A new synthesis of 3-fluoro- and 3-chlorocyclobutenes from dihalocyclobutanes. The five isomers of chlorofluorocyclobutane

Norman C. Craig*, Steven S. Borick, Michael A. Fisher, Thomas R. Tucker and Yong-Zhuang Xiao†

Department of Chemistry, Oberlin College, Oberlin, OH 44074 (USA)

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Abstract

3-Fluorocyclobutene (**1**) and 3-chlorocyclobutene (**2**) have been obtained by simpler syntheses and in higher yield than previously reported. One of the synthetic steps involves a three-phase-transfer–catalysis technique that could be of wider utility. New examples are cited of applying AgF_2, an underutilized reagent, as a fluorinating agent near room temperature. Compounds **1** and **2** have been characterized by mass, NMR and vibrational spectroscopies. The NMR spectra have been fully analyzed. Useful group frequencies in the vibrational spectra of halocyclobutenes have been identified. The five monochloromonofluorocyclobutane precursors of fluorocyclobutenes have also been separated and characterized. From NMR coupling constants, conformer mixtures have been identified for three of the isomers.

Introduction

Initially, 3-fluorocyclobutene (**1**) and 3-chlorocyclobutene (**2**) were sought as potential precursors of the cyclobutenyl cation [1, 2]. In the meantime, a complex, low-yield (0.7% overall) synthesis of **1** was published in conjunction with the study of its electrocyclic ring opening [3]. A synthesis of **2** was also mentioned as part of a similar study [4]. Since our method of synthesizing these two substances is appreciably simpler than the published ones, especially for making small quantities, we describe the method here. As part of this work, we have used silver difluoride as a mild fluorinating agent and have developed further a three-phase-transfer–catalysis method for undertaking dehydrohalogenation reactions. The five isomers of chlorofluorocyclobutane have been prepared and characterized. The NMR spectra not only assist in the characterization but provide some information about conformers. A complete assignment of the NMR spectra of **1** and **2** is given.

†Permanent address: Taiyuan University of Technology, Taiyuan, Shanxi Province, China.

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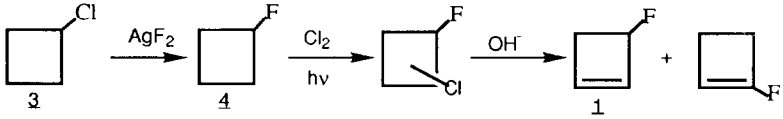
Results and discussion

The reaction sequence for preparing **1** was:



The conversion of chlorocyclobutane **3**, which is commercially available, to fluorocyclobutane **4** [5, 6] was essentially quantitative by our methods. The chlorination reaction [7] gave the five isomers of chlorofluorocyclobutane, which were separated by preparative chromatography. *trans*-1-Chloro-3-fluorocyclobutane was converted into **1** by passing gaseous material through a column packed with Ascarite (NaOH on support) coated with a mixture of tetraglyme and crown ethers. The *cis*-1,3- and *trans*-1,2-isomers also gave **1** when passed through the coated Ascarite column. Characterization of the isomer of **1**,1-fluorocyclobutene, has been reported elsewhere [8].

Compound **2** was prepared in a manner analogous to that shown in the scheme above. Compound **3** was further chlorinated to a mixture of the isomers of dichlorocyclobutane [7]. This isomeric mixture was dehydrohalogenated by distilling the gaseous mixture through the coated Ascarite column. The two isomers of monochlorocyclobutene were separated by preparative gas chromatography. The spectral properties of the isomer, 1-chlorocyclobutene, have been reported elsewhere [8].

Fully resolved proton NMR spectra were recorded for both **1** and **2**, and a fully resolved fluorine spectrum was recorded for **1**. These essentially first-order spectra were completely assigned. Table 1 gives the full set of assignments for **1** and **2**. The intensity patterns for the two CH_2 protons in both substances show some AB character. Proton-decoupled ^{13}C NMR spectra were also obtained for both species. Some doubt exists about the proper association of chemical shifts with the two different vinyl carbon atoms and their protons. The pattern of shifts found in the various isomers of dichlorocyclobutenes are consistent, however, with the choices for the protons given here [9]. The choice of the ^{13}C shifts is based on the smaller J_{CF} value for the carbon atom more distant from the CFH group. The assignments of the two CH_2 protons seem certain based on the relative magnitudes of the larger J_{HH} (*cis*) and smaller J_{HH} ('*trans*') coupling constants.

The gas-phase infrared spectra of **1** and **2** contained several group frequency bands that are common to the two molecules and close to values for the related molecules, cyclobutene (**5**), *cis*-3,4-dichlorocyclobutene (**6**) and *trans*-3,4-dichlorocyclobutene (**7**) [10], which also have no substituents on the carbon atoms of the C=C bond. The assignments for **1** and **2** are summarized in Table 2. When the carbon atoms of the C=C bond have substituents, a strong absorption in the C=C stretching region is observed [8]. Thus, the absence of absorption in the infrared spectrum due to the C=C mode is diagnostic for a cyclobutene with no substituent on the carbon atoms of the double bond. To the contrary, strong bands in the Raman

TABLE 1. NMR parameters for 3-chlorocyclobutene and 3-fluorocyclobutene[a]

^{1}H	δ_1	δ_2	δ_4	δ_5	δ_6	$J_{1,2}$ vinyl	$J_{1,4}$ cross	$J_{1,5}$ *vic*	$J_{1,6}$ *vic*	$J_{2,4}$ *vic*	$J_{2,5}$ cross	$J_{2,6}$ cross	$J_{4,5}$ *trans*	$J_{4,6}$ *cis*	$J_{5,6}$ *gem*
Cl	6.21	6.06	4.87	2.73	3.12	2.6	1.4	1.0	1.0	0.7	1.3	0.4	1.3	3.8	13.8
F	6.27	6.08	5.27	2.64	2.81	2.8	2.1	1.0	1.0	0.6	1.6	0.9	1.1	3.5	13.4

^{13}C	δ_1	δ_2	δ_3	δ_4	$J_{C1,F}$	$J_{C2,F}$	$J_{C3,F}$	$J_{C4,F}$
Cl	138.7	137.7	55.1	43.2				
F	139.2	138.1	87.5	40.1	16.3	19.9	214.5	20.6

^{19}F	δ	$J_{H1,F}$ cross	$J_{H2,F}$ *vic*	$J_{H4,F}$ *gem*	$J_{H5,F}$ *cis*	$J_{H6,F}$ *trans*
F	−170.9	8.1	0.4	56.6	7.1	3.8

[a]Chemical shifts in ppm relative to TMS or $CFCl_3$; coupling constants in Hz.

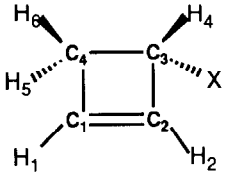


TABLE 2. Group frequencies for 3-chlorocyclobutene and 3-fluorocyclobutene (in cm^{-1})

Mode		
sym. =C−H stretch	3064[a,b]	3067[a,b]
asym. =C−H stretch	3066 A[c]	3066 A
XC−H stretch	2980 C	2979 C
asym. CH_2 stretch		2950 C
sym. CH_2 stretch	2939 B	~2940
C=C stretch	1559[a]	1560[a]
CH_2 scissors	1444 A	1444 A
asym. CH_2 bend	1420 C	1423 C

[a]From liquid-phase Raman spectrum.
[b]Additional bands at 3134 cm^{-1} (**2**) and 3142 cm^{-1} (**1**) in the gas-phase IR spectra are due to the overtone of the C=C stretch in Fermi resonance with the sym. CH_2 stretch.
[c]Approximate shapes of bands in the gas phase: A, B or C.

spectra for **1** at 1560 cm^{-1} and for **2** at 1559 cm^{-1} are due to this mode. For compounds **5**, **6** and **7**, the frequencies of comparable bands are 1570, 1559 and 1555 cm^{-1}, respectively. A common feature of the vibrational spectra of these latter species as well as of **1** and **2** is a band above 3200 cm^{-1} as a consequence of Fermi resonance mixing of the overtone of the C=C stretching mode and the symmetric H−C=C−H stretching mode. As a consequence of this mixing, the frequency of the apparent symmetric H−C=C−H stretching mode is somewhat decreased to make it almost coincident with the frequency of the antisymmetric H−C=C−H stretching mode. As shown in Table 2, the methylenic CH stretching modes and the CH_2 bending modes are also useful group frequencies.

The structures of the five isomers of monochloromonofluorocyclobutane were assigned from their NMR spectra. The 1,1-isomer, which has been reported before [8], is distinguished by having three CH_2 contributions to the proton spectrum. Klaboe and coworkers have used vibrational spectroscopy to show that a mobile equilibrium exists for this molecule between the two forms in which the C−Cl and C−F bonds are equatorial [11]. The ^{19}F NMR spectrum is consistent with this finding. Were the C−F bond locked in the equatorial position, the coupling constant between the fluorine nucleus and the axial protons, and between the fluorine nucleus and the equatorial protons on the neighboring carbon atoms, would be substantially different. Wiberg and coworkers found values of 20.6 and 6.14 Hz for **4** in which the C−F bond appears to be equatorial [12]. The corresponding J_{HF} constants observed for the 1,1-isomer are 9.6 and 15.0 Hz. Being intermediate in magnitude, these constants are consistent with a mobile equilibrium between axial and equatorial C−F bonds. In addition, coupling constants of 3.5 and 1.9 Hz acting between the fluorine nucleus and the two protons on the distant carbon atom are intermediate between the values of 8.54 and −0.03 Hz reported by Wiberg and coworkers for the C−F equatorial bond [12].

For the 1,3-isomers, the bilateral symmetry of these molecules and the consequent equivalence of the two CH_2 carbon atoms distinguishes their spectra from the spectra of the 1,2-isomers. Within the pair of 1,3-isomers, the *cis* isomer is in a single conformation with the C—Cl and C—F bonds equatorial. As a consequence, the coupling between each axial CXH proton and the four CH_2 protons gives undifferentiated quintet splittings, essentially in agreement with the findings of Wiberg and coworkers for the corresponding coupling constants in **3** and **4** [12]. The equatorial C—F bond gives two distinctly different HF coupling constants, 23.2 and 7.3 Hz, for interaction with the two types of neighboring pairs of protons. For the *trans*-1,3-isomer, a mobile equilibrium undoubtedly exists between the forms with C—F axial and C—F equatorial. As a consequence, the coupling constants for the two CXH protons with the neighboring CH_2 protons are intermediate between being undifferentiated as for CX—H axial and well differentiated as for CX—H equatorial [12]. The nearly equal HF coupling constants of 17.1 and 19.5 Hz are also consistent with the fluorine atom being averaged between axial and equatorial positions.

For the *trans*-1,2-isomer, the C—Cl and C—F bonds should be locked in equatorial positions. As a consequence, the two CXH protons are axial and thus coupled in undifferentiated quartets to the three protons on the neighboring carbon atoms. The fluorine nucleus in its equatorial position gives two substantially different HF coupling constants of 15.6 and 3.6 Hz.

The spectral data for the *cis*-1,2-isomer was compromised by an incompletely identified impurity. This isomer presumably has a mobile equilibrium between the C—Cl bond axial and the C—F bond axial. The quintets of the CF—H and CCl—H protons imply significant axial C—H contributions in both cases. The fluorine spectrum, which, besides a doublet due to $J_{HF}(gem) = 56$ Hz, is a triplet of triplets with J_{HF} constants of 20.7 and 8.5 Hz. Such differentiation is consistent with the C—F bond having a significant equatorial contribution. The impurity, which is probably 1,3-dichloro-1-fluorocyclobutane, contributes substantially to the intensity in the 2.8 to 3.5 ppm region of the proton spectrum and gives significant intensity at −84.8 ppm in the ^{19}F spectrum and at 103.8 ppm in the ^{13}C spectrum.

In the chlorination of **4** roughly equal amounts of the four isomers other than the *cis*-1,2-isomer were formed. This outcome is comparable to that for the production of the dichlorocyclobutane isomers from **3** [7]. Though still the lesser product, relatively more *cis*-1-chloro-2-fluorocyclobutane is formed than cis-1,2-dichlorocyclobutane in the comparable chlorination reaction.

An exploratory experiment showed that **1** could also be prepared by passing **2** through a column containing a short packing of a mixture of solid silver difluoride and potassium fluoride. This method was previously used to convert 3-chlorocyclopropene into 3-fluorocyclopropene [13]. Although we have not developed this latter method fully, we believe it may be the most efficient method for making small amounts of **1**.

The flow-system reaction methods used in these syntheses deserve consideration for generalization. In effect, the dehydrohalogenation on coated Ascarite is a three-phase-transfer–catalysis method, except one of the phases is a solid and a third is a gas passing over the liquid phase. The coating of the mixture of tetraglyme and crown ethers provides a medium in which the solid sodium hydroxide can dissolve and react efficiently with the halocyclobutanes as they repeatedly enter the liquid phase while being moved along in the gas phase. The product cyclobutenes are more volatile and thus spend less time in the liquid phase where they might be vulnerable to further reaction. The liquid phase also mobilizes the product sodium halides. The mixture of tetraglyme and crown ethers is sufficiently involatile to be used in a moderate vacuum system.

The other flow system reactor involves a mixture of solid silver difluoride and potassium fluoride. The high reactivity of silver difluoride towards chlorocyclobutenes is controlled by the brief contact as the gas passes over the solid and by the dilution of the silver difluoride with potassium fluoride. In addition to the reactions described here, this method has been useful in coverting *cis*-3,4-dichlorocyclobutene into the two isomers of 3-chloro-4-fluorocyclobutene and *trans*-3,4-difluorocyclobutene [14].

We had prepared compounds **1** and **2** as precursors of the cyclobutenyl cation. Unfortunately, we were unable to control the reactions of these halocyclobutenes with SbF_5 in SO_2 or in SOFCl solvents at low temperature in NMR sample tubes [1, 2]. Polymerization processes dominated and gave outcomes that were unsuited to NMR or Raman spectroscopy. Also, BF_3 proved to be too weak as a Lewis acid in SO_2 solution or in direct reaction in the glassy phase [2].

Despite our not succeeding in preparing spectroscopically worthy samples of the cyclobutenyl cation from **1** and **2**, we note that the mass spectrum of **2** had a prominent ion at 53, which must be the $C_4H_5^+$ species. Although this ion was low intensity in the mass spectrum of **1**, it was also prominent in the mass spectra of both *trans*-1,2- and *trans*-1,3-chlorofluorocyclobutane. In addition, the cyclobutenyl cation is presumably an intermediate in the conversion of **2** to **1** by AgF_2.

Experimental

NMR spectroscopy of the halocyclobutanes was undertaken mostly on a JEOL FX90Q FT instrument at the University of Toledo. Spectra of **1** and **2** were obtained on an IBM/Bruker AC200 FT instrument. Halocyclobutanes were dissolved in $CFCl_3$ and referenced to internal TMS and $CFCl_3$ (downfield shifts positive). Compounds **1** and **2** were dissolved in $CDCl_3$ and referenced to external TMS and $CFCl_3$. IR spectra were recorded on a Perkin-Elmer 580B dispersive instrument. MS spectra were obtained on a Hitachi RMS4 instrument, and GC–MS were obtained with a Hewlett Packard 5970 quadrupole mass-selective filter coupled to a 5890A gas chromatograph (phenyl methyl

silicone OV2 capillary column). Preparative gas chromatography was done with a home-built unit having a Gow–Mac thermal conductivity detector.

Fluorocyclobutane and monochloromonofluorocyclobutanes

15 mmol of compound **3** (Fairfield Chemical) was condensed onto 2 g of vacuum-dried AgF_2 (Aldrich) and some short Teflon tubing in the bottom of a 50 ml flask at liquid nitrogen temperature. Reaction occurred while the flask was dipped in ice water and shaken. The process was repeated after condensing the product in a second flask containing 1 g of AgF_2. Byproduct SiF_4 was distilled off at pentane slush (−130 °C) temperature. Conversion to **4** was essentially complete, but the crude product did not store well unless frozen in liquid nitrogen.

15 mmol of crude **4** was condensed at liquid nitrogen temperature in the test-tube bottom of a 2 l flask that contained some Teflon tubing mixers. 15 mmol of Cl_2 (Matheson Gas Products) was condensed in a separate band above **4**. In near darkness, the flask was allowed to warm to room temperature whilst being vigorously shaken. With continuing shaking, the flask was moved into low fluorescent light. The reaction was completed by direct exposure to two 100 W tungsten lights for several hours. (Premature exposure to light caused a runaway flame reaction in the flask.) Product HCl and byproduct SiF_4 were distilled off at pentane slush temperature. The crude mixture of chlorofluorocyclobutanes was separated by preparative gas chromatography at 90 °C on a 5 m×12 mm column packed with tricresylphosphate on Chromosorb. Relative elution times on the Chromosorb-supported column were: **4**, 0.42; 1-chloro-1-fluorocyclobutane, 1.0; **3**, 1.3; *trans*-1-chloro-3-chlorocyclobutane, 4.5; *trans*-1-chloro-2-fluorocyclobutane, 5.4; *cis*-1-chloro-3-fluorocyclobutane, 6.8; *cis*-1-chloro-2-fluorocyclobutane, 7.6. The last two peaks were not completely resolved. Small amounts of dichloromonofluorocyclobutanes followed. Approximate relative amounts of the isomers of chlorofluorocyclobutane from GC areas were: 1,1,1.0; *trans*-1,3,1.06; *trans*-1,2,1.44; *cis*-1,3,0.87; *cis*-1,2, ~0.25. Chlorination of **4** was essentially complete.

3-Fluorocyclobutene

In a representative reaction, a few tenths mmol of *trans*-1-chloro-3-fluorocyclobutane was distilled several times bulb-to-bulb through a 30-cm column packed with Ascarite (NaOH on inert support) coated with (11% w/w) of a 3:3:2 mixture of tetraglyme, 18-crown-6-ether and 15-crown-5-ether. Before use, the Ascarite column was activated by heating it to 50 °C. Coated Ascarite columns should not be pumped below 20 μHg due to a slight volatility of the liquid coating. The *cis*-1,3- and *trans*-1,2-isomers also gave **1** when distilled over coated Ascarite. Compound 1 was isolated by gas chromatography on a 4-m Apiezon M-on-Fluoropack column at 35 °C and dried by distillation through a column containing P_2O_5. (Compound **1** is irreversibly adsorbed to some degree and presumably hydrolyzed on a Chromosorb support. Subsequent work has shown that Fluoropak coated

with TCP is a more effective column for separating reactive halocyclobutenes. Such a column should allow working with the product of passing a crude mixture of monochloromonofluorocyclobutanes through an Ascarite column.) B.p. (Clausius–Clapeyron-based extrapolation of sub-25 °C vapor pressure data), 45 °C. GC–MS: 72 (Intens. = 67), parent peak; 46(100), C_2H_3F; 39(62), C_3H_3. ^{13}C proton-decoupled NMR δ: 40.1 (J_{CF} = 20.6 Hz); 87.5 (J_{CF} = 214.2 Hz); 138.1 (J_{CF} = 19.9 Hz); 139.2 (J_{CF} = 16.3 Hz) ppm. ^1H NMR δ: 2.64, d(J_{HH} = 13.4 Hz) of d(J_{HF} = 7.1 Hz) of d(J_{HH} = 1.6 Hz) of t(J_{HH} = 1.1 Hz); 2.81, d(J_{HH} = 13.4 Hz) of d(J_{HF} = 3.8 Hz) of d(J_{HH} = 3.5 Hz) of t(J_{HH} = 0.9 Hz) with some AB character; 5.27, d(J_{HF} = 56.6 Hz) of d(J_{HH} = 3.5 Hz) of d(J_{HH} = 2.2 Hz) of d(J_{HH} = 1.1 Hz) of d(J_{HH} = 0.6 Hz); 6.08, d(J_{HH} = 2.8 Hz) of d(J_{HH} = 1.6 Hz) of d(J_{HH} = 0.9 Hz) of d(J_{HH} = 0.6 Hz) of d(J_{HF} = 0.3 Hz); 6.27, d(J_{HF} = 8.2 Hz) of d(J_{HH} = 2.8 Hz) of d(J_{HH} = 2.1 Hz) of t(J_{HH} = 1.0 Hz) ppm. ^{19}F NMR δ: −170.9, d(J_{HF} = 56.6 Hz) of d(J_{HF} = 8.1 Hz) of d(J_{HF} = 7.1 Hz) of d(J_{HF} = 3.8 Hz) of d(J_{HF} = 0.4 Hz) ppm. IR, gas phase, approximate A, B or C band shapes, cm^{-1}: 3142 w, B; 3066 m, A; 2979 s, C; 2950 vs, C; 2856 w, C; 1444 m, A; 1423 w, C; 1338 vs, A; 1304 s, A; 1199 s, C; 1189 s, C; 1136 vs, A; 1044 s, A; 1005 s, A; 983 m, C; 930 m, B; 823 vs, C; 679 s, C; 494 m, A; 386 w, B. The less complete spectral data in ref. 3 is in satisfactory agreement with these results.

Dichlorocyclobutanes [9] and 3-chlorocyclobutene

A mixture of all five dichlorocyclobutanes was prepared by reaction of **3** with an equal number of mmol of Cl_2 in the same manner as described for the chlorofluorocyclobutanes. Byproduct HCl was distilled off at pentane-slush temperature.

A mixture of the two isomers of chlorocyclobutene was made by distilling the mixture of dichlorocyclobutanes bulb-to-bulb through the coated Ascarite column. Each isomer of chlorocyclobutene was isolated by gas chromatography on the TCP column at 65 °C and dried by distilling through P_2O_5. Relative elution times: 1-chlorocyclobutene, 1.0; **2**, 1.5.

For compound **2**; GC–MS: 90 (I = 7), parent (^{37}Cl); 88(22), parent (^{35}Cl); 53(100), C_4H_5. ^{13}C NMR δ: 43.2; 55.1; 137.7; 138.7 ppm. ^1H NMR δ: 2.73, d(13.8 Hz) of t(1.3 Hz) of d(1.0 Hz); 3.12 d(13.8 Hz) of d(3.8 Hz) of d(1.0 Hz) of d(0.45 Hz) with some AB character; 4.87, d(3.8 Hz) of t(1.3 Hz) of d(0.8 Hz); 6.06, d(2.6 Hz) of d(1.2 Hz) of d(0.7 Hz) of d(0.5 Hz); 6.21, d(2.6 Hz) of d(1.4 Hz) of t(1.0 Hz) ppm. IR, gas phase, cm^{-1}: 3134 w, B; 3066 s, A; 2980 s, C; 2939 s, B; 2859 w; 1444 w, A; 1420 w, C; 1293 s, A; 1240 vs, A; 1228 s, Q: 1213 m, C; 1121 m, A; 1090 m, A; 1004 m, C; 994 m, C; 929 m, A; 888 s, A; 864 m, C; 763 vs, A; 596 m, C; 417 m, A.

Chlorofluorocyclobutanes

1-Chloro-1-fluorocyclobutane: MS: 110 (I = 0.3), parent (^{37}Cl); 108 (0.7, parent (^{35}Cl); 82 (30), $C_2H_2F^{37}Cl$; 80 (100). $C_2H_2F^{35}Cl$: 73 (77), C_4H_6F; 53 (32), C_4H_5. ^{19}F NMR δ: −85.9, t(J_{HF} = 15.0 Hz) of t(J_{HF} = 9.6 Hz) of t(J_{HF} = 3.5

Hz) of d(J_{HF} = 1.9 Hz) ppm. For other NMR spectra and IR spectrum, see ref. 8.

trans-1-Chloro-2-fluorocyclobutane: MS: 110 (I = ~0.4), parent (^{37}Cl); 108 (1.2), parent (^{35}Cl); 73 (48), C_4H_6F; 72 (37), C_4H_5F; 64 (43), $C_2H_3{}^{37}Cl$; 62 (99), $C_2H_3{}^{35}Cl$; 53 (53), C_4H_5; 46 (44), C_2H_3F; 28 (77), C_2H_4; 27 (100), C_2H_3. ^{13}C NMR δ: 22.8 (J_{CF} = 19.5 Hz); 25.5 (J_{CF} = 19.6 Hz); 55.6 (J_{CF} = 21.5 Hz); 92.8 (J_{CF} = 227 Hz) ppm. ^1H NMR δ: 4H, 1.7, m; 2.3, m; 1H, 4.2, d(J_{HF} = 15.6 Hz) of quartet (J_{HH} = 7.6 Hz): 1H, 4.7, d(J_{HF} = 54 Hz) of quartet (J_{HH} = 7 Hz) ppm. ^{19}F NMR δ: −163.9, d(J_{HF} = 55 Hz) of quartet (J_{HF} = 15 Hz) of d(J_{HF} = 3.6 Hz) ppm. IR, gas phase, cm^{-1}: 3020 s; 2980 s; 2890 m; 1465 m; 1450 m; 1370 s; 1290 s; 1245 s; 1235 s; 1180 m; 1120 vs; 1005 m; 960 s; 920 m; 890 m; 790 w; 740 m; 570 m; 465 m.

cis-1-Chloro-2-fluorocyclobutane: ^{13}C NMR, proton number by off-resonance decoupling δ: including impurity, 41.1 (J_{CF} = 15.5 Hz), CHX; 43.7 (J_{CF} = 21.4 Hz), CH_2; 53.2 (J_{CF} = 21.5 Hz), CH_2; 55.5 (J_{CF} = 23.5 Hz), CH_2; 81.3 (J_{CF} = 212.9 Hz), CFH; 103.8 (J_{CF} = 289 Hz), CFCl ppm. ^1H NMR δ: approx. 9H (approx. 5H impurity), 3.1 and 3.3, complex multiplets; 1H, 4.26 quintet (J_{HF}? = J_{HH} = 7.5 Hz) of d(J_{HH} = 5.1 Hz); 1H, 5.16, d(J_{HF} = 55.6 Hz) of quintets (J_{HH} = 6.3 Hz) of d? ppm. ^{19}F NMR δ: impurity at −84.8, m; −176.8, d(J_{HF} = 56 Hz) of t(J_{HF} = 20.7 Hz) of t(J_{HF} = 8.5 Hz) ppm. IR, gas phase (purity in doubt), cm^{-1}: 3030 s; 2980 m; 1425 m; 1365 s; 1275 s; 1250 s; 1210 vs; 1135 vs; 1090 s; 995 vs; 770 m; 735 m; 660 m; 620 s; 485 m.

trans-1-Chloro-3-fluorocyclobutane: MS: 100 (I = 0.3), parent (^{37}Cl); 108 (0.7), parent (^{35}Cl); 72 (44), C_4H_5F; 64 (42), $C_2H_3{}^{37}Cl$; 62 (100), $C_3H_3{}^{35}Cl$; 53 (52), C_4H_5; 46 (39), C_2H_3F. ^{13}C NMR δ: 43.0 (J_{CF} = 21.5 Hz); 48.2 (J_{CF} = 9.7 Hz); 86.6 (J_{CF} = 205 Hz) ppm. ^1H NMR δ: 4H, 2.52, m; 2.76, m; 1H, 4.47, d(J_{HF} = 4.0 Hz) of t(J_{HH} = 7 Hz) of t(J_{HF} = 4 Hz); 1H, 5.28, d(J_{HF} = 55.8 Hz) of t(J_{HH} = 6.4 Hz) of t(J_{HH} = 4.6 Hz) ppm. ^{19}F NMR δ: −177.9, d(J_{HF} = 55.5 Hz) of t(J_{HF} = 19.5 Hz) of t(J_{HF} = 17.1 Hz) of d(J_{HF} = 3.7 Hz) ppm. IR, gas phase, cm^{-1}: 3020 s, 2990 s; 1420 m; 1355 s; 1280 s; 1250 s; 1190 s; 1110 vs; 1060 m; 970 s; 935 s; 835 m; 740 w; 650 m; 570 m; 470 m; 435 m.

cis-1-Chloro-3-fluorocyclobutane: ^{13}C NMR δ: 42.0 (J_{CF} = 23.4 Hz); 43.8 (J_{CF} = 19.5 Hz); 81.2 (J_{CF} = 215 Hz) ppm. ^1H NMR δ: 4H, 2.9, m; 2.4, m; 1H, 3.81, quintet (J_{HH} = 7.3 Hz) of d(J_{HF} = 2.8 Hz); 1H, 4.68 d(J_{HF} = 54.9 Hz) of quintet (J_{HH} = 6.4 Hz) ppm. ^{19}F NMR δ: −167.6, d(J_{HF} = 55.5 Hz) of t(J_{HF} = 23.2 Hz) of t(J_{HF} = 7.3 Hz) of d(J_{HF} = 3.0 Hz) ppm. IR, gas phase, cm^{-1}: 3020 s, 2970 s; 1455 m; 1435 m; 1370 s; 1290 vs; 1250 m; 1195 s; 1100 s; 1055 m; 975 s; 885 m; 800 w; 725 s; 535 w; 435 m.

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