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THE REGIOSELECTIVE CHEMISTRY OF ALKOXYXENON FLUORIDE

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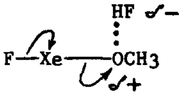
Xenon difluoride reacts with methanol to form the unstable reactive species methoxyxenon fluoride (1). In the absence of unsaturated hydrocarbons, this specie quantitatively disproportionates to formaldehyde and hydrogen fluoride; however, in the presence of alkene substrates a competitive methoxyfluorination reaction results. During methoxyfluorination, the highly reactive intermediate (1) displays a novel ambivalent addition character depending upon whether catalysis is accomplished by protonic acids (H_2SO_4 & HF generated in-situ) or Lewis acid species (BF_3 & BF_3 etherate). Catalysis with protonic acids produces an apparent fluorine electrophilic intermediate (2) where fluorine adds first and results in Markownikoff fluoromethoxy products predominating. Reaction in the presence of Lewis acids provides a positive oxygen electrophile as intermediate (3) where the methoxy group adds first and produces

$F—Xe—OCH_3$

1



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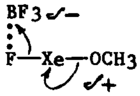

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mainly anti-Markownikoff fluoromethoxy products. The reaction mechanism involving species 1, 2, and 3 were studied by using five alkenes with varying structural features; in the case of the very electron rich alkene dihydropyran, reaction with XeF_2 occurred before 1 could form. Current mechanistic studies of this alkoxyfluorination reaction involve varying the alcoholic substrate with electron-donating and electron-withdrawing alkoxy moieties.