl halides. The contributions of these forms would furthermore be favored by the steric compression present in secondary and tertiary alkyl halides, and it would thus be in precisely these substances that the reversal in trend would be more likely to appear. The shielding of the β-protons in the series ethyl, *i*-propyl and *t*-butyl halides decreases slightly. A marked decrease is observed in the shielding of β-protons in the series alkyl chloride, alkyl bromide, alkyl iodide. These observations are also in accord with the increase in importance of the forms II, III and IV as contributors to the resonance with increasing atomic number of the halogen and with increasing branching on the α-carbon.

(2) **Bond Anisotropy in Remote Parts of the Molecule.**—The importance of this factor has been particularly emphasized by Pople.[2] Anisotropy in aromatic systems arising from the diamagnetic circulation of the π-electrons has been the basis of successful treatment of a number of problems, including the question of the difference in shielding between aromatic and olefinic protons,[2] the anomalous susceptibilities exhibited by aromatics used as solvents in n.m.r. measurements,[12] the shieldings in the paracyclophanes,[13] and the nature of chloroform–aromatic complexes.[12,14] The magnetic polarizability of a bond, although varying between limits, is roughly constant, as shown by the applicability of Pascal's numbers for the calculation of gross magnetic susceptibilities. As an extrapolation, one may propose that a given type of bond has roughly the same magnetic anisotropy as well. This means that characteristic longitudinal and transverse susceptibilities (χ_L and χ_T) may be assigned to single or triple bonds, while possibly three different susceptibilities are required for double bonds. In the general case of a single or triple bond with the proton located at a distance r and at an angle β off the axis of the bond, the local field produced by the bond at the proton is given by

$$\langle \mathcal{H}_{\text{loc}} \rangle = \frac{1}{3} \mathcal{H}^0 (3 \cos^2 \beta - 1)(\chi_L - \chi_T) r^{-3} \quad (9)$$

the thermal tumbling motion of the molecule having been taken into account.[3] If one assumes $\chi_L - \chi_T$ to be of the order of magnitude of 20% of the observed bond susceptibility, then calculations for methyl chloride, methyl bromide and methyl iodide show effects in the shielding of 25×10^{-8}, 32×10^{-8} and 38×10^{-8}, respectively.[15] In such a bond as a C–X bond, one may consider magnetic anisotropy arising in two ways. The quenching of the orbital angular momentum about an axis perpendicular to the bond leads to a paramagnetism perpendicular to the bond. This arises from the off-diagonal matrix elements connecting ground and excited electronic states. A method for the estimation of this contribution has been given by Pople, and applied in the cases of hydrogen fluoride, water, ammonia and methane.[2] The observed shieldings in these compounds are thereby satisfactorily explained. If overlap is neglected between atoms in a molecule, the diamagnetic term in the expression for the shielding is isotropic for each atom and hence for the molecule as a whole. In fact, however, the electrical properties of interatomic bonds are markedly anisotropic, as may be deduced from an examination of Kerr constant data.[16] Most bonds (the H–H bond is an exception) possess a greater longitudinal electric polarizability than transverse, and a classical extrapolation would predict a greater transverse diamagnetic susceptibility than longitudinal. A partial cancellation is thus expected. Application of (9) shows that in alkyl halides the α-hydrogen would be shielded by paramagnetism transverse to the C–X bond, unshielded by diamagnetism.

In a series of compounds in which the C–X bond is becoming more nearly ionic, the paramagnetic term would tend to diminish since the halogen more nearly approaches the state of the halogen ion for which no paramagnetic contribution is possible. Considering this, one can rationalize the relative shieldings in the methyl, ethyl and *i*-propyl halides. In the methyl halides, electronegativity and second-order paramagnetism work together to result in least shielding for the protons of methyl chloride, most for those of methyl iodide. With the isopropyl and cyclopentyl compounds the diamagnetic contribution is sufficiently important to cancel the effects of relative electronegativity, while with the cyclohexyl compounds, the large diamagnetic anisotropy of the C–I bond unshields the α-proton more effectively than does that of the C–Cl bond.[17]

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[12] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

[13] J. S. Waugh and K. W. Fessenden, THIS JOURNAL, **78**, 846 (1957).

[14] L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957).

[15] The distance r is taken to the halogen atom, rather than to the mid-point of the bond; this seems in order since the unshared electrons on the halogen contribute the largest part to the C–X bond susceptibility.

[16] C. G. LeFevre and R. J. W. LeFevre, *Rev. Pure Appl. Chem.* (*Australia*), **5**, 261 (1955).

[17] A particularly satisfying interpretation of the effect of hydrogen bonding on the position of the hydroxyl proton resonance is based on these ideas. The electron pair on the oxygen of the solvent molecule which is used in forming the hydrogen bond certainly is subject to a strong electrostatic attraction by the proton, and in consequence a large transverse diamagnetism will develop which unshields the hydrogen bonded proton. The α-protons of the alcohols are essentially

Dipole Moment Correlation.—Whichever viewpoint is adopted in interpreting the way in which the disposition of electrons within a haloalkane molecule affects the shielding of the α-hydrogens, the conclusion is reached that the shielding should be directly relatable to the degree of transfer of negative charge to halogen. A second property of the molecule which is also closely related to the degree of charge transfer is the molecular electric dipole moment. The moment in a haloalkane probably resides largely in the C–X bond. In fact, for methyl, ethyl and isopropyl halides, the shielding is an exact linear function of the dipole moment as measured in the gas phase. Figure 2 shows a plot of $(\sigma_{Rx} - \sigma_{CH}) \times 10^8$ *vs.* dipole moment for eight halides. The fit is even better than could reasonably be expected, considering the probable error in the measurement of electric dipole moments in the gas phase.

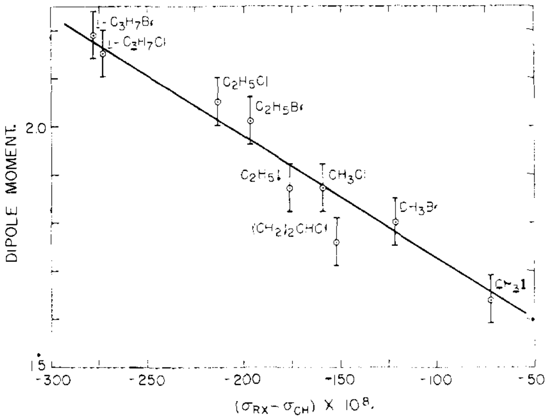


Fig. 2.—Plot of α-proton shieldings *vs.* molecular electric dipole moment for 9 haloalkanes (dipole moments as compiled by C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 269).

Yet another way of considering the effect of the halogens on the shielding of the α-protons is to postulate that the C–H bonds contribute very little to the total molecular electric dipole moment and are themselves polarized linearly by it. The electron density and hence the shielding would thus be inversely proportional to the molecular electric dipole moment in these compounds. In such a case the projection of the measured molecular electric dipole moment on the C–H bond should be a more general measure of the shielding than the moment itself. In Fig. 3 are plotted data for both mono- and polyhaloalkanes treated in this way. It is assumed that the moment resides in the C–X bonds, and the orientation of the moment in the molecule is deduced therefrom.[18] The agreement is again quite satisfactory. Although the moment of cyclopropyl chloride has not been measured in the gas phase, measurements[19] in solution indicate a very low value of the dipole moment. The low value is rationalized[19] on the basis of contributions by a resonance form such as V

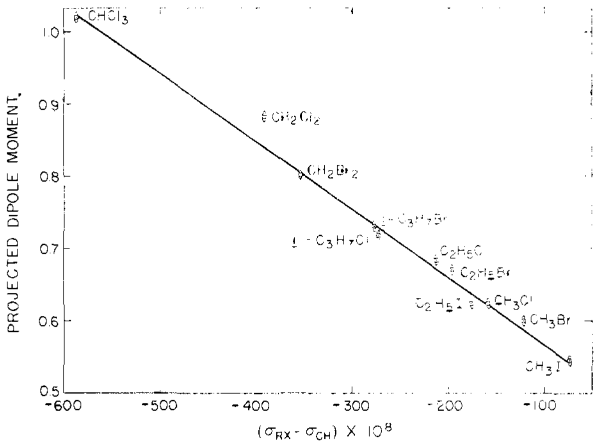
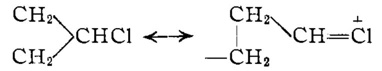


Fig. 3.—Plot of α-proton shielding *vs.* projected dipole moment in haloalkanes (dipole moments as compiled by C. P. Smyth, Fig. 2, pp. 269, 271).



V

The point corresponding to cyclopropyl chloride also falls roughly on the straight line of Fig. 2, however, so that it appears that the precise way in which the charge is transferred to the halogen makes little difference in the effect which the moment has on the proton shielding.[20]

Shielding in the Alkanes.—The alkanes *per se* do not fit the relationship between shielding and dipole moment. This is scarcely surprising since the zero electric dipole observed with saturated hydrocarbons is in no wise comparable with a zero dipole in a hypothetical haloalkane. The few observations made here corroborate previous findings on the general trends in alkane proton shieldings. Proton resonance in methyls occur at practically constant field, about 37 parts/10^8 higher than open-chain methylene. This shift can be accounted for either on the basis of the slightly greater electronegativity of carbon compared to hydrogen, or on the basis of an anisotropy in the carbon–carbon bond. The anisotropy must take the form of a transverse diamagnetic susceptibility equal to several times the longitudinal susceptibility. The electronegativity of carbon alone does not seem sufficient to account for the magnitude of the shift to lower fields. The relationship suggested by Dailey and Shoolery[5] connecting electronegativity and proton shielding would require carbon to have an electronegativity of less than 2.0.

In normal long chain alkyl halides the influence of the halogen ceases to be important to the shielding when 3–4 carbons have been interposed in the chain

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unaffected because their orientation with respect to the magnetic anisotropy results in almost complete cancellation of the net field through tumbling and internal rotation.

(18) For example, in methyl halides the moment is colinear with the C–X bond, in methylene halides it is along the axis bisecting the X–C–X angle, etc.

(19) M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946).

(20) We wish to thank Professor J. D. Roberts for a gift of some cyclopropyl chloride.

between the proton and the halogen. This coincides with the usual limit for the transmission of inductive effects along a chain; shielding values for protons further removed on the carbon chain are effectively identical with those for protons in alkanes.

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CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE RICHMOND LABORATORY, CALIFORNIA RESEARCH CORPORATION]

Silicate Esters and Related Compounds. I. Synthesis of Certain Tetraalkoxysilanes, Polyalkoxysiloxanes, Bis-(trialkoxysilyl)-alkanes and Related Intermediates[1]

BY J. R. WRIGHT, R. O. BOLT, A. GOLDSCHMIDT AND A. D. ABBOTT

RECEIVED FEBRUARY 4, 1957

Methods for the synthesis of silicate esters, disiloxanes (disilicates), trisiloxanes (trisilicates), bis-(trialkoxysilyl)-alkanes, alkoxychlorosilanes, alkoxysilylamines and alkoxysilanols are described. It is shown that the selection of reactants and reaction conditions to obtain a given compound must be based largely on the structure of the hydrocarbon radicals involved. New methods of synthesis and modifications of existing methods were developed to make a number of previously unreported compounds. The present paper describes these preparations. Future papers will describe the properties of the new esters.

Discussion

The shielding of functional linkages by the adjacent alkyl groups accounts for necessary variations in the general procedures to be described for the syntheses of silicates and related intermediates. The degree of shielding determines, for example, the reactivity of the chlorine atom in trialkoxychlorosilanes. It also governs the hydrolytic stability of silicate esters generally. The influence of this steric effect determined the preparation procedures used in the following cases.

Alkoxychlorosilanes and Tetraalkoxysilanes.—Reaction 1 is the most generally applicable for the preparation of these compounds.[2,3]

The concentrations of the individual reaction products depend upon the structure of the alcohol and upon the mole ratio of alcohol to tetrachlorosilane used. Because the rate of reaction decreases as chlorine atoms are successively replaced, lower temperatures tend to reduce the proportion of higher substitution products.

$$SiCl_4 \xrightarrow{ROH} \text{mixture of } ROSiCl_3 + (RO)_2SiCl_2 + (RO)_3SiCl + (RO)_4Si + HCl \quad (1)$$

Primary and secondary alcohols react readily with no complicating side reactions. However, tertiary alcohols require acid acceptors[4] to prevent dehydration of the alcohol and subsequent hydrolysis of chlorosilane derivatives. Even with this change, tri-(*t*-alkoxy)-chlorosilane is the highest substitution product obtainable by this method even with a large excess of tertiary alcohol.[5]

Temperature and steric hindrance effects for primary and secondary alcohols in reaction 1 are both illustrated by the reaction of three moles of alcohol with one mole of tetrachlorosilane.[6] Straight-chain primary alcohols produce mixtures of all four substitution products with no single one predominating even at −15°. On the other hand, 2-ethylhexanol yields 75 mole per cent. of the trialkoxychlorosilane at −15°. With 2-butanol, 85 to 95 mole per cent. of the trialkoxychlorosilane is obtained at 0°.

Tetraalkoxysilanes. (A) Derived from Primary Alcohols.—Reaction 1 yields tetraalkoxysilane readily when an excess of alcohol is employed. Method 2 is also satisfactory.[7,8] In most cases,

$$(EtO)_4Si + (\text{Excess})\ ROH \xrightarrow{NaOR} (RO)_4Si + 4EtOH \quad (2)$$

the latter is inferior to the alcoholysis of tetrachlorosilane because of the slow replacement of the fourth ethoxy group. However, reaction 2 was the only satisfactory means found for preparing tetrabenzyloxysilane.[6]

(B) Derived from Secondary Alcohols.—Method 1 is generally best for this synthesis. However, the reaction is very different from that with primary alcohols because of the relatively slow rate of replacement of the last chlorine atom. The tetrasubstitution stage is reached only after prolonged heating even when an excess of the alcohol is used. An acid acceptor increases this replacement rate. Only the trialkoxychlorosilane could be obtained from 2,4-dimethyl-3-pentanol, apparently because of steric hindrance.[6]

(C) Derived from Tertiary Alcohols.—Breederveld and Waterman[9] reported the preparation of tetra-(*t*-butoxy)-silane by the two steps shown in

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(1) Presented in part at a Meeting of the American Association for the Advancement of Science, Berkeley, Calif., December, 1953.

(2) C. R. Morgan, W. F. Olds and A. L. Rafferty, THIS JOURNAL, **73**, 5193 (1951).

(3) H. W. Post, "Silicones and Other Silicon Compounds," Reinhold Publishing Corp., New York, N. Y., 1949, p. 122.

(4) C. S. Miner, L. A. Bryan, R. P. Holysz and G. W. Pedlow, *Ind. Eng. Chem.*, **39**, 1368 (1947).

(5) H. J. Backer and H. A. Klasens, *Rec. trav. chim.*, **61**, 500 (1942).

(6) Based upon unpublished results from this Laboratory.

(7) H. W. Post, "The Chemistry of Aliphatic Orthoesters," ACS Monograph Series, Reinhold Publishing Corp., New York, N. Y., 1943, p. 133.

(8) D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, 73 (1946).

(9) H. Breederveld and H. I. Waterman, *Rec. trav. chim.*, **73**, 871 (1954).