# FREE RADICAL ADDITION OF F-ALKYL COMPOUNDS TO UNSATURATED CARBOXYLIC ANHYDRIDES AND THEIR DERIVATIVES

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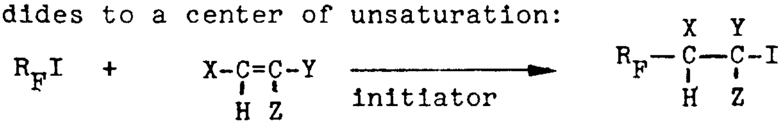
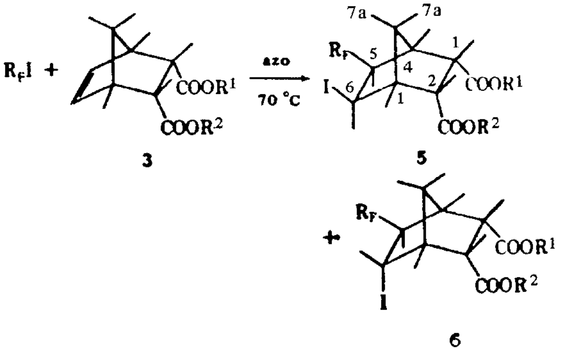
Many perfluoroalkyl-substituted organic compounds have been obtained through free radical addition of F-alkyl iodides to a center of unsaturation:



$$R_FI \quad + \quad X-\underset{H}{C}=\underset{Z}{C}-Y \xrightarrow[\text{initiator}]{} R_F-\overset{X}{\underset{H}{C}}-\overset{Y}{\underset{Z}{C}}-I$$

X, Y, and Z may include carbon chains, rings and various substituents. During the course of these synthetic studies--done over a span of several years--significant discoveries in mechanism and structure have been made.

Today I wish to report some free radical additions of F-alkyl iodides to unsaturated anhydrides and their derivatives. Among the compounds recently discovered are the norbornene products 5 to 10.



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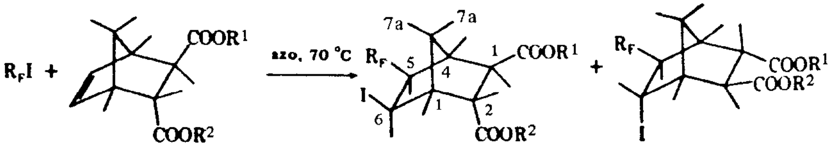

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Spectroscopic properties of the adducts varied with position and nature of the substituents. Somewhat surprisingly, the chemical shift of protons on the $R_F$ side of the molecule was affected by changes in substituents on the other side of the molecule.

Various reactions of the adducts were studied. Unusual stereospecificity in lactone formation and in base-induced cyclization to nortricyclene derivatives was observed. Only when the iodo group was in an endo position did these reactions occur.

Analogous free radical addition of fluorinated thiols ($R_FCH_2CH_2SH$) to norbornene anhydrides produced a series of 5-polyfluoroalkylthionorbornane-2,3-dicarboxylic acid anhydrides(11, 12; U S Patent 3,989,725 (1976). As in previous studies the entering group took up the exo position exclusively. Reaction with acids, esters or norbornenecarboxylic imides of the fluorinated thiol also gave analogous products.

Because of the hydrophobic nature of the F-alkyl groups the entire range of compounds displayed pronounced surface-activity and would appear to have utility in a wide range of applications.

**Scheme III. Stereoselective Radical Addition of Iodo-*F*-alkanes to Isomeric** 5-Norbornene-2,3-dicarboxylic Anhydrides