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A SELECTIVE SUBSTITUTION OF UNACTIVATED TERTIARY HYDROGENS IN SMALL MOLECULES BY THE MOST REACTIVE ELEMENT – F_2

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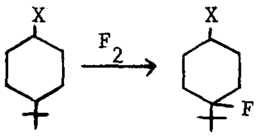
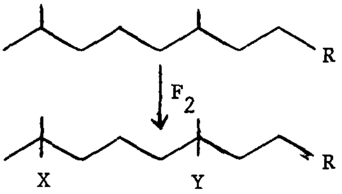
Only few works, mainly with paracids, which deal with ionic reactions on tertiary unactivated centers are described in the literature. Most of them involve only parafins since any oxygenated function complicates or even stops the reaction. On the other hand we have described some preliminary results from which it is evident that such a function does not prevent elemental fluorines from reacting and substituting unactivated tertiary hydrogens in many molecules.

Is the electronegative group necessary in the fluorination reactions as its absence is a condition for the reactions with peracids? We examined pairs of similar molecules with and without electronegative oxygenated functions: e.g.



X=H, OCOR, CH_3

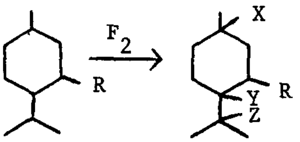


R=OCOR', X=F, Y=H

R=alkyl (X=F,Y=H or X=H,Y=F)

When competition is allowed one can see that the tertiary center in the parafin reacts much faster than the one in the oxygenated derivative.

Many times however this faster reaction is less selective than the one with compounds possessing electronegative end. The mechanism for such differences will be discussed.



R=OCOR' { X=Y=H, Z=F 60%
X=Z=F, Y=H 5% }

R=H all three mono fluoro derivatives.