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PREPARATION OF OXYDIFLUORAMINES FROM FLUOROOLEFINS

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Monosubstituted fluoroolefins, including functionalized olefins such as perfluoroacryloyl fluoride and perfluoroethylvinyl ether, react under electrophilic conditions with the Lewis acid adduct of trifluoramine oxide to give novel oxydifluoramines. Additionally, nitroso and nitrito derivatives are identified as significant byproducts of the reaction. The synthesis of several new oxydifluoramines, nitroso compounds and nitrites will be described, along with spectroscopic, physical and chemical characterization supporting their structures.

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HgF_2-ASSISTED ADDITIONS TO THE CN-TRIPLE BOND

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α, α-Difluoro-N, N-dihaloamines $R-CF_2-NX_2$ are simply prepared from nitriles and halogens in the presence of stoichiometric amounts of HgF_2, e.g.

$$R - CN + 2X_2 + HgF_2 \longrightarrow R - CF_2NX_2 + HgX_2$$

(X=Cl, R=CF_3, C_6H_5; X = Br, R = CF_3)

$$ClCN + 2\,Cl_2 + HgF_2 \xrightarrow{exc} CF_3NCl_2 + CF_2ClNCl_2 + HgCl_2$$

Sometimes also small amounts of the N-halo-imines (e.g. $CF_3CF{=}NBr$) are observed. These HgF_2-assisted additions avoid halogenomonofluorides, they occur under mild conditions (below r.t.) and with high yields (80-90%). Similar reactions are possible with cyanogen:

$$(CN)_2 + Cl_2 + HgF_2 \xrightarrow[-HgCl_2]{} Cl_2N-CF_2-CF = NCl + Cl_2N-CF_2-CF_2-NCl_2$$

$$(CN)_2 + (CF_2NCl_2)_2 \longrightarrow ClN = CF - CF = NCl$$

$$(CN)_2 + Br_2 + HgF_2 \xrightarrow[-HgBr_2]{} Br_2N - CF_2 - CF = NBr + BrN = CF-CF = NBr$$

The NN'-dichloro- and NN'- dibromo-ethanediimidoyldifluorides are colorless solids. The structure of the dibromide was determined by X-ray-investigations. The spectroscopic and some of the chemical properties of these N-halogeno-derivatives will be discussed.