

MECHANISM OF THE PHOTOCHEMICAL REDUCTION OF C-Cl BOND IN FLUORINE COMPOUNDS

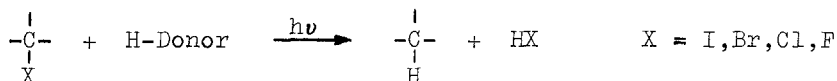
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The photochemically initiated substitution of a halogen for hydrogen atom represents a preparative reaction, that can be expressed by the general scheme:



The reaction is characterized by a high selectivity in poly-halogeno compounds as demonstrate examples of successfully performed preparations: $\text{CF}_3\text{-CBr}_2\text{Cl} \longrightarrow \text{CF}_3\text{-CHBrCl}$, $\text{CCl}_2\text{F-CClF}_2 \longrightarrow \text{CHClF-CClF}_2$, $\text{CF}_3\text{CClF-CCl}_3 \longrightarrow \text{CF}_3\text{CClF-CHCl}_2$.

A marked directive effect on the regioselectivity of the reduction is exhibited by the ester group in fluorinated propanoates: $\text{CFXY-CClZ-COOR} \longrightarrow \text{CFXY-CHZ-COOR}$ ($\text{X, Y} = \text{F, Cl}$). The quantum yields of this reduction in 2-propanol are as high as several hundreds of units, which is indicative of the chain mechanism. The photo-reduction is auto-sensitized by the resulting acetone.

The kinetic model of the reduction indicates, under a definite ratio of the terminal reaction rates, a rate limit independent of the concentration of the starting substance. The kinetic model of the reduction initiated by α -phenyl benzoin and benzoin isopropyl ether was verified also using the Stern-Volmer dependence of a total quantum yield of HCl.