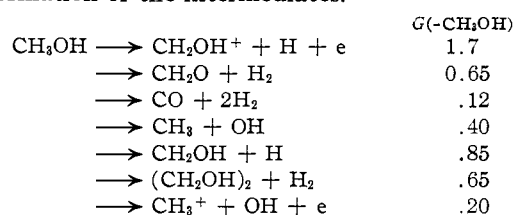**Yields of Intermediates.**—The product yields in various experimental conditions can be reasonably well accounted for in terms of intermediates formed from methanol according to the equations given below. The equations are chosen to express yields and do not necessarily represent the mechanism of formation of the intermediates.

$$
\begin{array}{ll}
& G(-CH_3OH) \\
CH_3OH \longrightarrow CH_2OH^+ + H + e & 1.7 \\
\longrightarrow CH_2O + H_2 & 0.65 \\
\longrightarrow CO + 2H_2 & .12 \\
\longrightarrow CH_3 + OH & .40 \\
\longrightarrow CH_2OH + H & .85 \\
\longrightarrow (CH_2OH)_2 + H_2 & .65 \\
\longrightarrow CH_3^+ + OH + e & .20
\end{array}
$$

We assume that CH_3^+ reacts rapidly with meth-

$$CH_3^+ + CH_3OH \longrightarrow CH_4 + CH_2OH^+$$

anol and is responsible for the unscavengeable methane, $G_m(CH_4)$.

In acid solution all the electrons combine with $CH_3OH_2^+$ as described above and we have

$$G(H_2) = G(e) + G(H) + G_m(H_2) = 6.0$$
$$G(CH_3) = G(CH_3) + G(CH_3^+) = 0.6$$
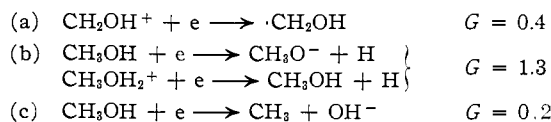$$G(CO) = 0.12, \quad G(CH_2O) = G_m(CH_2O) +$$
$$G(CH_2OH^+) + G(CH_3^+) = 2.55$$

$$G(R) = G(e) + G(H) + G(CH_3) + G(CH_2OH) +$$
$$G(OH) = 6.3$$
$$G(glycol) = \tfrac{1}{2}G(R) + G_m(glycol) = 3.8$$

in agreement with the experimental results in Table II. In neutral solution $G(H_2)$ and $G(CH_2O)$ are lower, $G(CH_4)$ is higher and quantitatively the change in $G(H_2)$ is balanced by that in $G(CH_4) + G(CH_2O)$. The yields in Table II are obtained if the fate of the electrons is

$$
\begin{array}{lll}
(a) & CH_2OH^+ + e \longrightarrow \cdot CH_2OH & G = 0.4 \\
(b) & CH_3OH + e \longrightarrow CH_3O^- + H \ \} & \\
& CH_3OH_2^+ + e \longrightarrow CH_3OH + H \ \} & G = 1.3 \\
(c) & CH_3OH + e \longrightarrow CH_3 + OH^- & G = 0.2
\end{array}
$$

We identify (a) as a reaction in the spurs and the electrons in (b) and (c) as those which are scavenged by low concentrations of solutes thus decreasing $G(H_2)$ from 5.4 to 4.1. Higher solute concentrations reduce $G(H_2)$ to $G_m(H_2)$ by scavenging H atoms.

In neutral methanol at $-78°$, CH_2OH^+ captures all the electrons because of their decreased mobility and/or a favorable activation energy thus decreasing $G(CH_2O)$ to 0.6 and $G(H_2)$ to 4.2. In acid at $-78°$ $CH_3OH_2^+$ captures all the electrons thus bringing the yields up to those in acid at $19°$.

The Dependence of Geminal Proton Spin–Spin Coupling Constants on Electron Delocalization in Molecules

BY MICHAEL BARFIELD AND DAVID M. GRANT

RECEIVED MAY 22, 1961

Geminal coupling constants for a number of substituted methanes have been measured via deuterium substitution. In compounds with substituents containing π electrons, larger geminal coupling constants were found than predicted by existing theoretical and experimental findings for the HCH angle. This increase in the spin–spin coupling is explained in terms of hyperconjugation of the adjacent π electrons with those of the geminal hydrogens in either a methyl or a methylene group.

Introduction

Using the Hamiltonian given by Ramsey[1] for spin–spin interaction, Karplus and co-workers[2-4] with a valence bond approach calculated the proton spin–spin coupling constant for methene. This work was extended by Gutowsky, Karplus and Grant[5] to include the HCH angular dependence of the geminal coupling by considering the methylene group as a four electron valence bond system. The effect of other substituents upon the geminal coupling constant was not considered.

Banwell and Sheppard[6] in studies of substituted vinyl compounds found significant negative deviations from the predicted values of Gutowsky, et al.[5] They concluded that the decrease was due

(1) N. F. Ramsey, Phys. Rev., 91, 303 (1953).

(2) M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, J. Chem. Phys., 27, 597 (1957).

(3) M. Karplus and D. H. Anderson, ibid., 30, 6 (1959).

(4) M. Karplus, ibid., 30, 11 (1959).

(5) H. S. Gutowsky, M. Karplus and D. M. Grant, ibid., 31, 1278 (1959).

(6) C. N. Banwell and N. Sheppard, Mol. Phys., 3, 351 (1960).

to the withdrawal of electrons from the methylene group by electronegative substituents.

This work presents a class of compounds having geminal coupling constants which are larger than the values predicted by a four electron calculation.

Experimental

Equipment.—The proton magnetic resonance spectra were obtained with a Varian Associates V-4311 high resolution spectrometer operating at a frequency of 60 Mc./sec. The instrument was equipped with standard accessories such as a superstabilizer, homogeneity controls, etc. The reported coupling constants and shifts were determined by the sideband technique and represent the average values obtained from as many as ten separate measurements.

Ethyl Cyanomonodeuterioacetate.—By refluxing ethyl cyanoacetate with heavy water containing a small amount of HCl to catalyze the exchange, we were able to synthesize ethyl cyanomonodeuterioacetate. No attempt was made to separate this product from either the parent or the corresponding di-deuterio compound which undoubtedly was formed during the reaction. Other impurities and by-products were, of course, separated.

The proton magnetic resonance spectra of the mono-substituted material consists of a deuterium coupled 1:1:1 triplet shifted 0.81 ± 0.07 c.p.s. upfield from the single peak
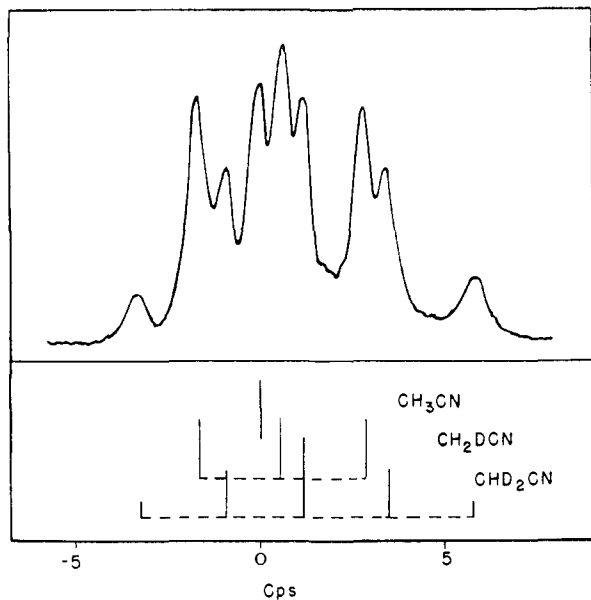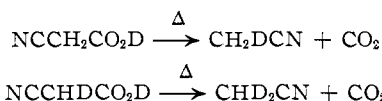
Fig. 1.—The proton magnetic resonance spectrum of aceto-nitrile and two of its deuteriated species.

corresponding to the parent compound. The H–D coupling constant was measured to be 2.86 ± 0.10 c.p.s. The di-deuterio compound would have no peaks in this region of the proton spectra.

Mono-deuterio- and Di-deuterioacetonitrile.—These compounds were prepared from deuteriated cyanoacetic acids in accordance with the pyrolytic reactions.

$$NCCH_2CO_2D \xrightarrow{\Delta} CH_2DCN + CO_2$$

$$NCCHDCO_2D \xrightarrow{\Delta} CHD_2CN + CO_2$$

The cyanodeuterioacetic acids were obtained in a manner similar to that used in making the corresponding deuteriated ethyl esters.

As before, no attempt was made to separate the "isomeric" species, and therefore the proton magnetic resonance spectra of the mixture, shown in Fig. 1, exhibit clearly the singlet of the parent molecule, the 1:1:1 deuterium-coupled triplet of the mono-substituted compound and the 1:2:3:2:1 deuterium-coupled multiplet of di-deuterioaceto-nitrile. The triplet was shifted 0.69 ± 0.03 c.p.s. and the quintet 1.35 ± 0.03 c.p.s. upfield from the singlet. The H–D coupling constant was determined to be 2.58 ± 0.04 c.p.s. by averaging the splitting in both the triplet and quintet.

Mono-deuterio- and Di-deuterioacetic Acid.—These compounds and possibly the completely substituted acid were prepared by the thermal decarboxylation of malonic acid which had been exchanged with heavy water. The synthesis is completely analogous to the preparation of the substituted acetonitriles from cyanoacetic acid. Furthermore the n.m.r. spectrum of the mixture of the deuterioacetic acids exhibits the same spectral features as the acetonitriles. The triplet is shifted 0.71 ± 0.07 c.p.s. and the quintet 1.51 ± 0.07 c.p.s. from the singlet of normal acetic acid. The H–D coupling recorded for these compounds is 2.32 ± 0.07 c.p.s.

Mono-deuterio and Di-deuterio Nitromethane.—Nitromethane was refluxed for 24 hr. with D_2O and $NaOD$ to effect exchange in a manner similar to that described by Leitch and co-workers.[7] As the n.m.r. spectrum for the resulting nitromethanes exhibited the same features as the substituted acetonitriles and the substituted acetic acids, it can be concluded that the mono-, di- and probably the tri-deuterium substituted nitromethanes are obtained in a statistical manner from the parent molecule. The chemical shifts of the triplet and quintet from the singlet are 0.95

(7) L. C. Leitch, P. E. Gagnon and A. Cambron, Can. J. Research, 28B, 256 (1950).

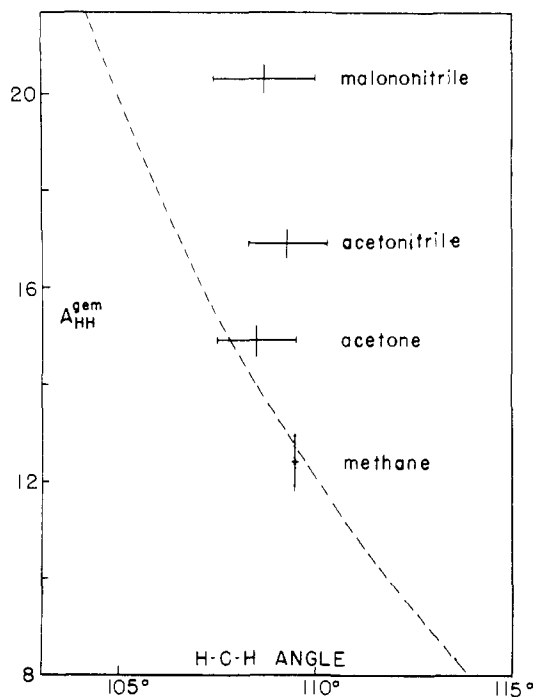Fig. 2.—Geminal H–H coupling constants as a function of H–C–H bond angle; the dashed line is the theoretical curve of Gutowsky, et al.[5] The error in the bond angle of aceto-nitrile is estimated as ±1.0°.

± 0.03 and 1.73 ± 0.04 c.p.s., respectively. The H–D coupling constant for the nitromethanes is 2.02 ± 0.03 c.p.s.

Results and Discussion

Our data for geminal H–H coupling constants are listed in Table I along with previously determined values appropriate to this discussion. Each of these values was obtained from the corresponding H–D coupling constants multiplied by the ratio of the hydrogen gyromagnetic constant to that of deuterium ($\gamma_H/\gamma_D = 6.55$). Compounds in Table I for which the HCH angle is known are entered in Fig. 2 along with the theoretical curve of Gutowsky, Karplus and Grant[5] which portrays the angular dependence of geminal coupling constants. As can be observed, large deviations from the theoretically predicted values are noted for aceto-nitrile and malononitrile.

By describing a molecule of the type $XYCH_2$ with a four electron valence bond treatment, the previous work failed to consider possible interactions of the methylene group with the remaining two substituents. In acetonitrile, the cyanide substituent leads to a positive deviation in the expected geminal coupling constant, whereas in malononitrile this deviation is about doubled as a result of the two cyanide groups. Furthermore, by making the reasonable assumption of tetrahedral or near tetrahedral HCH angles for ethyl cyanoacetate and acetic acid, significant positive deviations in the expected geminal coupling constants in these compounds are also noted. In each of these cases the X and/or Y substituents contain an adjacent π electron system which we feel will make a contribution to the geminal coupling by means of hyperconjugation.

GEMINAL H–H COUPLING CONSTANTS AND H–C–H BOND
ANGLES FOR SOME SUBSTITUTED METHANES

Compound	A_{HH}^{gem}	HCH angle
Malononitrile	20.3 ± 0.3^a c.p.s.	$108.7° \pm 1.3^{ob}$
Ethyl cyanoacetate	$18.7 \pm .6$	
Acetonitrile	$16.9 \pm .3$	$109.3°,^c$ 109.1^{cd}
Acetic acid	$15.2 \pm .5$	
Acetone	$14.9 \pm .3^a$	$108.5° \pm 1.0^{ca,e}$
Nitromethane	$13.2 \pm .2$	
Methane	$12.4 \pm .6^f$	$109.5°$

^{a} H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959). ^{b} E. Hirota and Y. Morino, *Bull. Chem. Soc. Japan*, **33**, 158 (1960). Gutowsky, *et al.*, used the value 105.5° for the H–C–H angle, based on the work of N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **80**, 3483 (1958). Several parameters were assumed in the latter study in order to calculate the structural values. As Hirota and Morino made an almost complete analysis based on isotopic substitution in the malononitrile molecule, it is felt that the larger value for the H–C–H angle is more reliable. ^{c} L. F. Thomas, E. I. Sherrard and J. Sheridan, *Trans. Faraday Soc.*, **51**, 619 (1955). No error was reported. ^{d} M. Kessler, H. Ring, R. Trambarulo and W. Gordy, *Phys. Rev.*, **79**, 54 (1950). Due to zero-point energy effects the error was estimated as about 1%. ^{e} The H–C–H angle can be calculated from the results reported by J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, **31**, 1562 (1959). In a private communication Dr. Swalen indicated that the error in the H–C–H bond angle of acetone would be as large as $\pm 1°$. ^{f} M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957).

The nature of this electron delocalization and its effect upon the spin–spin coupling constant can be visualized with a six electron valence bond model represented in Fig. 3.
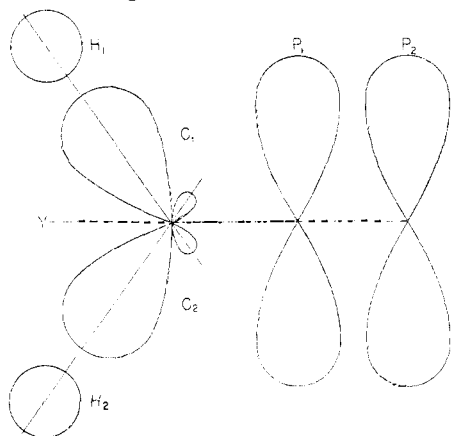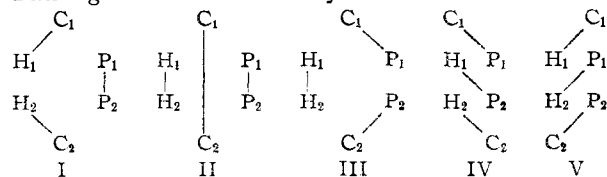

Fig. 3.

To the four electron model of the previous work consisting of the hydrogen orbitals (H_1 and H_2) and the hybrid carbon orbitals (C_1 and C_2) directed towards the hydrogen atoms, we have added a π electron pair (P_1 and P_2) centered on the α carbon and its adjacent atom. The five Rumer–Pauling structures for this system are

I   II   III   IV   V

In structures I and II the P electrons form the normal π bond and therefore do not interact with the remaining four electrons. It is the contribution of structure II to the ground state wave function which leads to a non-zero spin–spin coupling constant discussed in the previous treatment and from which the theoretical curve in Fig. 2 was calculated.

Structures III and IV both represent forms of hyperconjugation with structure III making a contribution to the geminal coupling constant in the same manner as structure II. Although the contribution of structure IV to the ground state wave function may well be comparable to structure III, its effect on the coupling constant will probably be small, coming in only to the extent that it effects the normalization constant of the over-all wave function. Structure V contains two long bonds and will therefore make a much smaller contribution to the wave function.

Applying this model to the acetonitrile molecule, we can therefore see that hyperconjugation of the type

$$\overset{H}{\underset{H}{|}}\ \overset{+}{CH}=C=\overset{-}{N},$$

corresponding to structure III, will contribute to the coupling, whereas hyperconjugation of the type $\overset{+}{H}\ CH_2=\overset{-}{C}=N$, typified by structure IV, while perhaps equally important to the energy, will not correlate the electron spins at the coupled protons and therefore will not affect the coupling. In malononitrile the increased possibility for electron delocalization would explain the considerably higher geminal coupling constant.

The larger coupling constant noted for ethyl cyanoacetate as compared with acetonitrile is attributed to further electron delocalization by the carboxyl group. This effect is supported by a similar increased value found in acetic acid. Furthermore the carbonyl group in acetone may lead to a slightly increased geminal coupling constant (see Fig. 2). Possible structures which could explain such contributions are:

$$\overset{H}{\underset{H}{|}}\ CH^+=C\overset{O^-}{\underset{OH}{\diagup}}$$

and

$$\overset{H}{\underset{H}{|}}\ CH^+=\overset{O^-}{\overset{|}{C}}-CH_3.$$

In the instance of nitromethane the structure exhibiting hyperconjugation which would increase the spin–spin coupling is as follows:

$$\overset{H}{\underset{H}{|}}\ \overset{+}{CH}=\overset{+}{N}\overset{O^-}{\underset{O^-}{\diagup}}.$$

As this structure violates the adjacent charge rule,[8] its contribution to the ground state wave function would be minimized, thereby explaining the more normal coupling constant. Furthermore the C–N bond distance, an additional criterion for hyperconjugation, in nitromethane is not shortened but equals 1.47 Å.,[9] a value within experimental error of a normal C–N single bond distance.

It is the conclusion of this study that adjacent π electron systems will lead to increased spin–spin

(8) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1960, p. 270.

(9) L. E. Sutton, "Interatomic Distances," The Chemical Society, Burlington House, London W.1, 1958.

coupling between geminal protons. Systems requiring hyperconjugative structures which violate the adjacent charge rule would be the exceptions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY EMORY UNIVERSITY, ATLANTA 22, GEORGIA]

Synthesis and Proton Magnetic Resonance Spectrum of Propargyl Cyanide

BY G. S. REDDY, LEON MANDELL AND J. H. GOLDSTEIN

RECEIVED APRIL 24, 1961

Propargyl cyanide has been prepared by the reaction between propargyl bromide and cuprous cyanide. The structure of the product was proved by detailed comparison of its n.m.r. spectrum with those of a series of propargyl halides and halo-allenes. Further confirmatory evidence was provided by the infrared spectrum of the product. The compound was stable on standing for ten months, as shown by the persistence of its n.m.r. spectrum. It is concluded that the previously reported preparations of cyanoallene might in fact have yielded propargyl cyanide.

It is well known that acetylenic nitriles are difficult to prepare. The first unsuccessful attempts in this field were made by Johnson[1] who explained the failure as due to acetylenic–allenic isomerism.[2] Later, for the first time an acetylenic nitrile having at least three methylene groups between the nitrile group and the triple bond was prepared by Newman and Wotiz.[3] These authors failed to obtain the nitrile by the general procedure of treating the chloride with AgCN. However, when they treated the corresponding bromide with cuprous cyanide at 150-160°, they were able to obtain the nitrile. Some attempts have been made by German workers[4] to synthesize acetylenic nitriles with only one methylene group between the nitrile group and the triple bond by refluxing a mixture of propargyl cyloride, cuprous chloride and hydrogen cyanide. In the reaction product no chloro-allene was detected. From the fact that CH_3-(CH_2)—$C{\equiv}C$—CH_2Cl ($n = 2,3$) under similar conditions gave a mixture of acetylene and allene, it was postulated that in the above reaction propargyl cyanide was first formed and subsequently rearranged to cyanoallene. This product, which was described as cyanoallene by these workers has the same boiling point and refractive index as the product we have prepared and have now shown to be propargyl cyanide. Thus, it is possible that the product previously reported as cyanoallene was in fact propargyl cyanide.

In this investigation the product of the reaction described below has been shown to be propargyl cyanide from its proton magnetic resonance (n.m.r.) and infrared spectra. It appears to be quite stable and does not undergo rearrangement on standing in a sealed tube at room temperature over a period of ten months. Since our n.m.r. proof depends upon comparisons with the spectra of other propargylic compounds, it was necessary to correct the chemical shifts of both the acetylenic and methylenic protons for the effect due to the diamagnetic anisotropy of the nitrile group. These corrections are given in detail below.

(1) A. W. Johnson, *J. Chem. Soc.*, 1009 (1946).

(2) A. W. Johnson, "Acetylenic Compounds," Vol. I, Edward Arnold and Company, London, 1946, p. 63.

(3) M. S. Newman and J. H. Wotiz, *J. Am. Chem. Soc.*, 71, 1292 (1949).

(4) German Patent 1,064,504; F21, 815 (1959).

Experimental

Preparation of Propargyl Cyanide.—One hundred twenty five grams of pure propargyl bromide was refluxed with fifty grams of cuprous cyanide for 48 hr. The copper salts were filtered off and the filtrate fractionated at 50 mm. After the low boiling fraction was removed a fraction of 15 g., b.p. 45-60 (50 mm.) was collected. The pot exploded at this point of the distillation. This happened on repetition of the synthesis and is due, undoubtedly, to copper acetylides formed during the reaction and present in the crude product. The distillate was filtered, to remove carbon blown over in the explosion, and redistilled to give 12.3 g. of material boiling at 45-48 (40 mm.). This product showed in its n.m.r. spectrum a sharp and fairly strong line at the water region (-212.5 c.p.s. from tetramethyl silane internal reference in carbon tetrachloride solution) as well as a triplet and a doublet in the region of propargyl bromide with spacing equal to that in propargyl bromide. This indicated the presence of water and propargyl bromide in the product. On refractionating the product the peak presumed to be due to water reduced greatly to about 1% and the peaks assigned to propargyl bromide disappeared completely. The refractive index is $n_D^{19} = 1.4610$. The physical properties of this material (boiling point and refractive index) corresponded well with those reported by the German workers.[4]

N.m.r. Spectrum.—The spectrum was taken on a Varian Associates Model 4300B High Resolution Spectrometer operating at 40 Mc./sec. and equipped with a Flux Stabilizer. Spinning 5 mm. o.d. Pyrex glass tubes were used for sample tubes, the solvent was CCl_4. (The product does not dissolve in inert materials such as cyclohexane or tetramethyl silane (TMS).) About 10% TMS was added to the solution to serve as internal reference. Since the sample and the reference are in the same medium, namely, CCl_4, there is no necessity to make any bulk magnetic susceptibility corrections in order to be able to compare effectively the chemical shifts with those of the compounds included in Table II which were taken in TMS. Calibrations were made by the usual side band technique. All the chemical shifts are expressed in cycles per second from the TMS internal reference. The coupling constants are expressed directly in cycles per second. Calibrations were repeated after storing the sample in a sealed tube for ten months to see if there was any rearrangement to the corresponding allenic compound. The spectra were unchanged after this time, and hence it was concluded that propargyl cyanide is stable under the conditions of storage at room temperature and does not rearrange to cyanoallene.

Infrared Spectrum.—The infrared spectrum was taken on a Perkin–Elmer Model 21 Spectrometer with rock salt optics. Carbon tetrachloride was again used as the solvent.

Discussion

The n.m.r. spectrum of the product, shown in Fig. 1, consists of a doublet and a triplet about 45 c.p.s. apart. The pattern is that of a first order A_2X system with the A_2 protons at lower field. The coupling constants and the chemical shifts can be readily obtained from the spacings