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FREE-RADICAL ADDITIONS OF AMIDES AND AMINES TO F-ALKENES

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Radicals derived from amides and amines are nucleophilic in character and are, therefore, especially reactive towards F-alkenes. We find that free-radical additions to F-alkenes occur in high yield with a range of amides

and amines, giving 1:1 and poly-addition products, depending on the conditions and the reactant. The scope of these processes will be described

e.g.
$$\text{Et}_3N + \text{CF}_2 = \text{CFCF}_3 \xrightarrow{\gamma} (\text{CH}_3\text{CHR}_F)_3N \quad (R_F = \text{CF}_2\text{CFHCF}_3).$$

Conversions of the adducts lead to new fluorinated amines

e.g.
$$0 \xrightarrow{\text{CF}_2\text{CFHCF}_3} \xrightarrow{\text{LiAlH}_4} \xrightarrow{\text{CF}_2\text{CFHCF}_3} \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}_3\text{CON(CH}_3)\text{CH}_2\text{CF}_2\text{CFHCF}_3} \xrightarrow{\text{H}_2\text{SO}_4} \xrightarrow{\text{CH}_3\text{NHCH}_2\text{CF}_2\text{CFHCF}_3}$$

Cyclic amines and amides show pronounced stereoelectronic effects and evidence for these effects will be presented. The very ready formation of products from (1) is attributed to the special stabilisation of radical (2)

by very favourable conformational interaction of non-bonding pairs on nitrogen with the adjacent singly occupied molecular orbital.