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SOME APPROACHES TO THE SYNTHESIS OF FLUORINE-CONTAINING ALCOHOLS AND ESTERS

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Among F-containing alcohols only trifluoroethanol, the so-called 'telomer alcohols' [$H(CF_2CF_2)_nCH_2OH$], and certain esters of 2-(F-alkyl)ethanols and 3-(F-alkyl)propanols, have achieved commercial importance. Their utilization has been limited by lack of suitable methods of synthesis and by their high cost. Yet F-containing alcohols and their esters have unique properties, and comprise a versatile class of compounds. It is to be noted that completely fluorinated esters have recently become available.

F-substituted alcohols must be made by special, less well-known methods. Routes based on tetrafluoroethylene (TFE) as starting material are of current interest. F-alkyl iodides (R_FI) are made in two steps from TFE. Reaction of R_FI with ethylene gives 2-(F-alkyl)-1-ethanes, and under suitable conditions, higher telomers in high yield. Displacement of iodine of $R_FCH_2CH_2I$ by an acyloxy group gives an ester, such as acrylate or fumarate of the F-substituted alcohol. Several methods have been discovered for this process, most recently by reaction with N-methylformamide or N,N-dimethylformamide and water. Free radical addition of R_FI to vinyl acetate and subsequent reduction provided 2-(F-alkyl)ethanols in excellent yield. Similar steps using allyl acetate gave both 3-(F-alkyl)-1-propanols and 3-(F-alkyl)-2-propanols; the latter compound also was formed by hydrolysis of the initial adduct. These various methods will be outlined and some recent results in a study of O-alkylation will be presented.

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A NEW METHOD FOR ELIMINATING CARBONYL FLUORIDE FROM α-TRIFLUOROMETHYLATED ACYL FLUORIDES

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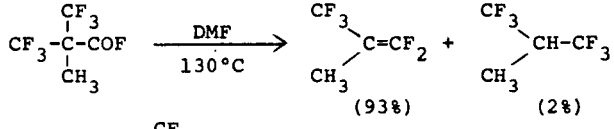
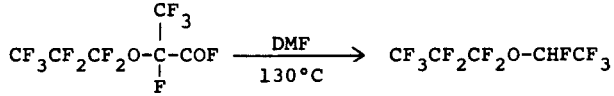
Carbonyl fluoride was found to be eliminated from α-trifluoromethylated acyl fluorides when they are treated with amides, e.g., dimethylformamide, dimethylacetamide, and dimethylthioamide, under mild condition, e.g.,





Possible reaction mechanism will be discussed.