A number of bending vibrations occur in octatetraene that would not occur in simpler molecules because there are two *trans* double bonds. Since an out-of-plane mode is lower than a corresponding in-plane mode, the band at 839 cm.$^{-1}$ was assigned as the C–H out-of-plane asymmetric deformation (ν_{25}). The band at 1096 cm.$^{-1}$ was assigned to the C–H in-plane asymmetric deformation (ν_{46}). The 1185 cm.$^{-1}$ band in the Raman spectrum was assigned as the *trans* C–H in-plane symmetric vibration (ν_{16}). The Raman band at 1080 cm.$^{-1}$ was assigned to the corresponding out-of-plane vibration (ν_{32}).

Skeletal deformations comprise the last large group of frequencies to be assigned. This type of vibration is usually found in the low frequency region of the spectrum. The selection rules for octatetraene indicate that there should be eleven observed skeletal deformations, five of which are Raman active and six, infrared active. It is possible, that several of these infrared frequencies lie below the range of available prism materials.

Hexatriene contains terminal and central angle in-plane bending modes which were assigned at 590 and 540 cm.$^{-1}$, in the infrared spectrum, respectively. The Raman active symmetric modes were assigned at 528 and 411 cm.$^{-1}$. The corresponding frequencies for the terminal angle bending motion (ν_{37} and ν_4) of octatetraene were assigned to bands at 649 and 528 cm.$^{-1}$. The central angle bending vibrations (ν_{38} and ν_7) were assigned at 565 and 288 cm.$^{-1}$. The symmetric and asymmetric middle angle bending modes (ν_5 and ν_{36}) were assigned at 470 and 627 cm.$^{-1}$, respectively.

The remaining skeletal deformations are the out-of-plane vibrations. These would be expected at lower frequencies than the in-plane type. The selection rules indicate three out-of-plane deformation frequencies should be observed in the infrared spectrum. Since there are no bands observed below 565 cm.$^{-1}$, it is concluded that these frequencies lie below the range of a CsBr prism. The remaining unassigned bands are three asymmetric skeletal deformation frequencies (ν_{18}, ν_{19} and ν_{20}). The Raman active symmetric skeletal deformations (ν_{26} and ν_{27}) are assigned to the band at 223 cm.$^{-1}$. Schematic diagrams of the modes of vibration of octatetraene are given elsewhere.[1] Tables II and III summarize this tentative frequency assignment. Table IV lists the assignment for this compound along with the assignment for related compounds.

Conclusions

The vibrational spectra of 1,3,5,7-octatetraene indicate that it is the all-*trans* structure. The lack of a sufficient number of coincidences between the infrared and Raman spectra rules out the combination *cis–trans* form and non-planar structures. The strong band in the accepted *trans* C–H frequency range, the lack of evidence for *cis* double bonds and the close relationship to the spectra of 1,3,5-hexatriene indicate but do not conclusively prove the presence of the all-*trans* configuration.

A number of weak bands are unassigned in both the infrared and Raman spectra. It is felt that these do not correspond to any fundamental frequencies of octatetraene. Quite a few are due to overtones and combination and difference tones. It is possible but improbable that some are due to small amounts of impurities in the octatetraene.

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Proton Magnetic Resonance Spectra of Propargyl Halides

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A reference procedure for measurement of relative intramolecular proton shieldings based on extrapolation to infinite dilution in saturated hydrocarbon solvents is used to (1) study the effects of solvent on the proton spectrum of propargyl bromide; and (2) measure the relative shieldings and long-range spin couplings in a series of propargyl halides. The medium shifts thus observed show a parallel with infrared stretching frequencies in the same solvents which suggests that intermolecular "H-bonding type" association is largely responsible for n.m.r. medium shifts in non-aromatic solvents. In a series of propargyl halides it is observed that the trans-acetylenic coupling and acetylenic proton shielding are virtually insensitive to the particular halogen substituent, which is taken to indicate that resonance forms involving the acetylenic π electrons are relatively unimportant in the propargyl system.

Following the original work of Meyer and Gutowsky[1] there have been various efforts to correlate nuclear magnetic resonance (n.m.r.) shifts in organic compounds with the qualitative predictions of electronic theory on the assumption that the chemical shielding tensor,[2] σ_i, arises principally from those electrons in the immediate vicinity of the nucleus under observation. More recent theoretical developments point, however, to the importance of "long range" shieldings in proton spectra,[3,4] and the acetylenic bond has been treated as a particular case in point.[5] In spite of the theoretical interest, comparatively few experimental

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

(2) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **86**, 243 (1952).

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

(4) J. A. Pople, *Proc. Roy. Soc.* (*London*), **A239**, 541 (1957).

(5) Pople, *ibid.*, **A239**, 550 (1957).

data is reported for proton shifts in acetylenic systems. The propargyl halides afford a simple, regular series in which may be observed two proton shifts and one long-range electron-coupled spin interaction across an acetylenic bond.

The experimental measurement of relative intramolecular shieldings for compounds in the liquid state is complicated by the high sensitivity of n.m.r. shifts toward environmental "medium effects."[7] Various reference techniques are employed which seek to eliminate, inasmuch as is experimentally feasible, resonance shifts from sources external to the molecule under consideration.[8]

A basic question in this context is whether medium shifts occur through environmental variations in the intramolecular shielding parameter itself or if the anomalous shifts result directly from influences in neighboring molecules. In a series of papers by Bothner-By and co-workers the latter viewpoint is stressed.[9] In the case of "regular" binary mixtures of non-aromatic components it is observed empirically that discrepancies between measured and classically predicted solvent shifts can be largely removed by a correction of about $0.5K$ in the classical volume susceptibility term. This general parallel between the anomalous medium shift and the volume susceptibility led to the suggestion that the shifts occur as the result of failures in the Lorentz cavity model due to a solute-induced solvent anisotropy.[10]

A different viewpoint is taken in a recent paper by Schneider, Bernstein and Pople in which the "liquid association shifts" in simple hydrides are attributed to reduced diamagnetic circulation in the H–X bond due to the electrostatic field about the donor.[11] Work in this Laboratory also suggests that liquid association, similar in type to ordinary hydrogen bonding, is generally involved to varying extents, depending on the proton type and the solvent.

We may consider that the magnetic field strength $\mathbf{H}_{ni}$ at a given nucleus i in an n.m.r. experiment differs from the applied field $\mathbf{H}_o$ due to small contributions from (a) bulk magnetization of the liquid medium, (b) specific effects from neighboring molecules and (c) intramolecular orbital shielding. Since all are small compared to $\mathbf{H}_o$, they may be considered as additive and varying linearly with the applied field:

$$\mathbf{H}_n = \mathbf{H}_o + \mathbf{H}_a + \mathbf{H}_b + \mathbf{H}_c = \mathbf{H}_o(1 + \alpha + \beta + \sigma) \quad (1)$$

Adopting Gutowsky's notation for the chemical shift with the convention $\mathbf{H}_n = \mathbf{H}_o$ for an external water reference we may write the relative screening of the ith nucleus in terms involving the experimental quantity

$$\delta = 10^6(\alpha + \beta + \sigma) \quad (2)$$

where the bulk term α has the classical expression $\alpha = 2\pi K/3$ with K representing the volume susceptibility of the liquid in a cylindrical container.[12] The solvent term β may arise from a variety of sources, including anisotropy of solvent, either permanent or induced, and liquid association effects. In the former case, σ for the solute is presumed to be unchanged, so that β and σ are in principle separable through studies in different media. To the extent that the second effect is operative, however, reference procedures exclusive of measurements on the vapor at low pressures are necessarily arbitrary. Admitting this, we may define for practical purposes $\bar{\sigma}$ as an experimental constant obtained for various molecules in a uniform environment by extrapolation of δ to infinite dilution in "inert" solvents and correcting for the volume susceptibility of the solvent[13]; *i.e.*

$$\bar{\sigma} = 10^{-6}\,\delta^{\infty} - \frac{2\pi K_s}{3} \quad (3)$$

Medium shifts in other solvents are now attributed to β regardless of the mechanism of their operation, so that β becomes an experimental quantity given by

$$\beta = 10^{-6}(\delta - \delta^{\infty}) + \frac{2\pi}{3}(K_s - K) \quad (4)$$

1. Solvent Effects on the Propargyl Bromide Spectrum.—We have applied equation 4 to determinations of the relative medium effects on the proton shifts of propargyl bromide extrapolated to infinite dilution in a number of solvents, choosing as our reference for δ^{∞} the extrapolated shifts in cyclohexane solution. These measurements are summarized in Table I.

Experimental

Spectra were obtained at 21° using the Varian Model 4300B High Resolution Spectrometer operating at 40 megacycles. Spinning 5 mm. Pyrex glass sample tubes with coaxially sealed H_2O reference capillaries were used in all shift measurements, displacements being determined by the side-band technique with a calibrated Hewlett–Packard Model 200J audio oscillator.[14] Reproducibility of measurements by superposition of marker on peak was ±0.5 c.p.s.

The spin multiplet pattern for propargyl bromide (see Fig. 1) is simply analyzed by first-order perturbation theory to give the shift positions at the center member of the $\equiv$C—H triplet and a point equidistant from the methylene doublet peaks.[15] The spin coupling constant is expressed directly as the separation between the doublet peaks or either the 1–2 or 2–3 triplet splitting.

The chemical shifts were observed to vary regularly over all concentrations in CCl_4 and CS_2 solutions. Extrapolations in other solvents were carried out from four or more points in the concentration range 0.5–25.0% by weight in the purest available commercial solvents. Values for β are accurate within the approximate limits ±0.03, assuming the volume susceptibilities are accurately known.

The infrared spectra were obtained with a Perkin–Elmer Model 21 double-beam recording instrument. In the region surveyed, $\sim 3\ \mu$, readings were reproducible to within 3–4 cm.$^{-1}$. The instrument was calibrated before and after the measurements using the NH_3 vapor band at 3337 cm.$^{-1}$.

It is at first sight reassuring to note that $\beta \cong 0$ within experimental limits for solutions in other

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(6) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

(7) See, for example, P. L. Corio and B. P. Dailey, *ibid.*, **25**, 1291 (1957); other cases are specifically mentioned in later discussion.

(8) J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).

(9) A. A. Bothner-By and C. Naar Cohen, THIS JOURNAL, **80**, 1728 (1958) and previous references cited there.

(10) H. A. Lorentz, "The Theory of Electrons," Dover Publications, Inc., New York, N. Y., p. 138, reprinted 1952.

(11) W. G. Schneider, H. J. Bernstein and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958). See also H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, **70**, 786 (1958).

(12) E. R. Andrew, "Nuclear Magnetic Resonance," Cambridge Univ. Press, New York, N. Y., 1956, p. 78.

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

(14) J. T. Arnold and M. G. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(15) See H. M. McConnell, A. D. McLean and C. A. Reilly, *ibid.*, **23**, 1152 (1955), for a general discussion.

TABLE I

MEDIUM EFFECTS ON THE CHEMICAL SHIFTS OF PROPARGYL BROMIDE AT INFINITE DILUTION IN DIFFERENT SOLVENTS

		$-CH_2-$		$\equiv C-H$				
Solvent	10^6K^a	δ	$10^6\beta$	δ	$(\Delta\delta/\Delta K)10^{-6}$	$10^6\beta$	$10^6\Delta\beta^b$	$\nu(\text{cm.}^{-1})^c$
Cyclohexane[d]	— 0.611	1.36	....	2.80	...	...	...	3314.5
n-Heptane	−0.582	1.45	0.03	2.90	3.45	0.04	0.01	3314.5
Trimethylpentane(224)	− .596	1.40	.01	2.83	2.00	.03	.01	3311.2
CCl_4	− .689	0.97	− .23	2.39	5.28	− .25	.02	3312.3
CS_2	− .743	.84	− .25	2.24	4.27	− .29	.04	3304.6
CH_2Cl_2	− .733	.84	− .27	2.15	5.33	− .39	.13	3298.1
$ClCH_2CH_2Cl$	− .755	.76	− .30	2.05	5.21	− .45	.15	3293.8
CH_2Br_2	− .941	.23	− .45	1.55	3.79	− .56	.11	3290.5
Acetone	− .462	1.33	− .35	2.29	−3.44	− .83	.48	3253.0
Benzene	− .616	2.38	1.02	3.58	....	0.79	.24	3292.7
Liquid	− .672[e]	0.66	−0.57	1.95	13.98	−0.73	.15	3290.5

[a] S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949); C. M. French and V. C. G. Trew, *Trans. Faraday Soc.*, **41**, 439 (1945); "International Critical Tables" and Landolt–Bornstein "Tabellen." Averages are used when several values in reasonable agreement are reported. [b] $\Delta\beta = \beta(CH_2) - \beta(\equiv C-H)$. [c] Acetylenic $\equiv C-H$ stretch at high dilution in the solvent indicated. [d] Reference solvent. [e] Susceptibility estimated from Pascal's constants.

hydrocarbons.[16] We further note in agreement with earlier observations that β is consistently negative in the remaining aliphatic solvents,[9,11] while there is a marked shift to higher field in benzene solution.[17] There is not, however, any general parallel between β and ΔK, so that the solutions cannot be described as regular in the sense noted by Bothner-By.[18] This is illustrated for the acetylenic proton in the sixth column of Table I.

Also apparent from column 8 of Table I is a quite general specificity of the medium shift toward the acetylenic proton, the direction being toward lower field relative to the methylene group. The recognized acidity of acetylenic protons suggests the presence of solvation interactions of the general type

$$S{:}\cdots H-C\equiv C-$$

In agreement with this interpretation we note a rough parallel between β and δ^∞ for other solutes in carbon tetrachloride solutions; *e.g.*, for cyclohexane ($\delta^\infty = 3.58$) $\beta = -0.05$, for 1,2-dichloroethane ($\delta^\infty = 1.48$) $\beta = -0.23$, and for chloroform ($\delta^\infty = -2.06$) $\beta = -0.28$. There is also a striking parallel between the medium effects on the acetylenic proton shielding and the infrared vibration frequency of the $\equiv C-H$ bond. This is evident in column 9 of Table I and in Fig. 2. A similar correlation was pointed out by Schneider, Bernstein and Pople, who discuss the association shifts in terms of increased asymmetry in the R–H shielding field due to the electrostatic field of the solvating group.[11]

Where anisotropic contributions from the solvent itself are large, as in benzene solutions, the parallel between β and the infrared medium shift no longer holds. It is interesting to note, however, that plots of β corrected for the corresponding shifts in the methylene protons show a parallel with the infrared shifts which includes the aromatic solvent, since the neighbor anisotropy effect largely cancels out. This is shown in Fig. 3. The correlation cannot be precise, since the negative association shifts might be partially cancelled by increases in the positive anisotropic shift in the configuration proposed by Reeves and Schneider for chloroform–benzene π complexes.[19] The results obtained by these authors for chloroform–benzene solutions are consistent with the shifts reported here.

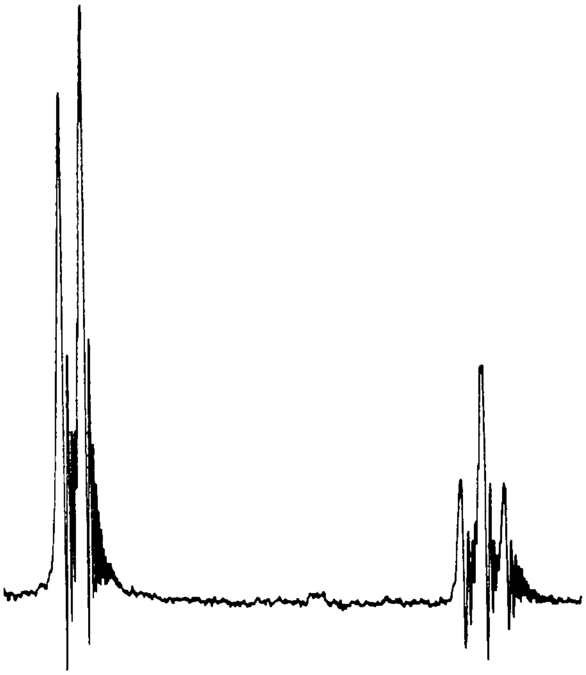

Fig. 1.—Typical propargyl bromide spectrum.

Since magnetic anisotropy of solvent would have negligible effects in the infrared spectra, the correlation between β and the n.m.r. medium shift in Fig. 2 may be taken to suggest that anisotropic shifts in aliphatic solvents are, at least for acetylenic protons, smaller in magnitude than association shifts. This is supported by simple calculations which show that intermolecular effects from anisot-

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(16) Extrapolated values for the acetylenic shift in hydrocarbons are somewhat more uncertain than the limit ±0.03 quoted for other solvents due to some interference from the leading edge of the solvent band at high dilutions. Use of Bothner-By's susceptibility correction, $2.60\Delta K$ gives smaller values for β in these cases, but the errors in $\Delta\delta$ and discrepancies among literature susceptibility values generally exceed the difference of $0.5\Delta K$.

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

(18) Bothner-By and Glick, *ibid.*, **26**, 1647 (1957).

(19) L. W. Reeves and W. G. Schneider, *Canad. J. Chem.*, **35**, 251 (1957).

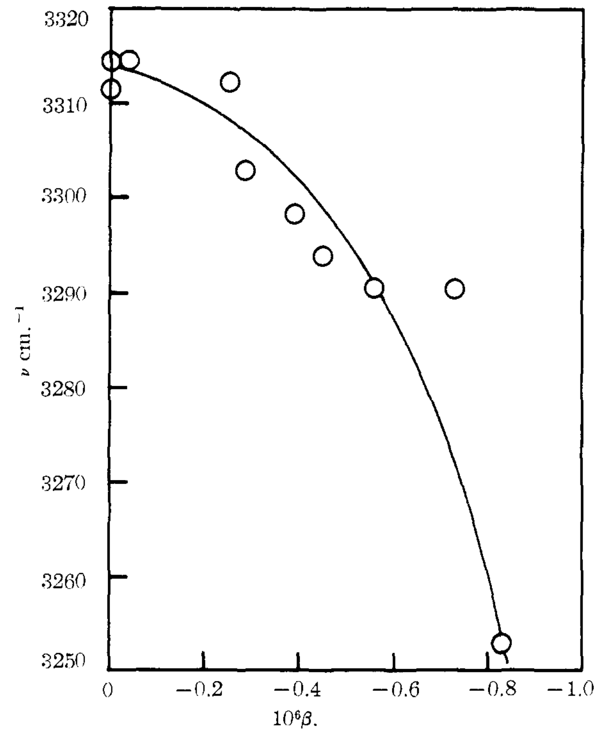

Fig. 2.—N.m.r. *vs.* medium shifts of the acetylenic proton in propargyl bromide solutions.

ropies of the order predicted from treatments of intramolecular shieldings are generally quite small and should average to zero for "spherical" molecules. Nevertheless, anisotropic shifts of the order $0.5\Delta K$ are not large enough to affect the parallelism observed in Fig. 2, so that our data cannot be taken to suggest that anisotropies of this order of magnitude are not involved. However, shifts of this magnitude cannot account for the β's listed in Table I for the methylene protons, where the effects of liquid association should be smaller. It is interesting in this respect to note the following more limited data for the methylene –C–H stretching frequencies in different solvents: for the symmetric and antisymmetric modes, respectively, we obtain 2953 and 3000 cm.$^{-1}$ in CCl_4, 2946 and 2994 cm.$^{-1}$ in CS_2, 2946 and 2991 cm.$^{-1}$ in benzene, and 2941 and 2989 cm.$^{-1}$ in acetone. Thus the smaller range of β in Table II is accompanied by a smaller range in infrared shifts for the methylene protons, and for the three aliphatic solvents the orders parallel as before. The infrared shift in benzene is, moreover, consistent with its position in Fig. 3. Finally, a threefold decrease in the molar extinction coefficient of the antisymmetric mode is observed on going from the pure liquid to very dilute solutions in CS_2, while the extinction coefficient for the symmetric stretch remains roughly constant. On the basis of these observations, it appears that association effects are important in the methylene as well as the acetylenic n.m.r. medium shifts.

We note finally that the long-range coupling shows no detectable medium effect; variations in the propargyl bromide coupling in the liquid and in tetramethylsilane, CCl_4 and benzene solutions were less than the experimental error of ± 0.1 c.p.s.

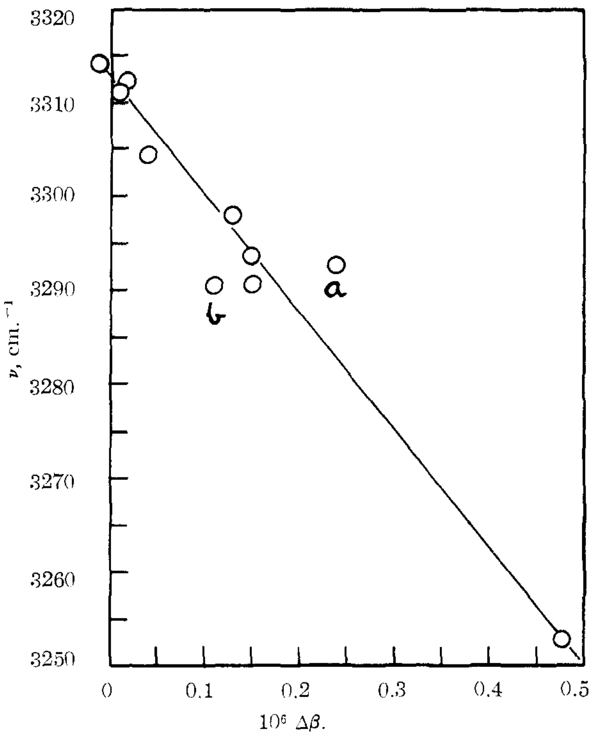

Fig. 3.—≡C—H stretch *vs.* "specific" medium shift of the acetylenic proton in propargyl bromide solutions: (a) benzene; (b) methylene bromide.

2. Relative Shieldings and Spin Coupling in Propargyl Halides.—The choice of saturated hydrocarbons as reference media for standardization of chemical shifts in the liquid state suffers the practical disadvantage of solvent interference in many cases. Tetramethylsilane (TMS) has been recommended as a solvent less often subject to this objection,[20] and our experiments justify its inclusion along with the hydrocarbons as an "inert" solvent. For example, the internal separation between cyclohexane and TMS lines in binary mixtures of the two is 58.0 c.p.s./40Mc.p.s. regardless of concentration, the latter absorbing at higher field.[21] Using this value together with the standard shift of 143.5 c.p.s./40Mc.p.s. for pure cyclohexane[22] gives 201.5 c.p.s./40Mc.p.s. as a standard conversion factor for shifts measured against the solvent line at high dilution in TMS. Applying this correction to the internally references ≡C—H shift of −89.6 c.p.s./40Mc.p.s. for propargyl bromide in TMS gives $\delta^\infty = (201.5 - 89.6)/40 = 2.80$, which is the same as the value obtained by direct measurement in Table I. Such regularity has been consistent in our measurements. Measurements of the relative shieldings in propargyl halides were hence

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(20) G. Van Dyke Tiers, Abstracts of April 13–18, 1958, American Chemical Society Meeting, p. 107-N.

(21) We may use this result together with the shift of liquid TMS, $\delta = 5.24$, to estimate the volume susceptibility by assuming $\beta = 0$ for TMS in cyclohexane. Taking $K = -0.611 \times 10^{-6}$ for cyclohexane, we obtain from equation 4 for TMS, $K = -0.516 \times 10^{-6}$. This agrees quite well with the value $K = -0.523 \times 10^{-6}$ calculated from Pascal's Tables using the factor -12.0×10^{-6} for Si according to Pacault, *Compt. rend.*, **232**, 1352 (1951).

(22) Standard shifts in this Laboratory, designated by δ^∞, refer to the infinitely dilute solution in cyclohexane relative to an external H_2O reference.

carried out in TMS solution to avoid complication by solvent absorption and the values converted to standard shifts in the manner indicated above.

Experimental

Spectra were measured at about 2% by volume concentration in purified[23] TMS. The doublet and triplet patterns (Fig. 1) were each "sandwiched" between modulation markers off the solvent peak while tracing on the Varian G-10 recorder, the modulating signal being switched out while sweeping through the actual pattern. The separation between reference markers was 8 and 10 c.p.s. for the doublet and triplet, respectively, and the sweep rate was maintained close to 0.1 milligauss sec.^{-1}. Peaks were located by interpolation and averaged over eight or more alternating forward and reverse traces. The maximum deviation in successive determinations was ±0.2 c.p.s. The analysis of the spectrum is described in the Experimental section of part 1.

TABLE II

PROTON SHIFTS AND COUPLINGS IN PROPARGYL HALIDES, $H—C\equiv C—CH_2X$

Substituent, X	Coupling[a]	Frequency[b] CH$_2$	Frequency[b] $\equiv$C—H	Chemical shift[c] CH$_2$	Chemical shift[c] $\equiv$C—H
Cl	2.6 ± 0.1	−157.5	−89.5	1.09	2.79
Br	2.7 ± .1	−147.3	−89.6	1.34	2.79
I	2.8 ± .1	−140.7	−87.7	1.51	2.83

[a] Sec.^{-1}. [b] Sec.^{-1} at $40 \times 10^6\ \text{sec.}^{-1}$ from TMS internal reference. [c] P.p.m. at high dilution in cyclohexane relative to H_2O external.

The results of these measurements are summarized in Table II. Having assumed that the measurement of chemical shifts at high dilution in "inert" solvents effectively cancels intermolecular contributions, the significant points in the n.m.r. data may be summarized as follows.

(1) The chemical shift of the acetylenic proton is relatively insensitive to the particular halogen substituent, $\Delta\omega \cong 3$ c.p.s. for the series. The total variation is about the same as observed for the γ-protons in a series of *n*-propyl halides.[9]

(2) Variations in the methylene shifts in the series are more pronounced and are roughly proportional to the halogen electronegativities.[24] Variations of the same order and approximate magnitude are observed in the α-proton shifts of alkyl halides.[9]

(3) Variations in the long-range spin coupling are quite small and are within the outside limits of experimental error. The apparent trend toward smaller coupling with increased substituent electronegativity is consistent with observations on other series[25] and with unpublished data we have obtained for other propargyl compounds.

Relatively little information is available which throws any light on the nature of the electron distributions in the propargyl halides. From electron diffraction studies, Pauling, *et al.*, have determined the C–halogen bond lengths to be 1.82, 1.95 and 2.13 Å., all ±0.02 Å., for Cl, Br and I, respectively.[26] These values are 0.06, 0.04 and 0.03 Å. longer than the "normal" bond lengths for the corresponding saturated alkyl halides. This has been interpreted as indicating a highly ionic C–halogen bond, stabilized by resonance as

$$\underset{\text{I}}{H—C\equiv C—CH_2{}^+X^-} \longleftrightarrow \underset{\text{II}}{H—C^+{=}C{=}CH_2X^-}$$

The amount of bond lengthening, and hence the degree of ionic character, parallel the electronegativities of the halogen atoms.

On the other hand, dipole moment values obtained by Rogers and co-workers for propargyl bromide and iodide, 1.49 and 1.21 *D*, respectively, do not support such an interpretation.[27] These results are, respectively, about 0.35 and 0.60 *D* lower than the vector sum of the methylacetylene moment and the appropriate *n*-propyl halide moment, and since such a decrease in resultant moment and in their relative magnitudes for the two halides is inconsistent with the existence of resonance forms I ⟷ II, Rogers has proposed an alternate pair of structures

$$\underset{\text{III}}{H—C\equiv C—CH_2{}^-X^+} \longleftrightarrow \underset{\text{IV}}{H—C^-{=}C{=}CH_2X^+}$$

All proposed structures I through IV involve the π electrons of the acetylenic bond and are presumed to vary in their relative contributions according to the halogen attached. There are, moreover, sound theoretical grounds for believing that the acetylenic π electrons make a substantial long-range contribution to the magnetic shielding of the terminal proton, the effect having been estimated to be as large as 10 p.p.m. in acetylene.[5] This long range shielding is most easily visualized in terms of the diamagnetic precession of the π electrons about their symmetry axis along the C≡C bond. Excluding a fortuitous cancellation of diamagnetic and paramagnetic terms, one might presume that any significant alterations of the π electron density at the terminal carbon due to halogen-sensitive resonance forms would lead to a detectable variation of the acetylenic proton shielding in a series, and the absence of such variation as evidenced by the data in Table II suggests strongly that resonance of either type I⟷II or III⟷IV is not appreciable.

A recent microwave investigation of propargyl chloride has yielded further information at variance with the original electron diffraction results.[28] The C–Cl bond distance was reported to be only 1.78 Å. and the dipole moment of 1.68 ± 0.04 *D* is in line with Rogers' values for the other propargyl halides. The Cl quadrupole coupling constants are reported to be about "normal" for C–Cl bonds.

Kinetic studies of the SN1 hydrolysis of propargylic halides are consistent with the absence of resonance-stabilized ionic forms. It has been observed, for example, that propargyl bromide and chloride hydrolyze too slowly for quantitative study in H_2O at 25° and that 1,1-dimethylpropargyl chloride in 80% EtOH at 25° has a rate constant $7.4 \times 10^{-4}\ \text{hr}^{-1}$ as compared with $550 \times 10^{-4}\ \text{hr.}^{-1}$ for *t*-amyl chloride and $138{,}000 \times 10^{-4}\ \text{hr.}^{-1}$ for 1,1-dimethylallyl chloride under similar conditions.[29]

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[23] Commercial "pure" grade TMS is shaken with concentrated H_2SO_4 and distilled from the mixture into an ice-cooled receiver.

[24] M. L. Huggins, THIS JOURNAL, **75**, 4123 (1953).

[25] R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956).

[26] L. Pauling, W. Gordy and J. H. Saylor, THIS JOURNAL, **64**, 1753 (1942).

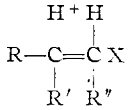
[27] M. T. Rogers and M. B. Pamish, *ibid.*, **77**, 3684 (1955).

[28] E. Hirota, T. Oka and Y. Morino, *J. Chem. Phys.*, **29**, 444 (1958).

[29] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 86–87, original references are cited here.

The decrease in rate of SN1 hydrolysis as well as the dipole moment results of Rogers can be attributed in large measure to the inductive effect of the H—C≡C— group.

Preliminary studies of the n.m.r. shifts in 1,1-dimethylpropargyl halides indicate somewhat different behavior, however. The relative methyl proton shifts with X = Br and X = Cl are opposite in direction from that expected on the basis of inductive withdrawal, but precisely this result has also been noted by Bothner-By for the β protons in alkyl halides,[9] and the latter has suggested resonance structures on the basis of which these data can be rationalized, *e.g.*



$$\mathrm{R}-\underset{\mathrm{R'}}{\mathrm{C}}=\overset{\mathrm{H^{+}\,H}}{\underset{\mathrm{R''}}{\mathrm{C}}}\,\mathrm{X^{-}}$$

Such forms can be expected to increase with the atomic number of X and to be favored by steric compression in secondary and tertiary halides. Shifts are also observed in the acetylenic protons, and like the methyl shifts, are opposite in order from the halogen electronegativities. In this connection it is noted that Rogers has measured the dipole moments of 1-methyl and 1,1-dimethylpropargyl bromides, obtaining values of 1.76 and 1.94 *D*, respectively.[27] The increased ionic character of the tertiary C-halogen bonds makes allenic resonance of the form I ⟷ II with consequent alteration of the terminal proton shielding more likely. The order of the shifts, as also evident in the β-methyl groups, appears to suggest that steric hindrance is more important than electronegativity in determining the relative contributions of these forms.

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A Mass Spectroscopic Appearance Potential Study of Some Boron Trihalides[1]

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The appearance potentials of the positive ion fragments from BCl_3, BBr_3 and BI_3 were measured mass spectroscopically. These measurements permitted a determination of the average B–I bond dissociation energy in BI_3. The value obtained was 2.77 ± 0.2 e.v. A B–I bond length of 2.03 Å. was estimated independently. A plot of the bond energy *versus* bond length in the boron trihalides gave a linear relation. A set of apparently self-consistent ionization potentials for the boron trihalides and fragments formed from these molecules has been estimated and compared with ionization potentials of other BY_3 molecules as well as for BY_2 and BY fragments (where Y can be H, halogen or alkyl substituents). Comparison of the ionization potentials of BY_2 radicals indicates an interesting correlation between the ionization potentials and the nature of the group attached to the boron. CY_3 radicals exhibit a similar behavior. The mass spectra of the boron trihalides were also run at 70 e.v. ionizing voltage to obtain a set of fragmentation patterns under constant conditions.

The appearance potentials of the positive ion fragments from BCl_3, BBr_3 and BI_3 were measured mass spectroscopically. The purpose of this research was twofold. First, to calculate a value for the average B–I bond dissociation energy in BI_3 since there is no thermochemical data available on this subject. Second, to attempt to calculate a self-consistent set of ionization potentials for the boron trihalides and the fragments formed from these molecules.

The method of obtaining bond dissociation energies and ionization potentials by electron impact has had considerable success especially in the field of hydrocarbons and related organic compounds. If one represents the process taking place as

$$R_1 - R_2 + e \longrightarrow R_1^+ + R_2 + 2e$$

then by the equation

$$A(R_1^+) = D(R_1\text{–}R_2) + I(R_1)$$

where $A(R_1^+)$ is the mass spectrometrically measured appearance potential of R_1^+, $D(R_1\text{–}R_2)$ is the dissociation energy of R_1–R_2, and $I(R_1)$ is the ionization potential of R_1, either the bond dissociation energy R_1–R_2 or the ionization potential of R_1 may be calculated directly from the measured $A(R_1^+)$, provided that one knows the value for the other unknown in the equation. A necessary condition for the above equation to hold true is $I(R_1) < I(R_2)$.[2] If $I(R_1) > I(R_2)$ then $A(R_1^+) > D(R_1\text{–}R_2) + I(R_1)$. In order to interpret correctly the appearance potentials of fragment ions, it is necessary to know what other fragments are simultaneously formed, the states of electronic excitation of the fragments and the molecule ion and the excess kinetic or vibrational energy present. In hydrocarbon dissociations, only neutral fragments are simultaneously formed, but in dissociations of halogen containing compounds, there is always the possibility that an X^- ion can be formed since the halogen atoms have high electron affinities. The X^- ions can be produced in two ways: by a resonance dissociative attachment process

$$BX_3 + e \longrightarrow BX_2 + X^-$$

or by an ion pair process

$$BX_3 + e \longrightarrow BX_2^+ + X^- + e$$

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1526. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).