CLAISEN REARRANGEMENTS OF FLUORINATED ENOL ETHERS: NEW ENTRIES TO α-MONOFLUORO AND α, α-DIFLUORO CARBOXYLIC ACIDS

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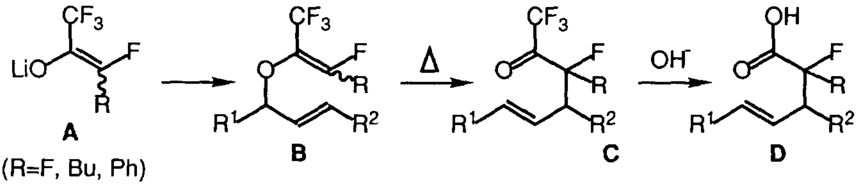
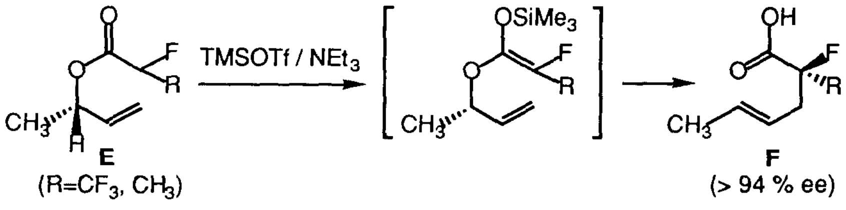
Reported herein are the two distinct types of Claisen rearrangement of fluorinated enol ether systems depicted by Eq. 1 and 2. The rearrangement of the fluorinated enol ethers of type **B**, prepared via *O*-allylation of lithium F-enolate **A** [1], was found to proceed at relatively low temperatures (40 ~ 65 °C) to afford, on hydrolysis, the α-monofluoro and α, α-difluoro acids **D**. Treatment of the chiral fluoro-esters of type **E** (100 % ee) with Me_3SiOTf / NEt_3 at 20 °C was found to provide the fluorinated carboxylic acids **F** in high enantiomeric purities. The unique features of the two Claisen processes, particularly the reversed HOMO-LUMO interaction in the former and the asymmetric transmission via the latter, will be discussed.



(1)



(2)

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[1] T. Nakai, et al., *Tetrahedron Lett.*, **29**, 4119 (1988); *J. Am. Chem. Soc.*, **112**, 4602 (1990).