SOME CHLORINE FLUOROSULFONATE AND PEROXYDISULFURYL-DIFLUORIDE REACTIONS

Academician A.V. Fokin
Academy of Sciences of the USSR, Moscow

Chlorine fluorosulfonate adds exceptionally easy not only to various alkenes, perfluorobenzene, but to alkynes too

$$c10S0_2F + HC=CH \xrightarrow{-30^\circ} CHC1_2CH(0S0_2F)_2$$

The addition of peroxydis::Ifuryldifluoride to alkyl- and perfluoroalkyliodides leads to unstable adducts, which decompose with the formation of alkylfluorosulfonates and iodine fluorosulfonate; the latter was trapped with fluoroalkenes

RJ +
$$(0S0_2F)_2 \xrightarrow{-50^{\circ}} RJ(0S0_2F)_2 \xrightarrow{20^{\circ}} JOS0_2F + ROS0_2F$$

$$JCF_2CF_2OS0_2F \xrightarrow{CF_2=CF_2}$$

The use of ClOSO₂F allows to substitute selectively for the fluorosulfonate group the chlorine atom in monochloroacetic acid esters as well as the fluorine atom in hexafluoroacetone N-fluoroimine

$$c10S0_2F \xrightarrow{C1CH_2COOR} FS0_2OCH_2COOR$$

$$FN=C(CF_3)_2 FS0_2ON=C(CF_3)_2$$

 ${\rm CloSO}_2{\rm F}$ serves as an exceptionally active chlorinating reagent for fluorinated alcohols, nitrosocompounds, perfluoroacid amides and particularly for benzene

The reaction of $(0S0_2F)_2$ with perfluoroacid amides leads to the corresponding N,N-bis(fluorosulfonate)amides, which easily rearrange into alkylfluorosulfonates

$$(0S0_2F)_2 + R_fC \xrightarrow{0} R_fC \xrightarrow{0} R_fC \xrightarrow{0}_{N(0S0_2F)_2} \rightarrow R_f0S0_2F + |0CN0S0_2F|$$

The hypochlorites of fluorinated alcohols are stable enough and they, similarly to ClOSO₂F, are able to add to alkenes, fluoroalkenes (but not to perfluoroisobutylene), bis(trifluoromethyl)ketene, trifluoromethylisocyanate and perfluoronitriles

The fluorosulfonatoacetic acid esters are unstable at the ambient temperature, but they can be widely used in situ as a very effective alkylating reagents

$$c_6H_5CH_2COOR \stackrel{C_6H_6}{\leftarrow 30^{\circ}} FSO_2OCH_2COOR \stackrel{R'2NH}{\longrightarrow} R_2'NCH_2COOR$$