was added to sodium hydride (0.72 g., 0.03 mole) in benzene (10 ml.). Dimethyl 1-methyl-1,2-cyclopropanedicarboxylate, b.p. 88–91° (10 mm.), 2.1 g. (40%), was obtained.

B.—Repetition of the experiment, but using benzene (15 ml.) and hexamethylphosphoramide (15 ml.) mixture, gave 2.4 g. (46%) of the cyclopropane diester, b.p. 90° (10 mm.).

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

Proton Magnetic Resonance Spectra of Cyclopropane Derivatives[1]

BY JOHN D. GRAHAM[2] AND MAX T. ROGERS

RECEIVED NOVEMBER 20, 1961

The proton magnetic resonance absorption of several cyclopropane derivatives has been studied at 60.000 mc. The observed chemical shifts and nuclear spin–spin coupling constants have been interpreted in terms of substituent effects and the structures of the molecules. Although the structure of the cyclopropane ring is often thought to be somewhat unusual, the observed proton–proton coupling constants for ring protons in the cyclopropane derivatives are not anomalous. The magnitude of, and variations in, the observed proton–proton coupling constants can be satisfactorily explained on the basis of the geometry of the molecules. Substituent effects have not been found to be important in the consideration of the proton–proton coupling constants, but the chemical shifts of the ring protons have been found to be strongly influenced by the nature of the substituents on the ring.

Introduction

Recently, the proton magnetic resonance spectra of some substituted cyclopropane derivatives have been reported. According to Jackman[3] the *cis* and *trans* coupling constants in *trans*-dibromocyclopropane are equal. However, Gutowsky[4] has shown that in A_2X_2 spin systems the invoking of accidentally equal J_{AX} coupling constants is not always correct. Also, Roberts[5] has suggested that the spectrum of *trans*-dibromocyclopropane is consistent with coupling constants of 8 and 2 c.p.s. for the *cis* and *trans* coupling constants. Closs[6] has assumed that the *trans* coupling constants are larger than the *cis* coupling constants in several substituted cyclopropanes. The vicinal coupling constants in 1-nitro-1,2-dicarboxylic anhydride have been reported[7] as 9.0 and 6.0 c.p.s., but the authors made no statement concerning which was *cis* and which *trans*. Muller and Pritchard[8] have reported that the C^{13} satellite lines in cyclopropane consist of a "normal" quintet, the coupling constant being equal to 7.5 c.p.s.

The purpose of the work reported herein was to determine the magnitudes of the coupling constants in several cyclopropane derivatives and to ascertain the effect of substituents and geometry upon the coupling constants in these molecules.

Experimental

The 60.000 mc. high-resolution proton magnetic resonance spectra were obtained with a Varian 4300–2 spectrometer and the usual side-band technique was used for calibration purposes. Spectra of the following pure liquids were obtained: 1,1-dichloro-2-methyl-2-phenylcyclopropane, *cis*-1,1-dichloro-2-methyl-3-phenylcyclopropane, 1,1-dichloro-2-methoxycyclopropane and 1,1-dichloro-2-ethoxycyclopropane. The spectrum of *trans*-1,2,3-tribenzoylcyclopropane[9] was obtained using a solution of this compound in CF_3COOH, and the spectra of cyclopropane-1,1,2-tricarboxylic acid and *trans*-3-methylenecyclopropane-1,2-dicarboxylic acid (Feist's acid) were obtained using solutions of these compounds in dilute NaOH.[10]

The 40.000 mc. spectrum of *trans*-1,2,3-tribenzoylcyclopropane has been reported by Shoolery[11] and the *trans* coupling constant in this molecule has been reported as 6.0 c.p.s. by Closs.[6]

The dichlorocyclopropanes were synthesized from the corresponding olefin by the dichlorocarbene reaction following the procedure of Doering.[12] The synthesis of 1,1-dichloro-2-ethoxycyclopropane has been reported by Doering and Henderson,[12] while the syntheses of the remaining three dichlorocyclopropanes have not been previously reported.

1,1-Dichloro-2-methoxycyclopropane was prepared by the addition of dichlorocarbene to vinyl methyl ether (Matheson Co., Inc.); b.p. 51°(mm.), $n^{20}D$ 1.4490.

Anal. Calcd. for $C_4H_6OCl_2$: C, 34.07; H, 4.26; Cl, 50.22. Found: C, 33.95; H, 4.37; Cl, 50.20.

The reaction of α-methylstyrene (Eastman Kodak Co., white label) with dichlorocarbene afforded 1,1-dichloro-2-methyl-2-phenylcyclopropane, b.p. 55–56° (0.3 mm.), $n^{20}D$ 1.5480.

Anal. Calcd. for $C_{10}H_{10}Cl_2$: C, 59.70; H, 4.98; Cl, 35.32. Found: C, 59.77; H, 5.03; Cl, 35.19.

β-Methylstyrene was obtained from Columbia Organic Chemicals Co. and a purity of greater than 99% was indicated by the results of the gas chromatographic separation. The refractive index of this material, $n^{20}D$ 1.5430, agrees with the literature value[13] for the *cis* isomer. The product of the reaction of this olefin with dichlorocarbene was *cis*-1,1-dichloro-2-phenyl-3-methylcyclopropane, b.p. 54–56° (0.2 mm.), $n^{20}D$ 1.5440.

Anal. Calcd. for $C_{10}H_{10}Cl_2$: C, 59.70; H, 4.98; Cl, 35.32. Found: C, 59.78; H, 5.06; Cl, 35.18.

Vinyl ethyl ether, purchased from Matheson Co., Inc., added dichlorocarbene to give 1,1-dichloro-2-ethoxycyclopropane,[12] b.p. 53–54° (28 mm.), $n^{20}D$ 1.4440.

Results and Discussion

The methods used to analyze the spectra of the cyclopropane derivatives have been discussed

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] Sterling Chemical Laboratory, Yale University, New Haven, Conn.

[3] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959.

[4] D. M. Grant and H. S. Gutowsky, *J. Chem. Phys.*, **34**, 699 (1961).

[5] J. D. Roberts, "An Introduction to the Analysis of Spin–Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961.

[6] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

[7] J. Smidt and Th. J. de Boer, *Rec. trav. chim.*, **79**, 1235 (1960).

[8] N. Muller and D. E. Pritchard, *ibid.*, **31**, 768 (1959).

[9] We are indebted to Prof. W. G. Brown of the University of Chicago for the gift of a sample of this compound.

[10] These two compounds were obtained from Dr. L. Brady of Abbott Laboratories, Chicago, Ill., to whom we are indebted for this assistance.

[11] J. N. Shoolery, *Svensk Kem. Tidskr.*, **69**, 185 (1957).

[12] W. E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, **80**, 5274 (1958).

[13] W. R. R. Park and G. F. Wright, *J. Org. Chem.*, **19**, 1435 (1954).

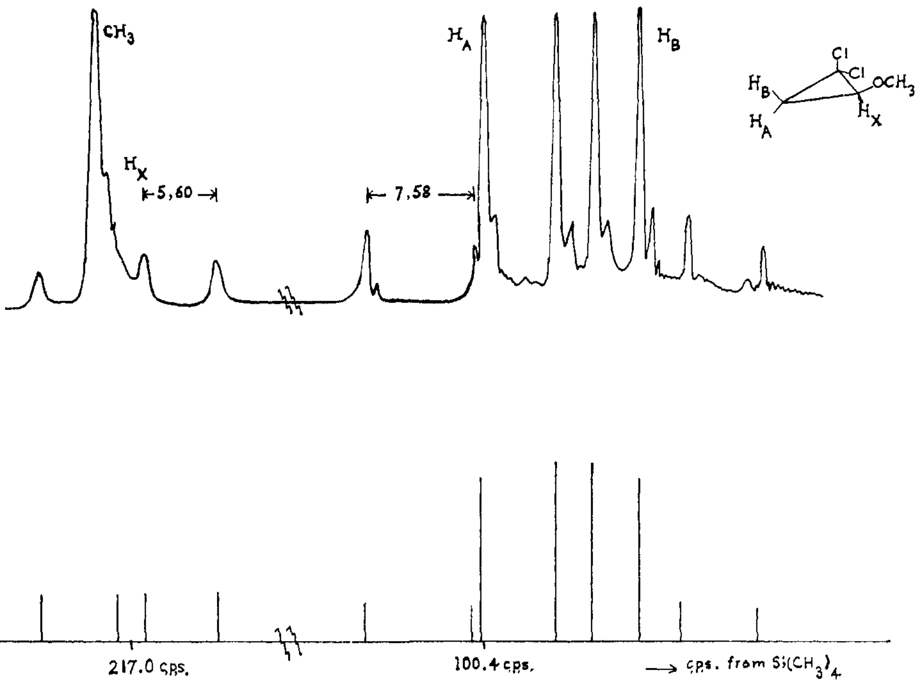


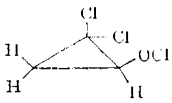
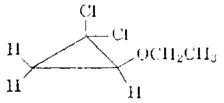
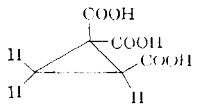
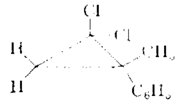
Fig. 1.—Experimental proton resonance spectrum (above) and theoretical spectrum (below) for pure liquid 1,1-dichloro-2-methoxycyclopropane; ν_0 = 60 mc.; the reference is tetramethylsilane. The intensities of the eight high-field lines are not on the same scale as those of the four low-field lines.

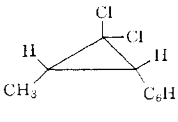
elsewhere.[14-16] The spectrum of 1,1-dichloro-2-methoxycyclopropane, shown in Fig. 1, is an ABX spectrum, for example. The proton resonance centered at 217.0 c.p.s. is due to the proton adjacent to the methoxy group. The theoretical spectrum computed from the parameters given in Tables I and II is also shown in Fig. 1 and is seen to agree well with the experimental spectrum. The remaining spectra were analyzed as AB, ABX or A_2B spin systems and the theoretical spectra for the final values of J and of chemical shift selected were compared with the experimental spectra. Values obtained for the ring proton coupling constants for the cyclopropane derivatives are given in Table I and the chemical shifts of the ring protons are summarized in Table II.

The data presented in Table I show that the *cis* and *trans* coupling constants are relatively insensitive to the nature of substituents while the data presented in Table II indicate that substituent effects are important in the case of chemical shifts. Although the cyclopropane ring is considered to have some π-electron character[17] the results for the coupling constants given in Table I indicate rather clearly that the most important mechanism for spin–spin coupling takes place through the σ-electronic structure. This follows because substituents would be expected to perturb the more easily polarized π-electrons, and hence the coupling constant, if the mechanism for spin–spin coupling proceeded through a π-electronic system.

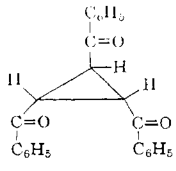
TABLE I

RING PROTON COUPLING CONSTANTS IN C.P.S. IN CYCLOPROPANE DERIVATIVES

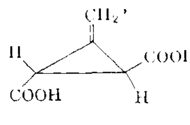
Compound	J_{cis}	J_{trans}	J_{gem}	(J_{cis} + J_{trans})	(J_{cis} + J_{trans} + J_{gem})
	7.90	5.28	8.38	13.18	21.56
	8.25	5.27	8.09	13.52	21.61
	9.33	6.55	4.80	15.88	20.68
			7.10		



J_{cis} 8.28



J_{trans} 5.61



$J_{H-H'}$ 2.63

The results for the *cis* and *trans* HCCH coupling constants are in good agreement with the predictions of valence-bond theory.[18,19] In particular the calculated coupling constant for dihedral angle ϕ equal to 0° is 8.2 c.p.s. and the average observed

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[14] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc. New York, N. Y., 1959.

[15] P. L. Corio, *Chem. Revs.*, **60**, 363 (1960).

[16] H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 596 (1957).

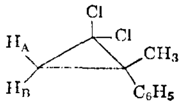
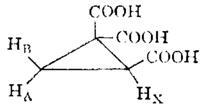
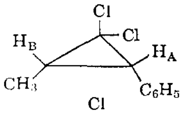
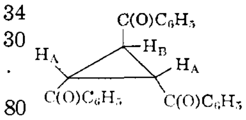
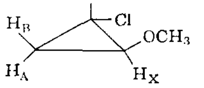
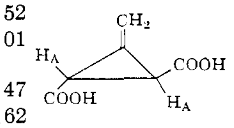
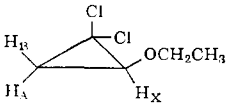
[17] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[18] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[19] M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960).

TABLE II

CHEMICAL SHIFTS OF RING PROTONS IN CYCLOPROPANE DERIVATIVES AT A SPECTROMETER FREQUENCY OF 60 MC.[a]

Compound	*A* *B* *X*	Compound	*A* *B* *X*
	102.36 85.53		137.78 145.53 190.47
	132.34 103.30		247.53 269.10 ....
	99.80 90.52 217.01		109.50 ....
	90.47 81.62 208.8		

[a] Chemical shifts are in c.p.s. relative to tetramethylsilane and are taken to be positive for protons on the low field side of TMS.

value of the *cis* coupling constant ($\phi = 0°$) for the substituted cyclopropanes listed in Table I is 8.44 c.p.s. The calculated value for $\phi = 146.5°$ is 6.3 c.p.s. and the average *trans* coupling constant observed ($\phi \cong 146.5°$) is 5.68 c.p.s. The values for ϕ quoted above are those which exist in the cyclopropane molecule when the HCH angle is 118°. The amount of data available concerning vicinal proton–proton coupling constants in molecules with known dihedral angles is limited. Musher[20] has found that in 1,1,4,4-tetramethylcyclohexyl *cis*-2,6-diacetate the vicinal proton-proton coupling constants for $\phi = 60°$ and $\phi = 180°$ are 4.25 and 12.35 c.p.s., respectively. Lemieux, *et al.*,[21] have studied a series of acetylated sugars and found that the average coupling constant for $\phi = 180°$ is 7 c.p.s. and for $\phi = 60°$ the average coupling constant is 3 c.p.s. Cohen, Sheppard and Turner[22] have estimated the proton–proton coupling constants in dioxane to be 9.4 c.p.s. for $\phi = 180°$ and 2.7 c.p.s. for $\phi = 60°$. The use of small ring compounds, such as those reported in this paper, to study the angular dependence of nuclear spin–spin coupling constants has the decided advantage that the nuclear framework is rigid and only one conformation exists. From the results reported here and from the above data it may be concluded that the theoretical values for vicinal proton–proton coupling constants are of the correct order of magnitude and that the angular dependence of these coupling constants is as predicted. The general agreement of the vicinal proton–proton coupling constants in cyclopropane derivatives with theory indicates that the electronic structure of the cyclopropane ring is not radically different from that of other saturated hydrocarbons.

The *gem* proton–proton coupling constants summarized in Table I vary over a larger range than do the *cis* and *trans* coupling constants. According to valence-bond theory[23] the *gem* coupling constant is a sensitive function of the HCH angle, and alterations in this angle should be reflected by changes in the value of the *gem* coupling constant. From the observed *gem* coupling constants (Table I) one would conclude that the HCH angle varies from 113 to 117.5° with an average angle of 115°. These angles are in the range of those calculated[17] and observed experimentally[24] for cyclopropane and its derivatives.

It may be noted from Table I that there is some variation in the values of similar coupling constants in different molecules but that in those molecules where the *cis*, *trans* and *gem* coupling constants are observable the sum of these coupling constants is virtually constant. Also, in the molecule 1-nitrocyclopropane-1,2-dicarboxylic anhydride,[7] the sum of these three coupling constants is 21.70 c.p.s. These data indicate that an increase in the HCH angle, which reduces the *gem* coupling constant and decreases the CCH angle, increases the vicinal coupling constants. The dihedral angle would also be affected, but theoretical calculations[18,19] show that the vicinal coupling constant is not very sensitive to small variations in the dihedral angle. Theoretical calculations of the vicinal coupling constants have employed a tetrahedral CCH angle, whereas in cyclopropane the CCH angle is 116° 29′ when the HCH angle is 118°. Theoretical calculations predict a decrease in the vicinal proton–proton coupling constants for the HCCH fragment when the CCH angle increases.[25] We would therefore expect that valence-bond calculations for the vicinal coupling constants in cyclopropane would lead to lower theoretical values than those calculated by Karplus[18] for ethane. Since the average values observed in cyclopropane for the vicinal coupling constants are rather close to the theoretical values of Karplus for ethane we might therefore expect valence-bond calculations made using the observed CCH angles in cyclopropane would turn out to be somewhat smaller than the observed values. Further theoretical calculations would be most desirable. Musher[20] has concluded from other evidence that valence-bond theory yields proton–proton coupling constants which are somewhat low.

The large coupling constant of 2.63 c.p.s. in Feist's acid between protons four bonds removed is of some interest.[26] The coupling constants for protons four bonds removed fall in the range of 1.4 to 1.8 c.p.s. in substituted propenes, and for allenes the coupling constants are in the range of 6.1 to 7.0 c.p.s.[27] A possible explanation for the magnitude of the coupling constant in Feist's acid is that the nature of the electronic structure of the cyclopropane ring imparts an allene-type character to this molecule. However, the role which the geometry of the molecule plays is hard to ascer-

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(20) J. I. Musher, *J. Chem. Phys.*, **34**, 594 (1961).

(21) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 2237 (1958).

(22) A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Roy. Soc. (London)*, **118** (1958).

(23) H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

(24) J. P. Friend and B. P. Dailey, *ibid.*, **29**, 577 (1958).

(25) H. S. Gutowsky and A. L. Porte, *ibid.*, **35**, 839 (1961).

(26) A value of 2.5 c.p.s. for this coupling constant has been reported by E. F. Ullman, *J. Am. Chem. Soc.*, **81**, 5386 (1959).

(27) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

tain and this might be the source of the large coupling constant.

As was mentioned previously, the chemical shift data presented in Table II vary over a wide range. The chemical shift of the protons of cyclopropane[3] is downfield by 13.2 c.p.s. with respect to tetramethylsilane (at 60 Mc.) and for the cyclopropane derivatives listed in Table II the resonance positions of the ring protons are shifted to lower fields. Substituents which are magnetically anisotropic, such as a phenyl or a carbonyl group, have a marked effect on the chemical shifts. It is also possible that there is a ring-current effect on chemical shifts comparable to that in benzene but of considerably smaller magnitude. It is interesting to compare the ring proton chemical shifts in 1,1-dichloro-2-methoxycyclopropane to those in 1,1-dichloro-2-ethoxycyclopropane. The replacement of a methoxy group by an ethoxy group increases the shielding of the ring protons. It is rather surprising that the changes in shielding are essentially equal for all three ring protons. It may also be noted that the proton *cis* to the substituent in these two compounds is more shielded than the *trans* proton while in cyclopropane-1,1,2-tricarboxylic acid the *trans* proton is more shielded.

[CONTRIBUTION NO. 2767 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

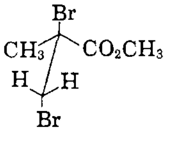
Nuclear Magnetic Resonance Spectroscopy. The Stereospecificity of the Long-range Spin–Spin Coupling in 1,2-Dibromo-2-phenylpropane[1]

BY DONALD R. DAVIS AND JOHN D. ROBERTS

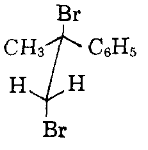
RECEIVED NOVEMBER 2, 1961

The stereospecific long-range, proton–proton spin coupling in 1,2-dibromo-2-phenylpropane has been shown by deuterium labeling to probably be a *trans* interaction. New preparations of the *cis*- and *trans*-α-methyl-β-bromostyrenes and the lithium reagents corresponding thereto are described.

Previously[2] we reported a stereospecific long-range, proton–proton spin coupling in methyl α,β-dibromoisobutyrate (I), which substance appears to exist in a preferred conformation Ia,[3] most likely that with the bromines *trans*. One of the non-equivalent[3] methylene protons of I is coupled to the protons of the C-methyl group with J = 0.75 c.p.s. It was not known whether the coupled proton is that which is *trans* or *gauche* to the methyl group.



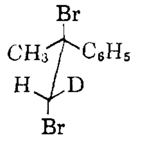
Ia



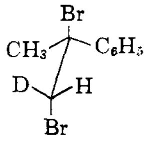
IIa

An analogous long-range splitting of 0.65 c.p.s. has been observed (*cf.* Fig. 1A) in the spectrum of 1,2-dibromo-2-phenylpropane (here and later shown in the conformation IIa with the bromines *trans;* this is expected to be the *favored* conformation by analogy with 1,1-difluoro-1,2,2-tribromo-2-phenylethane).[2,3] If the conformation is correctly assigned, then the spectra of the stereospecifically deuterium-labeled isomers IIb and IIc are only consistent with the long-range coupling involving the proton disposed *trans* to the methyl group. The evidence is deduced from the n.m.r. curves of Fig. 1 which shows the methylene resonances of the following mixtures of IIa-IIc

Fig.	IIa, %	IIb, %	IIc, %
1A	100	..	..
1B	18	29	54
1C	36	43	21



IIb



IIc

Figure 1B shows the broad peak of the methylene proton of IIc located between the low-field pair of peaks of IIa. The smaller, broadened triplet of IIb is likewise in the expected position[4] with respect to the high-field resonances of IIa. The weakly coupling deuterium nucleus, which possesses a spin of 1 and therefore has three equally probable orientations in a magnetic field, causes an adjacent proton to appear approximately as a triplet.[5] Clearly, that proton of IIc, which is presumed to be *trans* to the methyl group, is the long-range coupled proton of IIa. The long-range coupling cannot easily be observed in the spectrum of IIc due to the additional small coupling (~1.5 c.p.s.) to the deuterium. Furthermore, as can be seen from methylene resonances of IIb, the lines due to the H–D coupling are broadened and distorted, almost surely by intermediate rates of magnetic relaxation arising from the interactions involving

[1] Supported in part by the Office of Naval Research and the Undergraduate Research Participation Program of the National Science Foundation.

[2] D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

[3] (a) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chap. 3; (b) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957).

[4] J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1961, Chap. 2.

[5] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chap. 10.