PHOTOREDUCTION OF CARBON-HALOGEN BONDS IN FLUORINATED ALIPHATIC COMPOUNDS: SOME SELECTIVITY RULES

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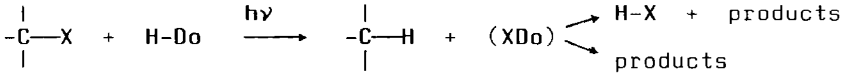
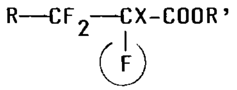
The photoreduction exhibits some favourable characteristics which make this reaction a convenient and specific method of monodehalogenation in particular structures. The reaction scheme can be expressed in the general form



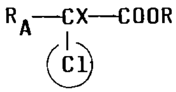
$$-\underset{|}{\overset{|}{C}}-X + H\text{-}Do \xrightarrow{h\nu} -\underset{|}{\overset{|}{C}}-H + (XDo) \begin{cases} \to H\text{-}X + \text{products} \\ \to \text{products} \end{cases}$$

where H-Do is a hydrogen donor. Generally, each halogen atom can be substituted with hydrogen in this manner including fluorine at special positions /1,2/.

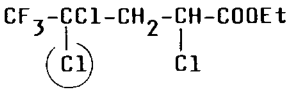
Advantages of the method concern the phenomenon selectivity which includes: chemo-selectivity (only halogen bonds are reduced); halogeno-selectivity (carbon-halogen bonds are reduced in the order: I > Br > Cl ≫ F); regio-selectivity, which is connected with the mechanism of electron transfer in the rate-limiting step. As a consequence of this fact, some groups exhibit strong directive effects (see examples) from which selectivity rules can be deduced /3/.



$R-CF_2-\underset{\textcircled{F}}{CX}\text{-}COOR'$



$R_A-\underset{\textcircled{Cl}}{CX}-COOR$



$CF_3\text{-}\underset{\textcircled{Cl}}{CCl}\text{-}CH_2\text{-}\underset{Cl}{CH}\text{-}COOEt$

$X = H,F$

$R_A = CF_2Cl,\ CFCl_2,\ CF_3\text{-}CHCl\text{-}CH_2,\ CF_2Cl$

$X = Cl \quad F \quad H \quad F\ (R = CH_2Cl)$

1 V.P. Shendrik, O. Paleta and V. Dědek, Collect. Czech. Chem. Commun., 41 (1976) 874.
2 C. Portella and J.P. Pete, Tetrahedron Lett., 26 (1985) 211.
3 V. Dadák, Dissertation, Prague, 1991.