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HYDROGEN FLUORIDE-ORGANIC BASE SOLUTIONS AS USEFUL FLUORINATING AGENTS

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Solutions of anhydrous hydrogen fluoride-organic base were investigated in the fluorination of organic compounds. In the hydrofluorination of alkenes, solutions of 14-23 wt% of melamine in hydrogen fluoride surpassed other amine-hydrogen fluoride reagents including the Olah's reagent (30 wt% of pyridine in hydrogen fluoride), with regard to its preparation, handling, hydrofluorinating activity and post-treatment. In general, hydrogen fluoride solutions of amines were extremely hygroscopic and such solutions having absorbed moisture usually showed remarkably low fluorinating activity. Whereas, a small influence of water on the deterioration of hydrofluorination ability was observed in a melamine-hydrogen fluoride solution compared with other amine-hydrogen fluoride solutions. Thus, it is stable as fluorinating agent for prolonged storage under ordinary conditions. A melamine-hydrogen fluoride solution containing a co-solvent such as pentane or carbon tetrachloride was found to result in a liquid-liquid two phase mixture. This was a highly convenient and a suitable system in its readily available separation of products to be found in a co-solvent layer. In addition to that, the recovered melamine-hydrogen fluoride solution layer can be used repeatedly without a remarkable decrease of the activity with a co-solvent.

Solutions of hydrogen fluoride-organic base with Cu_2O were used successively in the halogen-exchange fluorination of organic halides, particulary for the cyclo or tertiary alkyl halides, without remarkable formation of olefinic products. Ethers were found to be the most suitable organic base in this case. Alkyl halide RX (X; Cl or Br) was initiated by cuprous cation Cu^+ to form alkyl cation R^+ and cuprous halide CuX. In the case of using a solution of Cu_2O in hydrogen fluoride without an organic base, cationically induced polymerizations and rearrangements of R^+ readily occurred because of the strongly acidic properties of anhydrous hydrogen fluoride solution. However, hydrogen fluoride behaves as a weaker acid in an organic base compared to the pure form and the nucleophilic activity of the fluoride anion is known to be much more enhanced so that undesirable reactions such as oligocondensation of R^+ are strongly suppressed in the hydrogen fluoride-organic base with Cu_2O. Consequently, the reaction of R^+ with fluoride anion occurs predominantly to give corresponding alkyl fluorides. Interestingly, such halogen-fluoride exchange reactions were observed without carbon skeletal rearangement in the substrate even in such an alkyl halide as 2-chloro-2,4-dimethyl-pentane.

An improved procedure for diazotization-fluorodediazoniation of anilines was also successfully accomplished to produce fluoroarenes in high yields by using hydrogen fluoride-organic base solutions, which are free of volatile hydrogen fluoride at the fluorodediazoniation step. For example, quantitative yield of fluorobenzene was obtained from aniline by the present procedure, i.e. 55°C for dediazotization using 30 wt% pyridine-HF or 36 wt% 2-hydroxy-pyridine-HF or 27 wt% pyradine-HF solutions, and 90 °C for dediazotization using 40 wt% pyridine-HF or 50 wt% 2-hydroxy-pyridine-HF solutions respectively. Whereas a 70% yield was reported of fluorobenzene from aniline by carrying out the dediazoniation step using Olah's reagent heated up to 85 °C in a stainless steel pressure vessel. In addition to such unsatisfactory yield, fluoroarenes were obtained inconveniently as a mixture of isomers in some cases. However, most substituted anilines were found to produce corresponding fluoroaromatics in high yields with complete regioselection by carrying out the fluorodediazoniation in our experimental procedure. Interestingly, although anilines having nitro or halogen group in their ortho position gave considerably low yields of corresponding fluoroarenes, aromatic heterocyclic compounds having the similar structure with these anilines gave the corresponding fluorides in high yields. An addition of pentane or chlorobenzene to diazotization agents (sodium nitrate in hydrogen fluoride-organic bases) was again found to result in a liquid-liquid two phase mixture. Thus, after completion of the diazotization-fluorination of anilines, fluoroarenes produced were found in the organic layer which was free of hydrogen fluoride. The agent layer separated from organic layer could be used for the next run without the remarkable deterioration in activity.