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Selective Hydrogenolysis of the C–F Bond

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It has been shown that the C–F bond may be selectively hydrogenolysed under the action of $HSiEt_3$ in the presence of $AlCl_3$, when the α-position of the C–F bond is occupied by a phenyl group or by a heteroatom with an unshared electron pair.

Organic chlorides and bromides are known[1] to undergo readily ionic hydrogenolysis under the action of the $HSiR_3$–$AlCl_3$ system (Scheme 1). Such reactions have not been reported for organic fluorides so far. However, heterolytic cleavage of the C–F bond is known to occur in the presence of Lewis acids, if the cleavage leads to the formation of carbocations which are stabilized by substituents (allyl-, benzyl-fluorides, *etc.*).[2–4] In this context, organic fluorides are likely to undergo ionic hydrogenolysis. This is even more important, as hydrogenolysis of the C–F bond *via* traditional methods (*e.g.* catalytic hydrogenolysis, reduction with metal hydride complexes) under the conditions required for hydrogenolysis of C–Cl and C–Br bonds occurs only with difficulty.[5]

$$\text{R–X} \xrightarrow{AlCl_3} \text{R}^+ \xrightarrow{AlCl_3,\,HSiEt_3} \text{R–H}$$

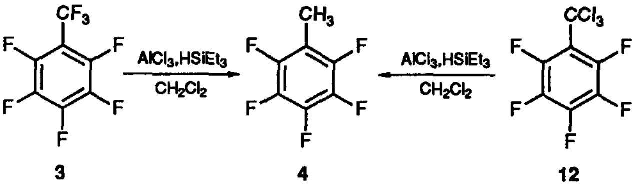
Scheme 1

We have shown that benzotrifluoride **1** readily interacts with $HSiEt_3$ and $AlCl_3$ in CH_2Cl_2, substituting all the fluorine atoms with hydrogen to yield toluene **2** (30%) (Table 1).† The low yield of toluene may be the result of further transformations caused by $AlCl_3$ under the reaction conditions. These by-processes are depressed in the case of perfluorotoluene **3**. The reduction of the latter *via* ionic hydrogenolysis results in pentafluorotoluene **4** (95%) (Scheme 2). The fluorine atoms in the benzene ring remain unaffected, in contrast to the reduction of perfluorotoluene by $LiAlH_4$, when the fluorine atom in the *para* position of the benzene ring[6] is substituted by a hydrogen atom.

Table 1 Ionic hydrogenolysis of C–F and C–Cl bonds in polyhalides with different structures

Starting compound	Mole ratio Substrate	 $AlCl_3$	 $HSiEt_3$	Reaction time/h	Product	Yield (%)
1	1	0.5	4	48	2	30
3	1	2	5	24	4[a]	95
5	1	1	5	2	6[b]	80
7	1	2	5	1	8[c]	97
9	1	1.3	2	2	10[d]	50[e]
9	1	2.5[f]	4	1	10	50[e]
11	1	1.5	3	1	8	97
12	1	0.5	4	1	4	95

[a] Ref. 11. [b] Ref. 12. [c] Compound **8**: δ −12.2 (d, CF_3), 41.7, 47.3, 52.2 and 60.6 [m, CF_2, $J(CF_{3-H})$ 7.5, $J(CF_{2-H})$ 49 Hz]; MS presence of $CH_2{=}O^+CH_2(CF_2)_4H$ (M^+ 245) and $CH_2{=}OCH_2CH(CF_3)H$ M^+ 195) molecular ions. [d] Compound **10**: **9** (6.4 g) was added at 0–5 °C to a solution of $LiAlH_4$ (1.0 g) in purified, dried diethyl ether (30 ml). After stirring (3 h, room temperature), the mixture was decomposed by water and treated with NaOH solution (50%) to alkaline pH. The ether layer was separated, dried over $MgSO_4$, saturated with HCl, dissolved in water, and, after adding $NaCHO_3$, the ether layer was dried and distilled *in vacuo*. Yield 1.9 g (38%), b.p. 67 °C (55 mm Hg). [e] Isolated as the picrate[13] (m.p. 110–111 °C).[14] [f] $BF_3 \cdot OEt_2$.



3 **4** **12**

Scheme 2

We have also established that compounds with a C–F bond in the α-position to a heteroatom (oxygen, sulphur, nitrogen) can readily undergo ionic hydrogenolysis. The reaction proceeds selectively and fluorine atoms in other positions remain unaffected. This was convincingly demonstrated by the following examples with sulphide **5**,[7] ether **7** and amine **9** (Scheme 3).

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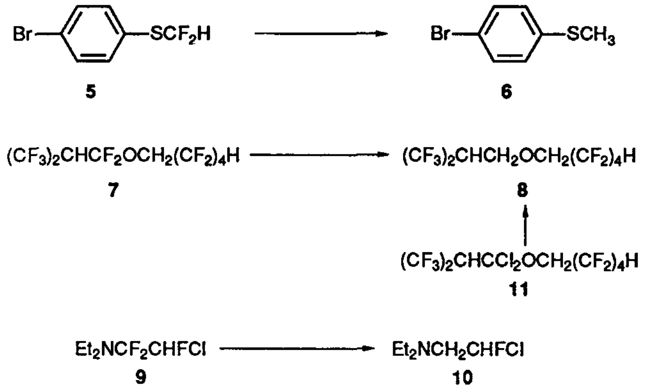
† Conversion products of compounds **1**, **3**, **5**, **11** and **12** were analysed *via* GLC [Chrom-5 instrument equipped with a flame ionization detector, 2400 × 3 mm (i.d.), 5% silicon SE-30 on Chromoton NAW (= 1,1,1,3,3,3-hexamethyldisilazane, HMDS) (0.16–0.20 mm), 3500 × 3 mm (i.d.), 10% polyethylene glycol adipinate on ribosorb BLK (0.2–0.3 mm), carrier gas nitrogen]. Quantitative analysis was run using internal standard technique. ^{19}F NMR spectra were obtained on a Bruker WP 200 SY instrument relative to CF_3CO_2H (external standard). Mass spectra were obtained on a VG-7070E spectrometer, ionizing electron energy 70 eV.



Scheme 3

The results obtained are indicative of the high selectivity of ionic hydrogenation towards C–F bonds of various natures, and are in agreement with the known mechanism.

During our investigation of the hydrogenolysis of ether **7**, we found that, in the initial stages, compound **11** was formed along with **8**. Compound **11** is later transformed into the reaction product **8**. This may be attributed to chlorine–fluorine exchange under the action of $AlCl_3$ followed by hydrogenolysis of the C–Cl bond as a result of the mutual action of $AlCl_3$ and $HSiEt_3$. This proposal is in conformity with reported data on fluorine–chlorine exchange concerning compounds of a similar type.[8] Moreover, we have established that **11**‡ and α,α,α-trichloro-2,3,4,5,6-pentafluorotoluene **12**,[9] synthesized independently, can easily be reduced by triethylsilane in the presence of $AlCl_3$, forming ether **8** and pentafluorotoluene **4**, respectively (see Table 1). Fluorine–chlorine exchange can be ruled out when BF_3 is used instead of $AlCl_3$. For this purpose we have investigated the possibility of hydrogenolysis for model fluorides under the action of Et_3SiH and $BF_3 \cdot OEt_2$ in CH_2Cl_2 and for **7** under the action of Et_3SiH and BF_3. Compounds **1**, **3**, **5** and **7** were established to be inert under these conditions. The results obtained are in good agreement with a proposal that the first stage of the interaction between the organofluorine compound and the silane in the presence of $AlCl_3$ is the substitution of fluorine by chlorine, followed by hydrogenolysis of the C–Cl bond.

However, amine **9** is reduced to amine **10** under the action of $HSiEt_3$ and $BF_3 \cdot OEt_2$. In this case, a highly stable carbocation may have been formed.[10]

Thus, the data obtained indicate that the mutual effects of the Lewis acid and the silane hydride on organofluorine compounds makes it possible to achieve selective hydrogenolysis of a C–F bond attached either to an aromatic ring or to a heteroatom which has a vacant electron pair.

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‡ Compound **11**: anhydrous $AlCl_3$ (3.3 g) was added to a vigorously stirred solution of **7** (8.3 g) in CH_2Cl_2 (40 ml) at room temperature. The reaction mixture was stirred for 3 h at room temperature until completion of the reaction. The organic layer was separated after hydrolysis, dried over $MgSO_4$ and then distilled *in vacuo*. Yield 6.1 g (68%), b.p. 65–68 °C (3 mm Hg), ^{19}F NMR (CH_2Cl_2) δ/ppm – 16.6 (d, CF_3), 41.5, 47.4, 52.3 and 60.0 (m, CF_2).