ADDITION OF SULFENYL CHLORIDES TO α-FLUOROACRYLATES

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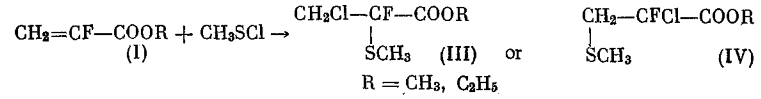
The addition of sulfenyl halides to α-halo acrylates and related systems has not been described, except for a patent communication on the reaction of alkylsulfenyl chlorides with α-chloroacrolein [1]. We studied the addition of methylsulfenyl chloride (I) and phenylsulfenyl chloride (II) to α-fluoroacrylic acid esters. The reaction of sulfenyl chloride (I) with the methyl and ethyl α-fluoroacrylates in CCl_4 is accompanied by slight exothermic heat, and the addition products are formed in quantitative yields. The presence of a single signal in the ^{19}F NMR spectrum of each of these adducts testifies to the fact that only one of two possible isomers, either (III) or (IV), is formed:

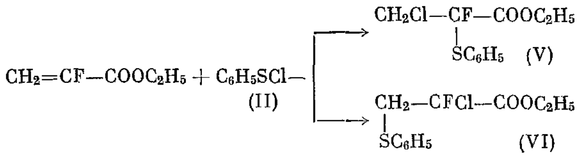


$$\underset{(I)}{CH_2{=}CF{-}COOR} + CH_3SCl \rightarrow \underset{SCH_3\ \ (III)}{CH_2Cl{-}CF{-}COOR} \text{ or } \underset{SCH_3}{CH_2{-}CFCl{-}COOR}\ (IV)$$

$R = CH_3, C_2H_5$

The ^{19}F NMR spectrum of the adduct of sulfenyl chloride (I) with $CH_2 = CFCOOCH_3$ is shown in Fig. 1. The ^{19}F signal represents a doublet of doublets. It is impossible to distinguish between isomers (III) and (IV) from the character of this signal, since it will be a doublet of doublets in both cases due to the diastereotopic nature of the protons of the β-carbon atom. In the NMR spectrum the signals of these protons are found in the range 3.22-3.62 ppm, which on the basis of the data given in [2, 3] makes it possible to assign them to the CH_2Cl group. The signal from the CH_2S group, which should be found in the 2.8 ppm region, is absent. The spectrum of this adduct remains unchanged either during storage or when the adduct is distilled. It is known that α-alkthio compounds are thermodynamically more stable than the β-isomers [2]. The above given data make it possible to assume that the adducts of the alkyl α-fluoroacrylates with sulfenyl chloride (I) have the (III) structure.

The reaction of sulfenyl chloride (II) with ethyl α-fluoroacrylate proceeds slowly at room temperature and is ended after 25 days (checked by the ^{19}F NMR method). The spectrum of the adduct contains two fluorine signals, with an intensity ratio of about 3 : 1 (Fig. 2). The spectrum fails to change when the adduct is distilled or stored for a long time. The assignment of the signals in this spectrum was made by analogy with the spectrum shown in Fig. 1; as a result, the α-(phenylthio) isomer (V) predominates. It is most probable that isomers (V) and (VI) under ordinary conditions are not converted into each other, and their formation is the consequence of the dual orientation in the addition of sulfenyl chloride (II) to ethyl α-fluoroacrylate:



$$\underset{(II)}{CH_2{=}CF{-}COOC_2H_5 + C_6H_5SCl} \begin{cases} \rightarrow \underset{SC_6H_5\ \ (V)}{CH_2Cl{-}CF{-}COOC_2H_5} \\ \rightarrow \underset{SC_6H_5}{CH_2{-}CFCl{-}COOC_2H_5}\ (VI) \end{cases}$$

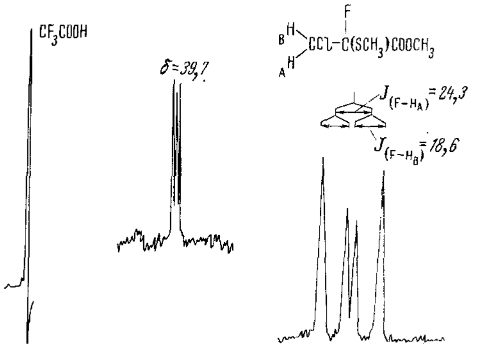


Fig. 1. ^{19}F NMR spectrum of methyl α-fluoro-α-methylmercapto-β-chloropropionate (56.4 MHz, external standard = CF_3COOH).

The numerous data that exist in the literature regarding the orientation of the addition of sulfenyl chlorides to olefins

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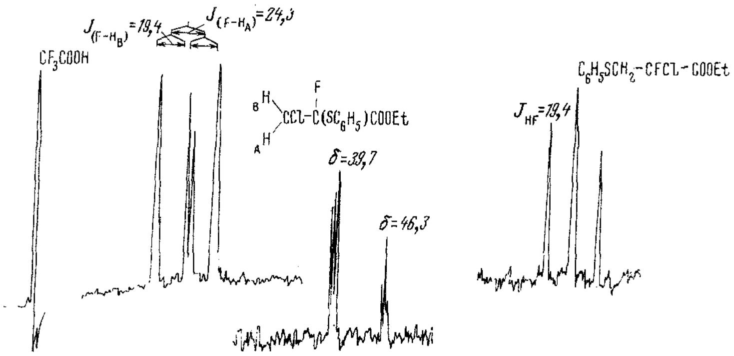

Fig. 2. ^{19}F NMR spectrum of mixed isomers, formed as the result of adding phenylsulfenyl chloride to ethyl α-fluoroacrylate (56.4 MHz, external standard = CF_3COOH).

and acrylic systems show that this is not a simple problem. Thus, according to [2], the addition of sulfenyl chloride (I) to an acrylic acid derivative, with a kinetic control of the reaction, leads to a mixture of adducts with a predominance of the α-chloro-β-(methylmercapto) isomer, while a mixture with a predominance of the thermodynamically more stable α-(methylmercapto)-β-chloro isomer is obtained on storage or when distilled. At the same time, in a number of papers on the addition of this sulfenyl chloride to α-substituted acrylic systems it was shown that in this case the α-(methylmercapto)-α-chloro isomers are formed immediately, which subsequently fail to isomerize. For example, the addition of sulfenyl chloride (I) to methacrylic acid and its anilide proceeds in specifically this manner [3, 4]. Consequently, in the discussed reaction the α-fluoroacrylic acid esters behave in the same manner as the methacrylic acid derivatives.

EXPERIMENTAL METHOD

Ethyl α-Fluoro-α-methylmercapto-β-chloropropionate (IIIb). With cooling in ice water, to 10.4 g of ethyl α-fluoroacrylate in 5 ml of CCl_4 was added a solution of sulfenyl chloride (I) in CCl_4 (obtained from 7 g of dimethyl disulfide and 10 g of sulfuryl chloride in 15 ml of CCl_4). The mixture was allowed to stand at ~20°C for a day, after which the solvent was distilled off, and the residue was vacuum-distilled. We obtained 16 g (90%) of adduct (IIIb), bp 72.5-73.5° (3.5 mm); n_D^{17} 1.4860. Found: C 35.78; H 5.07; F 8.52; Cl 18.53%. $C_6H_{10}FClO_2S$. Calculated: C 35.91; H 5.02; F 9.42; Cl 17.67%. Infrared spectrum: 1750, 1770 (C=O) cm^{-1}.

Methyl α-Fluoro-α-methylmercapto-β-chloropropionate (IIIa) was obtained in a similar manner, bp 73.5-75° (8 mm). The compound by treatment with aqueous ammonia was converted to the amide, mp 89-91° (from hexane). Found: F 11.21; N 8.28%. $C_4H_7FClOSN$. Calculated: F 11.07; N 8.16%.

Reaction of Phenylsulfenyl Chloride with Ethyl α-Fluoroacrylate. To 7.7 g of ethyl α-fluoroacrylate in 5 ml of CCl_4 was added 9 g of sulfenyl chloride (II) in 8 ml of CCl_4. The mixture was allowed to stand at ~20° for 25 days (until the signal of the α-fluoroacrylate in the ^{19}F NMR spectrum had disappeared). The residue from distilling off the solvent was vacuum-distilled. We obtained 12.4 g of mixed isomers (V) and (VI), bp 154-156° (9 mm). Found: C 50.91; H 4.57; F 6.76%. $C_{11}H_{12}FClO_2$. Calculated: C 50.30; H 4.60; F 7.24%. Infrared spectrum: 1740, 1765 (C=O) cm^{-1}.

CONCLUSIONS

α-Fluoroacrylates add sulfenyl chlorides in such a manner that the methylthio group adds exclusively, and the phenylthio group adds predominantly, to the α-carbon atom.

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