A Stereospecific 1,2 Cycloaddition of Trifluoroethylene with Vinyl Chloride. Nuclear Magnetic Resonance Spectrum of 1-Chloro-2,3,3-trifluorocyclobutane

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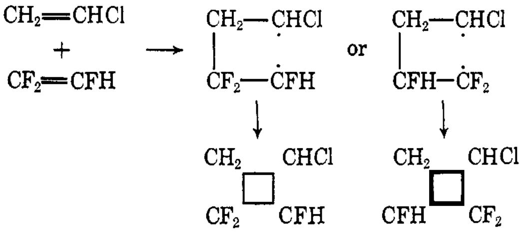
Trifluoroethylene and vinyl chloride have been shown to undergo a stereospecific 1,2 cycloaddition under thermal conditions to give 1-chloro-2,3,3-trifluorocyclobutane with the 1-chlorine and 2-fluorine *trans* to each other.

In general, only ethylenes of the type $CF_2{=}CX_2$ (where X = halogens) react readily with themselves or with allenes, ketenes, or activated alkenes, dienes, or alkynes to undergo 1,2 cycloadditions to yield cyclobutanes.[2] These reactions have been reported to give roughly equal amounts of *cis* and *trans* isomers where this possibility exists.[2]

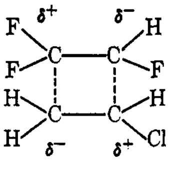
Trifluoroethylene has been shown to undergo no reaction with itself when heated in a sealed tube at 180° for 30 hr.[3]

The thermal high pressure reaction of trifluoroethylene with vinyl chloride was studied in order to ascertain if the cyclic dimer 1-chloro-2,3,3-trifluorocyclobutane could be obtained, in analogy to the thermal codimerizations of 1-halo-1,2,2-trifluoroethylenes with 1,1-dihalo-2,2-difluoroethylenes. Two possible cyclobutanes (I and II) might be formed as depicted below.



I II

Two factors favor the formation of the first isomer, I. First, $-\dot{C}FH$ is probably a more stable radical than either $-CH_2\cdot$ or $-CF_2\cdot$, since the predominant peak in the mass spectrum of the product of the reaction is $[CFH{=}CHCl]^{+\cdot}$. All $[CF_2{=}CX_2]^{+\cdot}$ fragments appear in rather low abundance. Second, the relative polarities of the two reacting olefins will favor the transition state leading to the isomer I. Further, one might expect the *trans* form of I (1-chlorine and 2-fluorine *trans* to each other) to predominate because of steric considerations.



Results

Trifluoroethylene and vinyl chloride were heated at 230° for 6 days. Vapor phase chromatography on three different columns (SE-30, Uconn, and Carbowax 20M) all indicated the product to be better than 95% pure and to consist of a single sharp peak. The infrared spectrum showed no significant absorption in the double-bond region, 1600–1800 cm^{-1}, indicating that the product is saturated.

The presence of structure I was indicated by potassium hydroxide induced dehydrohalogenation, which gave about a 68% yield of 2,3,3-trifluorocyclobutene.

The mass spectrum and nmr results proved the presence of structure I. The mass spectrum contained peaks expected from the cleavage of I into the four possible ethylene type fragment ions. The base peak was due to $[CFH{=}CHCl]^{+\cdot}$, which could only come from I and not II.

The nmr spectrum shows the presence of three symmetrical fluorine multiplets and four symmetrical proton multiplets from one isomer of I. The spectrum is nearly first order. The chemical shift between H_Y and H_Z is only 75 Hz and $J_{H_Y,H_Z} = -14.21$ Hz, resulting in second-order perturbations in the spectra of these two nuclei. Each nucleus is split into 64 lines from coupling to the other 6 nuclei. Many of these transition frequencies were accidentally degenerate, but it was always possible to pick out the 64 peaks for each nucleus by considering the amplitude of the degenerate lines. An iterative nmr computer program[4] was used to determine the best values of the nmr parameters using 156 of the 448 transition frequencies, including 54 lines from H_Y and H_Z. The rms error between calculated and observed frequencies was 0.10 Hz, and the probable errors of the parameters is under 0.05 Hz. The signs of all the vicinal and cross-ring coupling constants were determined relative to the signs of the geminal coupling constants using homonuclear spin tickling.[5] Other experiments have shown that J_{FF} (*gem*) and J_{HF} (*gem*) are positive[6,7] and J_{HH} (*gem*) is negative.[8] The results are given in Table I.

The J_{HH} couplings between the CF_CH_W and CH_YH_Z group, J_{WY} and J_{WZ}, are -1.43 and 1.85 Hz. The dihedral angle dependence of vicinal J_{HH} is well known,[9]

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[1] This paper represents part of a Ph.D. Thesis submitted by R. O. Michael to the Graduate School, University of Colorado, 1968.

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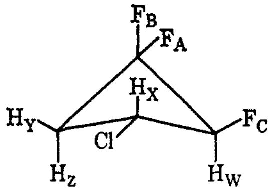
Table I

Nmr parameters for 1-Chloro-2,3,3-trifluorocyclobutane[a]



Chemical shifts (ppm)

Fluorine[b]	Hydrogen[c]
δ_A 93.72	δ_W 4.98
δ_B 124.64	δ_X 4.12
δ_C 188.76	δ_Y 2.97
	δ_Z 2.33

Coupling constants (Hz)

J_{FF}	J_{HF}	J_{HH}
J_{AB} (*gem*) = 210.19	J_{AW} (27°) = 7.81	J_{WX} (136°) = 6.11
J_{AC} (81°) = 0.93	J_{AX} (ea) = 2.70	J_{WY} (ae) = −1.43
J_{BC} (27°) = −3.69	J_{AY} (81°) = 2.49	J_{WZ} (aa) = 1.85
	J_{AZ} (27°) = 9.16	J_{XY} (27°) = 9.70
	J_{BW} (136°) = 8.17	J_{XZ} (136°) = 9.00
	J_{BX} (aa) = 3.45	J_{YZ} (*gem*) = −14.25
	J_{BY} (27°) = 15.99	
	J_{BZ} (136°) = 20.02	
	J_{CW} (*gem*) = 50.95	
	J_{CX} (27°) = 14.70	
	J_{CY} (ee) = 11.58	
	J_{CZ} (ea) = −3.32	

[a] Approximate dihedral angles are given for the vicinal couplings (see discussion) assuming the puckering angle of the cyclobutane ring is 27°,[10] and the cross ring couplings are labelled according to their stereochemistry, axial (a) or equatorial (e). [b] Upfield from $CFCl_3$. [c] Downfield from tetramethylsilane.

and these values are not consistent with the dihedral angles of the two vicinal couplings, differing by about 109°. Thus, the nmr shows that CFH and CH_2 cannot be vicinal as in II.

Discussion

Comparison of the vicinal J_{HF} couplings between the CH_2 and CF_2 groups with those observed by Lambert and Roberts[10] in other cyclobutanes strongly suggests that the chlorine and adjacent fluorine are both *trans* and equatorial in the isomer of I formed in the reaction. Lambert and Roberts[10] showed that 1,1-difluoro-2,2-dichloro-3-deuterio-3-phenylcyclobutane (III) consists predominantly of one conformer with the phenyl group equatorial, whereas 1,1-difluoro-3-bromo-3-phenylcyclobutane (IV) approximately equal populations of equatorial and axial conformers. In the former case, they found that the vicinal couplings between the CH_2 and CF_2 groups were 1.75, 8.57, 12.59, and 20.52 Hz, which corresponded to dihedral angles of approximately 80, 27, 27, and 136°, respectively. In IV the vicinal J_{HF} values were 8.90, 10.60, 12.45, 12.52 Hz;[5] the couplings are all averaged to about 12 Hz owing to interconversion between the two possible conformers. We find in I that the vicinal couplings between the CF_2 and CH_2 groups are 2.49, 9.16, 15.99, and 20.02 Hz. Consequently, I probably exists predominantly in one conformer. Since vicinal J_{HF} values follow approximately the same dihedral angle dependence as vicinal J_{HH} values,[10,11] the 2.49 Hz coupling is assigned to that between the equatorial H_Y and equatorial F_A. We would expect from simple steric arguments that the chlorine and F_C are both equatorial. This prediction is substantiated by the absence of small vicinal couplings to the protons in the CH_XCl and CH_WF_C groups. If H_W were equatorial, then the vicinal coupling to the equatorial F_A should be smaller than the observed 7.81 Hz. Similarly, the vicinal coupling of H_X to the equatorial H_Y is 9.70 Hz. The above arguments enabled the assignment of the stereochemistry of all the couplings in I given in Table I. To the best of our knowledge, this is the first determination of the signs of the J_{HF} cross-ring couplings in a cyclobutane. The cross-ring J_{HF} equatorial-equatorial coupling is much larger than the axial-axial coupling (11.58 and 3.45 Hz, respectively). Nmr studies on several other substituted cyclobutanes are necessary before it is possible to generalize these results. The large variations in the vicinal J_{HF} couplings with electronegativity, C–C bond length, and H-C-C-F bond angle at constant dihedral angle observed by Williamson, *et al.*,[11] suggest that cross-ring couplings should also vary considerably with molecular structure.

The cross-ring J_{HH} values are consistent with other studies which have shown that *trans* cross-ring couplings are negative whereas *cis* cross ring couplings vary from −0.5 to 2.3 Hz.[8] We obtained −1.43 and 1.85, respectively. As expected from previous measurements of vicinal J_{HH} and J_{HF} in saturated systems, the signs of all these couplings are positive.[8,12] The results of Williamson, *et al.*[11], mentioned above show that the

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[11] K. L. Williamson, Y. L. Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *ibid.*, **90**, 6717 (1968).

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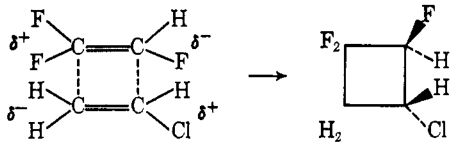
large variation of the 27° vicinal J_{HF} in the CH_2CF_2 group observed by us in I (9.16 and 15.77 Hz) and by Lambert and Roberts[10] in III (8.57 and 12.59 Hz) is probably due to small differences in C–C–F bond angles between axial and equatorial fluorines.

This is also the first determination of vicinal J_{FF} in a CF_2–CFH grouping in a cyclobutane ring. The opposite signs for the two vicinal couplings is expected from analogy to previous results for cyclobutenes and cyclobutanes.[13–15]

Conclusions

The interpretation of the nmr spectrum of 1-chloro-2,3,3-trifluorocyclobutane shows that the trifluoroethylene and vinyl chloride undergo a stereospecific 1,2 cycloaddition. Two explanations are possible for formation of only the *trans* isomer: (1) that it is an equilibrium reaction in which the most stable isomer predominates; (2) that it has an ionic rather than a diradical or a four-centered intermediate and that only the most electrostatically stable configuration of reactants leads to products.



Experimental Section

Infrared spectra were taken on a Perkin-Elmer Infracord. Nuclear magnetic resonance spectra were taken on a Varian HA-100 analytical spectrometer. Product analysis and fine 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 a CEC 21 103C mass spectrometer equipped with an all glass heated (150°) inlet system. Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

Codimerization of Trifluoroethylene with Vinyl Chloride.—Following the procedure of Park, Lacher, and Holler,[3] about 472 g of trifluoroethylene and 433 g of vinyl chloride were transferred into a sealed 1.5-l. autoclave containing 3 ml of *d*-limonene (added to prevent polymerization). The autoclave was heated to 230° for about 6 days. Upon cooling, 445 g of gaseous material and 284 g of a black liquid were obtained. Distillation of the liquid in a 3-ft glass helix packed column yielded 34.2 g (3.8% of theory) of 1-chloro-2,3,3-trifluorocyclobutane; bp 73–76° (627 mm); $n^{27}D$ 1.3683; d^{27} 1.3648. Molar refractivity: calcd, 23.76; found, 23.76.

Anal. Calcd for $C_4H_4ClF_3$: C, 33.24; H, 2.79; F, 39.44; Cl, 24.53. Found: C, 33.21; H, 2.77; F, 39.52; Cl, 24.73.

Tetramethylsilane and trichlorofluoromethane were added to the next liquid as internal reference lock signals for the nmr spectra. The sample was distilled *in vacuo* to remove oxygen.

Reaction of 1-Chloro-2,3,3-trifluorocyclobutane with Potassium Hydroxide.—Following the procedure of Park, Lacher, and Holler,[3] about 9.5 g of 1-chloro-2,3,3-trifluorocyclobutane was added dropwise over about 3 hr to a suspension of 18 g of potassium hydroxide suspended in 27 ml of heavy white mineral oil at room temperature in a 50-ml three-neck flask equipped with a stirrer and reflux condenser. After 44 hr, about 4.8 g (68% of theory) of a volatile product was obtained whose infrared spectrum was identical with that of known 2,3,3-trifluorocyclobutene. About 0.1 g each of *t*-butylpyrocatechol and diphenylamine was placed in the reaction flask and the gas trap to prevent polymerization of the cyclobutene. Catechol may be used in place of *t*-butylpyrocatechol.

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Registry No.—Trifluoroethylene, 359-11-5; vinyl chloride, 75-01-4; 1-chloro-2,3,3-trifluorocyclobutane (*trans*), 20445-03-8.

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Reactions of Dehydroacetic Acid and Related Pyrones with Secondary Amines

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A study of the reactions of dehydroacetic acid (**1**) and related pyrones with secondary amines has been undertaken. Pyrrolidine reacts readily with dehydroacetic acid (**1**), 3-propionyl-4-hydroxy-6-methyl-2-pyrone (**6**), and 3-benzoyl-4-hydroxy-6-methyl-2-pyrone (**10**) to yield **3**, **7**, and **12**, the respective products of nucleophilic attack at the 6 position of the pyrone, followed by ring opening and decarboxylation; with 3-acetyl-4-hydroxy-6-phenyl-2-pyrone (**14**) and dehydrobenzoylacetic acid (**16**), it gives in each case the product of condensation at the carbonyl of the side chain. Reaction of enediones **3** and **7** with pyrrolidine gives the corresponding dienones **4** and **9** which could also be obtained directly from dehydroacetic acid (**1**) and 3-propionyl-4-hydroxy-6-methyl-2-pyrone (**6**) and excess pyrrolidine. Enedione **12**, however, gives **13**, the pyrrolidinamide of benzoylacetic acid, when treated with pyrrolidine. When morpholine and diethylamine are employed as amines, a more complex reaction produces in the case of dehydroacetic acid (**1**) not only enediones and dienones but also acetoacetamides formed by attack at the 2 position of the pyrone. Mechanisms for these various transformations are discussed.

A primary or secondary amine could conceivably attack dehydroacetic acid (**1**) at any of four possible sites: the carbonyl of the acetyl side chain at the 3 position, the carbon atom terminating the conjugated carbon chain at the 6 position, the lactone carbonyl at the 2 position, and the carbon atom at the 4 position (the carbon of a potential carbonyl group). Actually, primary aliphatic and aromatic amines were shown to react preferentially and exclusively with the carbonyl of the acetyl side chain at the 3 position to form the Schiff