

DIFLUOROMETHYL PERFLUOROALKANESULFONATES AND THEIR REACTIONS

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In contrast to the nucleophilic reactions of $R_FSO_3CH_2R$ (1) (R =hydrogen, alkyl and perfluoroalkyl) and $R_FSO_3CF_2R_F$ (2) it was found that the reactions of $R_FSO_3CF_2H$ (3) with nucleophiles were more complicated. Halide ions, X^- ($X=F, Cl, I$) and ethanol only attacked the alkoxyl carbon atom, causing the C-O bond cleavage to give HCF_2X (4) and HCF_2OEt (5). Other reagents such as RCO_2^- ($R=CH_3, CF_3$), C_6H_5S etc can either attack the carbon or sulfur atom of 3 to give the corresponding products of C-O and S-O bond cleavage respectively. More basic nucleophiles, RO^- ($R=C_6H_5, C_2H_5$) mainly abstracted the hydrogen atom of the CF_2H moiety to produce difluorocarbene. Ether and benzene, which can be alkylated by methyl perfluoroalkanesulfonate, did not react with 3 under similar conditions. The reaction rate of 3 with KF was much slower than that of 1 ($R=H$). All these data seem to indicate that the shielding effect caused by the two fluorine atoms on the methyl carbon prevents to some extent the nucleophilic attacking on the carbon, but not so completely as in 2 due to the presence of a hydrogen atom.