F^{19} Coupling Constants and Chemical Shifts in Trifluorocyclopropanes[1]

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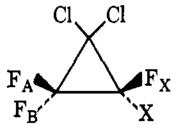
Abstract: The chloro, bromo, and iodo derivatives of 1,1-dichloro-2,2,3-trifluorocyclopropane have been synthesized and the F^{19} chemical shifts and coupling constants have been determined. The vicinal and geminal couplings have been shown, by frequency sweep double resonance, to be of opposite sign. Relative chemical shifts for the geminal fluorine atoms have been calculated. A linear correlation between the coupling constants and the substituent electronegativity has been noted in which J_{trans} is much more sensitive to changes in electronegative substituents than is J_{cis}. No obvious correlation between vicinal J_{FF} and dihedral angle is found.

To gain better insight into the steric and electronic effects which influence the magnitude of fluorine nmr chemical shifts and coupling constants we have synthesized the three trifluorocyclopropanes I–III. In this system the geometry of the molecule is fixed and known. The introduction of the three different halogens should not materially alter the geometry of the system and therefore we can evaluate the effect of substituents of varying electronegativity on the vicinal and geminal F–F coupling constants and the fluorine chemical shifts. We also can learn something of the dihedral angle dependence of J_{FF} in a saturated (although strained) system.



I, X = Cl
II, X = Br
III, X = I

We have previously shown that monosubstituted 1,1-dichlorocyclopropanes exhibit a linear relationship between the size of the various proton–proton coupling constants and the electronegativity of the substituents as well as a linear relationship between the chemical shifts of the protons and the substituent electronegativity.[3] The trifluorocyclopropanes studied in the present work show qualitatively the same behavior, but the quantitative differences may shed some light on the mechanism of F–F interactions.

Synthesis

The trifluorocyclopropanes I–III were prepared by the addition of dichlorocarbene to the appropriate trifluoroolefin. The best yields of 1,1-dichlorocyclopropanes are generally obtained from the reaction of potassium *t*-butoxide with ethyl trichloroacetate as the carbene precursor,[4] but any method employing a strong base is ruled out in the present work because of the possibility of undesirable formation of ethers from the trifluoroolefins.[5] Therefore we generated dichlorocarbene by one of two methods: the pyrolysis of sodium trichloroacetate[6] or the pyrolysis of phenyltrichloromethylmercury.[7] The chloro derivative I was prepared in 8.5% yield by pyrolysis of a monoglyme solution of sodium trichloroacetate in the presence of chlorotrifluoroethylene in a sealed tube. The bromo compound II was similarly prepared in 59% yield. It was also prepared in 18% yield by the pyrolysis of phenyltrichloromethylmercury in the presence of sodium iodide[8] and the bromoolefin in a sealed tube. The iodo compound III was prepared in 18% yield by the pyrolysis of phenyltrichloromethylmercury in the presence of the iodoolefin in a sealed tube (no sodium iodide). Seyferth has recently reported similar low yields in the synthesis of hexachlorocyclopropane using phenyltrichloromethylmercury and sodium iodide,[8] so it would appear that the method of choice for preparing highly halogenated cyclopropanes is by pyrolysis of the sodium salt of the appropriate trihalo acid.

In an attempt to prepare the chloro compound I by the addition of difluorocarbene to fluorotrichloroethylene it was found that the olefin was recovered unchanged, even though decarboxylation (at 150°) of the sodium salt of chlorodifluoroacetic acid had occurred. It was noted also that fluorotrichloroethylene was formed by the thermal decomposition of 1,1,2-trichloro-2,3,3-trifluorocyclopropane (I). It has recently been shown[9] by trapping experiments that the thermal decomposition (at 160–200°) of highly halogenated cyclopropanes of this type is an efficient source of difluorocarbene.

The infrared spectra of the three perhalocyclopropanes were strikingly similar; the infrared bands were assigned (see Experimental Section) by analogy with the assignments of Heicklen, *et al.*,[10] for perfluorocyclo-

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[2] National Science Foundation Undergraduate Research Participant and Petroleum Research Fund Scholar.

[3] K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964).

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[5] P. Tarrant and H. Brown, *J. Am. Chem. Soc.*, 73, 1781 (1951).

[6] (a) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959); (b) W. M. Wagner, H. Kloosterziel, and S. Van der Ven, *Rec. Trav. Chim.*, **80**, 740 (1961).

[7] D. Seyferth, J. Y-P. Mui, M. Gordon, and J. M. Burlich, *J. Am. Chem. Soc.*, **87**, 681 (1965).

[8] D. Seyferth, M. E. Gordon, J. Y-P. Mui, and J. M. Burlich, *ibid.*, **89**, 959 (1967).

[9] J. M. Birchall, R. N. Haszeldine, and D. W. Roberts, *Chem. Commun.*, 287 (1967).

[10] J. Heicklen, F. Wachi, and V. Knight, *J. Phys. Chem.*, **69**, 693 (1965).

Table I. Coupling Constants and Chemical Shifts for Trifluorocyclopropanes

	Electronegativity[a]	$\phi_X{}^{*b}$	$\phi_A{}^*$	$\phi_B{}^*$	J_{AB}	J_{AX}	J_{BX}
I, X = Cl	3.16	149.8	143.2	136.2	155.0	−4.1	−1.3
II, X = Br	2.94	148.6	143.2	131.0	153.0	−5.4	−5.4
III, X = I	2.65	148.8	142.7	122.9	150.5	−6.8	−10.0

[a] R. J. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1962). [b] Chemical shift in parts per million upfield from $CFCl_3$ (G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 671 (1959)).

propane and the assignments of Oliver, *et al.*,[11] for 1-chloro-1-fluoro-2,2-dimethylcyclopropane. The cyclopropane structures for I, II, and III are assigned on the basis of their method of preparation, elemental analyses, and infrared and nmr spectra.

Results and Discussion

The coupling constants and chemical shifts for the trifluorocyclopropanes I–III are given in Table I.

The geminal fluorine atoms A and B were assigned on the basis of their coupling constants ($J_{FF,gem}$ = 150.5–155 Hz);[12] however it is not immediately obvious which of the geminal fluorine atoms is *cis* and which is *trans* to the adjacent fluorine atom (F_X). The relationship between $J_{FF,vic}$ and dihedral angle is unknown so the assignment cannot be made on the basis of coupling constants. It is possible, however, to make the assignment on the basis of chemical shifts. It will be noted in Figure 1 that the chemical shift of F_B is markedly dependent on the electronegativity of the adjacent substituent (Cl, Br, I), while the chemical shift of F_A varies very little with changing substituent. This suggests that the relative chemical shifts of F_A and F_B might be calculated by consideration of the time-dependent dipole moments produced by the substituents which cause this van der Waals shift.

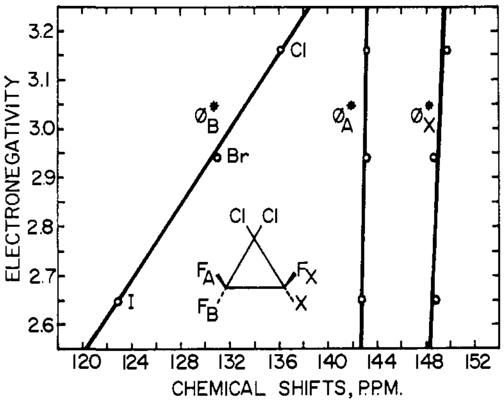

Figure 1. Chemical shifts *vs.* substituent electronegativity.

If we consider only the electric field effects on the shielding contributions to a fluorine nucleus, then the difference in chemical shift between F_A or F_B in a substituted cyclopropane (I, II, or III) and the analogous nucleus in 1,1,2,2-tetrafluoro-3,3-dichlorocyclopropane is given by[13]

$$\Delta S = -A\Delta E_Z - B(\Delta E^2 + \Delta\langle E^2\rangle) \qquad (1)$$

where E is the electric field produced at the fluorine nucleus by point dipoles placed at the center of any polar bonds in the molecule, E_Z is the component of this field acting along the bond direction, and $\langle E^2\rangle$ is the time-averaged square of the electric fields produced at the nucleus by fluctuating dipoles in the bonds. The effect of these time-dependent dipole moments gives rise to a nonzero time-averaged value $\langle E^2\rangle$ which is given approximately by[13]

$$\langle E^2\rangle = 3(PI/r^6) \qquad (2)$$

where P is the polarizability of the atom, I is its first ionization potential, and r is the distance between the fluorine nucleus and the center of the C–X bond. It has recently been shown by Feeney, Sutcliffe, and Walker[14–16] that the contribution to the chemical shift from changes in E_Z and E^2 are negligible when calculating fluorine chemical shifts in a series of halogenated fluoro compounds. This is because of the similarity in the size of the dipole moments of the C–X bonds and the compensating effect of the internuclear distance, r, as well as the relative sizes of the constants A and B. Thus the relative chemical shifts of F_A and F_B can be given simply by

$$\Delta S = -B\Delta\langle E^2\rangle \qquad (3)$$

These authors have used this relationship to calculate the relative chemical shifts in a series of halogenated ethanes and cyclobutanes[14] as well as in fluorinated cyclopentenes.[15]

Using the following parameters we have calculated r_1, the distance between F_A and the center of the C–X bond, and r_2, the distance between F_B and the center of the C–X bond, in I, II, and III: $\measuredangle$F–C–F = $\measuredangle$F–C–X = 114.5°, bond lengths: C–C = 1.53 A, C–F = 1.30 A, C–Cl = 1.70 A, C–Br = 1.85 A, and C–I = 2.05 A.[17] Employing these values of r_1 and r_2 and the bond parameters shown in Table II we calculated $\langle E^2\rangle$ and ΔS. The calculated chemical shifts result from subtracting ΔS from 144.3 ppm, the chemical shift of tetrafluorodichlorocyclopropane.[12] A value of $B = 15 \times 10^{-18}$ esu gives the best over-all fit to the experimental data and is also consistent with the values of B found by Feeney, *et al.*[15–17]

Inspection of Table II indicates that this rather simple calculation agrees fairly well with the experimental

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(11) J. P. Oliver, U. V. Rao, and M. T. Emerson, *Tetrahedron Letters*, 3419 (1964).

(12) $J_{FF,gem}$ = 157 Hz in 1-methyl-2,2-difluorocyclopropane (W. D. Phillips, *J. Chem. Phys.*, **25**, 949 (1956)) and in some pentafluorocyclopropanes $J_{FF,gem}$ = 188–207 Hz (R. A. Mitsch, *J. Heterocyclic Chem.*, 1, 27 (1964)). By contrast $J_{FF,gem}$ in tetrafluorocyclobutanes is about 220 Hz and in perfluorocyclohexane $J_{FF,gem}$ = 284 Hz.

(13) A. D. Buckingham, H. J. Bernstein, and W. T. Raynes, *J. Chem. Phys.*, **36**, 3481 (1962).

(14) J. Feeney, L. H. Sutcliffe, and S. M. Walker, *Mol. Phys.*, **11**, 117 (1966).

(15) J. Feeney, L. H. Sutcliffe, and S. M. Walker, *ibid.*, **11**, 129 (1966).

(16) J. Feeney, L. H. Sutcliffe, and S. M. Walker, *ibid.*, **11**, 137 (1966).

(17) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

Table II. Calculated Chemical Shifts

Compd	P_{C-X} $\times 10^{24}$ cm^3	$I \times$ 10^{12} ergs	r_1, A	r_2, A	$\langle E \rangle^2$ $\times 10^{12}$ esu	Chemical shifts Obsd	Chemical shifts Calcd	
I, X = Cl	2.604	20.8	2.573		0.5598	136.2	135.9	F_B
				3.131	0.1725	143.2	141.7	F_A
II, X = Br	3.754	18.8	2.594		0.6955	131.0	133.9	F_B
				3.183	0.2037	143.2	141.3	F_A
III, X = I	5.752	16.7	2.631		0.8701	122.9	131.3	F_B
				3.270	0.2360	142.7	140.8	F_A

data, except for the calculated shift of F_B in the iodo compound. A large number of factors have been neglected and the validity of this calculation for substituents other than halogens in these cyclopropanes is, of course, unknown. The lack of agreement for the chemical shift of F_B in the iodo compound could be due to some marked alteration in geometry of the molecule (although variation of the F–C–X bond angle and the C–C bond length over reasonable ranges does not improve the agreement between the calculated and experimental values). It is more likely that the unique hybridization of the cyclopropane ring system has caused a change in the C–X bond polarizability. In this regard eq 2 is very approximate in that the electron groups are regarded as point dipoles at the center of the C–X bond. Also, as noted by Feeney, *et al.*,[16] eq 2 was derived for intermolecular situations[13] in which r is greater than 3.5 A while for these cyclopropanes r is as short as 2.6 A. More refinement is needed in these calculations, but it is gratifying that a reasonable amount of agreement is found between observed and calculated fluorine chemical shifts in these rigid cyclopropanes. At the very least we have obtained unequivocal assignments for the chemical shifts of F_A and F_B.

Coupling Constants. As previously indicated[12] the value for J_{AB}, the geminal coupling constant (150.5–155.0 Hz), for these three trifluorocyclopropanes is in the range expected. From the work of Evans, Manatt, and Elleman[18] the positive sign for $J_{FF,gem}$ has been established for a number of saturated compounds. It is quite unlikely that $J_{FF,gem}$ should change from +200 Hz in fluorinated ethanes to −150 Hz in fluorinated cyclopropanes so we have assumed that $J_{FF,gem}$ in the present study has a positive sign. From frequency-sweep double-resonance experiments[19] we have established that both vicinal coupling constants have signs opposite to J_{gem} and are therefore presumably negative in sign. It would have been difficult to predict, *a priori*, the signs of these vicinal couplings since they are near zero in magnitude and since J_{vic} in alkenes is positive while in alkanes it is negative.[18c]

A plot of coupling constants *vs.* substituent electronegativity (Figure 2) reveals some interesting relationships. First of all, unlike vicinal H–H coupling, it is clear that substituent effects on J_{FF} far outweigh the dihedral angle dependence of J_{FF}. It would obviously have been impossible to assign the *cis* or *trans* couplings in these cyclopropanes simply on the basis of magnitude since $J_{FF,cis}$ for the chloro compound is smaller than $J_{FF,trans}$ while for the iodo compound the situation is just reversed. In this regard it has been noted by Harris and Sheppard[20] in some substituted perfluoroethanes that J_{trans} is more sensitive to substituent effects than is J_{gauche}.

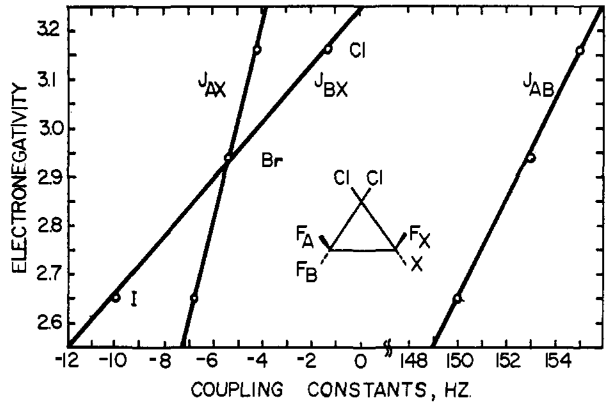

Figure 2. Coupling constants *vs.* substituent electronegativity.

Another consequence of the crossover in coupling constants as a function of electronegativity is that there can be no simple relationship between the internuclear F–F distance and J_{FF} as was once proposed by Sederholm[21] to account for fluorine–fluorine coupling. This concept of "through-space" coupling has previously been criticized by Roberts,[22] Evans,[23] and Sutcliffe, *et al.*[24,25]

These trifluorocyclopropanes constitute one of the few examples of molecules in which vicinal fluorine atoms are held in a fixed and known dihedral angle relationship to each other. We have recently shown[26] that vicinal J_{HF} has a dependence on dihedral angle which is quite similar to the dependence shown by vicinal J_{HH}.[27] If such a dependence were to hold for J_{FF} as well we would expect J_{AX} (dihedral angle = 0°) to be much larger than J_{BX} (dihedral angle = 140°). Feeney, Sutcliffe, and Walker[25] have studied $J_{FF,vic}$ in 1,2,4-trichloroheptafluorocyclohexene. Although the exact conformation of this molecule is not known it appears to exist primarily in one conformer having pseudo-axial and pseudo-equatorial fluorine atoms. It

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(18) (a) D. F. Evans, *Discussions Faraday Soc.*, **34**, 139 (1962); (b) S. L. Manatt and D. D. Elleman, *J. Am. Chem. Soc.*, **84**, 1305 (1962); (c) D. F. Evans, S. L. Manatt, and D. D. Elleman, *ibid.*, **85**, 238 (1963).

(19) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **36**, 2349 (1962).

(20) R. K. Harris and N. Sheppard, *Trans. Faraday Soc.*, **59**, 606 (1963).

(21) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964).

(22) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1339 (1965).

(23) D. F. Evans, *Discussions Faraday Soc.*, **34**, 139 (1962).

(24) N. Boden, J. Feeney, and L. H. Sutcliffe, *J. Chem. Soc.*, 3482 (1965).

(25) J. Feeney, L. H. Sutcliffe, and S. M. Walker, *ibid.*, 2650 (1966).

(26) K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *J. Am. Chem. Soc.*, **88**, 5678 (1966).

(27) M. Karplus, *ibid.*, **85**, 2870 (1963).

was found that the largest couplings (13–18 Hz) occurred between axial and equatorial fluorine atoms ($\phi \simeq 60°$) while eclipsed fluorine atoms ($\phi \simeq 0°$) gave small couplings (1–8 Hz). Merritt has found $J_{FF,vic}$ = 12 Hz in 4α,5α-difluorocholestan-3-one[28] ($\phi \simeq 60°$) and $J_{FF,vic}$ = 0.1 Hz in *trans*-1,2-difluoroacenaphthene ($\phi \simeq 120°$), 9 Hz in *cis*-1,2-difluoro-2-methylindan ($\phi \simeq 90°$), and 16.4 Hz in *cis*-1,2-difluoroacenaphthene ($\phi \simeq 120°$).[29] In neither of these previous studies were the signs of J_{FF} determined so a precise comparison with the present work is difficult. We see, however, in the bromo-substituted cyclopropane (II) that both J_{AX} and J_{BX} = −5.4 Hz when the dihedral angles are 0° in one case and *ca.* 144° in the other. Obviously no simple relationship between vicinal J_{FF} and dihedral angle is discernible at the present time.

In a careful study of the effect of substitution on vicinal J_{FF} in alkanes Abraham and Cavalli[30] found that $J_{FF(av)} = 91.4 - 6.15\Sigma E$ where ΣE is the sum of the Huggins electronegativities of the first atom of all the substituent groups on the C–C fragment considered. It is a bit difficult to know exactly how to apply this to these cyclopropanes; however one can readily calculate that J_{FF} should decrease in magnitude by 3.1 Hz when one replaces an iodine atom by a chlorine atom. $J_{FF,cis}$ changes by 6.3 Hz and $J_{FF,trans}$ changes by 13.9 Hz when one replaces an iodine atom by a chlorine atom in fluoroolefins.[31] In the present work we find that in going from compound III to compound I J_{AX} ($\phi = 0°$) decreases by 2.7 Hz and J_{BX} ($\phi \simeq 144°$) decreases by 8.7 Hz (Table I). It would seem therefore that the coupling constant behavior (as far as the effect of substituents goes) in these cyclopropanes is roughly intermediate between alkanes and alkenes. We have previously noted this effect in vicinal J_{HH} in a series of substituted cyclopropanes.[32]

Experimental Section

All infrared spectra were determined as 10% w/v solutions in carbon disulfide on a Perkin-Elmer Model 237 spectrometer. Nmr spectra were determined as 20% solutions in carbon disulfide using fluorotrichloromethane as an internal standard on a Varian DP-60 spectrometer operating at 56.4 MHz. Calibration was done by the audio side-band technique. Frequency-sweep double-resonance experiments were determined on a Varian HA-100 spectrometer operating at 94.1 MHz. Gas chromatography was done on a Cenco Model 70130 vapor-phase analyzer using helium as the carrier gas.

1,1,2-Trichloro-2,3,3-trifluorocyclopropane (I) was prepared following a modification of Wagner's method. Into a 3 × 21 cm Pyrex tube was placed 25 ml of monoglyme (distilled from sodium) and 27.8 g (0.15 mole) of sodium trichloroacetate (K & K, dried over phosphorus pentoxide). The tube was cooled and 55.6 g (0.48 mole) of chlorotrifluoroethylene (Peninsular ChemResearch, Inc.) was condensed in. The tube was sealed in a Parr bomb and heated to 100° overnight. After venting excess chlorotrifluoroethylene the crude product was taken up in ether, washed with water, and dried over anhydrous sodium sulfate. The ether was removed by careful distillation and the residue was chromatographed on a 0.25 in. × 10 ft Cenco Carbowax 600 column at room temperature. The yield (as determined by gas chromatography) was 8.5%, bp *ca.* 56–62°. The infrared spectrum showed: 7.01, 7.89, 8.45, 9.50, 9.61, 10.53, 10.70, 12.92, and 13.24 μ.

Anal. Calcd for $C_3Cl_3F_3$: C, 18.07; Cl, 53.34. Found: C, 18.44; Cl, 52.80.

An attempt to prepare this compound by an alternate method gave only starting material. In a Parr bomb was placed 10.55 g (0.07 mole) of freshly distilled fluorotrichloroethylene (Peninsular ChemResearch, Inc.), 30 ml of monoglyme (distilled from sodium), and 30.23 g (0.2 mole) of sodium chlorodifluoroacetate (dried over phosphorus pentoxide). The sealed tube was heated at 150° overnight. Treatment as described above gave primarily starting material after the final distillation. No cyclopropane could be detected.

Thermal Decomposition of I. A sample of I in a sealed glass tube was heated at 200° for 12 hr. The infrared spectrum taken at the end of this time showed a marked decrease (although not the entire disappearance) of the cyclopropane and the appearance of bands at 6.08, 8.54, 10.20, 11.76, and 11.93 μ attributed to fluorotrichloroethylene.

2-Bromo-1,1-dichloro-2,3,3-trifluorocyclopropane (II) was prepared by the method of Seyferth. Into a 24 × 125 mm Pyrex tube was sealed 8.0 g (0.02 mole) of phenyltrichloromethylmercury (mp 110.5–112°), 3 g (0.02 mole) of anhydrous sodium iodide, and 8.3 g (0.05 mole) of bromotrifluoroethylene. The tube was heated for 5 hr at 95°, cooled, and opened, and the product was removed by distillation. The crude yield was 17.5%.

This compound was also prepared by the method of Logan. Into a constricted Pyrex ignition tube was placed 7.92 g (0.02 mole) of phenyltrichloromethylmercury (mp 110–111°) and 14.4 g (0.08 mole) of bromotrifluoroethylene was condensed in. The sealed tube was heated at 95° for 24 hr, then allowed to stand some months before opening. The contents were removed by distillation to give 2.90 g (59.2%), bp 28–29° (39–44 mm). The infrared spectrum showed peaks at 7.07, 7.90, 8.52, 9.51, 9.60, 9.93, 10.10, 10.44, 10.63, 13.09, and 13.40 μ. A sample was purified for analysis by gas chromatography using a 0.25 in. × 10 ft Cenco Carbowax 600 column at 90.5°.

Anal. Calcd for $C_3BrCl_2F_3$: C, 14.77; Cl, 29.08; Br, 32.77. Found: C, 14.58; Cl, 29.17; Br, 32.84.

1,1-Dichloro-2-iodo-2,3,3-trifluorocyclopropane (III) was prepared by the method of Seyferth. Into a 25 × 125 mm Pyrex tube was sealed 9.29 g (0.023 mole) of phenyltrichloromethylmercury, mp 110–111°, 3.62 g (0.024 mole) of anhydrous sodium iodide, 10 ml of benzene, and 8.56 g (0.04 mole) of iodotrifluoroethylene (Peninsular ChemResearch, Inc.). The tube was heated at 95° for 5 hr, cooled, and opened. After removal of the benzene the product was distilled at *ca.* 50° (12 mm). The yield was 1.20 g (18%). A spectroscopic sample was purified on a 0.25 in. × 10 ft silicone column at 80°. The infrared showed peaks at 7.13, 7.99, 8.56, 9.57, 9.66, 10.12, 10.2, 10.71, 11.00, 13.3, and 13.6 μ.

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(28) R. F. Merritt and T. E. Stevens, *J. Am. Chem. Soc.*, **88**, 1822 (1966).

(29) R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, 31, 1859 (1966).

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

(31) M. G. Barlow, *Chem. Commun.*, 703 (1966).

(32) See ref 3.