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NEW APPROACHES TO P-F COMPOUNDS. AMINE-HF-ADDUCTS AS FLUORINATING AGENTS IN PHOSPHORUS CHEMISTRY

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Amine-HF adducts are excellent fluorinating agents. Their reaction with P(III)-compounds, PX_3 (X = OR, NR_2, halogen), gives HPF_5^- in high yield. From this product PF_3 can be generated in a convenient way.[1] . Organylchlorophosphanes, $RPCl_2$, react with $Et_3N \cdot n$ HF yielding RPF_2, $RPHF_4^-$, RPF_5^- and $(RP)_n$, resp., in dependence on the amine/HF ratio.

The reaction of $Et_3N \cdot n$ HF with PCl_5 results in the formation of hexafluorophosphate, PF_6^-. In the presence of sec. amines, however, PF_5-amine adducts, $PF_5 \cdot HNR_2$, are obtained. These adducts react with alcohols forming $(RO)PF_5^-$. [2].

Combined with CCl_4 organylammonium fluorides are useful agents for oxidative fluorination of tervalent phosphorus compounds.

Thus, $(RO)PF_5^-$, $(RO)_2P(O)F$, $(Et_2N)_2P(O)F$, $(Et_2N)_2(EtO)PF_2$, $(Et_2N)_3PF_2$ and $[(Et_2N)_3PF]^+$ are obtained from $P(OR)_3$, $P(OEt)(NEt_2)_2$ and $P(NEt_2)_3$, resp.. In the system $CCl_4/Et_3N \cdot n$ HF/sec. amine even elemental phosphorus, P_4, is oxidized yielding HPF_5^-, $R_2NH \cdot PF_5$ and $(R_2N)_2P(O)F$. If alcohols are added to this system $(RO)PF_5^-$, $(RO)_3PO$ and $(R_2N)_2P(O)F$ are the reaction products. [3].

1 L. Riesel, M. Kant: Z. Chem. 24, (1984) 382.

2, 3 L. Riesel, M. Kant: submitted to Z. anorg. allg. Chem. (1985).