A. V. Fokin, V. A. Komarov, A. F. Kolomiets, A. I. Rapkin, and T. M. Potarina UDC 542.91:547.465.5'161-38:546.49

Difluoronitroacetic acid (I) is one of the strongest carboxylic acids ($K_a = 97,000 \cdot 10^{-5}$ [1]) and, in contrast to nitroacetic acid, is stable when stored, heated moderately, and in aqueous solutions. A large number of (I) derivatives has been described: esters, acid halides, amides, etc. [1, 2]. However, the salts of this acid have not been obtained up to now. It is easily decarboxylated in the presence of basic compounds to give difluoronitromethane [2]. An analysis of the literature discloses that the synthesis of only the highly dissociated salts of (I) has been attempted previously. Consequently, it seemed of interest to evaluate the possibility of using the cations of the heavy metals, in particular mercury, as the counterion.

It was shown by us that (I) reacts smoothly with either mercuric acetate or yellow mercury oxide. The pure Hg salt of difluoronitroacetic acid (II) is formed in the latter case, which is easily separated from the starting products.

$$2O_2NCF_2CO_2H + HgO \xrightarrow[-H_1O]{} (O_2NCF_2CO_2)_2Hg$$
(I)
(II)

The reaction can be run in water and various organic solvents. The most suitable proved to be ether, in which (II) dissolves as it is formed. After evaporation using a water-jet pump the salt separates as solvates of variable composition with water and the solvent. The latter are removed by azeotropic distillation with CH_2Cl_2 and by drying in vacuo (1 mm) over P_2O_5 .

Pure (II) is a white crystalline compound that decomposes at 145-150°C. In the IR spectrum of (II) the ν (CO) is shifted toward higher frequencies by ~150 cm⁻¹ when compared with the acid and its esters. This testifies to a strong shift of the electron density from the carbonyl group to the Hg atom. At the same time, ν_{as} (NO₂) is also shifted toward higher frequencies by ~40 cm⁻¹. The signal in the ¹⁹F NMR spectrum is shifted downfield when compared with the other derivatives of the acid. All of this shows that quite strong donor—acceptor (DA) interaction exists between the Hg atom and the O₂NCF₂CO₂ group, in which the Hg atom functions as an electron acceptor.

Salt (II) is moderately soluble in water, ether, polar halohydrocarbons, and benzene, and is readily soluble in acetonitrile. The salt does not hydrolyze when dissolved in water. Intense decomposition occurs only above 80°, the character of which was not studied by us. In the presence of strong bases the salt undergoes decarboxylation, which is customary for such compounds, to give diffuoronitromethane.

$$(II) - \frac{\begin{bmatrix} Na_2CO_1, H_1O \\ [HgCO_3] \end{bmatrix}}{\begin{bmatrix} Na_2O_1, H_2O \\ Na_2OH, H_2O \end{bmatrix}} \rightarrow O_2NCF_2H$$

Salt (II) readily reacts in ether with alkyl iodides and the lower alkyl bromides, and also with allylic bromides and chlorides. In these reactions the salt apparently reacts as the solvates with the solvent. For this reason the process is complicated by the side formation of ethyl difluoronitroacetate and the corresponding alkyl ethyl ether by the following overall scheme:

(II) + RHal
$$\xrightarrow{\text{Et}_{2}O}_{-\text{HgHal}} O_2 \text{NCF}_2 CO_2 R + O_2 \text{NCF}_2 CO_2 Et + ROEt$$

R = Me, Et, *n*-Pr, *n*-Bu; Hal = I, Br

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TABLE 1. Propert	ies of Sy	nthesize	d Comp	ounds									
	bp.°C	50	20		Found,	0/0		Empirical	Ŭ	alculate	ed, <i>%</i>		19F NMR
Compound	of Hg)	4	Qu	IJ	н	E.	z	formula	υ	н	ſs,	z	tandard = CE.COOH
(02NCF2C02)2Hg	mp 149 (decompn)	1	I	10,21	1	15,50	5,47	C,H,HgN ₃ O ₈	9,98	1	15,80	5,82	12,70
O2NCF2CO2Me *	113-114	1,402	1,3553	23,49	1,57	24,61	9,32	C ₃ H ₃ F ₂ NO ₄	23,23	1,94	24,52	9,03	15,43
O2NCF2CO2Et *	125-127	1,298	1,3601	28,67	3,08	22,83	8,04	C ₄ H ₅ F ₂ NO ₄	28,40	2,96	22,49	8,28	15,27
O2NCF2CO2Pr-n *	140142	1,231	1,3720	33,02	3,81	21,00	7,57	C ₅ H ₁ F ₂ NO ₁	32,79	3,83	20,77	7,65	15,23
0_NCF2C0_B0-n *	158	1,187	1,3781	36,82	4,93	19,51	7,03	CeH _s F ₂ NO	36,55	4,57	19,29	7,11	15,25
02NCF2CO2CH2CH=CH2*	69 (80)	1,280	1,3825	32,96	2,85	20,90	8,15	C ₃ H ₄ F ₂ NO ₄	33,15	2,76	20,99	7,74	15,15
O ₂ NCF ₂ CO ₂ CH ₂ Ph	70-72(1)	1,321	1,4660	46,52	3,08	16,02	6,35	C.H.F2NO.	46,75	3,03	16,45	6,06	15,01
C ₂ H ₅ OB ₁₁ - <i>n</i>	33	0,761	1,3810	70,53	14,07	1	I	C ₆ H ₁₄ O	70,59	13,73	I	1	1
HGF ₃ NO ₂ †	42	1,465	1,3167	12,11	0,80	39,37	14,71	CHF2NO2	12,37	1,03	39,18	14,43	25,52
• See [3]. † See [4].													

Compounds
Synthesized
roperties of
ABLE 1. F

The yield of the secondary products decreases as the reactivity of the alkyl halide increases. Thus, in the reactions of the salt with MeI, n-PrI, n-BuI, and n-PrBr the ratios of the ethyl and n-alkyl esters of difluoronitroacetic acid are respectively 1:5, 1:3, 2:3, and 2:3, and they correlate with the amounts of formed alkyl ethyl ethers.* It was shown by direct experiment that the ether does not function as an alkylating agent in the discussed process in the absence of alkyl halides. With benzyl bromide and benzyl chloride the reaction proceeds unambiguously without the formation of secondary products.

$$(II) + PhCH_2Hal \xrightarrow{Bt_2O}_{-HgHal_2} O_2NCF_2CO_2CH_2Ph$$

Hal = Br, Cl

Salt (II) is easily alkylated by alkyl halides in acetonitrile, and side processes are not observed here.

(II) + RHal
$$\xrightarrow{\text{MeCN}}_{-\text{HgHal}_r} O_2 \text{NCF}_2 CO_2 R$$

R = Me, *n*-Pr, CH₂ = CHCH₂; Hal = Br, I

EXPERIMENTAL

<u>Mercury Difluoronitroacetate (II)</u>. With stirring, to a solution of 16 g (0.113 mole) of difluoronitroacetic acid (I) in 30 ml of anhydrous ether was added 11.5 g (0.053 mole) of yellow mercury oxide in several portions. The stirring was continued for 5 h, and then the reaction mass was let stand overnight. The solution was separated from any residual mercury oxide and then evaporated in vacuo to dryness, after which 50 ml of anhydrous CH_2Cl_2 was added and the mass was again evaporated to dryness. The solid residue was washed with anhydrous CCl_4 and dried in vacuo (1 mm) over P_2O_5 . We obtained 21 g (82.4%) of (II) as white crystals. Found: mol. wt. (cryoscopy) 475. Calculated: mol. wt. 481.

<u>Difluoronitromethane</u>. A suspension of 10 g (0.0208 mole) of (II) in 10 ml of H_2O was placed in a distillation flask and a solution of 2.9 g (0.0274 mole) of Na_2CO_3 in 15 ml of H_2O was added. The mixture was heated on the steam bath and 3.1 g (76.8%) of difluoronitromethane was distilled off.

Reaction of (II) with n-Butyl Iodide in Ether. With stirring, 13.8 g (0.0751 mole) of n-BuI was added in drops to a suspension of 30 g (0.0624 mole) of (II) in 50 ml of anhydrous ether. The stirring was continued for 5 h at ~20°C and for 2 h at reflux. Most of the ether was distilled off through an efficient column while the residual liquid products were separated by heating in vacuo (1 mm) to give 13 g of a mixture of butyl ethyl ether, ethyl difluoronitroacetate, and butyl difluoronitroacetate in an ~1:1:1.5 ratio. The indicated products were isolated in the pure state by repeated fractional distillation.

Using equimolar ratios of the reactants, the reaction of (II) with MeI, n-PrBr, n-PrI, PhCH₂Cl, and PhCH₂Br in ether was run under similar conditions. The presence and amounts of alkyl ethyl ethers and ethyl difluoronitroacetate were established by GLC using authentic specimens of these compounds.

<u>n-Propyl Difluoronitroacetate</u>. With stirring and cooling with water, 7 g (0.0412 mole) of n-PrI was added in drops to a solution of 12 g (0.0248 mole) of (II) in 10 ml of anhydrous acetonitrile. The stirring was continued for 3 h, and then the volatile products were collected in a cooled trap (-78°) by heating the mixture on the steam bath in vacuo (1 mm). The contents of the trap were poured into 30 ml of water, and the organic layer was washed 6 times with equal volumes of water and then dried over MgSO₄. Fractional distillation gave 5.4 g (71.5%) of n-propyl difluoronitroacetate.

Methyl difluoronitroacetate and allyl difluoronitroacetate were obtained in a similar manner. The properties of the synthesized compounds are given in Table 1.

CONCLUSIONS

1. We obtained and characterized the stable mercury salt of difluoronitroacetic acid, which exists as the intramolecular donor-acceptor complex.

^{*} The analysis of the mixtures and proof of the purity of the synthesized compounds employing GLC were run on an LKhM-8MD chromatograph; two columns were used: 1) a 3 m \times 3 mm column packed with 5% SE-30 deposited on Chromaton N-AW-DMCS, particle size 0.20-0.25 mm; 2) a 1 m \times 3 mm column packed with 5% XE-60 deposited on Chezasorb AW-HMDSc, particle size 0.20-0.36 mm; the carrier gas was helium and the flow rate was 18.7 ml/min.

2. The alkylation of the mercury salt of difluoronitroacetic acid with alkyl halides in ether and acetonitrile was studied.

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BROMOMETHYL- AND IODOMETHYLACETOXYSILANES

M. G. Voronkov, L.P. Ignat'eva, O. A. Zasyadko, E. O. Tsetlina, and A. A. Stotskii UDC 542.91:547.1'128

The possibility of making practical use of carbofunctional derivatives of methylacetoxysilanes has remained relatively unstudied up to now, while compounds of this type have hardly been described. At the same time, such compounds should have considerable interest for the surface modification of highly diverse inorganic, and especially organic, materials. As an expansion of our studies in this field, we set ourselves the goal of synthesizing the previously unknown bromomethyl- and iodomethylacetoxysilanes of general formula $(CH_3)_{3-n}XCH_2Si(OCOCH_3)_n$, where X = Br, I, and n = 1-3.

In most cases the literature conditions for the preparation of organosilicon compounds that contain the

grouping $\sum Si(CH_2)_n X$ [1], where X = Br, I, and n = 1-3, are not suitable for the direct synthesis of the cor-

responding halomethylacetoxysilanes due to the presence of the highly reactive acetoxy groups in their molecules. It was shown by us that chloromethylacetoxysilanes of type $(CH_3)_{3-n}ClCH_2Si(OCOCH_3)_n$; where n = 1-3, smoothly exchange the chlorine atom for bromine and iodine atoms when reacted with the corresponding lithium and sodium halides in anhydrous acetonitrile or acetone. The reaction proceeds by the scheme: $(CH_3)_{3-n}ClCH_2-$ Si· $(OCOCH_3)_n + MX \rightarrow (CH_3)_{3-n}XCH_2Si(OCOCH_3)_n + MCl$, where M = Li, Na, X = Br, I, and n = 1-3.

The iodomethylacetoxysilanes are formed more easily than the corresponding bromomethylacetoxysilanes (Table 1). The exchange reactions with NaI in acetone proceed at a faster rate than in acetonitrile, while the reverse relationship is observed in the case of NaBr. However, the yield of the halomethylacetoxysilanes in acetone is 7-10% lower than in acetonitrile. Replacing chlorine by bromine is an equilibrium reaction, since the starting chloromethylacetoxysilane is always present in the reaction mixture even when a large excess of either LiBr or NaBr is added. Besides this, chloromethylacetoxysilanes are formed when solutions of the bromomethylacetoxysilanes are refluxed with NaCl for a long time. A substantial increase in the yields of the bromo derivatives when using LiBr is apparently associated with the higher concentration of bromide ion due to the better solubility of LiBr, which has a favorable effect on S_N^2 reactions, to which class the reactions of substitution in the chloromethylacetoxysilanes probably belong.

The elemental analysis data, yields, and constants of the synthesized compounds are given in Table 1. The parameters of the NMR spectra, and of the IR frequencies that belong to the more characteristic structural fragments, are summarized in Table 2. The obtained halomethylacetoxysilanes, except the bromomethyland iodomethyltriacetoxysilanes, are high-boiling liquids with a sharp odor, colorless, and are easily hydrolyzed. They assume a dark color when stored for a long time. The obtained compounds are soluble in most

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. S. M. Kirov Leningrad Institute of the Textile and Light Industry. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 710-712, March, 1978. Original article submitted June 29, 1977.