ELECTROPHILIC REACTIONS OF HIGH FLUORINATED DIENES

V. A. Petrov*, G. G. Belen'kii and L. S. German

A. N. Nesmeyanov's Institute of Organo-Element Compounds Academy of Sciences U.S.S.R., Vavilov str., 28, Moscow (U.S.S.R.)

Conjugated addition of >N-Hal compounds to perfluorobutadiene (1) and 2-Cl-perfluorobutadiene (2) in solution of HOSO₂F has been studied. The reaction mixture contains only products of 1,4-addition and in the case of diene (2) electrophilic attack proceeds only at trifluorovinyl group:

In the presence of catalytic amounts of SbF₅ internal perfluoro dienes 1,4-cyclization has been found:

The use of excess of SbF₅ in the case of dienes (4) and (5) yields to the corresponding dialkylcyclopentens only:

4
$$\frac{\text{SbF}_{5}, \text{ex.}}{100^{\circ}, 15 \text{ min.}}$$
 $\frac{\text{CF}_{3}}{\text{c}_{2}^{\text{F}_{5}}}$ yield 90-95% $\frac{\text{SbF}_{5}, \text{ex.}}{100^{\circ}, 3-5 \text{ h.}}$ $\frac{\text{CF}_{3}}{\text{c}_{4}^{\text{F}_{9}}}$ + $\frac{\text{C}_{2}^{\text{F}_{5}}}{\text{c}_{3}^{\text{F}_{7}}}$ yield 85-90%

The reaction pathways of perfluorodienes 1,4- and 1,5-cyclizations are discussed.