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^{1}H and ^{19}F NMR Spectra of Some Fluorocyclobutane Derivatives

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Synopsis. ^{1}H and ^{19}F NMR spectra were observed at 60.00 and 56.46 MHz, respectively, for ten 1,1,2,2-tetrahalo-1,2,2a,7a-tetrahydro-7*H*-cyclobut[*a*]inden-7-ones. NMR parameters, thus obtained, are discussed in connection with molecular structures and properties. The structures were partly confirmed by NOE measurements. The signs of all coupling constants observed for six compounds were determined by a selective decoupling technique (except for one with a small magnitude). A deshielding effect of the carbonyl group to a particular ^{19}F atom has also been obtained; it is useful for a structural determination.

Although many fluorocyclobutanes have been synthesized by the thermal cycloaddition of fluoroolefines, only a few NMR spectral parameters of cyclobutanes have been reported.[1] Recently, we obtained several title compounds by the photocycloaddition of indene to chlorofluoroethylenes as a part of studies on the syntheses of fluorine-containing fused polycyclic compounds.[2] During these studies, ^{1}H and ^{19}F NMR spectral data were found to be potentially useful in determining the structures of the compounds. Therefore, we wish to report on some NMR data in this article in order to contribute to the structural determination of similar compounds. This article makes clear that the configuration between fluorine and proton can be ascertained by NOE measurements. The signs of several fluorine-proton and fluorine-fluorine coupling constants were also determined relative to the vicinal proton-proton coupling constants.

Experimental

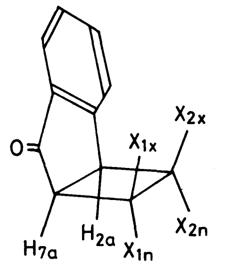
All ^{1}H and ^{19}F NMR spectra were recorded on a Hitachi R-20B spectrometer at a probe temperature (31.5 °C). ^{19}F and ^{1}H selective decoupling and tickling experiments were performed with the aid of a R-201SD decoupler, a R-209PA power amplifier, and a MG-514C synthesizer(Anritsu Electric Co., Ltd).

Chemical shifts were measured at 60 and 56.46 MHz for ^{1}H and ^{19}F nuclei, respectively; accuracies were within 0.2 Hz for ^{1}H and 0.4 Hz for ^{19}F measurements. All iterative calculations of the spectral analyses were carried out with a Hitachi-8450 computer system using a modification of LAOCN3 program.[3]

Samples of the title cyclobutane derivatives were synthesized from chlorofluoroethylenes and indene and the preparative methods were published.[2] The samples were dissolved in CCl_4 or $CDCl_3$ with small amounts of TMS and C_6F_6 served as internal references for ^{1}H and ^{19}F spectra, respectively. All sample solutions were degassed by the freeze-pump-thaw technique and sealed in 5-mm NMR sample tubes under vacuum.

Results and Discussion

The compounds studied are shown in Table 1;



X= F or Cl

Scheme 1.

Table 1. ^{1}H and ^{19}F Chemical Shifts of Fluorocyclobutanes in Carbon Tetrachloride

Compound No.	Conc. wt%	Chemical Shift/ppm					
		H_{2a}	H_{7a}	F_{1x}	F_{1n}	F_{2x}	F_{2n}
1	5.7	4.43	3.94	62.48	Cl	Cl	Cl
2	7.5	4.40	3.95	Cl	74.93	Cl	Cl
3	7.5	4.30	3.94	63.35	70.35	Cl	Cl
4	2.6	4.32	3.88	55.85	Cl	62.78	Cl
5	ca. 10	a	a	Cl	51.8	Cl	55.0
6	3.8	4.40	3.75	Cl	68.35	60.95	Cl
7	5.0	4.43	3.77	46.40	Cl	Cl	49.24
8	4.1	4.30	3.76	51.00	67.43	44.92	Cl
9	10.1[b]	4.25	3.90	59.65	55.80	Cl	45.07
10	7.1[c]	4.29	3.67	48.1	52.8	50.1	47.9

a) Uncertain because **5** could not be isolated. b) The sample contains **8** in the amount of 40%. c) In $CDCl_3$ solution.

Scheme 1 shows the numberings of positions (x=exo and n=endo). The NMR spectral parameters obtained from iterative refinements are shown in Tables 1 and 2. The parameters for compound **5** could not be obtained since the sample was impure.

^{1}H and ^{19}F Chemical Shifts. As shown in Table 1, the ^{1}H chemical shifts fall in a narrow range. The H_{2a} chemical shifts are always larger than those of H_{7a}. ^{19}F chemical shifts show a range of variations. The ranges of the chemical shifts for H_{2a}, H_{7a}, F_{1x}, F_{1n}, F_{2x}, and F_{2n} are about 0.18, 0.28, 16.95, 23.1, 17.9, and 9.9 ppm, respectively. The range is larger for H_{7a} than for H_{2a}; among fluorine nuclei, the F_{1n} shows the largest variation and the F_{2n} shows the smallest. The introduction of a chlorine atom instead of a fluorine atom caused a shielding effect for the fluorine chemical shift. This tendency is contrary to the strong inductive effect of fluorine, and is interpreted by the magnetic anisotropy effect of the chlorine atom.

When a carbonyl group was introduced to the 7-position of a precursor hydrocarbon, a large effect was observed on the ^{19}F chemical shifts of F_{1x}. The effect on the chemical shift of F_{1x} amounts to about 10 ppm while that of F_{1n} is smaller than 2.5 ppm in magnitude. This deshielding of F_{1x} is ascribed to a magnetic anisotropy effect of the 7-positioned carbonyl group; it seems to be useful for assigning of the F_{1x} signal. The observed chemical-shift displacements of F_{1x} and F_{1n} are given in Table 3. The values for F_{1x} are about 9.5 ppm. However, those for the F_{1n} are separated into two groups: one group falls at about 0.5 ppm and the other is at about −2.5 ppm. Compounds **2** and **6**, which belong to the latter group, have a trans-dichloro configuration. These chlorine atoms seem to contribute to the displacement.

Spin–Spin Coupling Constants. The coupling constants obtained from the spectral analyses of the compounds studied (except for **5** and **10**) are given in Table 2. Among the values, the relative signs of the coupling constants were determined by using selective decoupling and tickling techniques (except for the values for **8** and **9**). Typical decoupled spectra of **1** are given in Fig. 1 as examples. The upfield doublet of H_{2a} was decoupled when the upfield doublet of F_{1x} was irradiated as shown in Fig. 1C. The result shows that the $^3J_{2a7a}$ and the $^3J_{7a1x}$ of **1** have the same sign. The sign of $^4J_{2a1x}$ of **7** could not be determined because of its small magnitude. From the values given in Table 2, the signs of $^2J_{FF}$, $^3J_{HF}$, and $^4J_{HF}$ are positive, while those of $^3J_{FF}$ are negative. The values of fluorine-proton and fluorine-fluorine coupling constants vary largely in magnitude, while the vicinal proton coupling constants are almost constant. Therefore, care should be taken for the use of the coupling constants in order to determine the structures of the samples. For example, $^3J_{2a2x}$ of **4** and **6** and the $^3J_{2a2n}$ of **7** and **9** vary largely in magnitude.

NOE Enhancement. NOE observations can give valuable informations for structural determination.[4] The results of the present investigation are shown in Table 4. The signals of the H_{7a} of **2** and **6** increase in intensity by about 15% when the F_{1n} resonance is irradiated; for H_{2a}, irradiation of the F_{2n} resonance is effective. The results are consistent both with the structures determined from other chemical and physical properties and with the relative positions of the atoms shown in Scheme 1.

Table 2. Coupling Constants of Fluorocyclobutanes in Hz[a)]

Compound	1	2	3	4	6	7	8	9
$^3J_{2a7a}$	+7.1	+7.3	+7.2	+7.4	+7.3	+7.1	7.4	7.5
$^4J_{2a1x}$	+0.8	—	+2.7	+0.3	—	(−)0.1	2.0	2.5
$^4J_{2a1n}$	—	+4.0	+5.6	—	+4.1	—	5.7	6.2
$^3J_{2a2x}$	—	—	—	+15.9	+2.9	—	2.1	—
$^3J_{2a2n}$	—	—	—	—	—	+2.8	—	17.2
$^3J_{7a1x}$	+10.6	—	+8.1	+8.8	—	+8.6	6.9	7.0
$^3J_{7a1n}$	—	+15.1	+10.1	—	+15.5	—	10.9	13.0
$^4J_{7a2x}$	—	—	—	+2.7	+1.3	—	0.5	—
$^4J_{7a2n}$	—	—	—	—	—	+0.6	—	3.9
$^2J_{1x1n}$	—	—	+188.0	—	—	—	200.7	202.9
$^3J_{1x2x}$	—	—	—	−8.8	—	—	10.0	—
$^3J_{1x2n}$	—	—	—	—	—	−8.5	—	1.4
$^3J_{1n2x}$	—	—	—	—	−1.2	—	4.8	—
$^3J_{1n2n}$	—	—	—	—	—	—	—	5.1

a) The signs of the coupling constants were determined relative to the $^3J_{2a7a}$ which is assumed to be positive.

Table 3. Fluorine Chemical-Shift Change for Introduction of a Carbonyl Group at the 7-Position of the Precursors Studied

Compound	1	2	3	4	5	6	7	8	9	10
F_{1x}	9.5	—	10.0	9.3	—	—	9.0	10.1	10.0	10.0
F_{1n}	—	−2.4	0.3	—	0.0	−2.5	—	0.4	0.8	0.2

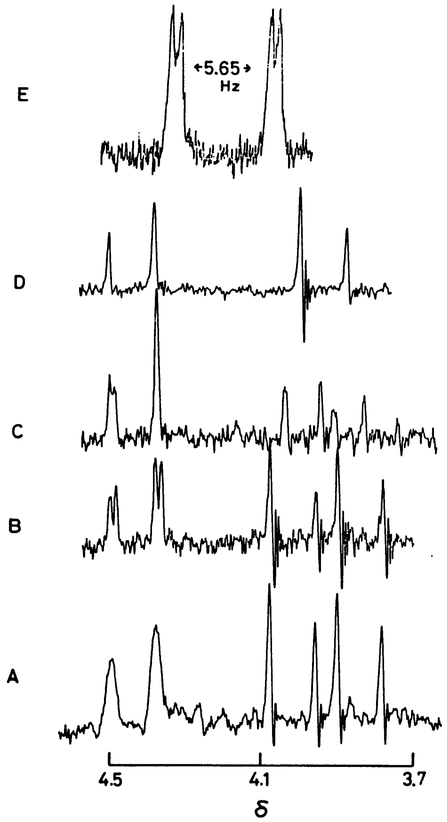


Fig. 1. ^{1}H and ^{19}F NMR spectra of the cyclobutane ring of **1** in CCl_4 at 60 and 56.46 MHz and 31.5 °C: (A) A normal ^{1}H spectrum, (B) an aromatic-proton decoupled ^{1}H spectrum, (C) a weak fluorine and aromatic-proton decoupled ^{1}H spectrum, (D) a strong fluorine and aromatic-proton decoupled ^{1}H spectrum, and (E) a ^{19}F spectrum.

Table 4. Proton-Fluorine Nuclear Overhauser Effects

Compound No.	^{19}F irradiated	% Enhancement observed[a]	
		H_{2a}	H_{7a}
1	1_x	2	4
2	1_n	0	14
4	1_x	2	−1
	2_x	3	2
6	1_n	0	13
	2_x	3	4
7	1_x	3	3
	2_n	10	1
8	2_x	2	−1
9[b]	2_n	5	

a) The area of the absorption was determined with an error of ±2%. b) The experiment was made in a mixture containing 40% of **8**. The enhancement of the H_{2a} and H_{7a} signals could not be obtained separately by overlapping of the signals. However, the result is significant.

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