

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE, SOUTH HADLEY, MASS.]

The Nuclear Magnetic Resonance Spectra of Three-Membered Ring Compounds: Substituent Effects on Monosubstituted 1,1-Dichlorocyclopropanes and Epoxides¹

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An algebraic decrease in the vicinal and geminal proton-proton coupling constants with an increase in substituent electronegativity has been observed in a series of monosubstituted 1,1-dichlorocyclopropanes and monosubstituted epoxides. The dependence of coupling constant and internal chemical shift on electronegativity in the 1,1-dichlorocyclopropanes is found to be intermediate between that of the saturated hexachlorobicyclo[2.2.1]-heptenes and that of the monosubstituted ethylenes, in keeping with the unique hybridization of the carbon atoms of the cyclopropane ring system.

Introduction

The purpose of the work reported herein was to determine the effect of various substituents on n.m.r. coupling constants and chemical shifts in three-membered ring compounds in order to determine if the unique electronic properties of these compounds are reflected in their n.m.r. spectra. This is part of a long-range investigation into those effects, other than changes in dihedral angle, that alter the coupling between protons on adjacent carbon atoms.

A linear correlation has been observed between coupling constants and substituent electronegativity in a series of monosubstituted ethanes,⁴ ethylenes,⁵ and in the rigid hexachlorobicyclo[2.2.1]heptene system.⁶ However, the presence or absence of any similar dependence in the cyclopropane and epoxide systems has not been established by previous studies. Reilly and Swalen^{7,8} have very carefully analyzed the n.m.r. spectra of a series of monosubstituted epoxides, but the electronegativity of the substituents varied only between 2.5 and 2.75 so that no clear relationship was observed. Graham and Rogers,⁹ in a study of some cyclopropane derivatives, stated that substituent effects are *not* important in the consideration of proton-proton coupling constants and that the electronic structure of the cyclopropane ring system is not radically different from that of other saturated hydrocarbons. Hutton and Schaefer,¹⁰ in a more recent study, suggest that the n.m.r. spectra of certain cyclopropane derivatives do show a deviation from the constants predicted by the Karplus equation¹¹ in the direction expected from electronegativity contributions, but they could find no clear dependence on substituent electronegativity. Furthermore they concluded that if the cyclopropane ring system shows any π -electron character, it does not contribute noticeably to the coupling.

Unfortunately these previous workers did not study a homologous series of compounds, so that unpredictable steric and multiple substituent effects mask any relationship among the compounds. To obviate these difficulties we have chosen to examine the n.m.r. spectra of a series of monosubstituted 1,1-dichlorocyclopropanes and epoxides. These systems contain just

three coupling protons facilitating complete, unambiguous analysis of the spectra by ABX methods.¹² By changing only one substituent in the system, the stereochemistry of the system should remain constant.

In a typical spectrum the X-proton (the proton on the substituent bearing carbon atom) quartet is found downfield from the A and B quartets as is to be expected from the proximity of the X-proton to an electron-withdrawing substituent. In the spectrum of the trimethylsilyl derivative the X-quartet is found upfield from the A and B quartets reflecting the electron-donating effect of this substituent. In all of the cyclopropanes studied in this work the A quartet (produced by the proton *cis* to the substituent) is upfield from the B quartet (produced by the proton *trans* to the substituent), except in the case of the carboxyl derivative.¹³ The assignments of lines to specific transitions were checked by the frequency sum rule of Fessenden and Waugh.¹⁴

Results

Since both the 1,1-dichlorocyclopropanes and the epoxides exist in only a single configuration for which the molecular geometry is known, any variation noted in coupling constants is expected to be due to some interaction of the substituent with the electronic structures of the ring. The dihedral angle between the X and B protons would be 0° and, since the HCH angle in cyclopropanes is $113.8 \pm 2^\circ$,¹⁵ the dihedral angle between the X and A protons would be 144°. Similar dihedral angles would occur in the epoxide ring system since the HCH angle for ethylene oxide ($116^\circ 41' \pm 2^\circ$)¹⁶ is about the same as in cyclopropane. Application of the Karplus equation¹¹ relating the coupling constant to the dihedral angle between adjacent protons would give coupling constants of 8.2 and 5.9 c.p.s. for dihedral angles of 0 and 144°, respectively.

Vicinal Coupling Constants.—In the 1,1-dichlorocyclopropanes J_{cis} is seen to vary from 7.9 to 12.6 c.p.s. and J_{trans} from 5.3 to 9.5 c.p.s. (see Table I). These variations are much too large to be accounted for by changes in geometry of the molecule but, as expected from our previous work,⁶ these values give a linear correlation with the electronegativity of the substituent. The electronegativity is defined, according to Cavanaugh and Dailey,¹⁷ by

$$\text{electronegativity} = 0.0114\delta + 1.78$$

where δ is the internal chemical shift in c.p.s. at 60 Mc.

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(2) N.S.F. Undergraduate Research Participant, summer, 1963.

(3) N.S.F. Undergraduate Research Participant, summer, 1962.

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

(5) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).

(6) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

(7) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **32**, 1378 (1960).

(8) C. A. Reilly and J. D. Swalen, *ibid.*, **34**, 980 (1961).

(9) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

(10) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **41**, 684 (1963).

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

(12) 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, p. 132.

(13) Similar behavior has been noted in four other cyclopropane carboxylic acids; see K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **85**, 2788 (1963).

(14) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **31**, 996 (1959).

(15) O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962).

(16) G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, W. D. Gwinn, and W. I. LeVan, *J. Chem. Phys.*, **19**, 676 (1951).

(17) R. J. Cavanaugh and B. P. Dailey, *ibid.*, **34**, 1099 (1961).

TABLE I
 COUPLING CONSTANTS AND CHEMICAL SHIFTS OF MONOSUBSTITUTED 1,1-DICHLOROCYCLOPROPANES^a

R	J_{cis}	J_{trans}	J_{gem}	δ_A	δ_B	δ_X	$\delta_X - \delta_A$	$\delta_X - \delta_B$	Electro- negativity	Reference
OAc	8.0	5.4	-9.1	95	110	257	162	147	3.74	^b
OCH ₃	7.9	5.3	-8.4	91	100	217	126	117	3.31	9
Br	9.4	6.6	-8.6	95	125	207	112	82	2.96	^b
C ₆ H ₅	10.5	8.6	-7.3	104	111	168	64	57	2.75	^c
COOH	11.0 ^d	6.8 ^d	-6.8	121	112	151	30	39	2.60	^b
Si(CH ₃) ₃	12.6 ^d	9.6 ^d	-4.9	67	86	35	32	52	1.8	^{b,e}

^a Chemical shifts are in cycles per second (at 60 Mc.) downfield from tetramethylsilane. ^b This work. ^c C. A. Reilly, Abstracts, 4th OCEANS, Mellon Institute, Pittsburgh, Penna., March 2, 1963. This compound has been erroneously analyzed as an AB₂ system with J 9.9 c.p.s. by H. Weitkamp, U. Hasserodt, and F. Korte, *Ber.*, **95**, 2280 (1962). ^d These coupling constants might vary 0.3 c.p.s. from these values if a complete ABC analysis of the spectra were carried out. See ref. 7 for a comparison of ABX and ABC analysis in the epoxide system. ^e The sample of 1,1-dichloro-2-trimethylsilylcyclopropane was kindly furnished by Prof. Dietmar Seyferth.

 TABLE II
 COUPLING CONSTANTS AND CHEMICAL SHIFTS OF
 MONOSUBSTITUTED EPOXIDES^a

R	J_{cis}	J_{trans}	J_{gem}	δ_A	δ_B	δ_X	Electro- nega- tivity	Refer- ence
OAc	2.2	1.4	4.5	155	166	320	3.74	^b
Cl	2.7	1.4	4.7	165	170	294	3.25	^c
C ₆ H ₅	4.0	2.5	5.7	151 ^d	169	217	2.75	7
CHO	4.9	2.0	5.5	186	190	201	2.69	8
COOH	5.0	1.9	6.3	176	179	209	2.6	7
CN	4.2	2.5	5.5	180	187	210	2.5	7

^a Chemical shifts are in cycles per second (at 60 Mc.) downfield from tetramethylsilane. ^b This work. ^c Coupling constants from C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, **84**, 3326 (1962), and chemical shifts from B. P. Dailey, A. Gawer, and W. C. Neikam, *Discussions Faraday Soc.*, **34**, 18 (1962). ^d The value of 156 c.p.s. reported by B. P. Dailey, A. Gawer, and W. C. Neikam, ref. *c*, must be a typographical error.

between the methyl and methylene protons of a series of monosubstituted ethanes. Since dihedral angles of 0° and about 144° would be expected in the monosubstituted epoxides, we would expect again to find coupling constants of 8.2 and 5.9 c.p.s. In this case, however, the vicinal coupling constants are considerably smaller than in the cyclopropane ring system, varying from 2.2 to 5.0 c.p.s. for J_{cis} and 1.4 to 2.5 c.p.s. for J_{trans} (see Table II). The change in coupling constants in the epoxides, relative to the vicinal coupling in cyclopropanes first noted by Mortimer,¹⁸ may be due in part to the generally lower electron density about the carbon atoms resulting from the electronegative character of the heteroatom. This feature is reflected in the lower shieldings and greater chemical shifts which are observed throughout the spectra of the epoxide series relative to those of the 1,1-dichlorocyclopropanes, indicating that the electron density on the epoxide protons is lower than on the cyclopropane protons, although it is high in comparison to that of other cyclic ethers.¹⁹

Again a linear correlation is found between the substituent electronegativity and the observed coupling constants in the monosubstituted epoxides.

A considerable scatter in the data is not surprising in the light of the nature of the three-membered ring compounds and the extensive delocalization of the unshared oxygen electrons in the epoxide ring. It is possible that some substituents contribute to this delocalization in a manner not indicated by their electronegativities. In particular, in substituents containing carbon doubly bonded to oxygen or nitrogen, the electron structure may be delocalized over the substituent as well. The effect of such delocalization is not reflected in the internal chemical shift of the ethane

series, upon which the definition of electronegativity is based. In the monosubstituted ethylenes an even greater scatter of data is observed in this correlation,⁵ reflecting the even more easily delocalized nature of the π -electrons in the ethylenic system.

Geminal Coupling Constants.— J_{gem} decreases algebraically with increasing electronegativity of the substituent in both the epoxides and dichlorocyclopropanes. This relationship is, of course, dependent on the sign of the geminal coupling constant. From the relative sign determinations in ethylene oxide²⁰ and styrene oxide²¹ it can be stated with some certainty that the *cis*, *trans*, and geminal couplings are all positive in the epoxides. From the recent relative sign determination in 1-chloro-2,2-dimethylcyclopropane²² it can similarly be presumed that the *cis* and *trans* couplings are positive and the geminal coupling is negative in the series of cyclopropanes reported upon in this work. It is noteworthy that given the above signs for the various coupling constants, the effect of an electronegative substituent on all of the coupling constants is the same: as the substituent electronegativity increases, the coupling constant decreases algebraically. Intuitively it would seem that such behavior should be noted for all coupling constants—as an electronegative substituent decreases the electron density about the coupling atoms, the coupling constant should decrease.²³

Internal Chemical Shifts.—In the 1,1-dichlorocyclopropanes two internal chemical shifts can be distinguished²⁴—the separation in c.p.s. at 60 Mc. between the X and A proton resonance peaks, $\delta_X - \delta_A$, and the corresponding separation between the X and B proton peaks, $\delta_X - \delta_B$. As in our previous work,⁶ a linear correlation is found between the internal chemical shifts and the electronegativity of the substituents. It is clear from the data in Table I that there will be a crossover in internal chemical shift in going from an electron-withdrawing substituent to an electron-donating one. The crossover point, where the internal chemical shifts are zero, corresponds to the electronegativity of the hydrogen atom in the 1,1-dichlorocyclopropane ring, 2.18, which can be compared to the Pauling electronegativity of 2.1.

From the expression given above as the Cavanaugh and Dailey definition of electronegativity,¹⁷ it is evident that the slope of the plot of electronegativity *vs.* chemical shift for the series of monosubstituted ethanes is 1.14×10^{-2} . The average slope of the plot of elec-

(20) P. C. Lauterbur and R. J. Kurland, *ibid.*, **84**, 3405 (1962).

(21) D. D. Elleman and S. L. Manatt, *J. Mol. Spectry.*, **9**, 477 (1962).

(22) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **41**, 1623 (1963).

(23) Cf., however, B. H. Arison, T. Y. Shen, and N. R. Trenner, *J. Chem. Soc.*, 3828 (1962), who report that $J_{HF(gem)}$ in CHF₂X derivatives has been found to increase with increasing electronegativity of X.

(24) Since many of the epoxides studied by Reilly and Swalen⁷ were run as neat liquids, it is not practical to compare internal chemical shifts reported for these compounds because of abnormal "solvent" effects.

(18) F. S. Mortimer, *J. Mol. Spectry.*, **5**, 199 (1960).

(19) See H. S. Gutowsky, R. L. Rutledge, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, **76**, 4242 (1954), for n.m.r. data pertaining to electron distribution in various cyclic ethers.

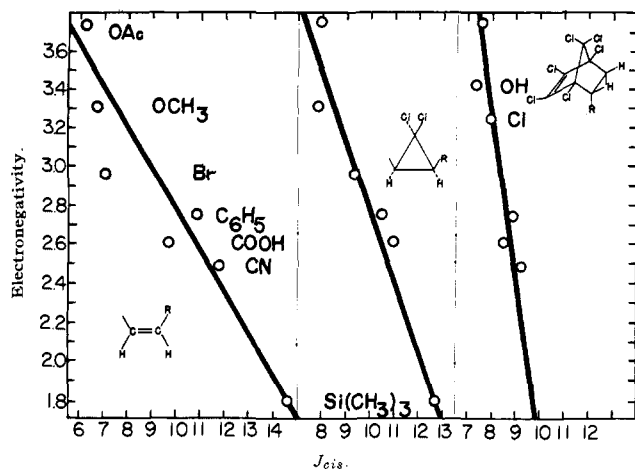


Fig. 1.— J_{cis} vs. electronegativity for a series of monosubstituted hexachlorobicycloheptenes,⁶ 1,1-dichlorocyclopropanes, and ethylenes. Coupling constants for the ethylenes are from W. Bruegel, Th. Ankel, and F. Krueckeberg, *Z. Elektrochem.*, **64**, 1121 (1960); C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960); and R. T. Hobgood, J. H. Goldstein, and G. S. Reddy, *J. Chem. Phys.*, **35**, 2038 (1961).

tronegativity vs. chemical shift for the 1,1-dichlorocyclopropanes is less than 0.85×10^{-2} , the slope of δ_{cis} being 0.91×10^{-2} and δ_{trans} being 0.78×10^{-2} . This indicates to us a greater withdrawal of electrons from the cyclopropane system than from the saturated system by groups of corresponding electronegativity and consequently a greater polarizability of the electron structure.

In our previous work on substituent effects in a series of monosubstituted hexachlorobicyclo[2.2.1]heptenes,⁶ an empirical equation of the form $\delta_{internal} = \text{electronegativity} (A - B \cos \phi) + C \cos \phi - D$ was proposed to relate the internal chemical shift in a given compound to the dihedral angle between the proton in question and the electronegativity of the substituent. That the proposed equation (where $A = 88.5$, $B = 21.8$, $C = 38.8$, $D = 157.5$) lacks generality is seen when an attempt is made to calculate the lines from the data for the cyclopropanes. As indicated above, the average slope of $(\delta_X - \delta_A)$ vs. E and $(\delta_X - \delta_B)$ vs. E is smaller than that which would be calculated. However, the equation is correct in predicting that the difference, at a given electronegativity, between the internal chemical shifts, $(\delta_X - \delta_A) - (\delta_X - \delta_B)$, should be smaller for a dihedral angle of 144° (the cyclopropanes) than for a dihedral angle of 120° (the hexachlorobicycloheptenes).²⁵ We can therefore state that the internal chemical shift is a function of substituent electronegativity, the polarizability of the system, and the dihedral angle between the protons in question.

Comparison of Cyclopropane Coupling with Couplings in Saturated and Unsaturated Compounds.—In Fig. 1 are presented plots of *cis* coupling constants vs. electronegativity for three systems. The saturated system used in this comparison is hexachlorobicyclo[2.2.1]heptene for which the variation of coupling constant with electronegativity has previously been reported.⁶ This system is rigid and the dihedral angle between the *cis* protons is therefore fixed at 0° . From the data plotted it is seen that the slope of the plot of electronegativity vs. coupling constant is -1.4 c.p.s. per unit electronegativity. The slope of the line defined by the *cis* coupling constant for ethylene derivatives plotted against electronegativity is at least -4.5 to -5.0 c.p.s. per unit electronegativity.

(25) See P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2709 (1963), for further examples from the norbornene system.

Hutton and Schaefer¹⁰ have noted that the dependence of coupling constants on substituent electronegativity is greater in vinyl compounds than in ethane derivatives, as would be expected by the greater polarizability of the electronic structure of the π -bonds in the ethylenes. Since, according to Bothner-By and Naar-Colin,²⁶ the contribution of σ -bonds to the coupling is not dependent on the hybridization of the carbon atoms, this variation seems to be due principally to substituent effects on whatever π -character exists in the C-C bond.

Inspection of Fig. 1 indicates that the dependence of the cyclopropane coupling constant on the electronegativity of the substituent is intermediate between that in the saturated and unsaturated compounds. The slope of the line is approximately -2.5 c.p.s. per unit electronegativity.

Conclusions

From the above comparison of the coupling constants of cyclopropanes with analogous saturated and unsaturated compounds (Fig. 1) as well as the lower slope of the plot of internal chemical shift vs. electronegativity for cyclopropanes compared to a saturated system, we conclude that the cyclopropane ring system has some π -electronic character that places it in a position intermediate between the saturated and unsaturated compounds.

There is, of course, much other evidence bearing on this unique electronic property of the cyclopropane ring system. It was shown many years ago in these laboratories that cyclopropanes have maximum absorption in the ultraviolet at a wave length between that for the corresponding saturated and unsaturated compounds,²⁷ indicating that the cyclopropane ring has some π -character as shown by its ability to enter into a conjugated system. A similar effect is exhibited by 3,4-epoxybutene and other epoxide containing compounds.²⁸

Streitwieser²⁹ attributed the unreactivity of cyclopropyl halides in solvolysis to the unusual amount of p-character in the C-C bonds. The high C-H stretching force constant in cyclopropane and ethylene oxide has been attributed by Linnett³⁰ to the large amount of s-character in the C-H bonds.

Coulson has applied the principle of maximum overlap³¹ as well as an elaborate valence bond calculation³² to show that the stability of cyclopropane is greatest when the angle between the ring orbitals is 104° and not the angle between the carbon atoms, 60° . This rehybridization means that the C-C bond has much p-character, being now $sp^{4.12}$, while the C-H orbital, now $sp^{2.28}$, has more s-character.³³

It has recently been postulated by Foote³⁴ that the C^{13} -H coupling constant is a linear function of the amount of s-character in the carbon orbital, following the initial proposal of Muller and Pritchard³⁵ that $J_{C^{13}-H}$ is a good measure of the extent of sp -hybridization at the carbon atoms. The $J_{C^{13}-H}$ of cyclopropane, 161 c.p.s., indicates that the C-H bond in this molecule has about 32% s-character.³⁵

(26) A. A. Bothner-By and C. Naar-Colin, *ibid.*, **83**, 231 (1961).

(27) E. P. Carr and C. P. Burt, *ibid.*, **40**, 1590 (1918).

(28) M. T. Rogers, *ibid.*, **69**, 2544 (1947).

(29) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

(30) J. W. Linnett, *Nature*, **160**, 162 (1947).

(31) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); correction, *ibid.*, 3161 (1963).

(32) C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(33) L. L. Ingraham in M. S. Newman, Ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 519.

(34) C. S. Foote, *Tetrahedron Letters*, 579 (1963).

(35) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **81**, 768, 1471 (1959).

That previous work on the proton-proton couplings in cyclopropanes and epoxides⁷⁻¹¹ has failed to reveal the correlation with substituent electronegativity and the π -electron character in the ring, we attribute primarily to the multiple substituent effects operative in the cyclopropanes previously studied and the limited range of electronegativity of substituents in the epoxides studied. Conformational changes would have to be quite large (and thus unlikely) to account for the large difference in coupling constants observed in poly-substituted cyclopropanes.

It is obvious from this work that structural assignments made simply on the basis of coupling constant magnitude, without taking into account substituent effects, could easily lead to the wrong structures; e.g., in these dichlorocyclopropanes J_{trans} in the trimethylsilyl derivative (9.4 c.p.s.) is larger than J_{cis} for the acetate derivative (7.9 c.p.s.) although simple consideration of the Karplus equation indicates that the *cis* coupling is larger than the *trans*.

We have discussed the coupling constants of these three-membered ring compounds in terms of the π -electron character of the ring and the hybridization of the carbon atoms involved. Rehybridization of the carbon atoms will necessarily change the C-C bond length and HCC' angle—two factors, in addition to substituent effects and dihedral angles, which Karplus has recently shown will also affect the coupling constant.³⁶

Experimental

The proton magnetic resonance spectra were obtained with a Varian Associates DP-60 high-resolution n.m.r. spectrometer operating at both 56.4 and 60 Mc./sec. Chemical shifts are reported in c.p.s. (at 60 Mc.) downfield from tetramethylsilane. Line positions were obtained by the side-band technique with graphical interpolation and are the average of at least six measurements. The frequency of the audio side band was measured with a Hewlett-Packard 521-C frequency counter. Chemical shifts are considered accurate to ± 1 c.p.s. and coupling constants to ± 0.2 c.p.s. Each sample was run as a 10% solution in carbon disulfide containing 1% tetramethylsilane as the internal standard.

2,2-Dichlorocyclopropyl acetate was prepared according to the procedure of Wagner, Kloosterziel, and van der Ven³⁷ in about 1% yield and separated from the contaminating 1-trichloromethyl ethyl acetate by preparative gas chromatography on a 2-ethylhexyl phthalate column.

Methyl trichloroacetate was prepared from A.R. trichloroacetic acid by Fischer esterification³⁸ using absolute methanol with concentrated sulfuric acid as the catalyst. The methyl

trichloroacetate used had b.p. 55.4–56.0° (19 mm.), reported³⁹ b.p. 52–54° (12 mm.).

2,2-Dichlorocyclopropyl bromide was prepared⁴⁰ following a modification of the procedure which Parham and Schweizer⁴¹ used to prepare 2,2-dichlorobicyclo[4.1.0]heptane from cyclohexene.

Into a three-necked, 100-ml., round-bottomed flask equipped with a Hershberg stirrer, pressure equalizing dropping funnel, thermometer, and nitrogen inlet was weighed 8.65 g. (0.16 mole) of sodium methoxide (Matheson Coleman and Bell) in a drybox under nitrogen. To this was added 40 ml. of ligroin (d 0.64), which had been washed with concentrated sulfuric acid and distilled. The mixture was stirred and cooled in an ice-salt bath while 30 ml. (45 g., 0.42 mole) of vinyl bromide was added. To the bright turquoise-blue mixture was added (under nitrogen) 14.8 ml. (0.125 mole) of methyl trichloroacetate over a 3-hr. period at such a rate that the reaction temperature was held to about 5° and did not exceed 12°. The mixture was stirred for 8 additional hours under nitrogen at 0°, and then for 9 hr. at room temperature. The reaction mixture was diluted with 200 ml. of water and extracted four times with 50-ml. portions of ether. The combined organic layers were washed twice with 10-ml. portions of a saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After removal of the ether and ligroin by distillation at atmospheric pressure, the product was distilled at reduced pressure to give 10.4 g. (44% yield), b.p. 102–103° (102 mm.), n_D^{22} 1.5102.

Anal. Calcd. for $C_3H_3BrCl_2$: C, 18.96; H, 1.59; Cl, 37.25; Br, 42.09. Found: C, 19.12; H, 1.68; Cl, 37.00; Br, 42.20.

2,2-Dichlorocyclopropanecarboxylic Acid.—To a solution of 7 g. (0.044 mole) of potassium permanganate in 70 ml. of water was added 2.45 g. (0.018 mole) of 1,1-dichloro-2-vinylcyclopropane (Columbia Organic Chemicals Co., Inc.). The mixture was stirred at room temperature overnight; then the manganese dioxide was removed by suction filtration and washed with water. The water clear filtrate was saturated with solid potassium chloride and extracted once with ether, which was discarded. The aqueous layer was acidified with dilute hydrochloric acid and the cloudy solution extracted with four 20-ml. portions of ether. The combined ether extracts were washed twice with 10-ml. portions of a saturated solution of sodium chloride and then dried over anhydrous magnesium sulfate. The ether was removed by distillation and the slightly yellow oil was then distilled through a small vacuum-jacketed Vigreux column. The product, b.p. 63° (1 mm.), spontaneously crystallized in the condenser. The yield was 1.25 g. (45%) of white prisms, m.p. 74–75°.

Anal. Calcd. for $C_3H_4Cl_2O_2$: C, 31.00; H, 2.60. Found: C, 30.78; H, 2.55.

Vinyl acetate epoxide was prepared by perbenzoic acid epoxidation of vinyl acetate according to the procedure of Gorton and Reeder.⁴² The material used for the n.m.r. spectrum had b.p. 35–37° (6 mm.).

Acknowledgment.—We wish to thank Professor Dietmar Seyferth for the sample of 1,1-dichloro-2-trimethylsilylcyclopropane.

(39) R. Anschütz and A. R. Haslam, *Ann.*, **253**, 121 (1889).

(40) Cf. the failure of dibromocarbene to add to vinyl bromide (P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956)).

(41) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(42) B. S. Gorton and J. A. Reeder, *ibid.*, **27**, 2920 (1962).

(36) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

(37) W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Rec. trav. chim.*, **80**, 740 (1961).

(38) S. G. Toole and F. J. Sowa, *J. Am. Chem. Soc.*, **59**, 1971 (1937).

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Rates of Rapid Ligand Exchange Reactions by Nuclear Magnetic Resonance Line Broadening Studies^{1a}

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The rates of exchange, or limits to the rates, of several unidentate and bidentate ligands coordinated to Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) have been measured by proton n.m.r. line broadening studies. The usual order of reactivity $Mn > Fe > Co > Ni \ll Cu$ has been found. The exchange reactions of copper complexes are clearly second order, in agreement with an S_N2 mechanism common for planar complexes. The exchange reactions of the octahedral complexes are mixed first and second order and are explained by a solvent assisted dissociation mechanism common for octahedral complexes. It is easier to measure rates of exchange in this way for ligands containing NH protons rather than OH protons, because rates of relaxation are very large for NH protons and hence exchange rates determine the line width.

In the past few years a great deal has been learned about the mechanism of ligand substitution reactions of

metal ions in aqueous solution. This has been possible because earlier work on slowly reacting systems such as

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