

PHOTOADDITION REACTIONS OF FLUOROOLEFINS WITH DIOLS AND CYCLIC ETHERS

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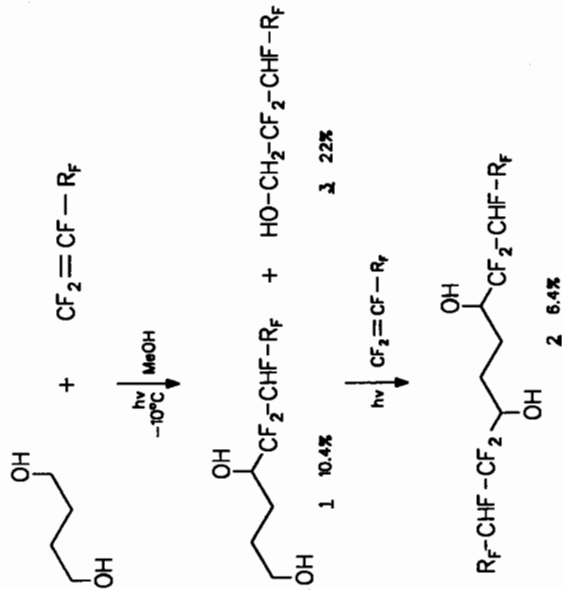
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Abstract: Fluoroalkylation of aliphatic diols, tetrahydrofuran and 1,3-dioxolanes with perfluoroolefins under photochemical initiation was studied. The aim of the study was the preparation of fluoroalkylated diols as intermediates for special fluorinated monomers. Fluoroalkylation was only partly successful in the case of 1,4-butanediol and quite successful with tetrahydrofuran and 2,2-dimethyl-1,3-dioxolane. The fluoroalkyl diols obtained were converted to monomethacrylates that are amphiphilic monomers.

Fluoroalkylated diols are intermediates for the preparation of mono- and bifunctional monomers and polymers such as poly(meth)acrylates, polyurethanes and polyesters. Some cyclic ethers can be transformed into diols by ring cleavage, e.g. tetrahydrofuran and 1,3-dioxolane derivatives. The aim of the study was to use aliphatic diols and their cyclic ethers for fluoroalkylation, which proceeds by a radical addition to fluoroolefins, to obtain fluoroalkylated diols. A radical chain mechanism was confirmed for the photo-induced addition of alcohols to fluoroolefins¹. For fluoroalkylation we used perfluoroolefins with terminal double bond which, as generally known, do not telomerize under radical conditions. The reactions were initiated photochemically.

Aliphatic alcohols can be fluoroalkylated under the atmospheric pressure by UV initiation with good results^{2,3}. Hence, the simplest route seemed to be photochemically induced fluoroalkylation of aliphatic diols. The reactions were carried out at low temperatures under atmospheric pressure. However, the results were not satisfactory: 1,2-ethanediol and 1,2-propanediol gave no products, 1,4-butanediol reacted with low conversion to mono- (1) and bis-fluoroalkylated product (2) while the yield of fluoroalkylation of methanol (3), which served as a solvent for the diols and which exhibited a low reactivity in the fluoroalkylation⁴, was even higher. The yields of fluoroalkylated 1,4-butanediol and fluoroalkylated methanol

Scheme 1

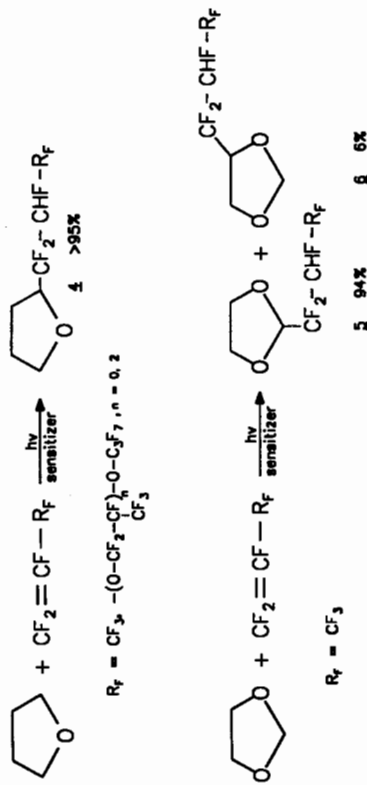


reflect the relative reactivity of both starting hydroxy compounds in fluoroalkylation. The complex of reactions mentioned above is depicted in Scheme 1.

Cyclic ethers can be fluoroalkylated in free-radical addition reactions with fluoroolefins which are initiated by peroxides^{5,6}, or gamma-radiation⁷. The ability of five-membered cyclic ethers to undergo fluoroalkylation under photochemical initiation was tested using tetrahydrofuran. This compound reacted easily under photochemical conditions with methyl 2,3,3-trifluoroacrylate⁸ which models properties of a terminal perfluoroolefin.

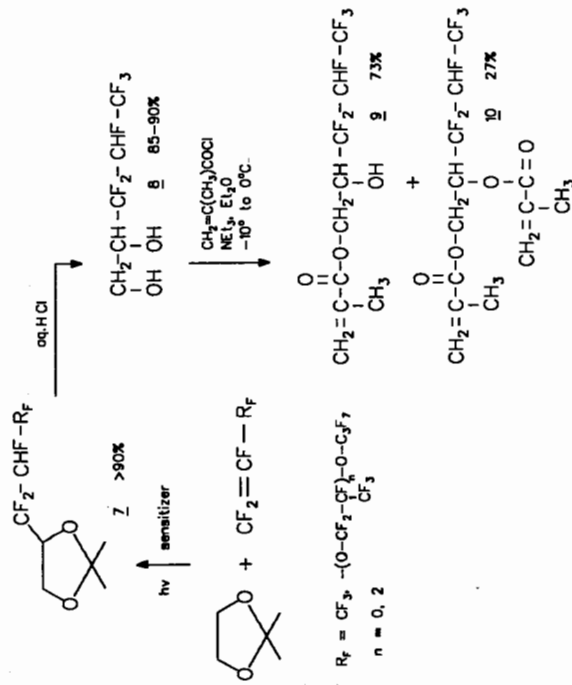
Tetrahydrofuran (THF) was also easily perfluoroalkylated with hexafluoropropene or with trifluorovinyl perfluoropolyethers in position 2 with 100% regioselectivity (product **4**). The conversion of fluoroolefins was complete in the presence of acetone as a photochemical triplet sensitizer.

Scheme 2



1,3-Dioxolane was fluoroalkylated with perfluoroolefins predominantly in position 2 (94%, product **5**) and in position 4 (6%, product **6**); its reactivity was high and the conversion of hexafluoropropene was complete. The reactions are depicted in Scheme 2.

Scheme 3



On the basis of these results we performed fluoroalkylation of 2,2-dimethyl-1,3-dioxolane in which position 2 is blocked for a displacement reaction. The fluoroalkylation took place in position 4 with 100% regioselectivity and with total conversion of fluoroolefins (product **7**); preparative yields were higher than 90%.

Hexafluoropropyl derivative **7** was converted to fluoroalkylated ethylene glycol **8** by acid hydrolysis with hydrochloric acid in preparative yield of 85-90%. Diol **8** was then submitted to monoacylation with methacryloyl chloride. This reaction was performed previously⁸ with 100% chemoselectivity. We obtained the monoacylated diol **9** in 73% relative yield together with 27% dimethacrylate **10**. In diol **8**, only the primary hydroxy group was acylated. The transformations of 2,2-dimethyl-1,3-dioxolane to methacrylates **9** and **10** is depicted in Scheme 3. Monoacrylate **9** represents an amphiphilic monomer that can be used, after polymerization, for contact lenses.

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