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1,1-Dihydroperfluoroalkylamines. Repor

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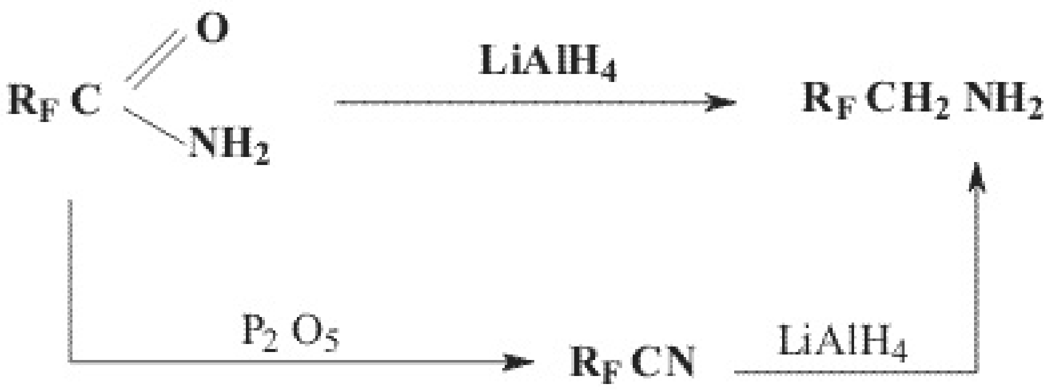
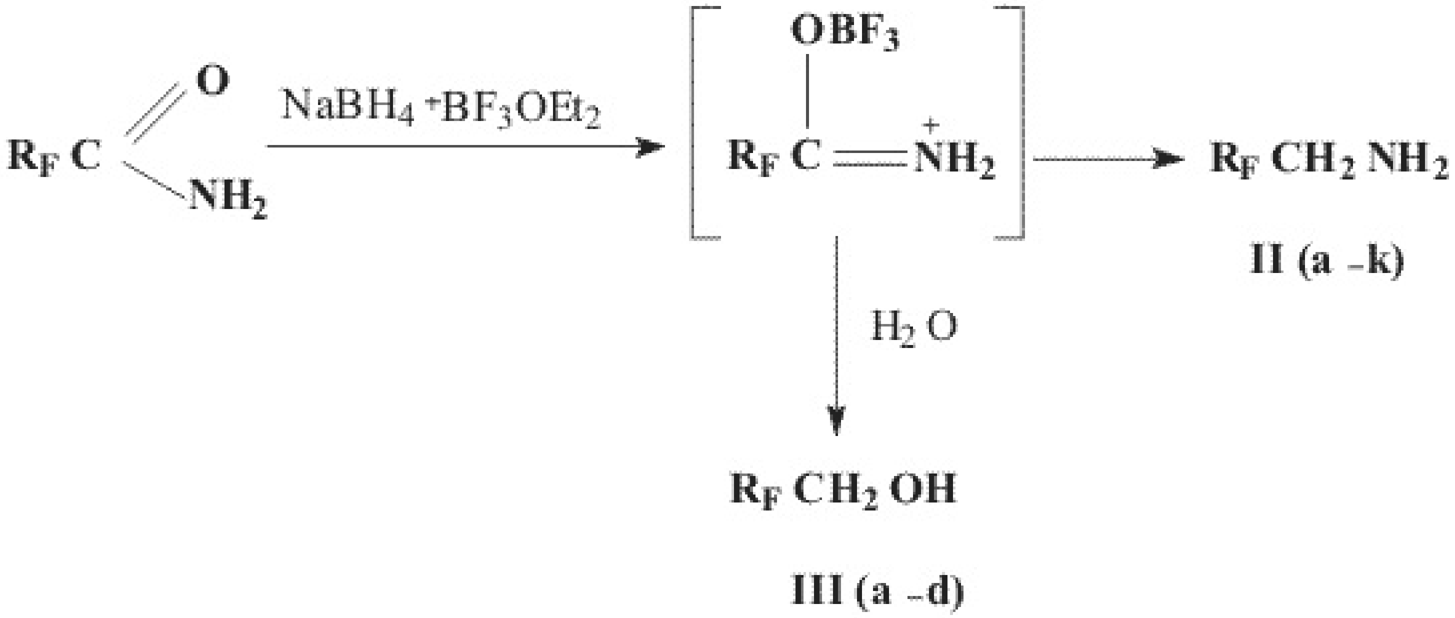
The main method to produce 1,1-dihydrofluoroalkyl amines is reduction of amides or nitr
lithium alumohydride [1-3].



This method has a number of disadvantages, first it is difficult to work with $LiAlH_4$ and it is
amines in a tangible quantity.

A more promising for the reduction is using diborane that may be obtained both separately
reaction mixture in the presence of amide to be reducted, for example from $NaBH_4$ and
earlier in obtaining dihydrotrifluoroethylamine [4]. A possibility to synthesize 1,1-dihydrofluor
BF_3*Et_2O system was studied in the present work. It has been found that amides of fluorocar
diglyme, dioxane) react exothermally with $NaBH_4$ at addition of BF_3*Et_2O.The amide re
directions- to form amine $RFCH_2NH2$ (II) and alcohol $RFCH_2OH$ (III).



After completion of the interaction the reaction mass was treated with hydrochloric acid, t were distilled, the latter was separated by pouring the strippant into water followed by rectific (III) was isolated in treatment of dry residue with water solution of alkali and distilla fluoroalkylamines (II a-g) are from 32 to 65%, the yields of alcohols (IIIa-g) are from 18 to 32%.

Table 1.

$R_FCH_2NH_2$ II	BP(°C)	Yield, % Method 1	Yield, % Method 2	R_F CH_2OH III	BP(°C)
HCF_2 (a)	68	55			96
CF_3 (b)	38	63			74-75
C_2F_5 (c)	45-50	60			80-81
C_3F_7 (d)	68	65			96-97
Cn Fg (e)	87	65			110-110
C_5F_{11} (f)	107	42	55		
C_6F_{13} (g)	+29	38	54		
C_7F_{15} (i)	45/15mm Hg	34	50		
C_8F_{17} (k)	56/15mm Hg	32	55		

We have also found that it is more easy to obtain higher dihydrofluoroalkylamines (R_f=C_5F action of $NaBH_4$ on perfluoroalkylnitriles (Method 2) because they are liquid products unlike low bp=-64°C; C_4F_9CN bp=150°C).See also [5].

Experimental

2,2-Difluoroethylamine(IIa)

A solution of amide of difluoroacetic acid (190 g, 2.00 mole) in 500 mL of abs. diglyme and Na a three-neck flask (2 L) fitted with a mixer, dropping funnel and a backflow condenser (the out flask with concentrated H_2SO_4). BF_3*Et_2O (306g, 2.16 mole) is added dropwise under stirring

After completion of addition the reaction mixture is stirred for an hour on a boiling water bat and hydrochloric acid (1L) is added dropwise. The obtained mixture is evaporated to dryness The strippant is collected in a cooled receiver, poured in water, the bottom layer is sepa difluoroethanol (IIIa), its boiling temperature and yield are given in Table 1.

A solution of NaOH (480g, 12.0 mol) in a minimal quantity of water is added dropwise to t

water is distilled to 100 °C. After rectification there is obtained 90 g (55%) of 2,2-difluoro
69°C).

1,1-Dihydroperfluoroalkylamines II (b-k) and alcohols III(b-d) are obtained analogously to IIa an

1H,1H-Perfluorohexylamine (IIe), method 2

Diglyme (1.5 L) and $NaBH_4$ (150 g. 3.95 mol) are placed and stirred in a four-neck flask (mechanical mixer, thermometer, dropping funnel and a backflow condenser, then perfluoroh added dropwise. The reaction mixture is heated up to 60°C. After completion of nitrile addition hours and is kept overnight.

Then the reaction mass is poured cautiously in portions, as foaming occurs, into a mixture of 300 mL water) with ice (1.5 kg). The formed mass is placed in a 6L flask and distilled wit strippant is separated to obtain 370g of the crude product that is then rectified to obtain 320 of 98% purity, BP 107°C in 55% yield. Amines (II b-k) are obtained in a similar way.

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