Journal "Fluorine Notes", Volume # 4(65), July - August 2009

1,1-DIHYDROPERFLUOROALKYL AMINES. Repo

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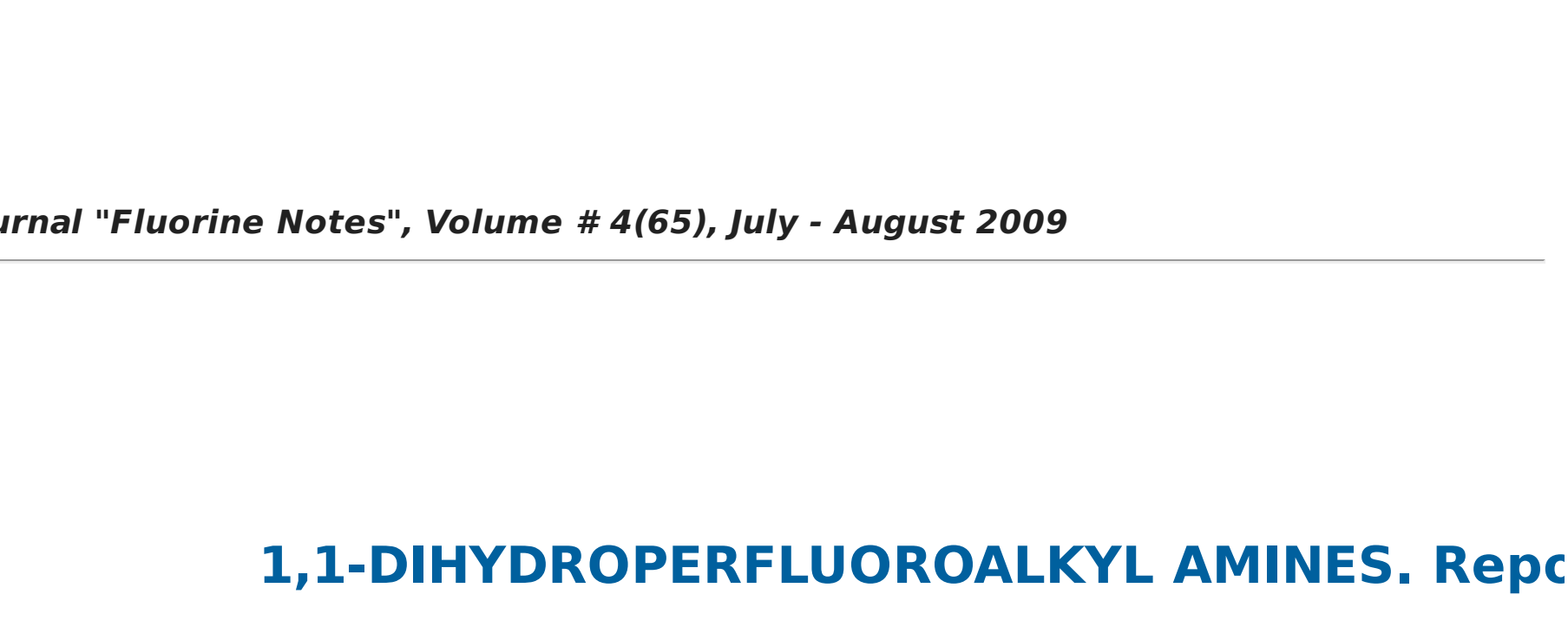
Reduction of primary amides of acids with borane (BH_3), generated in Situ by addition of Et_2O amide and $NaBH_4$ in an aprotic solution is well known [1,2]. We have shown earlier [3] tha mixture of corresponding primary amine and alcohol.

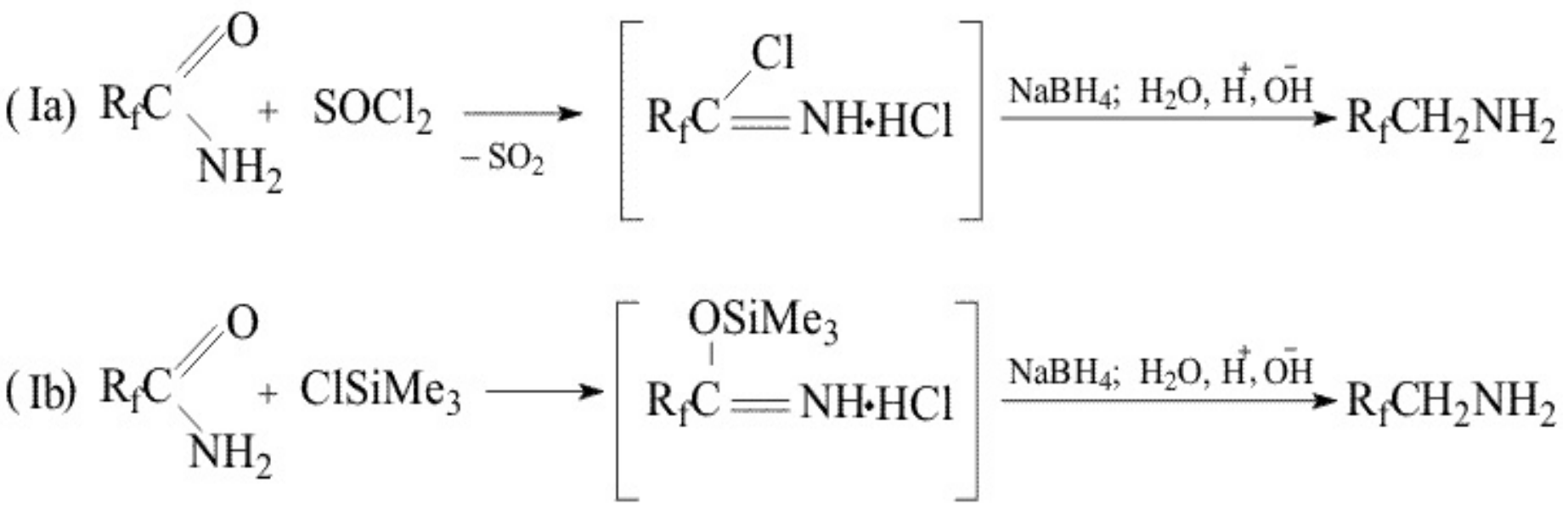


Throughout the research a new method has been developed, that makes possible the redu perfluoroacids to amines excluding formation of alcohols.

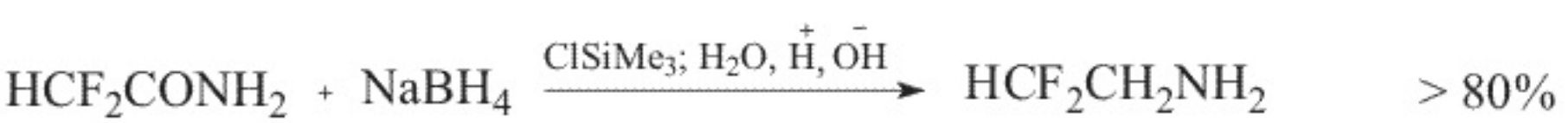
The method consists in treatment of the mixture of the amide and $NaBH_4$ in an aprotic chloride or chlorotrimethylsilane.

Probably in the first case ($SOCl_2$) the formation of imidoylchloride takes place and in the seco of aminoacid is formed. As a result, in the first case oxygen is absent in the initial molecule t alcohol formation, in the second case oxygen is bound with silicon that suppresses the process

The use of such a system results in a yield increase of the desired amine up to 80% ap suppression of the competitive reaction of the alcohol formation.



The latter variant was scaled by us in production of 1,1dihydrodifluoroethylamine up to 10.0 k



Experimental

Method Ia

Sodium boron hydride (5.07g, 0.15 mol) was added to the solution of difluoroacetamide dioxane at 20°C and thionyl chloride (18g, 015 mol) was added dropwise. The reaction ma heated up to 100°C and kept for 1 hour, then cooled to 50°C and the solution of NaOH (8g) dropwise (with simultaneous distillation of the desired product boiling before 70°C) .

There was obtained 5.05 g of the distillate with the product content of 67% (Gas liquid chron

Method Ib

Sodium boron hydride (3 kg, 75 mol) was added at stirring to the solution of difluoroa dioxane(15.8 kg).Trimethylchlorosilane (7.6 kg, 68 mol) was adding to the obtained suspens the temperature of the reaction mixture stable. Then the temperature was gradually incre reaction mixture was kept for another 5-6hours, then cooled to 75-80°C and the solution o water was added at such a rate that the raw would be distilled evenly. The product residue reactor to 100-105°C.

There was obtained 12.4 kg of the raw with the product content of ~35%. After rectification of the amine with BP= 68-63°C in 84% yield, 97% + purity.

References

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3. A.F.Gontar, V.L.Don, E.V.Igoumnova, S.M. Igoumnov, 1,1-DIHYDROPERFLUOROALKYL AMIN