The Alternation of Substituent Effects. The Nuclear Magnetic Resonance Spectra of Mono- and Difluorocyclopropanes

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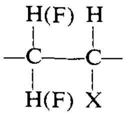
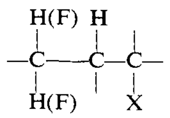
Abstract: A series of mono- and difluorocyclopropanes has been synthesized and subjected to complete nmr analysis. Clear evidence is presented that J_{HF} in the system XCCHCF *increases* as the electronegativity of X increases while J_{HF} in XCHCF *decreases* as the electronegativity of X increases. A rationale for this behavior in terms of alternating charge densities is offered. $^3J_{HF}$ in cyclopropanes is found to have values ranging from -2.3 to $+17$ Hz. Substituent effects on the H–F couplings are angularly dependent and found to be intermediate between those for alkanes and alkenes.

It is a well-established fact that vicinal HH (and HF) coupling constants in the fragment



$$\begin{array}{cc} \text{H(F)} & \text{H} \\ | & | \\ -\text{C}- & -\text{C}- \\ | & | \\ \text{H(F)} & \text{X} \end{array}$$

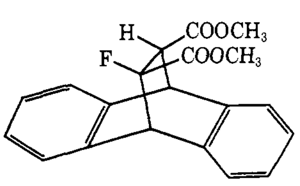
decrease as the electronegativity of the substituent X increases. We wish to present evidence that vicinal HF (and HH) coupling constants *increase* in the fragment



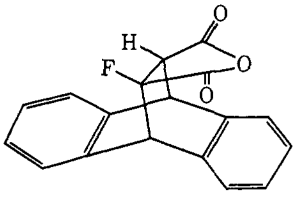
$$\begin{array}{ccc} \text{H(F)} & \text{H} & \\ | & | & | \\ -\text{C}- & -\text{C}- & -\text{C}- \\ | & | & | \\ \text{H(F)} & & \text{X} \end{array}$$

and to offer a possible explanation of this phenomenon. This observation is an outgrowth of a study of fluorinated cyclopropanes.

We have recently demonstrated that vicinal proton–fluorine coupling ($^3J_{HF}$) exhibits a dihedral angle dependence very similar to vicinal proton–proton coupling, having maxima at 0 and 180° dihedral angles and a minimum at 90°.[2] In addition, $^3J_{HF}$ is markedly dependent on the F–C–C and C–C–H bond angles in the fragment F–C–C–H. In molecules with dihedral angles fixed at 0° $^3J_{HF}$ is *ca.* +30 Hz in unstrained systems like **1a** (109.5° bond angles) and decreases monotonically in various compounds (like **1b**, **c**, **d**, and **e**) to 0.9 Hz in **2** (bond angles about 118°) as the F–C–C and C–C–H bond angles are widened.[2] Extrapolating this behavior to the cyclopropane ring one would expect an even smaller $^3J_{HF}$. But in the one case we examined, **3**, $^3J_{HF_{vic}}$ (0° dihedral angle) was found to be +17 Hz. The possibility exists that this large coupling constant arises from an unusually large substituent effect in **3**.

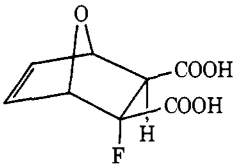


1a, $^3J_{HF} = 30$ Hz

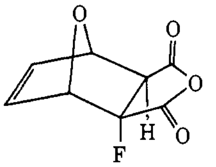


1b, $^3J_{HF} = 22$ Hz

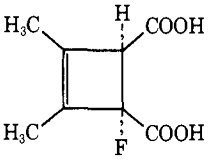
In the light of these facts the present research was undertaken to investigate further the proton–fluorine coupling in cyclopropanes.



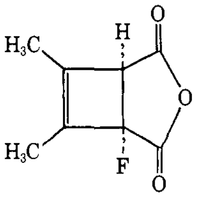
1c, $^3J_{HF} = 22$ Hz



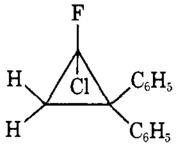
1d, $^3J_{HF} = 10.5$ Hz



1e, $^3J_{HF} = 6.25$ Hz



2, $^3J_{HF} = 0.9$ Hz



3, $^3J_{HF_{cis}} = +17$ Hz

Discussion

Syntheses of Fluorocyclopropanes. Attempts to prepare **4** by pyrolysis of sodium chlorodifluoroacetate[3] in the presence of vinyl acetate gave no detectable cyclopropane. The sample used was prepared by the pyrolysis of trimethyltrifluoromethyltin in dimethoxyethane.[4,5] The acetyl nitrate nitration of **6**[4] according to the procedure used by Ketcham, *et al.*,[6] for the nitration of phenylcyclopropane gave a 60% yield of **5** accompanied by 40% of the ortho isomer. The desired para nitro compound **5** very conveniently crystallized from the reaction mixture. Reduction of **5** with stannous chloride–hydrochloric acid[7] gave **7**; similarly **9** gave **11**. Compound **8** was prepared by the pyrolysis of sodium chlorodifluoroacetate[3] in the presence of vinyltriethoxysilane in diglyme.

Compounds **10** and **12** were prepared by the addition of chlorofluorocarbene to styrene. *In situ* generation of methoxide which reacted with *sym*-difluorotetrachlo-

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[1] National Science Foundation Undergraduate Research Participant, Summer 1967.

[2] K. L. Williamson, Y.-F. Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, **90**, 6717 (1968).

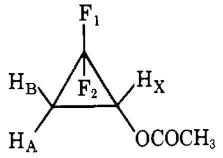
[3] J. M. Birchall, G. W. Cross, and R. N. Haszeldine, *Proc. Chem. Soc.*, 81 (1960). See also S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 1027 (1965).

[4] D. Seyferth, H. Dertouzos, R. Suzuki, and J. Y.-P. Mui, *ibid.*, **32**, 2980 (1967).

[5] We are indebted to Professor Seyferth for a sample of this compound.

[6] R. Ketcham, R. Cavestre, and D. Jambotkar, *J. Org. Chem.*, **28**, 2139 (1963).

[7] R. B. Woodward, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 453.



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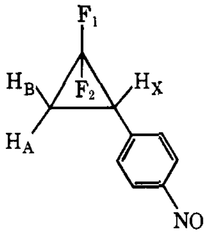

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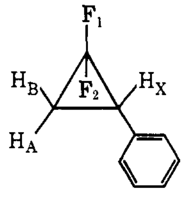

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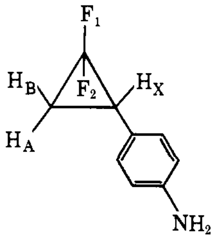

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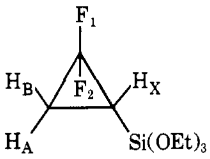

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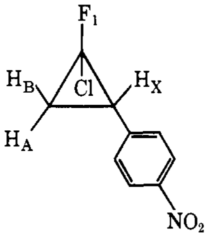

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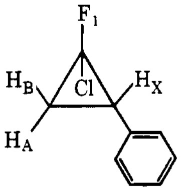

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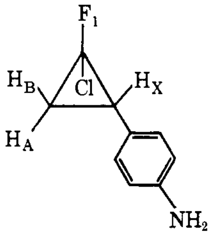

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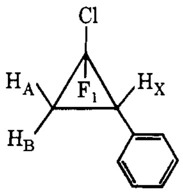

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roacetone to give the carbene[8] produced a mixture of **10** and **12** in 38% yield.[9] The fluorine nmr spectrum of the mixture (which could be separated by glc) showed it had the expected 1:1 ratio of the cis and trans isomers. Since $^3J_{HF_{cis}}$ (0° dihedral angle) is greater than $^3J_{HF_{trans}}$ (140° dihedral angle)[2] the isomer exhibiting $^3J_{H_XF}$ = 17.1 Hz was assigned structure **10** and that having $^3J_{H_XF}$ = 1.8 Hz was assigned structure **12**.

Nitration of **10**, where the phenyl group is cis to the chlorine atom, gave only one product, the crystalline para nitro compound **9**, while nitration of **12** in which the phenyl ring is cis to the fluorine atom gave a 1:1 mixture of ortho and para nitro products that were not studied further.[10] When the mixture of **10** and **12** was nitrated the desired **9** again conveniently crystallized from the reaction mixture.

Analyses of Nmr Spectra. Although it is a five-spin system, the nmr spectrum of the difluoroacetoxycyclopropane (**4**) could be analyzed easily by first-order methods. The proton, H_X, on the acetate-bearing carbon atom is over 2.5-ppm downfield from the resonances of the adjacent A and B protons. From our previous analysis of the nmr spectrum of 1,1-dichloro-2-acetoxycyclopropane[13] we know that $^3J_{HH_{cis}}$ = 8.0, $^3J_{HH_{trans}}$ = 5.4, and $^2J_{HH_{gem}}$ = −9.1 Hz. In compound **4** the cis, trans, and geminal couplings are 9.3, 5.0, and −9.7 Hz, respectively. The HF couplings are simply superimposed on the proton spectrum. Since $^3J_{HF}$ shows a dihedral angle dependence[2] similar to $^3J_{HH}$ we have assumed that the larger vicinal coupling constants are between cis protons and fluorines (dihedral angle 0°). In this way the upfield fluorine (F_2) is found to be cis to the substituent.

Since the spectrum of **4** can be analyzed by first-order approximations, changing the signs of the various coupling constants has very little effect on the frequencies and intensities of the lines. As the substituent electronegativity decreases, the chemical shifts of the three protons converge giving ABC spectra and then changes in the signs of J_{HF} cause marked changes in the frequencies and intensities of both the proton and fluorine spectra. In the present work we have assumed that the geminal proton coupling is negative and the vicinal proton coupling is positive in sign as has been shown for other cyclopropanes;[13,14] similarly we have assumed that the geminal fluorine coupling is positive.[15] This leaves only the signs of $^3J_{HF}$ to be determined.

The spectra were analyzed with the aid of the LAOCOON III computer program.[16] After initial iterations using both the proton and fluorine spectra the fluorine lines (not as well resolved as the proton lines) were dropped for the final iterations. For all compounds but **4** changing the signs of $^3J_{HF}$ from those listed in Table I caused noticeable changes in line intensities and frequencies on attempted iteration. (Note that both positive and negative signs for $^3J_{HF}$ were found.) We believe the signs thus determined are unique; this could be proved experimentally by heteronuclear spin tickling.

Results

The three difluorocyclopropanes **4**, **6**, and **8** constitute a series in which the substituent varies from the electron-withdrawing acetate group to the electron-donating triethoxysilyl group. As expected from our previous work[13] we note that the geminal and vicinal HH coupling constants, both cis and trans, decrease algebraically as the substituent electronegativity increases (Figure 1). Not surprisingly, $^3J_{F_1X}$ and $^3J_{F_2X}$ also decrease as the substituent electronegativity increases (Figure 2); Abraham and Cavalli have shown that $^3J_{HF}$ in a series of substituted ethanes is a linear function of substituent electronegativity which decreases with increasing electronegativity.[17]

The most interesting finding in the present work is the dependence of $^3J_{F_2A}$, $^3J_{F_2B}$, $^3J_{F_1A}$, and $^3J_{F_1B}$ on the electronegativity of the substituent. It will be noted in Figure 2 that these four coupling constants *increase*

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(8) T. Ando, H. Yamanaka, S. Terabe, A. Horike, and W. Funasaka, *Tetrahedron Lett.*, 1123 (1967).

(9) Compounds 10 and 12 have been prepared in 45% yield by a different procedure. See P. Weyerstahl, D. Klamann, C. Finger, F. Nerdel, and J. Buddrus, *Chem. Ber.*, **100**, 1858 (1967).

(10) This is noteworthy in that three groups of workers,[6,11,12] have found that the ortho:para ratio for the nitric acid–acetic anhydride nitration of phenylcyclopropane is 66:33 to 82:18. In the present work we have found that nitration of the difluorocyclopropylbenzene (6) gives a 40:60 ortho:para ratio indicating that the fluorine atoms do not severely block substitution at the ortho position. This decrease in the per cent of ortho isomer compared to cyclopropylbenzene may simply be due in part to the inductive effect of the two fluorine atoms. This is confirmed for the nitration of 12 where one of the fluorines is replaced by the less electronegative chlorine and the amount of ortho isomer goes up 10%. The nitration of 10, on the other hand, with the chlorine cis to the phenyl group, gives *no* ortho isomer, indicating steric hindrance to substitution. These results substantiate the finding of Shechter, *et al.*,[12] on the enhanced ortho substitution of cyclopropylbenzene.

(11) Yu. S. Shabarov, V. K. Potapov, and R. Ya. Levina, *J. Gen. Chem. USSR*, **34**, 3171 (1964).

(12) R. C. Hahn, T. F. Corbin, and H. Shechter, *J. Amer. Chem. Soc.*, **90**, 3404 (1968).

(13) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964).

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

(15) D. F. Evans, S. L. Manatt, and D. D. Elleman, *J. Amer. Chem. Soc.*, **85**, 238 (1963).

(16) A. A. Bothner-By and S. M. Castellano in "Computer Programs for Chemistry," Vol. 1, DeLos F. D. Detar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10.

(17) R. J. Abraham and L. Cavalli, *Mol. Phys.*, **9**, 67 (1965).

Table I. Chemical Shifts and Coupling Constants for Mono- and Difluorocyclopropanes

Compd	Chemical shifts, ppm[a]					Coupling constants, Hz										RMS error[b]
	F_1	F_2	X	B	A	F_1F_2	F_1X	F_1B	F_1A	F_2X	F_2B	F_2A	BX	AX	AB	
4	133.20	147.25	4.265	1.709	1.455	171.4	9.9	14.2	4.8	−2.3	6.7	15.5	9.3	5.0	−9.7	0.08
5	125.94	143.53	2.825	1.964	1.719	155.2	12.5	12.0	4.0	0.24	5.2	12.5	11.6	8.0	−8.2	0.11
6	126.11	143.58	2.673	1.729	1.550	154.4	13.4	12.5	3.8	0.40	5.0	12.6	11.8	8.2	−7.8	0.08
7	126.53	142.95	2.580	1.647	1.420	154.5	13.5	12.7	4.0	−0.01	4.6	12.2	11.7	7.9	−7.7	0.12
8	126.25	131.60	0.647	1.420	1.362	150.2	15.7	10.3	3.3	6.9	1.8	9.1	13.3	9.8	−5.8	0.06
9	124.81		2.947	2.116	1.714		16.2	15.4	6.2				11.5	8.5	−8.0	0.04
10	124.31		2.806	1.887	1.545		17.1	15.7	6.2				11.5	8.5	−7.7	0.08
11	124.12		2.723	1.864	1.478		17.0	15.7	6.2				11.6	8.5	−7.6	0.07
12	143.84		2.638	1.776	1.689		1.8	16.0	7.5				8.3	11.1	−7.8	0.04

[a] Upfield from $CFCl_3$, downfield from TMS. [b] See C. J. Macdonald and T. Schaefer (*Can. J. Chem.*, **48**, 1033 (1970)) for pertinent remarks regarding this value derived from the LAOCOON III computer program. See also the Experimental Section.

as the electronegativity of the substituent increases. This constitutes the first unambiguous observation of this behavior for H–F coupling constants and is one of the clearest examples of a phenomenon which has previously been observed for H–H coupling. In the case of H–H coupling the effect is quite small and consequently difficult to pin down with certainty. Schaefer[18] first noted this when he observed that $^3J_{\text{cis}}$ and $^3J_{\text{trans}}$ in his 2-substituted 1,1-dimethylcyclopropanes were larger than $^3J_{\text{cis}}$ and $^3J_{\text{trans}}$ in the series of 2-substituted 1,1-dichlorocyclopropanes which we had analyzed;[13] *i.e.*, replacement of the two methyl groups by two electronegative chlorine atoms caused $^3J_{\text{HH}}$ to *increase.* However, since the substituents in the two series of compounds differed he found a direct comparison difficult. More recently, Cohen and Schaefer[19] have critically examined the literature and found that an alternation in substituent effects with the number of intervening bonds is a general phenomenon, but the effect is very small for J_{HH}, *e.g.*, for coupling between the 2 and 3 protons in 1-substituted propanes, $^3J_{23}$ increases by 0.10 ± 0.12 Hz per electronegativity unit. In 1-substituted aromatic systems, $^3J_{23}$ increases by 0.4 Hz, in alkenes by 0.3 Hz, and in cyclopropanes by 1.3 Hz per electronegativity unit.

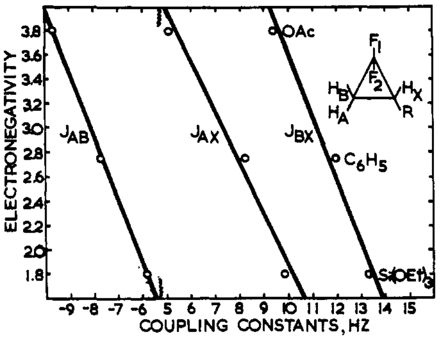


Figure 1. Vicinal and geminal proton–proton coupling constants *vs.* substituent electronegativity.

The effect is obviously larger for $^3J_{\text{HF}}$ in these cyclopropanes. It will be noted in Figure 2 that $^3J_{F_1A}$, $^3J_{F_2A}$, $^3J_{F_1B}$, and $^3J_{F_2B}$ all increase with increasing substituent electronegativity. Furthermore, it will be noted that $^3J_{F_2B}$ and $^3J_{F_2A}$ increase more per unit of electronegativity change than do $^3J_{F_1B}$ and $^3J_{F_1A}$. This indicates an angular dependence of the substituent effect. The larger substituent effect in cyclopropanes by comparison with *n*-propanes is undoubtedly due to the partially unsaturated character of the cyclopropane ring and the fact that there are two pathways leading from the substituted carbon to the carbons bearing the coupling atoms.

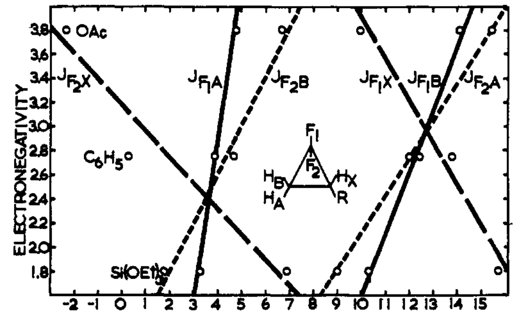
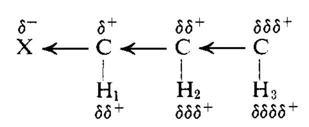


Figure 2. Vicinal proton–fluorine coupling constants *vs.* substituent electronegativity.

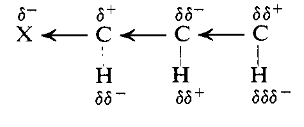
In ethylene oxide, sulfide, and imine, as the electronegativity of the heteroatom increases, $^3J_{\text{cis}}$ and $^3J_{\text{trans}}$ decrease,[20] behavior which is just the opposite of that observed for $^3J_{\text{HH}}$ in the substituted cyclopropanes.

If one reasons that an electronegative substituent induces charges that diminish steadily with distance down a chain of carbon atoms



$$\overset{\delta^-}{X} \longleftarrow \overset{\delta^+}{C} \longleftarrow \overset{\delta\delta^+}{C} \longleftarrow \overset{\delta\delta\delta^+}{C}$$
$$\begin{matrix} & H_1 & H_2 & H_3 \\ & \delta\delta^+ & \delta\delta\delta^+ & \delta\delta\delta\delta^+ \end{matrix}$$

then it is difficult to see why the effect of substituents on $^3J_{H_1H_2}$ should be different in sign than for $^3J_{H_2H_3}$—we would simply expect the effect on $^3J_{H_2H_3}$ to be smaller. However, Pople and Gordon[21] have recently performed some extremely interesting CNDO calculations on the changes in electronic structure of hydrocarbons caused by the introduction of substituents. They find that induced charges alternate in a decaying manner down the chain, so that the β position is normally negative.



$$\overset{\delta^-}{X} \longleftarrow \overset{\delta^+}{C} \longleftarrow \overset{\delta\delta^-}{C} \longleftarrow \overset{\delta\delta^+}{C}$$
$$\begin{matrix} & H & H & H \\ & \delta\delta^- & \delta\delta^+ & \delta\delta\delta^- \end{matrix}$$

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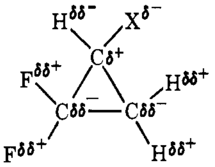
[18] T. Schaefer, F. Hruska, and G. Kotowycz, *Can. J. Chem.*, **43**, 75 (1965).

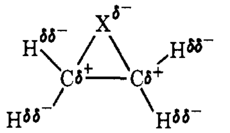
[19] A. D. Cohen and T. Schaefer, *Mol. Phys.*, **10**, 209 (1966).

[20] F. S. Mortimer, *J. Mol. Spectrosc.*, **5**, 199 (1960).

[21] J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

If we apply this type of charge distribution to substituted cyclopropanes and the heterocyclic three-membered rings, we see that the substituent has opposite effects on the electron densities at the coupling atoms.

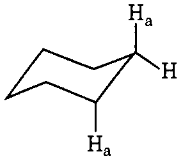




Coupling constants as well as these charge densities are ultimately derived from the same wave equation for these molecules. If we assume that coupling will be greater between protons and fluorine having the higher electron densities, then an electronegative substituent in a cyclopropane will cause an increase in the charge on the β atoms and a consequent increase in coupling, but will have an opposite effect on the three-membered heterocycles, as is observed.

Castellano and Kostelnik[22] have used a similar rationale to explain the alternation of substituent effects observed in monosubstituted benzenes and N-substituted pyridines. In agreement with the earlier work of Cohen and Schaefer, the change in $^3J_{23}$ for 1-substituted aromatic systems is found to be 0.54 Hz per electronegativity unit. Castellano argues at length that the effects observed are transmitted by the polarization of the σ electrons in the aromatic system and do not involve to any great extent π electrons or changes in bond lengths and angles due to substituents.

Booth, *et al.*,[23] have noted that in replacing the equatorial hydrogen of compounds of type **13** with an electron-donating methyl group to give compounds of type **14** results in a decrease in $^3J_{aa}$ of 0.9–1.3 Hz, while changing compounds of type **15** to **16** causes an increase in $^3J_{aa}$ of 0.6–1.0 Hz. Sardella[24] has found that as the electronegativity of X increases $^4J_{HH}$ also increases in **17**.



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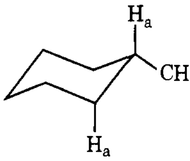
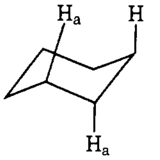
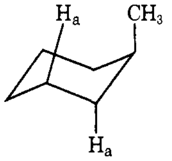


14



15



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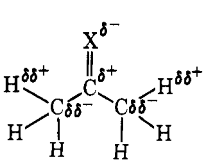

17, X = C,N,O

He states that these results can be accommodated by an extension of the Pople–Bothner-By theory[25] of geminal coupling; however, it appears this may be simply another example of the alternation of substituent effects under discussion here.

Goldstein, *et al.*,[26] have carried out an extensive and careful analysis of J_{HF} in a large number of benzene derivatives. Small alternations in substituent effects can be noted by comparing J_{23} in the 1,3- and 1,4-disubstituted fluorobenzenes.

Recently, Pople, *et al.*,[27] have calculated vicinal proton–proton coupling constants involving SCF–MO wave-function calculations in the INDO approximation under the influence of a Fermi contact perturbation. Their calculations show that the dependence of $^3J_{23}$ upon the electronegativity of X is opposite in sign from that of $^3J_{12}$ in systems of the type $CH^3CH^2CH^1X$. Such alternation was not expected on the basis of earlier valence bond views of inductive mechanisms. Their calculations indicate that, in agreement with experiment,[18,19,22] $(\partial {}^3J_{23}/\partial \chi_X)/(\partial {}^3J_{12}/\partial \chi_X)$ is approximately $-{}^1/_6$. In the present work we find this to be about $-{}^1/_2$ for HF coupling in these cyclopropanes.

The calculations of Pople, *et al.*,[27] also indicate an angular dependence of the substituent effect. For instance, $^3J_{cis}$ in the ethylene part of methyl vinyl ketone is calculated to vary from 9.8 to 12.0 Hz depending on the orientation of the acetyl group with respect to the ethylene part of the molecule. Unfortunately, virtually all of the couplings Pople, *et al.*, have calculated are, like the various conformers of methyl vinyl ketone, not amenable to experimental verification. In the present work we can see clearly (Figure 2) that $^3J_{F_2B}$ and $^3J_{F_2A}$ are more sensitive to electronegativity changes than are $^3J_{F_1A}$ and $^3J_{F_1B}$. It must follow also that the geometric relationship of the fluorines and not the hydrogens to the substituent is the dominant factor in this effect.

On the basis of the present work we conclude that the dependence of $^3J_{HF}$ on substituents alternates with the number of intervening bonds, just as $^3J_{HH}$ does and that there is an angular dependence of this substituent effect as well. The dependence is larger in the same way that the dihedral angle and bond angle dependence of $^3J_{HF}$ is larger than $^3J_{HH}$, further confirming the similarities of HF and HH coupling. In addition, the alternation in substituent effects on both $^3J_{HH}$ and $^3J_{HF}$ with the number of intervening bonds may be rationalized by the alternating charge densities which Pople's recent CNDO calculations indicate.

Effects of Cyclopropane Hybridization on Nmr Spectra. Substituent effects in these compounds seem to be transmitted primarily by the σ electrons of the bonds, but evidence can be seen for the π character of the cyclopropane ring. In this regard we note that $^3J_{HH_{cis}}$ ($^3J_{BX}$) *vs.* electronegativity for **4**, **6**, and **8** has the slope -2. For ethylenes the slope of $^3J_{cis}$ *vs.* electronegativity has the slope -0.7.[28] Thus, as previously noted,[13] the behavior of $^3J_{HH}$ as a function of substituent electro-

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[22] S. Castellano and R. Kostelnik, *J. Amer. Chem. Soc.*, **90**, 141 (1968).

[23] H. Booth and P. R. Thornburrow, *Chem. Ind.* (*London*), 685 (1968).

[24] D. J. Sardella, *Chem. Commun.*, 1613 (1968).

[25] Similar relationships do not hold for $^3J_{FF}$ in cyclopropanes; see M. G. Barlow, R. Fields, and F. P. Temme, *ibid.*, 1671 (1968).

[26] J. E. Loemker, K. M. Pryse, J. M. Read, Jr., and J. H. Goldstein, *Can. J. Chem.*, 47, 209 (1969); see also, J. E. Loemker, J. M. Read, Jr., and J. H. Goldstein, *J. Phys. Chem.*, 72, 991 (1968).

[27] G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4497 (1970).

[28] C. N. Banwell and N. Sheppard, *Mol. Phys.*, 3, 351 (1960).

negativity in cyclopropanes appears to be intermediate between that of saturated and unsaturated compounds. Similarly, ${}^3J_{\mathrm{HF_{cis}}}$ (${}^3J_{\mathrm{F_1X}}$) *vs.* electronegativity for **4**, **6**, and **8** has the slope −2.9, while for ethanes ${}^3J_{\mathrm{HF_{cis}}}$ *vs.* electronegativity has the slope −2.2.[17]

As noted above we have previously found that ${}^3J_{\mathrm{HF}}$ decreases as the H–C–C and C–C–F bond angles increase in a number of compounds, but in cyclopropanes, ${}^3J_{\mathrm{HF}}$ is much larger than expected. This cannot be attributed to some sort of anomalous substituent effect because ${}^3J_{\mathrm{HF_{cis}}}$ in all the compounds we have examined here falls in the range 9.1–17 Hz. It is not near zero or below as might be expected on the basis of the bond angles in cyclopropane; the large values of ${}^3J_{\mathrm{HF_{cis}}}$ in cyclopropanes (compared to cyclobutenes) must be due to the short C–C bond lengths in these molecules.

A negligible difference in ${}^3J_{\mathrm{F_1X}}$ (and ${}^3J_{\mathrm{BX}}$ and ${}^3J_{\mathrm{AX}}$ as well) is found in compounds **9**, **10**, and **11** (see Table I) in which the phenyl group is substituted at the para position with a nitro group, a hydrogen atom, and an amine group. So even though ${}^3J_{\mathrm{HF}}$ is four times more sensitive to substituent effects than ${}^3J_{\mathrm{HH}}$, remote substitution on the phenyl ring still does not perturb the electron density on the cyclopropane ring enough to be reflected in the coupling constants.

Experimental Section

Nmr spectra were recorded on a Varian HA-100 spectrometer operating at either 100 or 94.1 MHz. All compounds were run as 10–15% solutions in deuterated chloroform with either tetramethylsilane (TMS) or fluorotrichloromethane as an internal reference. Chemical shifts are reported in parts per million downfield from TMS and upfield from fluorotrichloromethane. Coupling constants are considered to be accurate to better than ±0.1 Hz on the basis of determining spectra on different samples and spectrometers over a period of time. Group electronegativity values are calculated by the method of Cavanaugh and Dailey[29] and are considered accurate to ±0.2 electronegativity unit. Infrared spectra were recorded as 10% solutions in carbon disulfide and/or chloroform on a Perkin-Elmer Model 137 spectrometer; ultraviolet spectra were recorded on a Perkin-Elmer Model 202 spectrometer in 95% ethanol. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were taken on a Thomas-Hoover capillary melting point apparatus. Vapor-phase chromatography was performed on an Aerograph Autoprep 705 gas chromatograph.

1,1-Difluoro-2-*p*-nitrophenylcyclopropane (5). This compound was prepared by the nitration of 1,1-difluoro-2-phenylcyclopropane (6)[4] following the method of Ketcham, *et al.*,[6] for the nitration of phenylcyclopropane.

To 4 ml of 98% acetic anhydride in a 25-ml three-necked round-bottomed flask was added 1.2 ml (25.7 mmol) of fuming nitric acid dropwise with stirring at −40°. To this was added 1.2 g (7.8 mmol) of **6** at such a rate that the temperature did not exceed −25°. The mixture was stirred for 0.5 hr at −30 to −15°. The reaction mixture was slowly added to warm water and then extracted with ether. The ether layer was washed with 25 ml of warm water and two 25-ml portions of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The ether was removed *in vacuo* and the product was distilled to give 0.90 g (58%) of a yellow liquid, bp 105° (0.6 Torr). Compound **5** crystallized and upon recrystallization from ethanol gave white needles, mp 51.5–53°, having infrared bands at 7.54, 8.15, 9.70, 9.90, 10.75, and 11.78 μ.

Anal. Calcd for $C_9H_7F_2NO_2$: C, 54.25; H, 3.55. Found: C, 53.46; H, 3.37.

The fluorine nmr spectrum of the crude mixture of nitrate product exhibited four octets centered at 125.9, 128.4, 138.7, and 142.2 ppm having peak areas in a ratio of 3:2:2:3. Pure **5** had fluorine nmr peaks at 125.9 and 138.7 ppm as well as an AA′BB′ aromatic proton spectrum characteristic of para substitution.

1,1-Difluoro-2-*p*-aminophenylcyclopropane (7). This compound was prepared from **5** according to the general procedure for the reduction of *p*-nitrobenzaldehyde.[7]

A 25-ml three-necked round-bottomed flask was charged with 0.55 g (2 mmol) of finely powdered stannous chloride dihydrate and 2 ml of concentrated hydrochloric acid. The mixture was cooled, with stirring, to 0°, 0,14 g (0.7 mmol) of **5** was added in one portion, and it was refluxed under nitrogen at 110° for 2 hr followed by gradual cooling. The mixture was dissolved in water, made slightly basic with a 10% sodium hydroxide solution, and extracted with ether. The ether extract was acidified with dilute hydrochloric acid and dried, and the solvent was evaporated. There was no evidence of unreacted **5**. The aqueous layer was made slightly basic, extracted with ether, washed with two 25-ml portions of saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The product, 94 mg (80%) of an orange solid, was obtained by evaporation of the solvent *in vacuo*. Further purification was not attempted. The compound exhibits characteristic infrared bands at 6.21, 9.68, 9.91, 12.20, and 12.50 μ.

1,1-Difluoro-2-triethoxysilylcyclopropane (8). Vinyltriethoxysilane, prepared according to the procedure of Nagel, *et al.*,[30] from vinyltrichlorosilane, 20 g (0.135 mol), and sodium chlorodifluoroacetate, 10 g (0.066 mol), were combined in a dry nitrogen atmosphere and heated to 150°. No decarboxylation was noted until 2 ml of diglyme was added at which time decarboxylation started and proceeded at a slow but steady rate. Carbon dioxide (1300 ml, 0.058 mol) was collected over a 21-hr period. The reaction mixture was cooled, sodium chloride was removed by filtration, and the filtrate was distilled on a spinning band distillation column to give 8.5 ml of unreacted olefin, bp 70–73° (25 Torr), and 0.5 g (4% yield) of **8**, bp 78–80°. The product, a colorless liquid, has $\lambda_{\max}^{\mathrm{CS_2}}$ 7.3, 7.4, 7.9, 8.6, 8.7, 9–9.5, 9.6, 9.8, 10.5, 11.1, 11.4, 12.8, and 13.7 μ. The proton and fluorine nmr coupling constants and chemical shifts are in complete accord with the proposed structure (see Table I). In order to reveal the majority of the cyclopropyl proton lines the methylene protons of the ethoxy groups were irradiated collapsing the methyl triplet to a singlet, at 1.13 ppm.

1-Chloro-1-fluoro-2-phenylcyclopropane (10 and 12). This mixture of isomers was synthesized according to the procedure of Ando, *et al.*,[8] for the preparation of 7-chloro-7-fluoronorcarane.

A 250-ml three-necked round-bottomed flask was charged with 12.6 g (0.30 mol) of a 57% dispersion of sodium hydride in mineral oil (Metal Hydrides), 50 ml of dry hexane, 52 g (0.5 mol) of styrene, and 23.2 g (0.10 mol) of freshly distilled *sym*-tetrachlorodifluoroacetone (Allied Chemicals). To this stirred mixture 10 ml (0.2 mol) of dry methanol was added dropwise at such a rate that the temperature did not exceed 50°. Stirring was continued overnight. The mixture was extracted with hexane, washed with 25 ml of water and two 25-ml portions of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. Removal of the hexane on a rotary evaporator under reduced pressure followed by distillation through a Vigreux column gave 12.9 g, 38%, of product, bp 46° (0.35 mm). Samples for analysis were separated by gas chromatography using a 20 ft × ³/₈ in. QF-1 column at 138°. Distillation on a Nester–Faust spinning band distillation column at 59.5° (5–6 mm) with a reflux ratio of 100:1 gave small amounts of extremely pure samples of Ia and Ib in addition to intermediate fractions containing the two isomers in varying ratios. Compound **10** (phenyl and chlorine cis) exhibited significant infrared bands at 8.09, 8.68, 8.79, 10.20, 10.68, 11.80, 13.15, and 14.50 μ, and ultraviolet absorption at $\lambda_{\max}$ 220 and 260 mμ (ε 9100, 460).

Anal. Calcd for C_9H_8ClF: C, 63.33; H, 4.74. Found: C, 63.33; H, 4.80.

For compound **12** (phenyl and fluorine cis) characteristic infrared peaks occurred at 7.92, 8.79, 10.43, 11.8–11.9, 13.00, and 14.50 μ; $\lambda_{\max}$ 220 and 260 mμ (ε 9000, 590).

Anal. Calcd for C_9H_8ClF: C, 63.33; H, 4.74. Found: C, 63.40; H, 4.77.

Attempts to prepare **10** and **12** by adding *sym*-tetrachlorodifluoroacetone to a stirred suspension of potassium *tert*-butoxide (MSA), styrene, and hexane at 0–5° (the method of Farah and Horensky[31]) gave a 6.3% yield. Inverse addition of potassium *tert*-butoxide to a mixture of styrene and the tetrachlorodifluoroacetone (the method

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[29] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

[30] R. Nagel, C. Tamborski, and H. W. Post, *J. Org. Chem.*, **16**, 1768 (1951).

[31] B. Farah and S. Horensky, *ibid.*, **28**, 2494 (1963).

of Moss and Gerstl[32] and Moore and Levine[33]) also resulted in a 6.3% yield of product.

1-Chloro-1-fluoro-2-*p*-nitrophenylcyclopropane (9). A 1:1 mixture of **10** and **12** was nitrated using the method of Ketcham, *et al.*,[6] for the nitration of phenylcyclopropane.

To 11.5 ml of acetic anhydride in a 100-ml flask was added dropwise 3.5 ml (0.075 mol) of fuming nitric acid at −40°. To this rapidly stirred mixture was added 4.0 g (0.023 mol) of the mixture of **10** and **12** at a rate such that the temperature did not exceed −30°. The mixture was stirred for 0.5 hr at −30 to −15° and then slowly added to warm water and extracted with ether. The ether layer was washed with 25 ml of warm water and two 25-ml portions of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The ether was removed *in vacuo* and the product distilled to give 3.4 g (69.5%) of a yellow liquid, bp 117–120° (0.2 mm). Compound **9** crystallized and upon recrystallization from ethanol gave white needles, mp 74.5–75.5°, having infrared bands at 7.59, 8.15, 8.74, 11.71, 11.89, and 14.60 μ, and having ultraviolet absorption at 216 and 274 mμ (ϵ 8900, 10,000).

Anal. Calcd for $C_9H_7ClFNO_2$: C, 50.12; H, 3.27. Found: C, 50.02; H, 3.11.

The crude nitration mixture from this experiment was examined by ^{19}F nmr and found to have three sets of peaks with relative area ratios of 2:1:1 at 124.8, 146.4, and 143.8 ppm. Crystalline **9** had a ^{19}F resonance centered at 124.8 ppm and had a proton spectrum that displayed the characteristic A_2B_2 pattern for aromatic protons, indicative of para substitution. In a separate experiment a sample of **12** was nitrated to give a 1:1 mixture of products having ^{19}F resonance patterns at 146.3 and 148.3 ppm and having an aromatic proton spectrum indicative of a mixture of ortho and para isomers. This mixture had infrared bands at 7.51, 7.90, 8.80, 11.60, 11.71, and 14.40 μ and ultraviolet absorption at 225 and 274 mμ (ϵ 8500 and 9600). Attempts to separate this mixture on QF-1 and Carbowax gas chromatography columns were unsuccessful as was column chromatography on silica gel and activated alumina.

1-Chloro-1-fluoro-2-*p*-aminophenylcyclopropane (11). This compound was prepared from **9** according to the general procedure of Woodward[7] for the reduction of *p*-nitrobenzaldehyde.

A 25-ml flask was charged with 0.738 g (0.003 mol) of finely powdered stannous chloride dihydrate and 2 ml of concentrated hydrochloric acid. The mixture was cooled with stirring to 0° and 0.232 g (0.001 mol) of **9** was added in one portion; the mixture was then refluxed under nitrogen at 110° for 2 hr followed by gradual cooling. It was dissolved in water, made slightly basic with a 10% sodium hydroxide solution, and extracted with ether. The ether extract was acidified with dilute hydrochloric acid and dried, and the solvent was evaporated. There was no evidence of unreacted nitro compound. The aqueous layer was made slightly basic, extracted with ether, washed with two 25-ml portions of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure to give an orange oil, having significant infrared bands at 2.95–3.05, 3.45–3.39, 6.20, 7.9, 8.10, 8.70–8.80, 9.00, 11.80, 12.20, and 13.50 μ and ultraviolet absorption at 216, 243, and 292 mμ (ϵ 5100, 5600, and 360).

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Type I and Type II Photochemical Reactions of Some Five- and Six-Membered Cycloalkanones[1]

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Abstract: The type I and type II photochemical reactions of a series of cyclopentanones and cyclohexanones have been studied. Quantum yields and rate constants for the various processes were determined. The results from the type I reactions show that α cleavage occurs predominantly from the triplet excited state, whereas the type II reactions occur from both the singlet and triplet excited states. Although the reactivities toward intramolecular γ-hydrogen abstraction of singlet and triplet states seem to be comparable, the triplet appears to be much more reactive than the singlet toward the α cleavage process. The efficiency of type II reaction from the singlet is generally higher than that from the triplet of the same molecule. These results are discussed in the light of other recent investigations in the field.

Since Norrish[6] in the 1930's discovered the type I (eq 1) and type II (eq 2) photochemical reactions of ketones, there have been numerous studies on both types of reactions. Both alkyl ketones[7,8] and aryl alkyl ketones[8] have undergone extensive and intensive investigation.

The type I cleavage of medium-ring alkanones is believed to result from photochemical production of a

$$R'COR \xrightarrow[\text{type I}]{} R'\dot{C}O + \dot{R} \qquad (1)$$

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