Mechanistic and Synthetic Aspects of the Simons Process. Electrochemical Synthesis of New Organo-Phosphorus Compounds

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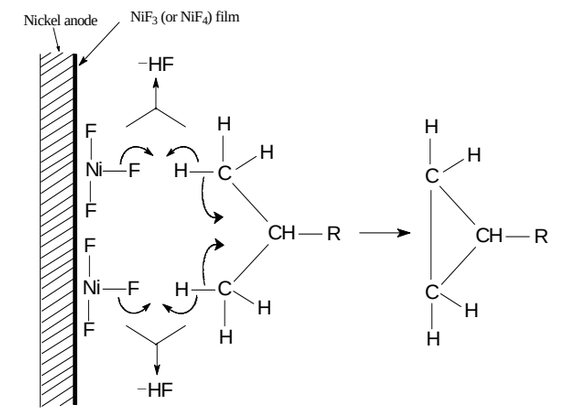
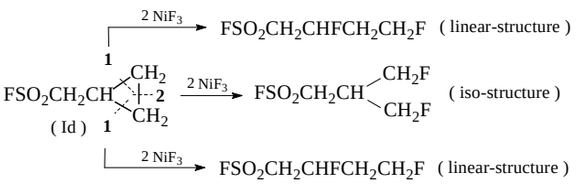
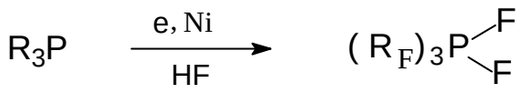
The compounds *i*-$C_4H_9SO_2F$, *i*-$C_3H_7SO_2F$ and *cyclo*-$C_3H_7C(O)F$ are subjected to electrochemical fluorination in anhydrous hydrogen fluoride. The resulting products from the cell and the volatile fluorinated material collected in the trap at -78° C are fully analysed by NMR spectroscopy. From the reaction balances, literature data and quantum chemical calculations a new mechanism of the carbon chain isomerization during the electrochemical fluorination (ECF) is proposed. The key step in the formation of isomeric products is the ring closure reaction via carbo-cationic or biradical intermediates [1].





ECF of trialkylphosphines in HF solution leads to the formation of tris(perfluoroalkyl)-difluorophosphoranes in high yield [2,3].



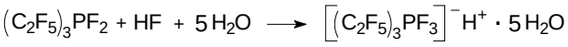
Yield: 49− 74 %

R = C_2H_5 ; C_3H_7 ; $n-C_4H_9$; $i-C_4H_9$

R_F = C_2F_5 ; C_3F_7 ; $n-C_4F_9$; $i-C_4F_9$

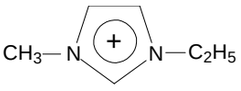
In the case of tris(i-butyl)phosphine a complex mixture of isomeric tris(perfluorobutyl)-difluorophosphoranes is formed [2,3].

Reaction of tris(perfluoroalkyl)difluoro-phosphoranes with aqueous hydrofluoric acid result in the formation of the corresponding tris-(perfluoroalkyl)trifluorophosphoric acid (I) [4].



(I)

The aqueous solution of acid (I) is stable at room temperature for a long time and can be used as a convenient starting material for the preparation of different salts containing the tris(perfluoroalkyl)trifluorophosphate-anion (FAP-anion) for application as new ionic liquids and conducting salts.



$[(C_2F_5)_3PF_3]^-$

$[(C_6H_{13})_3(C_{14}H_{29})P]^+$

$[(C_2F_5)_3PF_3]^-$

The properties of ionic liquids containing the FAP-anion and possible applications in the electrochemical processes will be discussed.

References.

1. N.V. Ignat'ev, U. Welz-Biermann, U. Heider, A. Kucheryna, S. von Ahsen, W. Habel, P. Sartori and H. Willner, *J. Fluorine Chem.*, in press.
2. N. Ignat'ev and P. Sartori, *J. Fluorine Chem.*, 103 (2000), p. 57-61.
3. Patent Application WO 00/21969, Merck KGaA, Darmstadt, Germany.
4. Patent Application DE 101 30 940.6, Merck KGaA, Darmstadt, Germany.