NMR Spectroscopy

Fluorine Coupling to $^1$H and $^{13}$C

Fluorine Coupling to $^1$H

Coupling between hydrogen and fluorine (spin 1/2) is very strong. Typical $^2J$ coupling constants are about 48 Hz. Longer range coupling is smaller. Typical $^4J$ coupling constants are about 4 Hz.

The figure below contains the NMR spectrum for fluoroacetone. The nuclear spin of fluorine is 1/2. This means that the proton signal is split into $n + 1$ parts.

Figure. NMR spectrum of fluoroacetone.

Fluorine Coupling to $^{13}$C

Coupling between carbon and fluorine (spin 1/2) is very strong. Typical $^1J$ coupling constants are about 185 Hz. Longer range coupling is smaller. Typical $^2J$ coupling constants are about 20 Hz.

The figure below contains the NMR spectrum for fluoroacetone. The nuclear spin of fluorine is 1/2. This means that the carbon signals are split into $n + 1$ parts.

Figure. NMR spectrum of fluoroacetone.
$^1J = 185 \text{ Hz}$

$^2J = 20 \text{ Hz}$

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SDBS-$^{13}$C NMR
SDBS No. 13226CDS-07-633

$C_3H_5FO$

fluoroacetone

50.18 MHz
0.05 ml : 0.5 ml CDCl$_3$

<table>
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<tr>
<th>ppm</th>
<th>Int.</th>
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http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi
and hexamethyldisilazide (HMPS) were purified by fractional distillation from calcium hydride. Cyclohexylamine and tert-butylamine were also distilled under a nitrogen atmosphere from calcium hydride before use.

A buffered acetic solution,18 prepared with 3.0 g of sodium acetate, 7.5 mL of glacial acetic acid, and 35 mL of distilled water, was used for hydrolyzing enolizable chiral α-fluoro ketimines. Determination of the enantiomeric excess by the use of tris[(heptfluoropropyl)hydroxypropyl]amine-[(+)-camphor-10-ol]europium(III) as the chiral shift reagent was accomplished by first purifying the ketone by preparative GC or by recrystallization. The purified ketone, 3-6 mg, was diluted with 1 mL of CDCl3, to which 100-μL amounts of a standard solution of (−)-Eu(tfc)3 were added dropwise. After stirring another hour, the reaction mixture was purified by preparative GC to yield 0.22 g (48%) of 1-fluoro-2-butanone: 1H NMR (CDCl3) δ 5.70–5.15 (m, 1 H, CH=CH2), 5.05–4.45 (m, 2 H, CH=CH2), 4.54 (d, JHF = 47 Hz, 2 H, CH2F), 3.00–2.51 (m, 2 H, CH2CH=CH2) 2.51 (dt, JHF = 5 Hz, J = 6 Hz, 2 H, CH2); 13C NMR (CDCl3) δ 206.3 (d, JCF = 19 Hz, C=O), 131.1 (CH=CH2), 119.0 (CH=CH2), 85.0 (d, JCF = 185 Hz, CH2F), 37.6 (CH2), 26.6 (CH3); 19F NMR (CDCl3) δ = 228.3 (t, JCF = 48 Hz). Anal. Calc'd for C4H9OF: C, 62.05; H, 7.81. Found: C, 62.16; H, 7.84.

1-Fluoro-2-heptanone was prepared by the addition of 1-iodobutane (0.02 g, 0.005 mol) to 4 deprotonated with LHMDS. Workup in the normal manner yielded 0.20 g (30%) of 1-iodo-2-heptanone. After the addition of 1.20 (4, 5 H, CH2CH=CH2) 0.87 (t, J = 7 Hz, 3 H, CH3); 19F NMR (CDCl3) δ = 227.9 (t, JCF = 48 Hz). Anal. Calc'd for C9H17OF: C, 64.8; H, 9.97.

Fluoro Ketimines

1-Fluoro-2-propanone was prepared by the addition of cinnamyl bromide (0.86 g, 0.005 mol) to 4 deprotonated with LHMDS. Workup in the normal manner yielded 0.84 g (70%) of 1-fluoro-4-phenyl-2-butane. A sample for analysis was purified by preparative GC: IR (neat) ν = 3150 (w), 3140 (w), 2950 (m), 1720 (s), 1600 (m), 1460 (w), 1040 (s), 760 (s), 710 (cm−1); 1H NMR (CDCl3) δ 7.81 (m, 5 H, Ar-H), 6.97 (m, 3 H, Ar-H), 2.20 (s, 3 H, CH3); 19F NMR (CDCl3) δ = 227.7 (t, JCF = 49 Hz). Anal. Calc'd for C9H7OF: C, 72.27; H, 6.67. Found: C, 72.60; H, 6.49.

1-Fluoro-2-butane was prepared by the addition of iodobenzene (0.08 g, 0.005 mol) to 4 deprotonated with LHMDS. Workup in the normal manner yielded 0.84 g (88%) of (E)-1-fluoro-2-butene. A sample for analysis was purified by preparative GC: IR (neat) ν = 3140 (w), 3020 (m), 2950 (s), 1720 (s), 1600 (m), 1460 (w), 1040 (s), 760 (s), 710 (cm−1); 1H NMR (CDCl3) δ 7.81 (m, 5 H, Ar-H), 6.97 (m, 3 H, Ar-H), 2.20 (s, 3 H, CH3); 19F NMR (CDCl3) δ = 227.7 (t, JCF = 49 Hz). Anal. Calc'd for C9H7OF: C, 72.27; H, 6.67. Found: C, 72.60; H, 6.49.

General Procedure for the Formation of 3-Fluoro-2-alkanones

To a magnetically stirred 50-mL three-necked flask containing lithium hexamethyldisilazide (LHMDS), prepared by the dropwise addition of 4.2 mL (0.007 mol) of methyllithium (1.6 M in ether) to 0.97 g (0.006 mol) of HMPS in 15 mL of THF at 0 °C, was added 1.07 g (0.006 mol) of HMPS folowed by dropwise addition at −35 °C of 0.75 g (0.005 mol) of 4 in 10 mL of THF. After a half hour, 0.005 mol of the alkyl halide in 5 mL of THF was added dropwise. After stirring another hour, the reaction mixture was poured over 10 mL of a saturated sodium bicarbonate solution and extracted with distilled hexanes (3 × 10 mL). The combined organic phases were dried over magnesium sulfate, and the solvent was removed in vacuo. The crude imine, dissolved in 20 mL of pentane, was hydrolyzed by treatment with 10 mL of a saturated sodium bicarbonate solution for 2 h, and the organic phase was washed with saturated sodium bicarbonate solution (2 × 10 mL). After drying over anhydrous magnesium sulfate, the solvent was removed to yield the crude fluoro ketone (see Table 1).