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Utilisation of Ammonium and Phosphonium Perfluorocyclobutane Ylides as Fluoride Anion Source

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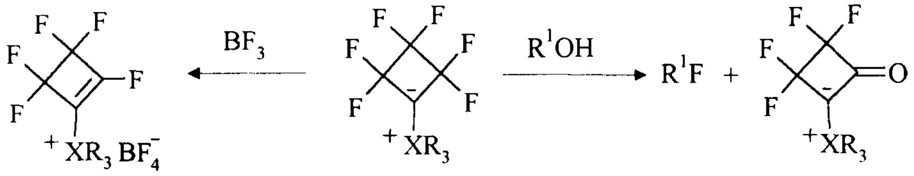
Abstract: Ammonium- and phosphoniumperfluorocyclobutane ylides **1** and **2**, prepared from perfluorocyclobutene and tertiary amines or phosphines can be used as a masked fluoride anion source. These properties have been demonstrated in several reactions. Ylides **1** and **2** cleave C-Si or O-Si bonds, cause dimerisation of fluoroolefins or react with acid chlorides or activated aromatic compounds under halogen exchange.

Reactions involving fluoride anion play an important role in organic and fluoroorganic chemistry, for instance for the generation of carbanions, cleavage of C-O, C-Si or Si-O bonds, halogen exchange or fluorodenitration reactions.[1-4] For these purposes alkali metal fluorides such as KF or CsF, tetraalkylammonium fluorides[4], or tris(dimethylamino)sulfonium (trimethylsilyl)difluoride (TASF)[5] are generally used. Some other F anion sources like phosphazenium-[6], hexamethylpiperidinium-[7], cobaltocenium fluorides[8], tetrabutylammonium(triphenylsilyl)difluorosilicate[9] and the complex tetrakis(dimethylamino)ethene/perfluoropropene[10] are also described in the literature.

Ammonium- and phosphoniumperfluorocyclobutane ylides **1,2** are easily prepared from perfluorocyclobutene and tertiary amines or phosphines and are soluble in a wide range of (even nonpolar) organic solvents.[11,12] They react with F anion acceptors such as BF_3 under elimination of an F atom and formation of stable tetrafluoroborate salts.[11] Recently, we have shown that ylides **1** and **2** react with alcohols and carboxylic acids under exchange of the OH group by fluorine.[12]

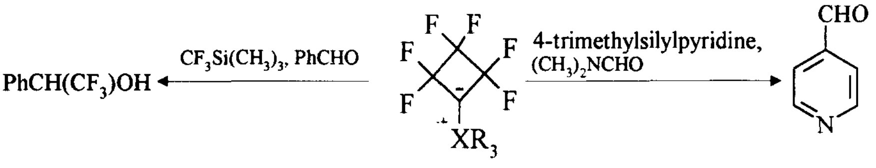


1,2

XR$_3$ = NEt$_3$ (**1**), P(NEt$_2$)$_3$ (**2**). R^1 = CH$_3$, C$_8$H$_{17}$, CH$_2$=CH-CH$_2$, Ph-CH$_2$, Ph-CH-COOEt, PhCO, C$_6$F$_5$CO.

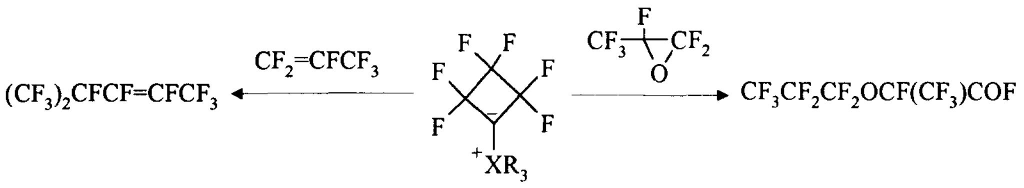
These results stimulated our interest in further evaluating the scope of applications and the synthetic potential of these compounds.

We found that ylides **1** and **2** transfer fluoride and therefore can be used as an easily soluble source of F anions. Although they contain no ionic fluoride they react with F anion acceptors such as Si derivatives with elimination of thermodynamically favoured $(CH_3)_3SiF$ to produce carbanions which can be quenched with suitable electrophiles. The reaction proceeds by slightly heating the reactants in THF or DMF solution.



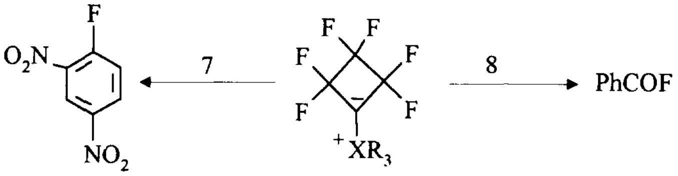
3 **1,2** **4**

Dimerisation of hexafluoropropene (3 % of higher oligomers) and hexafluoropropene oxide catalysed by the action of ylides **1** or **2** occurred spontaneously at room temperature simply by agitating the reagents in a pressure vessel in acetonitrile solution.



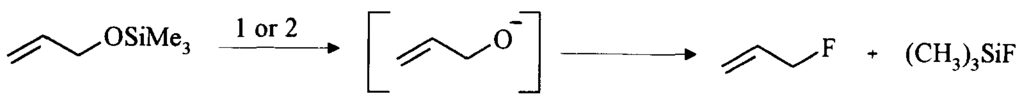
5 **1,2** **6**

The application of ylides **1** and **2** for halogen exchange processes is limited due to their low thermal stability and therefore they can only be used for the substitution of highly activated halogen atoms as for instance in dinitrochlorobenzene (**7**) or benzoyl chloride (**8**).



9 **1,2** **10**

The properties of ylides **1** and **2** (as fluorinating agents[12] and F-anion sources) can be used for the fluorination of silylated alcohols where the cleavage of the O-Si bond followed by fluorination proceeds in one step.



11 **12** **13**

EXPERIMENTAL SECTION

Commercially available chemicals were of analytical grade and used without further purification. NMR spectra were recorded on an AMX 300 spectrometer (^{19}F: 282.1 MHz, ^{1}H 299.8 MHz). A positive chemical shift denotes a resonance occurring downfield from the external standard CCl_3F and internal TMS. All reactions were carried out in N_2 atmosphere. The reaction products were analysed by GLC on a Hewlett Packard 5890 Series 2 Chromatograph using a 10 m • 0.53 mm column HP-1 (dimethylpolysiloxane). Ylides **1, 2** were prepared according to literature methods.[11 12]

2,2,2-Trifluoro-1-phenylethanol (3)

To a solution containing 1.06 g (10.0 mmol) of benzaldehyde and 1.69 g (12.0 mmol) of (trifluoromethyl) trimethylsilane in 20 ml THF 0.20 g of ylide **2** was added at 40°C and stirred for 1 h. To the reaction mixture which contains crude 1-trimethylsilyloxy-1-phenyl-2,2,2-trifluoroethane are added 3 ml of tetrahydrofuran and 5 ml of 3 N hydrochloric acid. The mixture was stirred at room temperature for 8 h. The product was extracted with diethyl ether, washed with water and dried over $MgSO_4$. After solvent evaporation the residue was distilled in vacuo. Yield 1.14 g (65 %). B.p. 93°C/15mbar (lit.[13]).

Pyridine-4-carbaldehyde (4)

To the solution of 1.51 g (10.0 mmol) of 4-trimethylsilylpyridine in 15 ml dimethylformamide 0.20 g of ylide **1** was added at 50°C (exothermic reaction). The reaction mixture was stirred 1h at 50°C and diluted with water. The product was extracted with diethyl ether, washed with water and dried over $MgSO_4$. For purification the product was distilled in vacuo. Yield 0.83 g (78 %), b.p. 77-78°C/12 mbar (lit.[14]).

1,1,1,2,3,4,5,5,5-Nonafluoro-4-trifluoromethylpent-2-ene (5)

A solution of 0.20 g of ylide **1** or **2** in 50 ml dry acetonitrile was placed in an autoclave and 15.00 g (0.10 mol) of perfluoropropene was condensed into it. After stirring for 2 h at ambient temperature the reaction mixture was transferred into a funnel and the lower layer was separated and distilled. Yield 1.44 g (96 %), b.p. 52°C. ^{19}F NMR ($CDCl_3$) trans isomer (94 %) δ: -68.8 (3F), -75.6 (6F), -155.8 (1F), -158.6 (1F), -188.2 (1F) ppm. Cis isomer (6 %) δ: -64.5 (3F), -75.3 (6F), -135.7 (1F), -139.5 (1F), -188.0 (1F) ppm (lit.[10,15]).

2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoyl fluoride (6), was obtained by treatment of 16.60 g (0.10 mol) hexafluoropropeneoxide with 0.30 g of ylide **1** in 30 ml CH_3CN in an autoclave during 2 h. The lower layer of the reaction mixture was separated and distilled. Yield 13.6 g (82 %) of **6**, b.p. 52-55°C (lit.[16,17]). Spectral data for **6**. ^{19}F NMR ($CDCl_3$) δ: 26.1 (1F), -79.1(1F), -81.6 (3F), -82.2 (3F), -86.5 (1F), -129.6 (2F), -130.1 (1F) ppm.

2,4-Dinitrofluorobenzene (9)

2.02 g (10.0 mmol) of dinitrochlorobenzene and 2.89 g (11.0 mmol) of ylide **1** were heated in 20 ml acetonitrile for 3 h at 70°C. After solvent evaporation the product was distilled in vacuo. Yield 1.26 g (68 %), b.p.178°C /25 mbar (lit.[14]).

Benzoyl fluoride (10), yield 87 %, b.p. 159-161°C (lit.[14]) was obtained by heating of 2.89 g (11.0 mmol) of ylide **1** and 1.40 g (10 mmol) of benzoyl chloride at 60°C for 3 h.

1-Fluoropropene-2 (12)

16.3 g (40.0 mmol) of betaine **2** and 2.60 g (20.0 mmol) of allyloxytrimethylsilane **(11)** were placed in a glass pressure-vessel and heated at 60°C for 6 h. The reaction mixture was cooled and volatile product was condensed into a cold trap. For further purification the product was distilled at low temperature. Yield 0.57 g (48 %), b.p. -3°C.[18] ^{19}F NMR δ: -216.3 (tm, $^2J_{F\text{-}H}$=48 Hz) ppm.

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