REACTION OF FLUORINATED β-DICARBONYL COMPOUNDS WITH ETHYLMERCAPTAN

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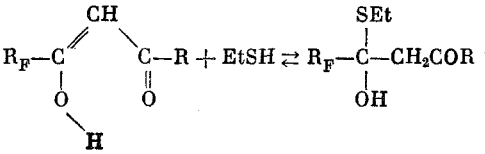
UDC 542.91:547.446:547.269.1

In the presence of HCl, β-dicarbonyl compounds (DCC) react with EtSH to form esters of β,β-di(ethylmercapto)acids [1, 2] or β,β-di(ethylmercapto)ketones [3]. The first stage of this reaction is apparently the addition of EtSH to the keto group. However, it is not clear at which of the two nonequivalent carbonyl groups in nonsymmetrical dienes the addition occurs nor which tautomeric form (keto or enol) of a DCC will react with mercaptans.

In the case of fluorinated compounds (FDCC) it has been shown by NMR that an equilibrium mixture is formed of the FDCC and its adduct with water or alcohol. Also, addition of the O-nucleophile occurs through the enol form of the FDCC [4, 5] and the rate of addition of the nucleophile exceeds the rate of establishment of the keto–enol equilibrium [6].

Study of the indicated equilibrium by NMR methods is possible only for FDCC derivatives due to the increased lifetime of the adducts. For DCC this is not possible because of the short lifetime on the NMR scale. In our work, using ^{1}H, ^{19}F, and ^{13}C NMR methods we have studied the reaction of ethanethiol with fluorinated β-ketoesters (I), (III), and (V) (FKE) and β-diketones (II), (IV), and (VI) (FDK) in chloroform. We have shown that addition occurs at the enol group bound to the fluoroalkyl substituent



$R_F = HCF_2$ (I), (II); CF_3 (III), (IV); $H(CF_2)_4$ (V), (VI); $R = CH_3$ (II), (IV), (VI); OCH_3 (I), (III), (V).

In the PMR spectra of solutions of FKE (I), (III), or (V) there are characteristic signals for the methine (5.50-5.64 ppm) and methylene (3.71-3.76 ppm) protons and also the protons of the methoxy groups (3.76-3.83 ppm) corresponding to the keto and enol forms of I and III (Table 1). An exception is FKE (V) which exists wholly in the enol form.

On addition of EtSH to solutions of FKE (I) and (III), there appears a signal at 2.81 ppm for the methylene groups of the β-hydroxy-β(ethylthio)fluorocarboxylic acids formed ((Ia), (IIIa); Table 1). In addition, the intensity of the methine signals for the enol form of the products FKE (I) or (III) decrease but the signals for the protons of the methylene remain unchanged. In the case of 4,4-difluoroacetoacetic ester (I) the methylene protons of the adduct (Ia) (Table 1) give an AB system due to the proximity to the asymmetric C atom. The PMR spectrum of FKE (V) remains unchanged after addition of EtSH.

In the ^{19}F NMR spectrum taken over a period of 1 h after addition of EtSH to solutions of FKE there also appear signals for the adducts (Ia), (IIIa) (Table 1) with simultaneous decrease in the intensity of the signals for the enol form.

In the case of 4,4-difluoroacetoacetic ester the relative enol-to-keto ratio in deuterochloroform solution is 0.62. One hour after the addition of EtSH this ratio falls to 0.47 and after 24 h to 0.29. This is in agreement with the results of investigation of the reaction of FKE with hydroxy-containing nucleophiles [5] and supports the conclusion that addition of EtSH proceeds through the enol form of FKE.

Chemistry Institute, Ural Science Center, Academy of Sciences of the USSR, Sverdlovsk. M. V. Lomonosov State University, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2293-2298, October, 1985. Original article submitted May 22, 1984.

0568-5230/85/3410-2123$09.50

TABLE 1. ^{1}H and ^{19}F NMR Spectra of Products of Reaction of Fluorinated β-Ketoesters with Ethylmercaptan in Deuterochloroform* (δ, ppm, J, Hz, PMR — TMS, ^{19}F NMR — HFB)

Number	Compound	PMR spectrum					^{19}F NMR spectrum			Content of adduct unchanged after 24 h, %
		OCH_3	CH_2	CH	C_2H_5	$H(CF_2)_n$ J_{HCF_2}, $J_{H(CF_2)_2}$	$H(CF_2)_n$ J_{HCF_2}	CF_3	CF_2	
(I)	$HCF_2COCH_2CO_2CH_3$	3,76 (k)† 3,80 (e)	3,71	5,5	–	5,88 t (k), 53,3 6,03 t (e), 53,3	34,19 (k); 53,2 35,68 (e); 53,2		–	
(Ia)	$HCF_2C(SC_2H_5)(OH)-CH_2CO_2CH_3$	3,79	2,83 $J_{AB}=55$ $\Delta_{AB}=0,1$	AB system	1,33 2,56	5,74 t, 54	33,16, 54			77
(III)	$CF_3COCH_2CO_2CH_3$	3,79 (k) 3,83 (e)	3,76	5,64				83,03 (k) 87,4 (e)		
(IIIa)	$CF_3C(SC_2H_5)(OH)-CH_2CO_2CH_3$	3,82	2,84		1,18 2,56			81,38		89
(V)	$H(CF_2)_4COCH_2CO_2CH_3$	3,83 (e)		5,6		6,04 tt 51,4; 4,6	24,91 d, 51,4		32,33 37,67 42,01	
(Va)	$H(CF_2)_4C(SC_2H_5)(OH)-CH_2CO_2CH_3$	Adduct signal not observed								

*NMR spectra of β-ketoesters (I), (III), and (V) and adducts (Ia), (IIIa), (Va) measured for reaction mixtures.

†k — keto; e — enol.

TABLE 2. ^{1}H and ^{19}F NMR Spectra of Products of Reaction of Fluorinated β-Diketones with Ethylmercaptan in Deuterochloroform* (δ, ppm, J, Hz, PMR — TMS, ^{19}F NMR — HFB)

Number	Compound	PMR spectrum, 24°C					^{19}F NMR spectrum			Content of adduct measured after 24 h, %
		CH_3	CH	CH_2	C_2H_5	$H(CF_2)_n$ J_{HCF_2}, $J_{H(CF_2)_2}$	$H(CF_2)_n$ J_{HCF_2}, Hz	CF_3	CF_2	
(II)	$HCF_2COCH_2COCH_3$	2,19	5,90	–	–	5,91 t, 53,3	34,98 d, 53,3			
(IIa)	$HCF_2C(OH)(SC_2H_5)-CH_2COCH_3$	2,29	–	2,89	1,42	5,74 , 55,1	33,06 d, 55,1			19
(IV)	$CF_3COCH_2COCH_3$	2,22	5,93					85,35		
(IVa)	$CF_3-C(OH)(SC_2H_5)-CH_2COCH_3$	2,32		2,9	1,41			81,2		25
(VI)	$H(CF_2)_4COCH_2COCH_3$	2,21	5,97	–	–	6,12 dd, 51,8, 5,14	25,06 d, 51,8	–	37,83 32,79 41,19	
(VIa)	$H(CF_2)C(OH)(SC_2H_5)-CH_2COCH_3$	Adduct signal not observed								

*NMR spectrum of β-diketones (II), (IV), (VI) and adducts (IIa), (IVa) measured for reaction mixtures.

TABLE 3. ^{13}C NMR Spectra of Products of Reaction of Fluorinated β-Diketones with Ethylmercaptan in Deuterochloroform*

Number	Compound	δ, ppm							J, Hz		
		C¹	C²	C³	C⁴	C⁵	C⁶	C⁷	$J_{1\text{-}F}$	$J_{5\text{-}F}$	$J_{3\text{-}F}$
(II)	$\overset{1}{H}\overset{2}{C}F_2\overset{3}{C}O\overset{4}{C}H_2\overset{5}{C}OCH_3$	109,6	180,2	96,8	195,1	25,5			246,8	25,7	2,9
(IIa)	$HCF_2\overset{\overset{OH}{\vert}}{\overset{3}{C}}-\overset{4}{C}H_2\overset{5}{C}OCH_3$ $\vert\ 6\ 7$ $S-CH_2CH_3$	114,7	57,7	43,5	210,1	22,4	32,5	17,1	248,3	23,1	
(IV)	$\overset{1}{C}F_3\overset{2}{C}O\overset{3}{C}H_2\overset{4}{C}O\overset{5}{C}H_3$	117,5	175,7	93,4	194,3	25,2			283,5	36,6	1,5
(IVa)	$\overset{1}{C}F_3\overset{\overset{OH}{\vert}}{\overset{3}{C}}-\overset{4}{C}H_2\overset{5}{C}OCH_3$ $\vert$ $S\overset{6}{C}H_2\overset{7}{C}H_3$	124,4	57,7	84,6	209,8	22,4	32,6	17,1	282,8	34,13	

*^{13}C NMR spectra of β-diketones (II) and (IV) and adducts (IIa) and (IVa) measured for reaction mixtures.

The adduct content, measured 24 h after addition of EtSH, was found to be 77 (Ia), 89 (IIIa), and 0% (Va) (see Table 1), i.e., as in the case of hydroxy nucleophiles, the amount of adduct falls with increasing length of the fluoroalkyl substituent.

The fluorinated β-diketones (II), (IV), and (VI) are fully enolized and in their PMR spectra in deuterochloroform there are observed signals for the methine protons (5.90-5.97 ppm, Table 2) and methyl groups (2.19-2.22 ppm). Upon addition of EtSH to solutions of FDK (II), (IV), and (VI) in deuterochloroform there appear signals at 2.8-2.9 ppm for the methylene proton groups in the adducts (IIa) and (IVa) formed as well as signals for the protons of the ethylmercapto groups. The intensity of the signals for the methine protons and the methyl groups of FDK (II) and (IV) also decrease but the PMR spectrum of FDK (VI) remains unchanged. Peaks for the starting FDK and adducts (IIa) and (IVa) are also seen after the addition in the ^{19}F NMR spectrum.

The adduct content of (IIa) and (IVa) measured 24 h after addition of EtSH is 19-25%. In general (as in the case of the reaction of FDK with hydroxy nucleophiles [4]) lengthening of the fluoroalkyl substituent leads to decrease in the adduct content. The octafluorobutyl-substituted diketone does not react with EtSH at all (Table 2).

In the ^{13}C NMR spectra it is seen that formation of adducts (IIa) and (IVa) (Table 3) is accompanied by shifts of about 120 ppm to high field for the C^2 signal (assignment of signals being made on the basis of the spin–spin coupling between ^{13}C and ^{19}F nuclei). This indicates a change from sp^2 to sp^3 hybridization on addition of EtSH at the carbon atom connected to the fluorinated substituent of greatest electron acceptor property.

EXPERIMENTAL

β-Diketones (II), (IV), and (VI) were prepared according to [7] and β-ketoesters (I), (III), and (V) according to [8]. The ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a Jeol JNMFX-100 instrument operating at 100 MHz (^1H, ^{19}F) and 25 MHz (^{13}C) using $CDCl_3$ solvent with TMS (^1H, ^{13}C) or hexafluorobenzene (HFB, ^{19}F) as internal standards. Solution concentrations were 1 M and the ratio of reagents 1:1. After EtSH addition the solutions were held for 24 h at ~20°C. All values were obtained by twofold integration of ^1H or ^{19}F spectral signals with an error of ±3%.

CONCLUSIONS

Addition of ethylmercaptan to fluorinated β-diketones proceeds through the enol form at the carbon atom bound to the fluoroalkyl substituent; with fluorinated β-ketoesters it is also the enol form which reacts with the mercaptan.

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