

*Anal.* Calcd. for  $C_{11}H_{18}O_2$ : C, 72.5; H, 10.0. Found: C, 72.4; H, 9.6.

A mixture melting point of the acid, m.p. 90.8–92.6°, above with a sample of bornylcarboxylic acid, m.p. 79.6–83.0°, prepared from bornylmagnesium chloride and carbon dioxide according to the method of Rupe and Hirschman,<sup>38</sup> showed a m.p. 85.0–90.0°.

**Acknowledgment.**—The authors wish to thank Mr. I. D. Calvert for operation of the spectrometer and for many of the subsequent measurements of chemical shifts.

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## Nuclear Magnetic Resonance Spectroscopy. Cyclopropane Derivatives<sup>1</sup>

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Chemical shifts and coupling constants have been determined from the analysis of proton nuclear magnetic resonance spectra for a series of cyclopropane derivatives. The geminal and vicinal cyclopropyl couplings have opposite signs. Additional <sup>13</sup>C–H coupling constants have been obtained for cyclopropanes which support the conclusion that the hybridization of the carbon–hydrogen bonding orbitals in cyclopropanes is close to sp<sup>2</sup>. The chemical shifts for several cyclopropane hydrocarbons seem consistent with a ring-current effect.

Proton n.m.r.<sup>3</sup> and fluorine n.m.r.<sup>4</sup> spectroscopy have been utilized for structure determinations of substituted cyclopropanes. Coupling constants and chemical shifts of cyclopropane derivatives<sup>5,6</sup> have recently been reported and interpreted in terms of substituent effects and molecular geometries.<sup>6</sup>

In the present research, the spin–spin splittings in the proton n.m.r. spectra of several substituted cyclopropanes have been analyzed using standard methods<sup>7,8</sup> with results shown in Table I.

The Wiberg,<sup>9</sup> the Bothner-By, and the Swalen<sup>10</sup> computer programs were used to obtain the best agreement between the observed and the calculated spectra. The AB cyclopropyl proton patterns in the n.m.r. spectra of tetrasubstituted cyclopropanes yielded the cyclopropyl couplings directly. The *trans*-cyclopropyl couplings in the ABX type spectra of *trans*-3-(*trans*-2'-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid and its dimethyl ester were determined directly from the AB portion of the spectrum, the downfield part of which was split by the adjacent vinyl hydrogen. The n.m.r. spectra of neat samples of 1,1-dimethylcyclopropanecarboxylic acid, dimethyl 1-methylcyclopropane-*cis*-1,2-dicarboxylate, and dimethyl 1-methylcyclopropane-*trans*-1,2-dicarboxylate were analyzed as ABC systems. Identification in the observed spectrum of the three quartets and repeated spacings between lines gave approximate values of the chemical shifts and coupling constants, respectively. Best calculated frequency fits for the four possible combinations of relative signs of couplings were then obtained using the Swalen program.<sup>10</sup> The best fit between observed and calculated intensities was found for the assignments with geminal coupling having an opposite sign to the vicinal couplings in the three ABC

systems studied. The analysis of the n.m.r. spectrum of dimethyl 1-methylcyclopropane-*trans*-1,2-dicarboxylate in benzene gave magnitudes and signs of couplings in agreement with the neat compound.

The <sup>13</sup>C satellite n.m.r. spectra of 1,1-dichlorocyclopropane, 1,1-dimethylcyclopropane, spiropentane, and spirohexane were analyzed as AA'XX' systems. The center of each multiplet of the <sup>13</sup>C satellites was determined by the moment method.<sup>11</sup> Similar calculated spectra in agreement with the observed spectrum were found with two geminal couplings having different magnitudes and opposite signs in each AA'XX' system studied. However, the best fit to the intensities was found for 1,1-dichlorocyclopropane with the geminal and vicinal couplings having opposite signs and this sign assignment was assumed for the other three AA'XX' systems. The *cis* and *trans* couplings which have the same sign are interchangeable without affecting the spectrum and have been assigned assuming the *cis* coupling has the greater magnitude. The errors involved in the determination of coupling constants are large owing to a low signal-to-noise ratio in the <sup>13</sup>C satellite spectra, and also because small changes in the geminal coupling do not have much effect on the calculated spectra.

The AA'BB' type proton n.m.r. spectrum of neat 1-phenyl-1-bromocyclopropane was solved with the aid of the Swalen program. The only satisfactory fit was obtained with the geminal coupling taken to have the opposite sign to the vicinal couplings. Interchange of the two *cis* couplings and interchange of the geminal and *trans* couplings does not affect the calculated spectrum. The assignment of geminal and *trans* couplings with opposite signs appears to be definite and is supported by analysis of the spectrum of 1-phenyl-1-bromocyclopropane in chloroform (where the chemical shifts are different).

Gutowsky and co-workers<sup>12</sup> on the basis of valence-bond calculations have predicted a positive geminal coupling for H–C–H angles less than 120°. However, a recent publication<sup>13</sup> on the proton n.m.r. spectra of small-ring compounds indicates that the geminal coupling has an opposite sign to the vicinal couplings in cyclobutane derivatives. With the aid of spin decoupling, Anet<sup>14</sup> has shown that the geminal proton–

(1) Supported in part by the Office of Naval Research and the National Science Foundation.

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proton coupling in  $\text{CH}_2\text{DOH}$  is opposite in sign to the  $^{13}\text{C}-\text{H}$  coupling. Since the latter coupling is almost sure to be positive,<sup>15</sup> the geminal coupling must have a negative sign. On the basis of this evidence we have assigned the geminal coupling a negative sign and the *cis* and *trans* vicinal couplings positive signs in cyclopropanes. It is very interesting that in ethylene oxides, the coupling constants have been reported to have the same relative sign.<sup>16</sup>

The geminal H-C-H angles in cyclopropanes appear to fall in the vicinity of  $114.5-118^\circ$ <sup>17</sup> and, for this range of angles, the theoretical valence-bond curve of Gutowsky and co-workers<sup>12</sup> predicts H-C-H spin-spin couplings of +4.5 to +7 c.p.s. We have investigated the coupling constants in a number of cyclopropanes with different kinds of substituent groups and find the geminal coupling constants between -3.1 to -6.0 c.p.s. (Table I). These results contrast with those of Weitkamp and co-workers,<sup>18</sup> who report geminal couplings of 7.0 to 9.0 c.p.s. for substituted 1,1-dichlorocyclopropanes. In monosubstituted epoxides, the geminal coupling constants have been reported<sup>16</sup> to fall in a narrow range of +5.0 to +6.3 c.p.s. for the compounds studied. In ethylene oxides, the H-C-H angle is around  $116^\circ$  and similar geminal couplings in cyclopropanes and ethylene oxides would be expected owing to the dependence of the coupling on H-C-H angle.

The valence-bond calculations made by Karplus<sup>19</sup> and the molecular-orbital treatment of Conroy<sup>20</sup> predict for  $\text{sp}^3$  hybridization a dependence of the vicinal coupling constant on the dihedral angle between the C-H bonds. For the geminal H-C-H angles of  $114.5-118^\circ$  for cyclopropanes<sup>17</sup> the corresponding dihedral angles are calculated to be  $131-134^\circ$  for *trans*-cyclopropyl hydrogens and  $0^\circ$  for *cis*-cyclopropyl hydrogens. The Karplus equations predict for these dihedral angles, a *cis* coupling of +8.2 c.p.s. and a *trans* coupling of +3.8 to +4.3 c.p.s., while the Conroy curve predicts *cis* and *trans* coupling of +8.0 and +6.4 to +7.0 c.p.s., respectively. The vicinal cyclopropyl coupling constants (Table I) are found to be +8.0 to +11.2 c.p.s. for *cis* hydrogens and +5.2 to +8.0 for *trans* hydrogens in cyclopropanes. The *cis* coupling was found to be greater than *trans* in cyclopropanes in agreement with theory. In monosubstituted ethylene oxides,<sup>16</sup> the *cis* and *trans* couplings have smaller magnitudes than in cyclopropanes, being +4.0 to +5.2 and +1.86 to +2.51 c.p.s. for *cis* and *trans* protons. The *cis* hydrogens in both cyclopropanes and ethylene oxides are eclipsed and the difference in couplings cannot be accounted for on the basis of dihedral angle. The differences in vicinal couplings may be due to the electronegativity of oxygen in the oxides.

Lynden-Bell and Sheppard<sup>21</sup> have analyzed the proton n.m.r. spectra of  $^{13}\text{C}$ -labeled acetylene, ethylene, and ethane and found the  $^{13}\text{C}-\text{H}$  coupling to be 249, 156.3, and 125 c.p.s., respectively. The fact that the  $^{13}\text{C}-\text{H}$  values for cyclopropanes (Table I) fall between 157.8 and 166.5 c.p.s. reinforces the suggestion<sup>22</sup> that the hybridization of the carbon-hydrogen bonding orbitals in cyclopropanes is close to  $\text{sp}^2$ . The  $^{13}\text{C}-\text{H}$  couplings in cyclopropanes are comparable with those

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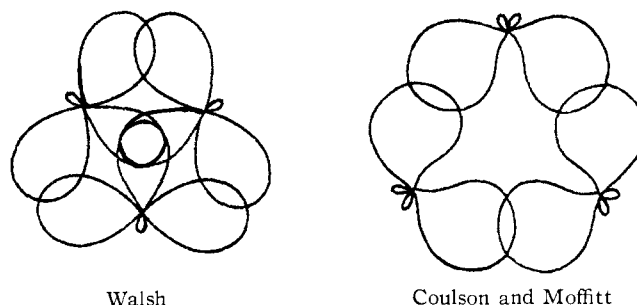
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Walsh

Coulson and Moffitt

Fig. 1.—Walsh and Coulson-Moffitt orbital models for C-C bonding in cyclopropane rings.

for allenes<sup>23</sup> which are in the range 166-168 c.p.s. and with those for three-membered heterocycles<sup>24</sup> which are in the range 168-176 c.p.s. The  $^{13}\text{C}-\text{F}$  coupling in octafluorocyclobutane<sup>25</sup> is 298.0 c.p.s. We find for the  $^{19}\text{F}$  spectrum of hexafluorocyclopropane a  $^{13}\text{C}-\text{F}$  coupling of 328.7 c.p.s. and a 6.4 c.p.s. upfield  $^{13}\text{C}$  isotope effect on the fluorine line positions. Not enough data are available to use the magnitude of  $^{13}\text{C}-\text{F}$  coupling in fluorocyclopropanes to indicate the hybridization of the carbon-bonding orbitals.

A study of chemical shift in cyclopropanes offers the possibility of giving new insight into the electronic structure of the cyclopropane ring. A large body of evidence has accumulated which supports the concept that the cyclopropane ring system possesses double-bond character.<sup>26</sup> The evidence is based on measurements of dipole moments, ultraviolet and infrared spectra, and ionization potentials as well as on chemical reactivity. Cyclopropane has been suggested by Walsh<sup>27</sup> to have bonding corresponding to a three-centered ethylene—the C-C bonds being formed by overlap in the plane of the ring of p-orbitals on neighboring carbon atoms and by overlap of three  $\text{sp}^2$  orbitals on adjacent carbon atoms directed toward the center of the ring (Fig. 1). The Walsh model assumes that two electrons occupy the central hybrid orbitals while four electrons occupy the molecular orbitals formed by overlap of the p-atomic orbitals. Some localized bond character was predicted for cyclopropane leading to hybridization between  $\text{sp}^3$  and  $\text{sp}^2$  but closer to  $\text{sp}^2$ . On the basis of a pure valence-state model with perfect pairing, Coulson and Moffitt<sup>28</sup> formulate the C-C carbon bonds of cyclopropane to involve hybrid orbitals which lie outside the internuclear angles. It was shown that the most favorable hybridization angle corresponds to having the C-C bond-forming orbitals at an angle of  $104^\circ$  which make the difference between internuclear lines and the hybrid orbitals be  $22^\circ$  (Fig. 1). The Coulson-Moffitt model predicts the C-H bond orbitals in cyclopropane to have less p-character than normal tetrahedral bonds and hence be more like ethylene than ethane.

Despite the fact that the theoretical models indicate that the C-H bonds in cyclopropane should be more closely akin to those of ethylene than those of ethane, the cyclopropyl resonances come very significantly upfield from the vinyl resonances. Clearly some factor(s) other than carbon hybridization determines the chemical shifts of cyclopropyl hydrogens. Comparison of the cyclopropyl chemical shifts for 1,1-dimethylcyclopropane, spiro-pentane, and spirohexane

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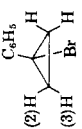
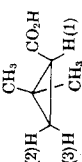
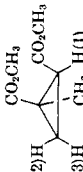
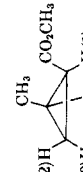



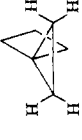
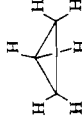
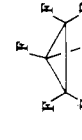
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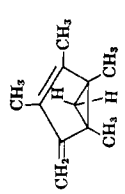
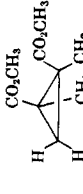
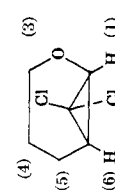
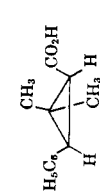
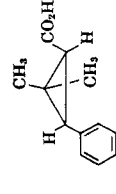
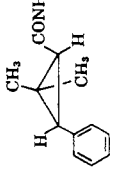
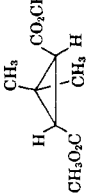
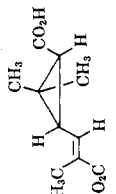
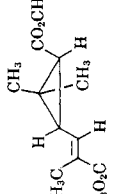
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TABLE I  
COUPLING CONSTANTS AND CHEMICAL SHIFTS IN CYCLOPROPANE DERIVATIVES

Formula	Compound	Solvent	Coupling constants, c.p.s.			Chemical shifts, c.p.s. <sup>k</sup>		
			$J_{gem}$	$J_{cis}$	$J_{trans}$	H(1)	H(2)	H(3)
 (2)H (3)H	1-Phenyl-1-bromocyclopropane	Neat <sup>b</sup>	-5.9 ± 0.2	+10.5 ± 0.3	+7.0 ± 0.2	..	53.1 <sup>a</sup>	70.1 <sup>a</sup>
 (2)H (3)H	1,1-Dimethylcyclopropanecarboxylic acid	Neat	-4.3 ± .3	+8.0 ± .3	+5.6 ± .3	83.4	59.4	47.5
 (2)H (3)H	Dimethyl 1-methylcyclopropane- <i>cis</i> -1,2-dicarboxylate	Neat	-4.7 ± .2	+8.6 ± .2	+6.3 ± .2	115.4	98.9	69.1
 (2)H (3)H	Dimethyl 1-methylcyclopropane- <i>trans</i> -1,2-dicarboxylate	Neat <sup>c</sup>	-4.2 ± .2	+8.8 ± .2	+6.6 ± .2	133.4	72.1	88.8
 H H	1,1-Dichlorocyclopropane	Benzene	-6.0 ± 2.0	+11.2 ± .5	+8.0 ± .5	$J^{13}CH$ 166.5	Chemical shifts, c.p.s. <sup>k</sup> 88.2	
 H H	1,1-Dimethylcyclopropane	Benzene	-4.5 ± 1.0 <sup>d</sup>	+9.2 ± .5	+5.4 ± .5	158.7		12.0
 H H	Spiropentane	Benzene	-3.9 ± 1.0 <sup>d</sup>	+8.9 ± .5	+5.2 ± .5	159.8 <sup>e</sup>		43.8
 H H	Spirohexane	Benzene	-4.6 ± 2.0 <sup>d</sup>	+9.7 ± .5	+6.3 ± .5	157.8		20.4
 H H	Cyclopropane	5% w./v. in CCl <sub>4</sub>				161.8 <sup>f</sup>		13.2
 F F	Hexafluorocyclopropane	CFCl <sub>3</sub>				$J^{19}CF$ , 328.7		8976 ± 122 <sup>g</sup>

	1,3,4,5-Tetramethyl-2-methylenecyclo-[3.1.0]hex-3-ene	Neat	-3.1 ± 0.2 <sup>d</sup>
	Dimethyl 1,2-dimethylcyclopropane- <i>cis</i> -1,2-dicarboxylate	Neat	-4.2 ± 0.2 <sup>d</sup>
	2-Oxa-7,7-dichloronorcaradiene	5% w./v. in CCl <sub>4</sub>	+8.6 ± 0.2 <sup>i</sup>
	2,2-Dimethyl- <i>cis</i> -3-phenylcyclopropane-1-carboxylic acid	Satd. in CHCl <sub>3</sub>	+9.1 ± 0.2 <sup>i</sup>
	2,2-Dimethyl- <i>trans</i> -3-phenylcyclopropane-1-carboxylic acid	Satd. in CHCl <sub>3</sub>	+5.7 ± 0.2 <sup>i</sup>
	2,2-Dimethyl- <i>trans</i> -3-phenylcyclopropane-1-carboxamide	Satd. in CHCl <sub>3</sub>	+6.0 ± .2 <sup>i</sup>
	Dimethyl 2,2-dimethylcyclopropane- <i>trans</i> -1,3-dicarboxylate	5% in CCl <sub>4</sub>	+5.6 ± .2 <sup>i,j</sup>
	<i>trans</i> -3-( <i>trans</i> -2'-Carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid	Satd. in CHCl <sub>3</sub>	+5.7 ± .2 <sup>i</sup>
	Methyl <i>trans</i> -3-( <i>trans</i> -2'-carbomethoxypropenyl)-2,2-dimethylcyclopropane-1-carboxylate	Satd. in CHCl <sub>3</sub>	+5.4 ± .2 <sup>i</sup>

<sup>a</sup> Assigned on the basis that the phenyl group in phenylcyclopropane deshields the *trans*-protons more than the *cis*-protons. <sup>b</sup> Magnitudes and signs of coupling constants verified with 1-phenyl-1-bromocyclopropane in chloroform solution. <sup>c</sup> Magnitudes and signs of coupling constants verified with dimethyl 1-methylcyclopropane-*trans*-1,2-dicarboxylate in benzene solution. <sup>d</sup> Sign assumed to be negative. <sup>e</sup> Taken as twice the frequency difference between the parent peak and the center of the upfield satellite. <sup>f</sup> In good agreement with the value of 161 c.p.s. reported in ref. 22. <sup>g</sup> At 56.4 Mc. relative to fluorotrichloromethane. <sup>h</sup> Chemical shift in c.p.s. from tetramethylsilane for 5% w./v. solutions in carbon tetrachloride. <sup>i</sup> Sign assumed to be positive. <sup>j</sup> Obtained from <sup>13</sup>C-satellite spectrum. <sup>k</sup> Chemical shift in c.p.s. from tetramethylsilane.

TABLE II  
 SUMMARY OF CALCULATIONS OF RING-CURRENT EFFECTS ON CHEMICAL SHIFTS IN CYCLOPROPANES<sup>a</sup>

Compound	Side chain, $\Delta c.p.s.$									
	Obsd.	Case A		Case B		Obsd.	Case A		Case B	
		4e	6e	4e	6e		4e	6e	4e	6e
Cyclopropane										
Nortricyclene (CH)	18.0 <sup>c</sup>	23.4	34.2	29.4	43.8	73.2 <sup>b</sup>	19.8	29.4	40.8	61.8
1,1-Dimethylcyclopropane <sup>d</sup>	-9.0 <sup>d</sup>	12.6	18.6							
Dicyclopropylmethane <sup>h</sup>	9.6 <sup>d</sup>	25.2	37.8							
Spirohexane (in-plane) <sup>e</sup>	-6.0	-8.4	-12.6	-11.4	-17.4					
Spirohexane (out-of-plane) <sup>e</sup>	-6.0	3.6	6.0	6.0	9.6					
Spiropentane <sup>f</sup>						-30.6	-3.6	-6.0	-3.6	-5.4

<sup>a</sup> A positive value of  $\Delta c.p.s.$  indicates an upfield shift while a  $-\Delta c.p.s.$  indicates a downfield shift due to ring-current effect; 4e and 6e in the headings refer to the number of electrons assumed to be involved in the ring-current in the Johnson-Bovey<sup>31</sup> treatment. <sup>b</sup> Compared with cyclohexane. <sup>c</sup> Bicyclo[2.2.1]heptane was taken as a model compound in which the cyclopropyl ring was absent. <sup>d</sup> Obtained by comparison with shifts in aliphatic hydrocarbons. <sup>e</sup> Cyclobutyl hydrogens coplanar or out-of-plane with the cyclopropyl ring; observed  $\Delta c.p.s.$  are relative to cyclobutane. <sup>f</sup> Calculated  $\Delta c.p.s.$  takes account of modification of ring current due to a geometry different from cyclopropane. <sup>g</sup> Calculated as the average for four conformations of the C-H bond. <sup>h</sup> Assumed to be twice that for 1,1-dimethylcyclopropane.

indicate that as the external C-C-C bond angle is decreased the cyclopropyl resonances are shifted to lower field (see Table I).

The contribution of magnetic anisotropy<sup>29</sup> of the C-C bonds in cyclopropanes to the proton shielding has been calculated by Wiberg and Nist<sup>30</sup> to be 15 c.p.s. The greater mobility of the carbon electrons in cyclopropane predicted on the basis of the theoretical models compared to ordinary saturated compounds suggests that part of this anomalous diamagnetic shift may be due to a cyclopropane ring-current effect. This could either oppose or reinforce the field of the magnet depending on the position of the attached hydrogen atom relative to the ring. Johnson and Bovey<sup>31</sup> have calculated the chemical shift changes in aromatic systems due to ring-current effects by considering the circular precession of the  $\pi$ -electrons in two regions above and below the plane of the aromatic ring under the influence of the component of the applied field which is perpendicular to this plane.

The Johnson and Bovey method<sup>31</sup> was applied to the calculation of expected chemical shifts for ring and side-chain hydrogens in several cyclopropanes. The mobile electrons, four for the Walsh model and six for the Coulson and Moffitt model, were assumed to precess in the plane of the cyclopropane ring. Molecular parameters given by Goldish<sup>17</sup> were used. Calculations were carried out for (case A) the radius of the ring current equal to that of the circle circumscribing the ring (0.88 Å. for cyclopropane) and (case B) of a circle passing through the center of maximum electron density (assumed to 0.5 Å. from the carbon atom) of a p-orbital oriented as in the Walsh model (1.01 Å. for cyclopropane). The results are summarized in Table II and compared with observed shifts.

The calculated values are in no more than qualitative agreement with the observed chemical-shift differences. Since some degree of localization of the C-C bond electrons in cyclopropane is likely, the calculated influence of ring currents probably represents upper limits of such effects. It is to be expected that the C-C and C-H bond anisotropies also make substantial contributions to the observed chemical shifts. The assumed ring current for cyclopropane suggests that a hydrogen located near the equatorial plane of the ring will experience a paramagnetic effect on its resonance position, and a diamagnetic effect is predicted for hydrogens inside the ring, or somewhere above it and reasonably close to its threefold axis. The compari-

son between experiment and theory shown in Table II cannot be taken as establishing the existence of ring current in cyclopropanes, but the trends are reasonably consistent with a ring-current effect which has also been invoked to explain the unusually large molar diamagnetic susceptibility of cyclopropane.<sup>32</sup>

### Experimental

The 60-Mc. proton n.m.r. spectra of the AB system and ABC, AA'XX', and AA'BB' systems were taken on the V-4300B and A-60 high resolution spectrometers, respectively. The chemical shifts on the V-4300B were measured by means of a Hewlett-Packard Model 200AB audio oscillator and Model 521C frequency counter. Line positions have been measured to an accuracy of 0.1 c.p.s. Tetramethylsilane was used as an internal reference in the study of AB systems and as an external reference for other systems. All proton chemical shifts are given in c.p.s. from tetramethylsilane. Proton and fluorine <sup>13</sup>C satellite n.m.r. spectra were taken for <sup>13</sup>C in natural abundance. The <sup>13</sup>C-H coupling constants were obtained as the difference between the chemical shifts of the centers of the low- and high-field satellites.

Hexafluorocyclopropane was a sample generously supplied by Dr. D. C. England of the Du Pont Company. The positions of the <sup>13</sup>C-satellite peaks were determined at 56.4 Mc., using side bands from the parent difluoromethylene peak. The chemical shift of the latter peak was measured by interpolation with a 50% solution of hexafluorocyclopropane in fluorotrichloromethane, by generating an approximately 600-c.p.s. side band and sweeping rapidly through to the fluorotrichloromethane peak.

1,1-Dichlorocyclopropane was obtained by photochlorination of cyclopropane. It was distilled through a center-rod fractionating column and the fraction with b.p. 74.5° (744.5 mm.), *n*<sub>D</sub><sup>20</sup> 1.4373 (lit.<sup>33</sup> b.p. 74-75°, *n*<sub>D</sub><sup>20</sup> 1.4400) was used.

1,1-Dimethylcyclopropane was prepared by Cox<sup>34</sup> and was used without further purification.

Spiropentane of b.p. 36-38° was obtained from Professor D. E. Applequist. It had been distilled after treatment with bromine and dried over calcium hydride.

Spirohexane was furnished by Professor D. E. McGreer.<sup>35</sup>

1-Phenyl-1-bromocyclopropane was prepared in these laboratories by Dr. D. I. Schuster.

Dimethyl 1-Methylcyclopropane-cis-1,2-dicarboxylate.—The parent diacid, m.p. 139-141°, was provided by Professor L. L. McCoy,<sup>36</sup> and was esterified with an excess of diazomethane in benzene. The product was microdistilled at 3 mm. with a bath at 80°.

Dimethyl 1-Methylcyclopropane-trans-1,2-dicarboxylate.—The parent diacid, m.p. ca. 170° from Professor L. L. McCoy, was esterified with excess diazomethane. The resulting dimethyl ester was microdistilled at 2 mm. with a bath at 65-70°.

Nortricyclene was a pure sample obtained from Professor H. Hart. The spectrum showed a small broad CH peak, large CH<sub>2</sub> peak, and a cyclopropyl peak at 114.6, 70.8, and 57.60 c.p.s., respectively, with areas 1:6:3. The chemical shift for the cyclopropyl peak was measured by side-band superposition from tetramethylsilane, and that for the CH<sub>2</sub> and CH peaks by interpolation from two tetramethylsilane side bands. Since the chemical shifts

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were critical, they were obtained from the maxima or geometric center of each resonance for volume fractions of nortricyclene in carbon tetrachloride of approximately 1, 0.25, 0.06, 0.016, and extrapolating to infinite dilution.

**1,3,4,5-Tetramethyl-2-methylene-bicyclo[3.1.0]hex-3-ene** was obtained from Dr. L. de Vries.<sup>37</sup> Two side bands from the vinyl peak were used to obtain the frequencies of the cyclopropyl peaks by interpolation, the chemical shift difference between the cyclopropyl hydrogens being 3.9 c.p.s. The chemical shift of the center of the cyclopropyl methylene quartet was measured by interpolation from side bands from tetramethylsilane for a 5% w./v. solution of the hydrocarbon in carbon tetrachloride and found to be 31.2 c.p.s.

**2-Oxa-7,7-dichloronorcarane** of b.p. 50–52° (1.6–1.9 mm.),  $n_D^{25}$  1.4981, was provided by Professor W. E. Parham.<sup>38</sup> The n.m.r. spectrum of a 5% w./v. solution of 2-oxa-7,7-dichloronorcarane in carbon tetrachloride showed two main groups of peaks, the larger group at high field being assigned to the methylene hydrogens at C-4, C-5, and the cyclopropyl methine hydrogen at C-6; and the smaller group at low field to the methylene hydrogens at C-3 and the cyclopropyl methine hydrogen at C-1. The latter gave a prominent unsymmetrical doublet on the low-field side of the lower group of peaks, due to *cis*-vicinal spin coupling with the cyclopropyl methine hydrogen at C-6. The frequencies of the peaks in this doublet were determined by side-band superposition from tetramethylsilane.

**Dicyclopropylmethane** was provided by Professor H. Hart.<sup>39</sup> The acyclic methylene resonance appeared as a broadened doublet near the cyclopropyl methine peaks. The chemical shift for the center of this doublet was obtained by extrapolation to infinite dilution and found to be 65.4 c.p.s. downfield from tetramethylsilane.

**trans-3-(trans-2'-Carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid** was the dextrorotatory enantiomer, m.p. 164–165°, obtained from Professor Y. Inouye.<sup>40</sup> The line positions were measured by superimposing side bands from chloroform.

**Methyl trans-3-(trans-2'-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylate**, m.p. 80°, was also provided by Professor Y. Inouye.

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**2,2-Dimethyl-trans-3-phenylcyclopropane-1-carboxylic acid** was provided by Professor F. Sorm<sup>41</sup> and had m.p. 102°. Approximate chemical shifts (accurate to  $\pm 1$  c.p.s.) were obtained for the methyl and cyclopropyl hydrogens by interpolation from a tetramethylsilane peak (internal reference) and the low-field cyclopropyl doublet, which has been accurately calibrated. The chemical shift differences were thus found to be 48 c.p.s. between the cyclopropyl hydrogens and 31 c.p.s. between the *gem*-dimethyl groups.

**2,2-Dimethyl-cis-3-phenylcyclopropane-1-carboxylic acid** was also provided by Professor Sorm and had m.p. 134°. The chemical shift between the cyclopropyl hydrogens was 39 c.p.s., and between the *gem*-dimethyl groups only 2 c.p.s.

**2,2-Dimethyl-trans-3-phenylcyclopropane-1-carboxamide** was obtained from Professor G. W. Perold.<sup>42</sup> The chemical shifts were approximately 55 c.p.s. between the cyclopropyl hydrogens and 27 c.p.s. between the *gem*-dimethyl groups.

**Dimethyl 2,2-Dimethylcyclopropane-trans-1,2-dicarboxylate**.—The parent diacid was obtained from Professors Y. Inouye and M. Matsui, who report m.p. 210–212° and 212–213°, respectively. The combined samples were esterified with excess diazomethane, and the product was microdistilled at 14 mm. with a bath at 125–130° and gave diester of  $n_D^{25}$  1.4434. The high-field cyclopropyl <sup>13</sup>C-satellite was a slightly unsymmetrical doublet. The resonances were calibrated by side-band superposition from the carbomethoxyl peak.

**Dimethyl 1,2-dimethylcyclopropane-cis-1,2-dicarboxylate** was provided by Professor L. L. McCoy and contained 7% of the *trans* isomer. Two side bands from the methyl peaks were placed on either side of the upfield cyclopropane doublet and the splitting determined by interpolation. The analysis of the cyclopropyl methylene quartet indicated that the chemical shift between the cyclopropyl hydrogens was 79.0 c.p.s.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SYNTEX, S.A., MEXICO D.F., MEXICO]

## Spectra and Stereochemistry. VII.<sup>1,2</sup> Long-Range Shielding by Nitrile Groups

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The long-range shielding of steroidal angular methyl protons by cyano groups has been calculated and compared with experimental values for the methyl proton resonance shifts. The importance of other factors which influence the methyl proton resonances is commented upon. Evidence is presented which suggests that in  $\delta\alpha$ -cyano-3-keto-steroids ring A is distorted from the chair form.

In recent years the utility of nuclear magnetic resonance (n.m.r.) spectra in steroid chemistry has developed rapidly. Shoolery and Rogers<sup>3</sup> in a classical opening study of steroid n.m.r. spectra demonstrated the close relation of the resonance frequency of angular methyl protons to the nature of, and orientation of, substituent groups on the steroid skeleton. Moreover, they observed the independent additivity of the frequency shifts of the angular methyl protons induced by several different functional groups. These concepts have been substantially extended,<sup>1,4–16</sup> though

it has become apparent that where ring conformational changes occur, considerable caution must be exercised when considering the additivity of angular methyl proton frequency shifts, especially where long-range shielding effects are operative.<sup>4,14</sup>

In connection with some studies of 16,17-disubsti-

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