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REACTION OF SULPHUR TETRAFLUORIDE WITH HALOGENATED ACETONES. THE EVIDENCE FOR PARTICIPATION OF FLUOROCARBOCATIONS

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1,3-Dihalopropanes-2 (X = Br, Cl) were reacted with sulphur tetrafluoride to give 1,3-dihalo-2,2-difluoropropanes 1 as main products (yield 60 - 70 %). In addition, bis(1,3-dihalo-2-fluoropropyl)ethers 2 (yield 5-20 %) and 1,2-dihalopropenes-1 3 (yield 1-3 %) were obtained. 1,3-Difluoropropanone-2 gave only products 1 and 2.

$$(CH_2X)_2\text{-}CO \xrightarrow[HF]{SF_4} (CH_2X)_2\text{-}CF_2 \quad 1$$

$$(CH_2X)_2\text{-}CF\text{-}{}_2O \quad 2$$

$$CH_2X\text{-}CF{=}CHX \quad 3$$

$$(CH_2Cl)_2\text{-}CO \xrightarrow[CF_4,\ HF]{C_6H_6} C_6H_6\text{-}CF(CH_2Cl)_2 \quad 4$$

Formation of compounds 2 and 3 is interpreted in terms of a mechanism involving fluorocarbonium ions of the type $(CH_2X)_2\text{-}\overset{+}{C}F$. The occurence of fluorocarbonium ions in the above reactions was confirmed by the reaction of 1,3-dichloroacetone with sulphur tetrafluoride and benzene followed by isolation of 1,3-dichloro-2-fluoroisopropylbenzene 4. The latter is an electrophilic substitution of benzene with fluorocarbonium ion, i.e. fluoroalkylation of benzene.