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EVIDENCE FOR THE EXISTENCE OF METHYL HYPOFLUORITE: METHANOLYSIS OF XENON DIFLUORIDE

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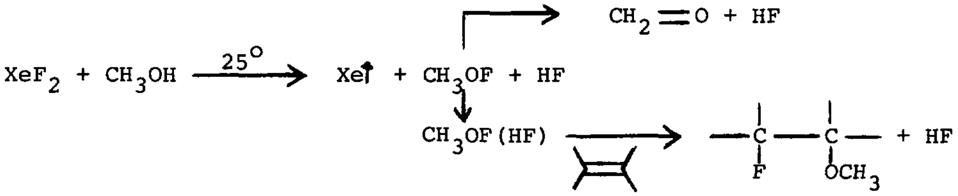
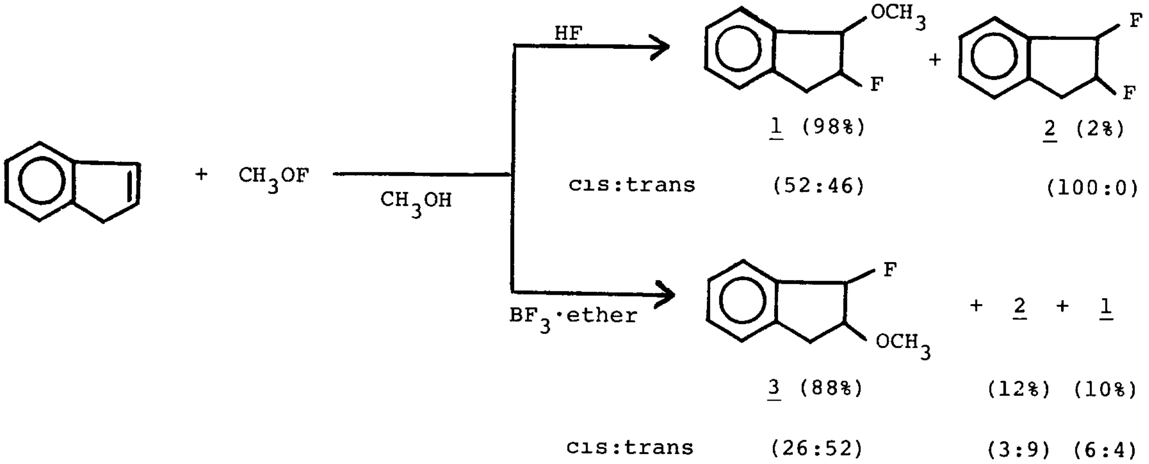
Abstract: Methyl hypofluorite is indicated as an intermediate in the reaction of xenon difluoride with alkenes in methanol as solvent.

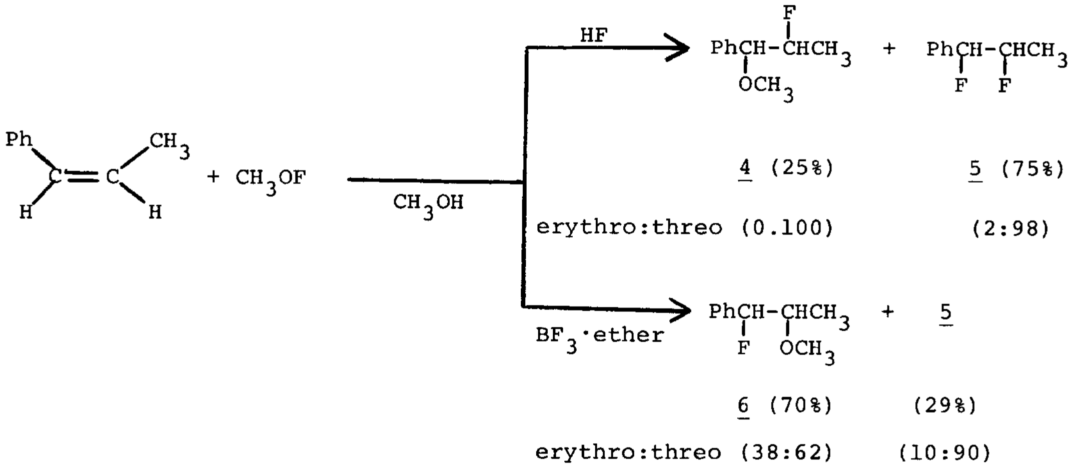
We would like to report the existence of methyl hypofluorite (CH_3OF) and describe some of its reactions. The chemistry of methyl hypoiodite,[1a] methyl hypobromite,[1b] and methyl hypochlorite[1b] is known.[2] Although perfluoroalkyl hypofluorites have been studied,[3] alkyl hypofluorites are unknown except for two theoretical calculations involving CH_3OF.[4]

Xenon difluoride (XeF_2) reacts with methanol to give CH_3OF. Methyl hypofluorite can be trapped by addition of an alkene to the reaction mixture. In the absence of alkene, disproportionation of CH_3OF to formaldehyde and HF is quantitative (eq.).[5]



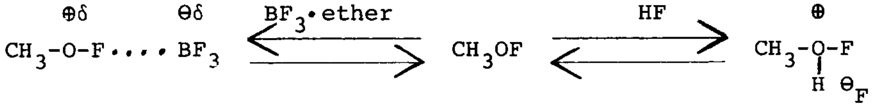
We were surprised to find that changing the acid catalyst produced different regioisomers when alkenes were added to intercept CH_3OF. Thus, reaction of CH_3OF with indene or 1-phenylpropene and hydrogen fluoride generated in situ gave compounds 1 or 4 in three hours.[6] However, addition of one equivalent boron trifluoride etherate as catalyst gave 3 or 6 in ten minutes.[7,8,9]





The possibility of a radical mechanism for the formation of 3 and 6 in the presence of boron trifluoride was ruled out on the basis of the following evidence: (1) Radical inhibitors such as 2,6-di-tert-butyl-4-methylphenol, isoamyl nitrite, or galvinoxyl do not inhibit the reaction. (2) Methyl crotonate does not intercept CH_3OF (α,β-unsaturated esters react slowly by an ionic process but rapidly by a radical pathway[10]). (3) Alkenes like 1-phenylpropene, indene, and 2-methyl-2-butene trap CH_3OF to give fluoro methoxy products, but 1-hexene is not sufficiently reactive to intercept CH_3OF and only formaldehyde is produced.

Products 3 and 6 can only be formed by an ionic reaction where CH_3OF functions as a positive oxygen electrophile.[11] Why should boron trifluoride complex with the fluorine of CH_3OF to produce a positive oxygen electrophile? Hard-Soft Acid Base Theory suggests that a mixed hard-soft ligature results in an unstable metal ion species, and therefore, boron trifluoride prefers to accept another hard fluoride ion rather than a softer base.[12] Thus, the boron trifluoride catalyst bonds to the fluorine of CH_3OF to give a positive oxygen electrophile (7), while proton catalysts[6] bind to the more basic oxygen of CH_3OF to induce an apparent fluorine electrophile (8). If CH_3OF does exist at room temperature, it collapses so rapidly to $CH_2{=}O$ and HF that reaction with very reactive alkenes seems unlikely. However, the protonated (8) or complexed (7) species are more plausible electrophilic intermediates, and they should be thermodynamically more stable than CH_3OF.[13]



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8

The reaction in methanol was found to be first order in XeF_2 and zero order in alkene over two or three half-lives. Therefore, XeF_2 is not reacting directly with the alkenes to form products. Kinetic data, and the formation of products 3, 6, and formaldehyde,[14] are consistent with 7 and 8 as the reactive species.

A fluoroxenon methoxide intermediate CH_3O-XeF (9) cannot be ruled out at this time. Stoichiometric reactions of XeF_2 with trifluoroacetic acid,[15a] nitric acid,[15a] fluorosulfuric acid,[15a,b,c] perchloric acid,[15c] and substituted benzoic acids[16] were shown to give xenon (II) fluoride compounds. Experiments to distinguish between intermediates 7, 8, or 9 are in progress.

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5. Aldehydes are formed by the oxidation of primary alcohols with XeF_2. See: I. Feher and M. Semptey, Mafy. Kem. Foly., 76, 141, (1970).
6. Addition of 0.02 eq. H_2SO_4 as catalyst gave product 1 or 4 and some difluorides in less than 30 minutes. Product 3 or 6 was not formed in these reactions.
7. The 360 MHz NMR data of products 2, 4, and 5 are in agreement with those reported in the literature. For 2 see: M. Zupan and A. Pollak, J. Org. Chem., 42, 1559. (1977). For 4 and 5 see: R. F. Merritt, J. Am. Chem. Soc., 89, 609, (1967).
8. Spectral data for 1, 3, and 6 are in excellent agreement with the assigned structures. There is about 5 percent of 1 and 4 formed in the BF_3 catalyzed reaction, presumably from the HF generated during the reaction.
9. All products were shown to be stable to analysis and reaction conditions.
10. D. R. Shellhamer, F. L. Heasley, J. E. Foster, J. K. Luttrull, and G. E. Heasley, J. Org. Chem., 42, 2141, (1977); V. L. Heasley, unpublished results.
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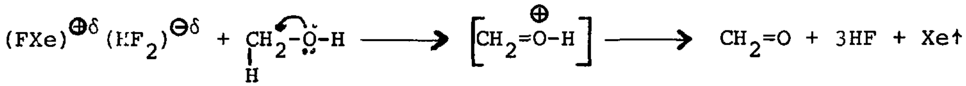
12. Tse-Loc Ho. "Hard and Soft Acids and Bases Principle in Organic Chemistry," pp. 21-22, Academic Press, New York, 1977.
13. The reaction was followed by quantitative iodometric titration and appearance of xenon gas formation. These results indicate that the stability of the intermediate is such that its concentration cannot be detected by these experiments. Thus an alkene more reactive than 1-hexene is required to trap this very reactive intermediate.
14. A referee suggested that Formaldehyde may be formed as follows:



$$(FXe)^{\oplus\delta}(HF_2)^{\ominus\delta} + \underset{H}{CH_2}-\ddot{O}-H \longrightarrow \left[CH_2=\overset{\oplus}{O}-H\right] \longrightarrow CH_2=O + 3HF + Xe\uparrow$$

Our data does not rule out a competing direct oxidation of methanol. However, products 3 and 6 cannot be formed via this pathway or by direct reaction of alkene with XeF_2.
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