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A COMPARISON OF THE REACTIVITY OF CF_3OX ($X = Cl, F$) WITH SOME SIMPLE ALKENES. EVIDENCE AGAINST ELECTROPHILIC FLUORINATION BY CF_3OF

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The chemistry of CF_3OF has been widely investigated, especially on its ability to serve as selective fluorination reagent. In many of these reactions it has been proposed that the reactions proceed by an electrophilic mechanism. In our work, reactions of CF_3OF and CF_3OCl were carried out with a variety of alkenes to compare the regio and stereoselectivity of the additions to the carbon-carbon double bonds. The observed addition products for CF_3OCl were consistent with an electrophilic mechanism involving syn addition where the positively polarized Cl is attached to the more nucleophilic carbon of the double bond. With CF_3OF , however, the observed addition products indicate a different regioselectivity and a low stereospecificity. The products are explicable on the basis of a free-radical mechanism where the additions are governed mainly by steric effects. Thus, our results go against the commonly held notion of 'electrophilic fluorination' by CF_3OF . Several examples will be presented and discussed.

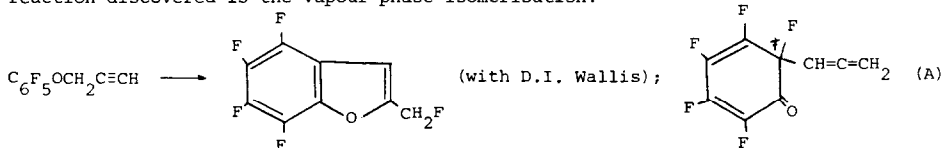
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THE FATE OF THE ORTHO-FLUORINE IN 3,3-SIGMATROPIC REACTIONS INVOLVING POLYFLUORO-ARYL and -HETEROARYL SYSTEMS

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Over the past twelve years, the thermal reactions of polyfluoroaryl prop-2-enyl-ethers and -thioethers and prop-2-ynyl ethers have been investigated. One truly remarkable reaction discovered is the vapour phase isomerisation:



In aromatic solvents at 150° , analogous 2-arylmethyl compounds are formed. The reactions proceed via the Claisen rearrangement \rightarrow (A) and it is the mechanism of cleavage of the aliphatic C-F bond[†] which is so interesting (homolytic and heterolytic fission reactions are possibilities).

In this Paper the results of some 3,3-sigmatropic shift reactions using some nitrogen-containing compounds will be presented. Some totally unforeseen products have been obtained in what are believed to be the most amazing reactions encountered in these investigations.