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SIGMATROPIC SHIFTS WITH POLYFLUOROAROMATIC COMPOUNDS

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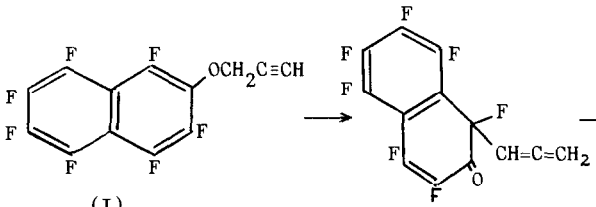
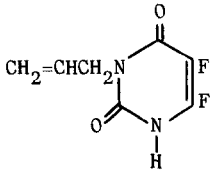
The prop-2-ynyl ether (I) is isomerised to the 2-fluoromethyl compound (III) at 360° in the vapour phase or at 150° in $CF_2ClCFCl_2$ via (II) the product of an initial [3,3] sigmatropic shift. In the presence of aromatic compounds ArH, the products are (IV) if the reactions are carried out in glass apparatus, but if nickel equipment is used, aromatic hydrocarbons largely behave as solvents and (III) is the main product once again.



(I) (II) (III) R = F; (IV) R = Ar

Evidence will be presented that the intriguing conversion of (II) to (III), in which the fluorine shifts from carbon to the fourth carbon along the chain, occurs via an ionic process. Also it will be shown that at 140°, glass is a most effective Lewis acid catalyst in promoting the conversion of (III) to (IV) with aromatic hydrocarbons.

Claisen rearrangement reactions have also been carried out with polyfluoropyrimidyl prop-2-enyl ethers. One synthetic sequence has yielded the uracil derivative (V).



(V)