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Unidirectional *cis* Addition of Iodine Chloride to 1,1,2-Trifluorocyclobutenes. Nuclear Magnetic Resonance Spectra of 2-Iodo-1,1,2-trifluorocyclobutanes

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Abstract: Iodine chloride was found to add unidirectionally to 2,3,3-trifluorocyclobutene and to 1-chloro-2,3,3-trifluorocyclobutene to give 1-chloro-2-iodo-2,3,3-trifluorocyclobutane (I) and 1,1-dichloro-2-iodo-2,3,3-trifluorocyclobutane (II), respectively. A small amount of 1,1,2-trichloro-2,3,3-trifluorocyclobutane (III) was formed in the latter case. The analysis of the nmr spectrum of I indicated that the iodine chloride added *cis* to the double bond. The dependence of the *cis* and *trans* vicinal J_{FF} on the electronegativity of the halogen substituent in 1-halo-1,2,2-trifluorocyclobutanes is similar to that observed in the cyclobutenes and cyclopropanes.

Iodine chloride has long been known to undergo Markovnikov-type electrophilic addition to ordinary olefins.[2] However, in 1952 Haszeldine[3] reported the addition of iodine chloride to chlorotrifluoroethylene to give almost quantitatively 1,2-dichloro-1,2,2-trifluoroiodoethane. Iodine bromide added analogously.

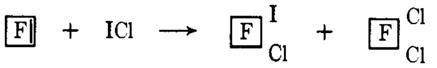
$$IX + CF_2{=}CFCl \longrightarrow CF_2X{\cdot}CFClI$$
$$X = Cl \text{ or } Br$$

The orientation of the addition is explained by back-donation of electrons from the vinylic fluorines to make the CF_2 group more positive in chlorotrifluoroethylene.

$$\overset{-}{F}\overset{+}{C}F{=}CClF \longleftrightarrow CF_2{=}CFCl \longleftrightarrow \overset{+}{F}{=}CF{\cdot}\overset{-}{C}ClF$$

However, Hauptschein, *et al.*,[4] found that iodine chloride added bidirectionally at high temperatures or in the presence of iron to give 1,1-dichloro-1,2,2-trifluoroiodoethane as well as 1,2-dichloro-1,2,2-trifluoroiodoethane. They also found that iodine chloride adds bidirectionally to 1,1-dichlorodifluoroethylene.

Haszeldine and Osborne[5] allowed a mixture of perfluorocyclobutene and iodine chloride to react at 180° for 1 day and obtained a 77% yield of 1-chlorohexafluoro-2-iodocyclobutane and a 10% yield of 1,2-dichlorohexafluorocyclobutane. In contrast, hydrogen iodide reacting with perfluorocyclobutene at 300° led to ring opening.[6]



No other examples of the addition of mixed halogens to fluorinated cyclobutenes have appeared in the literature. We report here the addition of iodine chloride to several asymmetrical fluorinated cyclobutenes. The nmr spectra of the products were studied in detail and compared with spectra of 1-halo-1,2,2-trifluorocyclopropanes and -cyclobutenes.[7,8]

Results

2,3,3-Trifluorocyclobutene was found to react readily with iodine chloride at 0° to give 1-chloro-2-iodo-2,3,3-

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(1) Taken in part from the Ph.D. dissertation of R. O. Michael, University of Colorado, 1968.

(2) C. K. Ingold and H. G. Smith, *J. Chem. Soc.*, 2742, 2752 (1931).

(3) R. N. Haszeldine, *ibid.*, 4423 (1952).

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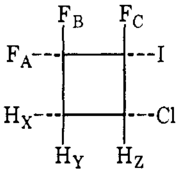
Table I. Chemical Shifts[a] and Coupling Constants[b] of 2-Chloro- and 2-Iodo-1,1,2-trifluorocyclobutenes, -cyclobutanes, and -cyclopropanes

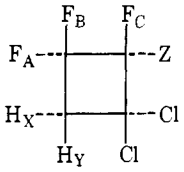
	I[c]	II	III[d]	III[e]	IV	V	VI[f]	VII[f]
δF_A	87.95	86.86	101.94	101.99	92.43	102.97	122.9	136.2
δF_B	108.53	112.30	111.35	111.34	111.32	110.49	142.7	143.2
δF_C	129.72	109.27	114.44	111.47	101.88	108.04	148.8	140.8
δH_X	3.09	3.33	3.33	3.32	6.15	6.57		
δH_Y	2.77	3.44	3.38	3.37	6.97	6.82		
J_{AB}	+197.62	+200.07	+202.89	+203.12	+190.08	+192.33	+150.0	+155.0
J_{AC}	−5.56	−5.05	+2.82	+2.80	+21.78	+28.62	−10.0	−1.3
J_{BC}	−8.92	−8.76	−9.46	−9.34	−11.74	−12.21	−6.8	−4.1
J_{AX}	+8.45	+8.99	+10.47	+10.40	−2.50	−2.04		
J_{AY}	+11.71	+9.49	+9.76	+9.76	+12.63	+11.85		
J_{BX}	+10.23	+10.59	+10.69	+10.50	−1.65	−1.62		
J_{BY}	+13.23	+11.78	+11.86	+11.79	+9.72	+10.19		
J_{CX}	−2.53	−3.03	−3.1	−3.3	+4.77	+6.85		
J_{CY}	+5.92	+6.87	+7.5	+7.6	−0.86	−0.85		
J_{XY}	−14.38	−15.00	−15.20	−15.11	3.07	3.24		

[a] Fluorine chemical shifts (nuclei A, B, and C) are in ppm upfield from $CFCl_3$ and proton chemical shifts (nuclei X, Y, and Z) are in ppm downfield from TMS. [b] In Hz. [c] In I, δH_Z = 4.57 ppm, $J_{AZ} = +5.64$, $J_{BZ} = +1.13$, $J_{CZ} = +6.85$, $J_{XZ} = +8.39$, and $J_{YZ} = +6.09$ Hz. [d] 50% by volume in $CFCl_3$. [e] 10% by volume in $CFCl_3$. [f] Reference 7.

trifluorocyclobutane (I). 1-Chloro-2,3,3-trifluorocyclobutene reacted with iodine chloride at room temperature



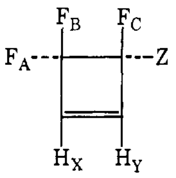
I



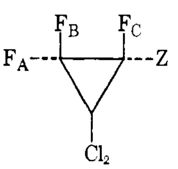
II, Z = I
III, Z = Cl

to give 1,1-dichloro-2-iodo-2,3,3-trifluorocyclobutane (II) plus a small amount of 1,1,2-trichloro-2,3,3-trifluorocyclobutane (III). 1,2-Dichloro-3,3-difluorocyclobutene was found to be inert to iodine chloride at room temperature but did appear to react at 100° to give small amounts of three extremely lachrymatory products which were not identified. 1,2-Dichlorotetrafluorocyclobutene was found to be inert to iodine chloride at room temperature, but at 195° gave a small yield of 1,1,2,2-tetrachlorotetrafluorocyclobutane. III was identified by comparison of its infrared spectrum with the spectrum of an authentic sample. I and II were identified by their nmr and mass spectra.

The structure of I is confirmed by the potassium hydroxide induced dehydrohalogenation, which yielded 3-iodo-3,4,4-trifluorocyclobutene (IV).



IV, Z = I
V, Z = Cl



VI, Z = I
VII, Z = Cl

The mass spectra of I, II, and IV all show strong peaks at *m/e* 208 as well as the appropriate molecular ion peaks. A study of all possible fragment ions from IV proved that a peak at *m/e* 208 could come only from an ion with composition C_2F_3I. For I and II, an ion with the composition $C_2HCl^{37}FI$ also has *m/e* 208. However, in the spectrum of I the *m/e* 206 peak ($C_2HCl^{35}FI$) is slightly less intense than the 208 peak and thus the 208 peak must consist predominantly of C_2F_3I. The mass spectrum of II is missing a significant peak at *m/e* 206, and thus its 208 peak must consist exclusively of C_2F_3I. Assuming that ICl adds to the double bond to give a cyclobutane, the only logical structure for an ion of this atomic composition would be $[CF_2{=}CFI]\cdot^+$, formed by reverse 1,2 cycloaddition. This moiety must therefore be present in all the iodine compounds obtained. No significant peaks at *m/e* 116, $[CF_2{=}CFCl]\cdot^+$, were present in the spectra of I, II, and IV, in contrast to the spectrum of 1,1,2-trifluoro-2,3,4-trichlorocyclobutane, where the 116 peak amounts to 61% of the base peak.

Nmr Spectra

The nmr spectra of I, II, and IV show that all three iodo compounds are structurally pure. Furthermore, the spectrum of I shows the presence of only one geometrical isomer. The nmr coupling constants and chemical shifts for the three new iodo compounds are given in Table I. The relative signs were determined from homonuclear spin-tickling experiments.[9] The absolute signs are given assuming the geminal J_{FF} and vicinal J_{HF} are positive,[10,11] and the geminal J_{HH} is negative.[12] The spectrum of I is first order except for protons X and Y (see Table I), and the multiplets of nuclei X and Y are almost first order since $\nu_X - \nu_Y$ is twice J_{XY}. Iterative calculations with the computer program LAOCN3 were used to determine the best values of the nmr constants.[13] The rms deviation between all 192 calculated and observed transitions was 0.04 Hz, and the probable errors of the coupling constants are less than 0.01 Hz. The spectra of II and III were more difficult to analyze since the chemical shift between X and Y was equal to J_{XY} in II and much less than J_{XY} in III. The signs of the HF coupling constants could be determined from first-order spin-tickling considerations in II,[9] and computer iterations gave an rms deviation between the calculated and observed transitions

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(9) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, 37, 2053 (1962).

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(12) I. Fleming and D. H. Williams, *Tetrahedron*, 23, 2747 (1967).

(13) LAOCN3 by A. A. Bothner-By and S. Castellano, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

of 0.05 Hz. An approximate spectrum for the analogous chloro compound, III, was calculated assuming the HF coupling constants were unchanged and halving the chemical shift between the geminal protons. The FF couplings were readily determined from the fluorine spectrum. Iteration with LAOCN3 then gave a rms deviation between all calculated and observed transitions of 0.04 Hz, and the spin-tickling experiments agreed with the calculated spectrum. The probable errors of the coupling constants in II and III are less than 0.02 Hz, except for the two cross-ring couplings where the probable error calculated by LAOCN3 is 0.13 Hz. Spectra of III were taken at 10 and 50% by volume in $CFCl_3$ (see Table I). Although the coupling constants and chemical shifts are clearly a function of concentration, the magnitude of the concentration changes are small compared to the differences between compounds discussed below. The nmr spectrum of III was independently analyzed by Harris and Robinson.[14] Their coupling constants for the neat liquid are all within 0.25 Hz of the values we found for the 50% solution.

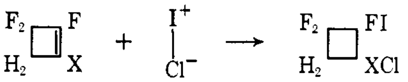
The analyses of the nmr spectra of IV and of the analogous chloro compound, 3-chloro-3,4,4-trifluorocyclobutene (V), have been discussed previously by us.[8] The coupling constants are included in Table I for comparison with the cyclobutane results. The nmr spectrum of IV unambiguously shows the presence of two different vinylic protons and three allylic fluorines, thereby proving the suggested structure.

The chemical shifts in I–III were assigned to particular nuclei as follows. The geminal fluorines constitute an AB system readily identified by the large value of J_{AB}, and the third fluorine is then unambiguously assigned. The A and B fluorines can be distinguished by considering the contribution of the electric fields in the CFCl or CFI group on the chemical shifts of the methylene fluorines. These calculations predict that the methylene fluorine *cis* to the fluorine in a CFX group in cyclopropanes should be 5.8 ppm upfield from the fluorine which is *trans*, for X = Cl, and 9.5 ppm upfield for X = I.[7] The calculations for cyclobutenes predict 8.0 and 16.2 ppm, respectively.[8] The calculated values for the cyclobutanes, 6.7 and 13.5 ppm, are intermediate between the values for the cyclopropanes and cyclobutenes.[8,15] Since the cyclobutane calculation is identical with the two previous calculations except for a slightly different proportionality coefficient, we will not give the details here, but the results enable the assignment of the fluorine nuclei given in Table I.

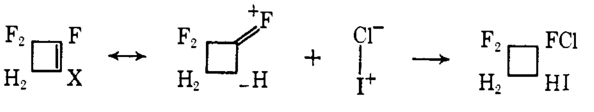
The geminal protons in I are identified by their large negative coupling constant, J_{XY}, and the remaining proton is then H_Z. The assignment of the geminal protons is not certain, but a reasonable guess may be made from a consideration of the cross-ring HF coupling constants. In 1-chloro-2,3,3-trifluorocyclobutane the two *cis* cross-ring couplings are +11.6 and +3.5 Hz (axial–axial and equatorial–equatorial, respectively), whereas the two *trans* couplings are +2.7 and −3.3 Hz.[11] In I, II, and III the cross-ring couplings to the CH_2 are about +6 and −3 Hz, and we have assigned the positive coupling to the *cis* proton and the negative coupling to the *trans* proton, relative to the fluorine in the CFX group.

Discussion

The addition of iodine chloride to 2,3,3-trifluorocyclobutene and 1-chloro-2,3,3-trifluorocyclobutene appears to be governed by simple polarity effects, wherein the fluorinated side of the ring is negative with respect to the protonated side. Just the opposite orientation



would be expected to occur in these additions if "back-donation" of electrons by the vinylic fluorine were occurring. Thus, the direction of addition is in the op-



posite direction to that found by Haszeldine[3] in iodine chloride addition to chlorotrifluoroethylene, 1,1-dichlorodifluoroethylene, and perfluoropropene. Since the double bonds in these noncyclic compounds have only highly electronegative substituents, these bonds would be relatively unpolarized, and weak effects such as "back-donation" would be important. Also, constraining the double bond into a four-membered ring might have an effect on the direction of addition, and further experiments are planned to understand the observed differences between cyclic and noncyclic olefins.

The order of reactivity was also just opposite to that found in nucleophilic substitution in fluorinated cyclobutenes[16] but the same as usually found for halogenation, highly halogenated systems being less active to further halogenation than less halogenated systems.[17]

A comparison of the couplings in the nmr spectrum of I with couplings in phenylcyclobutanes showed that the ICl added *cis* to the double bond. Lambert and Roberts[18] showed that 1,1-difluoro-2,2-dichloro-3-deuterio-3-phenylcyclobutane consists predominantly of one conformer with the phenyl group equatorial, whereas 1,1-difluoro-3-bromo-3-phenylcyclobutane contains approximately equal populations of equatorial and axial conformers. In the former case the vicinal couplings between the CH_2 and CF_2 groups were 1.75, 8.57, 12.59, and 20.52 Hz. In the latter case the four vicinal couplings were 8.90, 10.60, 12.45, and 12.52 Hz; the couplings are all averaged to about 12 Hz due to interconversion between the two possible conformers. We find in I that the four vicinal couplings (J_{AX}, J_{AY}, J_{BX}, and J_{BY}) are 8.45, 10.23, 11.71, and 13.23 Hz. This strongly suggests that I contains approximately equal amounts of both possible interconverting conformers, and that the iodine and chlorine are *cis*. If the iodine and chlorine were *trans*, then we would expect the conformer with both substituents equatorial to have a much lower free energy than the conformer with the substituents axial, and we would expect J_{AX} to be much smaller and J_{BY} much larger than observed.

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(14) R. K. Harris and V. J. Robinson, *J. Magnetic Resonance*, 1, 362 (1969).

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

(16) J. D. Park and R. O. Michael, unpublished results.

(17) H. Adams, Ph.D. Thesis, University of Colorado, 1965.

(18) J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, 87, 3884, 3891 (1965).

Previously,[19] it was shown that the photochemical or catalytic chlorination of perfluorocyclobutene yielded a dichloride which was identified as *trans*-1,2-dichlorohexafluorocyclobutane. The ICl reaction is the first instance where a *cis* addition occurs.

Our observation of the opposite signs of the vicinal FF coupling constants in cyclobutenes and cyclobutanes was the original inspiration to carry out the complete sign determination of the couplings in the cyclobutanes discussed above.[20] It is known that vicinal HF couplings in cyclobutanes follow approximately the Karplus dihedral angle dependence,[18,21,22] and we expected that the FF couplings in cyclobutanes would provide a good example of the dihedral angle dependence of vicinal J_{FF}. During the course of this work we discovered that Ernst[23] had independently studied the dihedral angle dependence of J_{FF} in a series of 1-chloro-1,2,2-trifluoro-3-substituted cyclobutanes, and we have limited our effort to observing the electronegativity dependence of the couplings in pairs of related compounds. We observe (see Table I) that J_{BC}, the 0° dihedral angle coupling, is unchanged in going from the 1-chloro-1,2,2-trifluoro derivative to the 1-iodo-1,2,2-trifluoro derivative, whereas J_{AC}, the approximately 109° coupling, decreases by approximately 8 Hz (in absolute magnitude) in the cyclopropanes, cyclobutenes, and cyclobutanes. In 3,3,4,4-tetrafluorocyclobutene the vicinal FF couplings are -12.92 and $+30.45$ Hz.[14] The latter result, combined with IV and V, shows the dependence of J_{AC} on electronegativity is not linear.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Infracord, and calibrated against the 1601.4-cm^{-1} line of polystyrene. Frequency sweep nmr spectra were taken on a Varian HA-100 analytical spectrometer. Tetramethylsilane was used as the reference for the proton spectra and trichlorofluoromethane for the fluorine spectra. Concentrations were about 30% by volume in trichlorofluoromethane. The samples were degassed by distillation under vacuum into the nmr tube. Transition frequencies were determined to ±0.03 Hz using the method reported previously.[8] The coupling constants and chemical shifts of the new compounds are given in Table I. Product analysis and small-scale preparations were carried out on an Aerograph Autoprep Model A-700, using a Texas Instruments Inc. Servariter model recorder. Refractive indices were taken on a Bausch & Lomb refractometer. Mass spectra were taken on either a Varian M-66 mass spectrometer, CEC 21-103C mass spectrometer equipped with an all-glass-heated (150°) inlet system, or a Varian MAT CH-5 mass spectrometer.

1-Chloro-2-iodo-2,3,3-trifluorocyclobutane (I). In a four-neck flask equipped with a magnetic stirring bar, reflux condenser, and a trap immersed in a Dry Ice–acetone bath, 11 g (0.10 mol) of 2,3,3-trifluorocyclobutene and 15 g of iodine chloride (0.09 mol) were mixed and stirred at 0° for 24 hr. The crude product was extracted with 30 ml of concentrated sodium bisulfite solution, washed with two 25-ml portions of water, and dried over anhydrous magnesium sulfate to yield 21 g (80%) of crude product. Preparative-scale glpc yielded a pure sample of 1-chloro-2-iodo-2,3,3-trifluorocyclobutane: $n^{25}\text{D}$ 1.4789; d^{25} 2.1270; molar refractivity, calcd 36.56, found 35.99; the mass spectrum gave a molecular ion at *m/e* 270.

1,1-Dichloro-2-iodo-2,3,3-trifluorocyclobutane (II). About 2.9 g (0.02 mol) of 1-chloro-2,3,3-trifluorocyclobutene and 7.6 g (0.05 mol) of iodine chloride were placed in a 50-ml stoppered round-bottom flask and allowed to stand at room temperature for 3 days. Washing with sodium bisulfite solution and water and drying over anhydrous magnesium sulfate yielded 2.9 g (50%) of product. Preparative scale glpc on SE30 yielded 90% 1,1-dichloro-2-iodo-2,3,3-trifluorocyclobutane (II) and 10% 1,1,2-trichloro-2,3,3-trifluorocyclobutane (III). The infrared spectrum of III was identical with that of a known sample. For II, $n^{27}\text{D}$ 1.4880; d^{27} 2.0887; molar refractivity, calcd 41.42, found 40.72; the mass spectrum gave a molecular ion at *m/e* 304.

Reaction of 1,2-Dichloro-3,3-difluorocyclobutene with Iodine Chloride. About 6 g (0.04 mol) of 1,2-dichloro-3,3-difluorocyclobutene and 7.7 g (0.05 mol) of iodine chloride were placed in a 6-dram bottle at room temperature for 3 days. The crude product was washed with 25 ml of saturated sodium bisulfite solution and dried over anhydrous magnesium sulfate. Glpc analysis indicated that only starting material was present.

About 3.1 g (0.02 mol) of 1,2-dichloro-3,3-difluorocyclobutene and 14 g (0.09 mol) of iodine chloride were placed in a 25-ml heavy-walled Pyrex glass tube which was then cooled in liquid nitrogen, evacuated, and sealed. After heating to 100° for 59 hr, the tube was cooled and opened and the crude product washed with 50 ml of concentrated sodium bisulfite solution. The mixture was extracted with methylene chloride and the organic layer dried over anhydrous magnesium sulfate. Glpc analysis indicated three possible products present in very small concentration. They were intensely lachrymatory and were not identified.

Reaction of 1,2-Dichlorotetrafluorocyclobutene with Iodine Chloride. About 6.2 g (0.03 mol) of 1,2-dichlorotetrafluorocyclobutene and 6.1 g (0.04 mol) of iodine chloride were placed in a 25-ml heavy-walled Pyrex glass tube which was then cooled in liquid nitrogen, evacuated, and sealed. The tube was heated to 195° for 67 hr, then cooled and opened to give 6.0 g of crude product. Comparing the glpc retention times with those of known samples indicated that the product was 89% 1,2-dichlorotetrafluorocyclobutane and 6% 1,1,2,2-tetrachlorotetrafluorocyclobutane. There was also present 1.6% of an unknown component whose retention time was intermediate between that of 1,2-dichlorotetrafluorocyclobutane and 1,1,2,2-tetrachlorotetrafluorocyclobutane.

Reaction of 1-Chloro-2-iodo-2,3,3-trifluorocyclobutane with Potassium Hydroxide. About 15.8 g (0.06 mol) of 1-chloro-2-iodo-2,3,3-trifluorocyclobutane was added to a well-stirred suspension of 30 g (0.54 mol) of potassium hydroxide in 100 ml of heavy white mineral oil cooled to 0°. After 24 hr of stirring at 0°, the reaction mixture was subjected to vacuum distillation to obtain about 12 g (70%) of crude product, shown to be 80% 3-iodo-3,4,4-trifluorocyclobutene (IV) by glpc. Preparative scale glpc yielded a pure sample whose structure was confirmed by its nmr spectrum. The mass spectrum gave a molecular ion at *m/e* 234.

Acknowledgment. The authors wish to express their appreciation to the Minnesota Mining and Manufacturing Co., St. Paul, Minn., for their support of this work through a grant-in-aid. R. A. N. also thanks the Research Corporation for support.

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