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SOME CHEMISTRY OF 2-CHLOROPERFLUORO-1,3-BUTADIENE AND N,N-DIETHYL-4-CHLORO-3,4,4-TRIFLUORO-2-BUTENAMIDE

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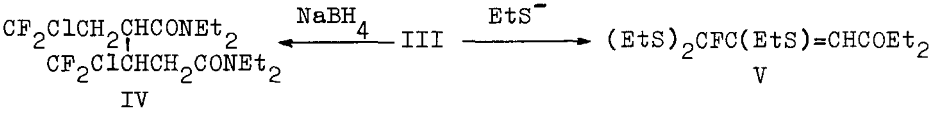
The mechanism of a novel photochemical synthesis of 2-chloroperfluoro-1,3-butadiene will be discussed and the regioselective course of addition of alkoxides or secondary amines on CF_2=CCl-grouping of I shown.

$$\underset{\text{I}}{CF_2{=}CFCCl{=}CF_2} \xrightarrow{Et_2NH} CF_2{=}CFCHClCF_2NEt_2 \xrightarrow{H_2O} \underset{\text{II}}{CF_2{=}CFCHClCONEt_2}$$

In the reaction of butadiene I with diethylamine N,N-diethyl-2-chloro-3,4,4-trifluoro-3-butenamide, (II) arises which undergoes easily an allylic rearrangement giving N,N-diethyl-4-chloro-3,4,4-trifluoro-2-butenamide (III) In contrast to II, amide III does not undergo an allylic rearrangement apparently due to the

$$\text{II} \xrightarrow{180^\circ C} \underset{\text{III}}{CF_2ClCF{=}CHCONEt_2} \xrightarrow{Nu:} \underset{Nu{=}\ MeO,\ Me_2N,\ Me,\ Ph}{CF_2ClCNu{=}CHCONEt_2}$$

conjugation of carbon-carbon double bond with the amide function and its reactions with nucleophiles (sodium methoxide, dimethylamine, Grignard reagents) proceed as a vinyl substitution of the fluorine atom in position 3. The reactions of amide III with sodium borohydride or sodium ethanthiolate have a more complicated course. In the first case N,N,N',N'-tetraethylamide of 2-(2-chloro-2,2-difluoroethyl)-3-chlorodifluoromethylpentanedioic acid (IV) and in the second one N,N-diethylamide of 3,4,4-tris(ethylthio)-4-fluoro-2-butenoic acid (V) is formed.



$$\underset{\text{IV}}{\begin{matrix}CF_2ClCH_2\underset{|}{C}HCONEt_2\\ CF_2ClCHCH_2CONEt_2\end{matrix}} \xleftarrow{NaBH_4} \text{III} \xrightarrow{EtS^-} \underset{\text{V}}{(EtS)_2CFC(EtS){=}CHCOEt_2}$$