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Addition Reaction of Halogens to Vinyl(pentafluorocyclopropanes): Competition between a Radical Addition and an Electrophilic Addition†

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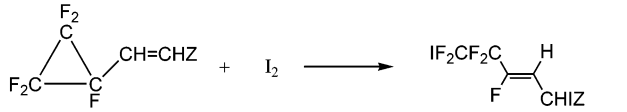
Abstract: Vinylpentafluorocyclopropanes **1** react with I_2 to give the (*Z*)-1,5-adduct **2**, whereas **1** reacts with Cl_2, Br_2 or I−Cl to produce (*Z*)-1,5-adduct **3** predominantly along with small amounts of 1,2-adduct **4**, which are formed by a radical mechanism and an ionic mechanism, respectively.

Halogenations of vinylcyclopropanes give 1,2-adducts predominantly through an electrophilic mechanism due to powerful stabilization of a carbocation by an adjacent cyclopropyl group.[1] Radical additions to vinylcyclopropane produces the 1,5-adduct along with small amounts of 1,2-adducts, particularly in a low concentration of a radical trap agent.[2] Introduction of fluorine into cyclopropane alters its properties due to an increase of ring strain energy and electron negativity.[3] The ring-opening of the difluorocyclopropylcarbinyl radical to a homoallyl radical is considered to be a hyperfast reaction with an estimated activation energy of 1.9 kcal/mol.[4] However, ring-opening of the difluoro cation analogue is much slower than its hydrocarbon counterpart since destabilization of the cation by difluorination essentially eliminates the cyclopropyl effect.[5] I previously discovered that a rapid radical polymerization of vinyl(pentafluorocyclopropane) **1** gave the ring-opened polymer exclusively.[6] It would be interesting to investigate reaction of vinylpentafluorocyclopropanes with halogens. The radical addition should give 1,5-adducts, whereas ionic addition may be diminished by pentafluorination of the cyclopropyl group. Herein I report the addition of halogens to **1** to test the two competitive mechanisms.

Vinylpentafluorocyclopropanes **1** underwent halogenation reactions under very mild conditions (0 °C to room temperature), whereas addition of halogens to perfluorocyclopropanes required much higher temperatures, usually above 150 °C.[7] The ring-opened 1,5-addition product and simple 1,2-addition product were obtained, depending on the halogens used and the reaction conditions. Addition of iodine to alkenes is well documented and an ionic addition mechanism is often proposed on the basis of kinetic data and product analysis.[8] However, iodination of fluoroolefins is considered to proceed through a radical mechanism.[9] When **1a** was treated with iodine in CH_2Cl_2 at room temperature to 40 °C, a rapid ring-opening addition reaction occurred to give **2a** in 92% yield. GC analysis gave only one peak, and ^{1}H NMR analysis revealed a doublet of triplets at 5.97 ppm with coupling constants of 30.1 and 9.0 Hz. The larger coupling is due to trans F−H coupling, indicative of the (*Z*)-olefin. Compound **1b** (*E*:*Z* = 5:1) also gave **2b** in 89% yield under similar conditions. The exclusive formation of ring-opened products **2** is consistent with the attack of the terminal carbon of the double bond by an iodine atom to give the pentafluorocyclocarbinyl radical, which isomerizes to the (*Z*)-allyl radical through a favorable transition state.[6] This kind of cyclopropylcarbinyl radical ring-opening is well-known in hydrocarbons with an activation energy of only 5.5 kcal/mol and a rate constant at 25 °C of almost 1×10^8 s^{-1}.[10] Fluorine substituents on the cyclopropylcarbinyl radical further enhances the rate.[4] Although the exact kinetic data has not been measured, the ring opening of the pentafluorocyclopropylcarbinyl radical is believed to be faster than that of the hydrocarbon and difluorinated analogues since the perfluorinated cyclopropane has much higher strain energy. Thus, the ring-opened products **2** were formed exclusively.



1

1a: Z = H
1b: Z = CH_3

2

2a: Z = H: 92%
2b: Z = CH_3: 89%

An ionic addition proceeds predominately in solution upon addition of bromine or chlorine to an electron-rich double bond.[2] However, a radical mechanism is operative with an electron-poor double bond, particularly in fluorinated olefins.[11] When **1** was treated with Br_2 or Cl_2 in solution, the major products were the ring-opened adducts, **3**, along with the simple addition products, **4**. In contrast to **1**, bromination or chlorination of vinyl cyclo-

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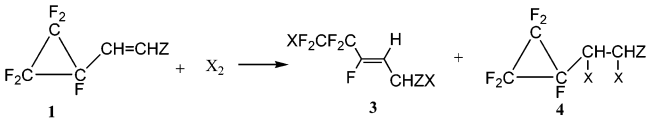
propanes predominately gave the 1,2-adducts through a cyclopropylcarbinyl cation intermediate.[1,2] The ratio of **3** to **4** depended on the halogens and reaction conditions. For example, bromination of **1a** in CH_2Cl_2 at 0 °C to room temperature gave **3a** and **4a** (X = Br) in a 4.4:1 ratio, whereas reaction of **1b** with Br_2 under the same conditions yielded a 6.3:1 mixture of **3b** and **4b** in 96% yield. In the presence of pyridine, the ratio changed to 3:1 under similar conditions. With Cl_2, **1a** produced a 5:1 mixture of **3a** and **4a** (X = Cl). The relative yield of **4b** (X = Cl) was increased when **1b** was treated with Cl_2.



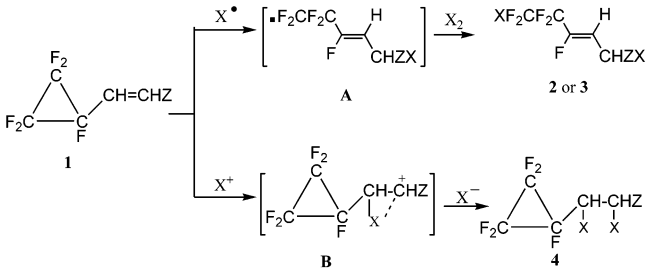
1: **1a**: Z = H, **1b**: Z = CH_3

3: **3a**: Z = H, **3b**: Z = CH_3

4: **4a**: Z = H, **4b**: Z = CH_3

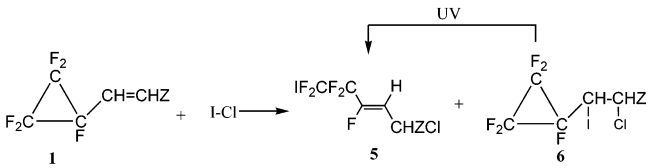
1a: X = Br, 84%; **3a**:**4a** = 4.4:1
1b: X = Br: 96%; **3b**:**4b** = 6.3:1
1a: X = Cl: 65%; **3a**:**4a** = 5:1
1b: X = Cl: 75%; **3b**:**4b** = 3:1

These results indicated that a radical mechanism dominated when **1** reacted with Br_2 or Cl_2. The ring-opening reaction proceeds through a radical intermediate **A** resulting in the 1,5-adduct, but the simple addition may involve a cationic intermediate. The bromine or chlorine cation first adds to the internal carbon of the double bond to form **B** due to electronic effects. In the presence of pyridine, the amount of ionic halogenation increased. This is due to the fact that pyridine promotes the electrophilic bromination through the formation of a bromine and pyridine complex.[12]



Interhalogens such as I−Cl are highly polarized halogens, although they are in equilibrium with small amounts of the pure halogens in solution.[2,13] When I−Cl reacted with **1a** in CH_2Cl_2 at room temperature, a 2:1 mixture of $ICF_2CF_2CF{=}CHCH_2Cl$ and c-$C_3F_5CHICH_2Cl$ was obtained in 92% yield. The amount of the electrophilic adduct **6a** was significantly greater than in reactions with I_2 and Cl_2. The regiochemistry of the addition reaction also supported an electrophilic mechanism. Other regioisomers such as c-$C_3F_5CHClCH_2I$ were not observed since attack of the iodonium ion to the internal carbon of the double bond is electronically favored by the electron-withdrawing effects of the fluorinated substituent. Upon reaction of **1b** with I−Cl, **6b** was found to be the major product with a ratio of **5b** to **6b** of 1:2.2. This is due, at least in part, to the increase in electronic density of the double bond by a methyl group, which favors the ionic mechanism.

Since alkyl iodides form radical intermediates under UV irradiation, it would be interesting to investigate if the ring opening of the pentafluorocyclopropylcarbinyl radical occurs when **6b** is irradiated with UV light. After a 1:2.2 mixture of **5b** and **6b** was irradiated with UV light in CCl_4 solution at room temperature for 1 h, ^{19}F NMR revealed that a significant amount of **6b** was converted into **5b** with some decomposition. The ratio of **5b** to **6b** changed from 1:2.2 to 5.9:1. This result further supports that the 1,5-addition proceeds through a radical intermediate.



1: **1a**: Z = H, **1b**: Z = CH_3

5: **5a**: Z = H, **5b**: Z = CH_3

6: **6a**: Z = H, **6b**: Z = CH_3

1a: 92%; **5a**:**6a** = 2:1
1b: 89%; **5b**:**6b** = 1:2.2

In summary, unlike nonfluorinated vinyl(cyclopropanes), vinyl(pentafluorocyclopropanes) react with halogens predominantly through a radical mechanism, along with a minor ionic mechanism, due to its electron-poor double bond and high strain energy. The two mechanisms can be readily differentiated by analysis of adducts. The radical addition gives the ring-opened 1,5-adducts, whereas the ionic addition affords the 1,2-adducts. The relative ratio of these two products depends on the halogens and reaction conditions. Iodination of **1** gives the 1,5-adducts exclusively, and bromination and chlorination produce a mixture of the adducts. The resulting adducts are useful intermediates for making other fluorinated materials.

Experimental Section

^1H NMR and ^{19}F NMR spectra were taken in $CDCl_3$ solvent using tetramethylsilane (TMS) and trichlorofluoromethane ($CFCl_3$) as respective internal standards. Preparation of **1** was described according to the literature.[14]

General Procedure for Reactcion of Vinyl(pentafluorocyclopropanes) 1 with Halogens. A mixture of 5.1 g (20 mmol) of I_2, 10 mL of CH_2Cl_2, and 3.4 g (21.5 mmol) of vinylpentafluorocyclopropane was stirred in a sealed tube at 50 °C for 3 h. After removal of solvent, 7.7 g of crude product was distilled to give 7.5 g (92%) of (*Z*)-$ICF_2CF_2CF{=}CHCH_2I$, **2a**, bp 85−86 °C/6.5 mmHg. ^{19}F NMR: δ −60.5 (m, 2F), −112.9 (m, 2F), −126.6 (m, 1F). ^1H NMR: δ 5.97 (dt, J = 30.1 Hz, J = 9.0 Hz, 1H), 3.92 (ddt, J = 9.0 Hz, J = 1.6 Hz, J = 1.6 Hz, 2H). HRMS: calcd for $C_5H_3F_5I_2$, 411.8244; found, 411.8246. Anal. Calcd for $C_5H_3F_5I_2$: C, 14.58; H, 0.73; F, 23.06; I, 61.62. Found: C, 14.50; H, 0.79; F, 21.41; I, 61.34.

Reaction of 1-Pentafluorocyclopropyl Propene 1b with Iodine. (*Z*)-$ICF_2CF_2CF{=}CHCHICH_3$, **2b**, was obtained in 89% yield, bp 68 °C/3 mmHg. ^{19}F NMR: δ −60.4 (m, 2F), −113.2 (m, 2F), −126.0 (m, 1F). ^1H NMR: δ 5.96 (dd, J = 30.3 Hz, J = 11.1

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Hz, 1H), 5.11 (dq, J = 11.1 Hz, J = 6.8 Hz, 1H), 2.00 (d, J = 6.8 Hz, 3H). HRMS: calcd for $C_6H_5F_5I_2$, 425.8401; found, 425.8381.

Reaction of Vinylpentafluorocyclopropane 1a with Bromine. A mixture of (*Z*)-$BrCF_2CF_2CF{=}CHCH_2Br$ and c-$C_3F_5CHBrCH_2Br$ was obtained in a ratio of 4.4:1 in 84% yield, bp 152−154 °C. ^{19}F NMR for (*Z*)-$BrCF_2CF_2CF{=}CHCH_2Br$: δ −65.9 (m, 2F), −115.9 (m, 2F), −126.0 (m, 1F). ^{19}F NMR for c-$C_3F_5CHBrCH_2Br$: δ −144.9 (d, J = 194.1 Hz, 1F), −154.6 (dd, J = 195 Hz, J = 5.6 Hz, 1F), −157 (s, 2F), −219 (dt, J = 10.4 Hz, J = 4 Hz, 1F). ^{1}H NMR for (*Z*)-$BrCF_2CF_2CF{=}CHCH_2Br$: δ 5.94 (dt, J = 30 Hz, J = 8.5 Hz, 1H), 4.04 (ddt, J = 8.5 Hz, J = 1.8 Hz, J = 1.5 Hz, 2H). ^{1}H NMR for c-$C_3F_5CHBrCH_2Br$: 4.40 to 4.24 (m, 1H), 3.83 (d, J = 10.4 Hz) and 3.82 (d, J = 6.3 Hz) total 2H. GC-HRMS: calcd for $BrCF_2CF_2CF{=}CHCH_2Br$, 315.8523; found, 315.8522. GC-HRMS: calcd for c-$C_3F_5CHBrCH_2Br$ − Br, 236.9337; found, 236.9295. Anal. Calcd for $C_5H_3F_5Br_2$: C, 18.89; H, 0.95; F, 29.88; Br, 50.27. Found: C, 18.75; H, 0.93; F, 28.70; Br, 50.48.

Reaction of 1-Pentafluorocyclopropylpropene 1b with Bromine. (*Z*)-$BrCF_2CF_2CF{=}CHCHBrCH_3$ and c-$C_3F_5CHBrCHBrCH_3$ were obtained in a 6.3:1 ratio in 96% yield, bp 81−85 °C/50 mmHg. ^{19}F NMR for (*Z*)-$BrCF_2CF_2CF{=}CHCHBrCH_3$: δ −65.9 (m, 2F), −116.1 (m, 2F), −126.2 (m, 1F). ^{19}F NMR for c-$C_3F_5CHBrCHBrCH_3$: δ −145.1 (dd, J = 195.5 Hz, J = 4.5 Hz, 1F), −155.0 (dm, J = 195 Hz, 1F), −156.6 (d, J = 199 Hz, 1F), −157.6 (dm, J = 199 Hz, 1F), −216.5 (dt, J = 26.6 Hz, J = 4.3 Hz, 1F). ^{1}H NMR for (*Z*)-$BrCF_2CF_2CF{=}CHCHBrCH_3$: δ 5.89 (dd, J = 30.2 Hz, J = 10.6 Hz, 1H), 5.00 (dq, J = 10.6 Hz, J = 6.8 Hz, 1H), 1.83 (d, J = 6.8 Hz, 3H). ^{1}H NMR for c-$C_3F_5CHBrCHBrCH_3$: δ 4.35 (dq, J = 10.6 Hz, J = 6.5 Hz, 1H), 4.04−4.23 (m, 1H), 1.96 (d, J = 6.5 Hz, 3H). HRMS: calcd for $C_6H_5F_5Br_2$, 329.8678; found, 329.8650. Anal. Calcd for $C_6H_5F_5Br_2$: C, 21.70; H, 1.52; F, 28.62; Br, 48.15. Found: C, 21.74; H, 1.54; F, 28.52; Br, 48.07.

Reaction of 1-Pentafluorocyclopropyl Propene 1b with Bromine in the Presence of Pyridine. After a mixture of 3.2 g of bromine and 3.2 g of pyridine in 10 mL of CH_2Cl_2 was stirred at temperatures between −9 and 0 °C for 10 min, 2.4 g of c-$C_3F_5CH{=}CHCH_3$ was added. The resulting mixture was stirred at 4 °C for 45 min and then at 9 °C for 1.5 h , diluted with 20 mL of CH_2Cl_2, and washed with 5% HCl. After removal of the CH_2Cl_2, 3.3 g of (*Z*)-$BrCF_2CF_2CF{=}CHCH_2Br$ and c-$C_3F_5CHBrCHBrCH_3$ in a 3:1 ratio were obtained.

Reaction of Vinylpentafluorocyclopropane with Chlorine. A mixture of (*Z*)-$ClCF_2CF_2CF{=}CHCH_2Cl$ and c-$C_3F_5CHClCH_2Cl$ was obtained in a ratio of 5:1 in 65% yield, bp 112 to 115 °C. ^{19}F NMR for (*Z*)-$ClCF_2CF_2CF{=}CHCH_2Cl$: δ −70.9 (m, 2F), −117.9 (m, 2F), −125.9 (m, 1F). ^{19}F NMR for c-$C_3F_5CHClCH_2Cl$: δ −146.1 (dd, J = 196.4 Hz, J = 5.4 Hz, 1F), −155.0 (dt, J = 196.0 Hz, J = 5.4 Hz, 1F), −155.6 (dd, J = J = 201.6 Hz, J = 8.3 Hz, 1F), −156.8 (dt, J = 201.3 Hz, J = 6.0 Hz, 1F), −221.9 (dt, J = 25.3 Hz, J = 6.2 Hz, 1F). ^{1}H NMR for (*Z*)-$ClCF_2CF_2CF{=}CHCH_2Cl$: δ 5.85 (dt, J = 30.2 Hz, J = 7.9 Hz, 1H), 4.21 (ddt, J = 7.9 Hz, J = 1.6 Hz, J = 1.6 Hz, 2H). ^{1}H NMR for c-$C_3F_5CHClCH_2Cl$: δ 3.88 (d, J = 9.6 Hz) and 3.86 (d, J 16.6 Hz) total 2H, 3.95 (m, 1H). GC-HRMS: calcd for $ClCF_2CF_2CF{=}CHCH_2Cl$, 227.9532; found, 227.9546. GC-HRMS: calcd for c-$C_3F_5CHClCH_2Cl$ − Cl: 192.9843; found: 192.978.

Reaction of 1-Pentafluorocyclopropyl Propene 1b with Chlorine. (*Z*)-$ClCF_2CF_2CF{=}CHCH_2Cl$ and c-$C_3F_5CHClCHClCH_3$ were obtained in a 3:1 ratio in 75% yield, bp 126 °C. ^{19}F NMR for (*Z*)-$ClCF_2CF_2CF{=}CHCHClCH_3$: δ −70.9 (m, 2F), −118.0 (m, 2F), −126.8 (m, 1F). ^{19}F NMR for c-$C_3F_5CHClCHClCH_3$: δ −145.9 (dd, J = 196.4 Hz, J = 6.4 Hz, 1F), −155.7 (dm, J = 196.6 Hz, 2F), −157.3 (dt, J = 201 Hz, J = 6.0 Hz, 1F), −220.1 (dt, J = 26.2 Hz, J = 5.5 Hz, 1F). ^{1}H NMR for (*Z*)-$ClCF_2CF_2CF{=}CHCHClCH_3$: δ 5.78 (dd, J = 30.7 Hz, J = 10.0 Hz, 1H), 4.96 (dq, J = 10.0 Hz, J = 6.7 Hz, 1H), 1.66 (d, J = 6.7 Hz, 3H). ^{1}H NMR for c-$C_3F_5CHClCHClCH_3$: δ 4.26 (dq, J = 10.1 Hz, J = 6.5 Hz, 1H), 4.06 (ddt, J = 25.5 Hz, J = 10.1 Hz, J = 2.0 Hz, 1H), 1.76 (d, J = 6.5 Hz, 3H). GC-HRMS: calcd for $C_6H_5F_5Cl_2$, 241.9868; found, 241.9866 for (*Z*)-$ClCF_2CF_2CF{=}CHCHClCH_3$ and 241.9977 for c-$C_3F_5CHClCHClCH_3$.

Reaction of Vinylpentafluorocyclopropane with Iodine Monochloride. A mixture of (*Z*)-$ICF_2CF_2CF{=}CHCH_2Cl$ and c-$C_3F_5CHICH_2Cl$ were obtained in a ratio of 2:1 in 92% yield, bp 85−91 °C/80 mmHg. ^{19}F NMR for (*Z*)-$ICF_2CF_2CF{=}CHCH_2Cl$: δ −60.6 (m, 2F), −112.5 (m, 2F), −125.0 (m, 1F). ^{19}F NMR for c-$C_3F_5CHICH_2Cl$: δ −145.0 (dd, J = 193.4 Hz, J = 6.6 Hz, 1F), −155.0 (dm, J = 193.6 Hz, 1F), −155.9 (dd, J = 199.8 Hz, J = 5.3 Hz, 1F), −156.9 (dt, J = 200 Hz, J = 5.3 Hz, 1F), −221.5 (dt, J = 25.5 Hz, J = 5.8 Hz, 1F). ^{1}H NMR for (*Z*)-$ICF_2CF_2CF{=}CHCH_2Cl$: δ 5.83 (dt, J = 30.5 Hz, J = 8.0 Hz, 1H), 4.19 (ddt, J = 8.0 Hz, J = 2.0 Hz, J = 1.6 Hz, 2H). ^{1}H NMR for c-$C_3F_5CHICH_2Cl$: δ 4.40−4.24 (m, 1H), 5.95 (d, J = 10.1 Hz, 2H). GC−HRMS: calcd for $C_5H_3F_5ICl$, 319.8890; found: 319.8848 for (*Z*)-$ICF_2CF_2CF{=}CHCH_2Cl$ and 319.8917 for c-$C_3F_5CHICH_2Cl$.

Reaction of 1-Pentafluorocyclopylpropene 1b with Iodine Monochloride. A mixture of (*Z*)-$ICF_2CF_2CF{=}CHCHClCH_3$ and c-$C_3F_5CHICHClCH_3$ was obtained in a 1:2.2 ratio in 89% yield, bp 83−84 °C/38 mmHg. ^{19}F NMR for (*Z*)-$ICF_2CF_2CF{=}CHCHClCH_3$: δ −60.6 (m, 2F), −112.8 (dt, J = 14.5 Hz, J = 7.7 Hz, 2F), −126.2 (m, 1F). ^{1}H NMR for (*Z*)-$ICF_2CF_2CF{=}CHCHClCH_3$: δ 5.76 (dd, J = 30.8 Hz, J = 10.0 Hz, 1H), 4.96 (dq, J = 9.9 Hz, J = 6.7 Hz, 1H), 1.66 (d, J = 6.7 Hz, 3H). ^{1}H NMR for c-$C_3F_5CHICHClCH_3$: δ −4.10 ∼ −4.40 (m, 2H), 2.13 (d, J = 6.6 Hz), 1.83 (d, J = 6.7 Hz), 1.73 (d, J = 6.8 Hz) total 3H. Anal. Calcd for $C_6H_5F_5ICl$: C, 21.55; H, 1.51; I, 37.47; Cl, 10.60. Found: C, 21.68; H, 1.53; I, 37.47; Cl, 9.88.

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