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SOME TRANSFORMATIONS OF FLUOROCHLORONITROALCOHOLS

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Polyfunctional nitro compounds, in particular, halonitroalcohols have a broad spectrum of biological activity [1]. In previous work [2], we reported on the methods for the synthesis of fluorochloronitroalcohols and their reactions with various acid halides and chlorosilanes. In a continuation of a study of the reactivity of fluorochloronitroalcohols (I)-(IV) relative to acid halide compounds [2], we investigated the reactions of these compounds with thionyl chloride,  $SOCl_2$ . Alcohols with electron-withdrawing substituents react with  $SOCl_2$  to form, as a rule, chloroalkanes and products of the replacement of chlorine in  $SOCl_2$  [3]. In contrast to the results of Krolevets et al. [3], the reaction of alcohols (I)-(IV) with  $SOCl_2$  leads only to bis(fluorochloronitroalkyl) sulfites (VI)-(IX), while chlorination products and monosubstituted chlorosulfites were not detected in significant amounts. Carrying out the reaction without solvent with flushing of hydrogen chloride by an inert gas or in a solvent with an acceptor leads to sulfites (VI)-(IX).

 $\begin{array}{c} O_2 \text{NCFClCHROH} + \text{SOCl}_2 \xrightarrow{-\text{HCl}} (O_2 \text{NCFClCHRO})_2 \text{SO} \\ (I) - (V) & (V1) - (IX) \end{array}$ 

 $R = H(I), (VI); CH_3(II), (VII); C_2H_5(III), (VIII); C_3H_7(IV), (IX); C_6H_5(V).$ 

Sulfites (VI)-(IX) are stable compounds, which are soluble in most organic solvents. These compounds are oxidized by  $KMnO_4$  to the corresponding sulfates. The structures of (VI)-(IX) were demonstrated by IR, PMR, and <sup>19</sup>F NMR spectroscopy, while their compositions were shown by elemental analysis. <sup>19</sup>F NMR spectroscopy indicated that (VI)-(IX) are diastereomer mixtures.  $SOCl_2$  forms stable donor-acceptor complexes with dimethylformamide (DMF) (the Weismeier-Haake reagent), which is active in the substitution of the OH group [5]. We have shown that the reaction of the Weismeier-Haake reagent with (I)-(V) gives the O-formylation of alcohols (I)-(V), leading to the formation of formate esters (X)-(XII), rather than chlorination.

(I), (III), (V)  $\xrightarrow{\text{SOCI}_2 - \text{DMF}} O_2 \text{NCFCICHROCH}$ (X) - (XII)

The reaction was carried out by analogy to the procedure of Golubok et al. [5] at from -5 to  $-15^{\circ}$ C in chloroform with subsequent isolation of (X)-(XII) by vacuum distillation. The structures of (X)-(XII) was established by spectral analysis. Thus, the IR spectra of these compounds have a strong characteristic band at 1720 cm<sup>-1</sup> (C=O), while their PMR spectra have a signal in the vicinity of 8.0 ppm, which confirms the presence of the -C(O)H fragment.

Fluorinated nitroketones remain difficult to prepare and have not been the subject of extensive studies. The literature contains information on the preparation and several trans-

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TABLE 1. Characteristics of (VII)-(XIX)

Com- pound	<sup>1</sup> HNMR spectrum, δ, ppm (J, Hz)	<sup>19</sup> F NMR spec- trum, 0, pmm (JH-F, Hz)	IR spectrum v, cm <sup>-1</sup>
(VI)	4,83 m (4H, 2CH <sub>2</sub> O)	-18,9 m	1330, $1597 (NO_2)$ , 1220 (S=O)
(VII)	5,32 m (1H, CH); 1,63 s (6H, 2CH <sub>3</sub> )	5,18m, -3,94m	1330, $1600 (NO_2)$ , 1210 (S=O)
(VIII)	5,12 m (1H, CH); 2.00 m (2H, CH <sub>2</sub> ); 1,13 t (3H, CH <sub>3</sub> )	-12,18 m, -13.84 m -20,86 m, -21,60 m	$\begin{array}{l} 1332, \ 1600 (\mathrm{NO}_2), \\ 1210 (\mathrm{S}{=}\mathrm{O}) \end{array}$
(IX)	5.06 m (1H, CH); 1.61 m (4H, 2CH <sub>2</sub> ); 0.88 t (3H, CH <sub>3</sub> )	-12.34 m13.24 m -20,52 m21.48 m	1330, $1600(NO_2)$ , 1210(S=O)
(X)	8,18 s (1H, CH); 5,11 m (2H, CH <sub>2</sub> )	-17,1 d (10,2)	1330, $1590(NO_2)$ , 1720(C=O)
(XI)	8,32 \$8,20 \$ (1H. CHO); 5,87 m (1H, CH); 2,19 9, 1,89 q (2H, CH <sub>2</sub> ); 1,02 t (3H, CH <sub>2</sub> )	-20.62 d (19,0); -13,61 d (12,0)	$1335, 1585(NO_2), 1720(C=0)$
(XII)	8,13 s, 7.91 s (1H, CHO); 7,45 m (5H, C <sub>6</sub> H <sub>5</sub> ); 6,70 d, 6,63 d (1H, CH)	-17.2 d (16.0), -24,1 (20,0)	$1300, 1565 (NO_2), 1720 (C=0)$
(XIII)	2,68 d (3H, CH <sub>3</sub> , $J_{H-F}=2,2$ )	-15,13	$1330, 1590(NO_2), 1750(C=0)$
(XIV)	$3,03 \text{ m}$ (2H, CH <sub>2</sub> , $J_{H-F}=3,5$ ); 1,47 (3H, CH <sub>3</sub> , $J_{H-H}=7,0$ )	14,97	$1320, 1590(NO_2), 1750(C=0)$
(XV)	2,82 m (2H, CH <sub>2</sub> , $J_{H-F}$ 3,0); 1,75 m (2H, CH <sub>2</sub> , $J_{H-H}$ =7,5); 1.0 t (3H, CH <sub>3</sub> ))	-13,84	1320, $1595(NO_2)$ , 1760(C=O)
(XVI)	8,11-7,54 m (5H, C <sub>6</sub> H <sub>5</sub> )	-5,88	1320, 1590 (NO <sub>2</sub> ), 1720 (C=O)
(XVII)	9,05-7,85 m (3H, C <sub>6</sub> H <sub>3</sub> ); 2,61 s (3H, CH <sub>3</sub> )	-4,12	1365, 1590 (NO <sub>2</sub> )
(XVIII)	9,05-7,83  m (3H, C <sub>6</sub> H <sub>3</sub> ); $3,05  m(2H, CH2); 1,23 \text{ t} (3H, CH3)$	-4,84	1360, 1590 (NO <sub>2</sub> )
(XIX)	9.06-7.86 (3H, C <sub>6</sub> H <sub>3</sub> ); 2,84 m (2H, CH <sub>2</sub> ); 1.83 m (2H, CH <sub>2</sub> ); 1,16 m (3H, CH <sub>3</sub> ) <sup>,</sup>	-3,02	1360, 1590 (NO <sub>2</sub> ) <sup>,</sup>

formations of difluoronitroalkyl ketones [6, 7] and pentafluoronitroacetone [8]. Only information on the preparation of  $\alpha$ -fluoro- $\alpha$ -nitroketones is given for these examples.

In order to obtain new fluoronitroketones, we carried out the oxidation of (II)-(V).

 $(II) - (V) \xrightarrow{K_2 Cr_2 O_7 - H_2 SO_4} O_2 NCFClCR$ 0(XIII) - (XVI)

 $\mathbf{R} = \mathbf{CH}_3(\mathbf{XIII}), \ \mathbf{C}_2\mathbf{H}_5 \ (\mathbf{XIV}), \ \mathbf{n}\text{-}\mathbf{C}_3\mathbf{H}_7 \ (\mathbf{XV}), \ \mathbf{C}_6\mathbf{H}_5 \ (\mathbf{XVI}).$ 

Ketones (XIV)-(XVI) were obtained in greater than 50% yield and proved to be stable, distillable liquids, which are highly soluble in organic solvents. These compounds were characterized by PMR, <sup>19</sup>F NMR, and IR spectroscopy. These spectra have signals characteristic for the R substituents. The protons of the methylene group bound to the carbonyl carbon atom form an AB spin system with  $J_{\rm HF}$  7 Hz due to their inequivalence. The <sup>19</sup>F NMR spectra have signals at 14-15 ppm. The IR spectra have bands corresponding to the NO<sub>2</sub> (1325 and 1590 cm<sup>-1</sup>) and C=O groups (1750 cm<sup>-1</sup>). In contrast to (XIV)-(XVI), fluorochloronitroacetone (XIII) is an unstable compound and could not be isolated in pure form. PMR spectral analysis of the fraction with bp 60-61°C (50 mm Hg) obtained upon distillation of the reaction mixture showed that this mixture contained 30% acetic acid and 70% (XIII). Limited information is available on the reactions of fluorinated nitroketones with hydrazines. Only the hydrazones of difluoronitroketones have been described [7]. Recently, Knunyants et al. [9] have reported the synthesis of hydrazones of pentafluoronitroacetone. We have found that fluorochloronitromethyl ketones react with 2,4-dinitrophenylhydrazone with the formation of stable hydrazones (XVII)-(XIX).

 $(XIII) - (XV) + H_2NNHC_6H_3(NO_2)_2 \rightarrow O_2NCFClC = NNHC_6H_3(NO_2)_2$ 

$$(XVII) - (XIX)$$

Com- Yield		Bp, °C	.,20	. 20	Found/Calcu- lated, %		Chemical formula
pound	*	Mp, °C	"D	<i>a</i> ,	с	N	
(VI)	63,8	117 - 119 (2.0)	1,4585	1,5745	<u> </u>	8.51	$C_4H_4Cl_2F_2N_2O_7S$
(VII)	45,0	135–137 (3.0) <sup>,</sup>	1,4550	1,5484	20.03 20.06	7.63	$C_6H_8Cl_2F_2N_2O_7S$
(VIII)	64,4	127 (1,5)	1,4597	1,4563	24.58	7,29	$C_8H_{12}Cl_2F_2N_2O_7S'$
(IX)	65,2	145–146 (1.5)	1,4594	1,3921	$\frac{24.00}{28.79}$	6.61	$C_{10}H_{16}Cl_2F_2N_2O_7S$
(X)	36,7	102 (80,0)	1,4216	1,5611	20.96	8,18 8,18	C <sub>3</sub> H <sub>3</sub> CIFNO <sub>4</sub>
(XI)	34,3	74(23,0)	1,4252	1,3647	29,99	7.04	C5H7ClFNO4
(XII)	51,6	81-83 (2.0)	1,4302	1,3952	45.25	5.66	C₂H7ClFNO₄
(XIV)	79,5	76 (40,0)	1,4166	1,3631	28.42	8,13 8,26	C4H5ClFNO3
(XV)	68,2	80 (35,0)	1,4193	1,3583	$\frac{32.64}{32.70}$	7.60	C5H7CIFNO3
(XVI)	68,5	80(3,0)	1,5294	4,4098	44.24	6,45 6,44	C <sub>8</sub> H <sub>5</sub> ClFNO <sub>3</sub>
(XVII)	64,6	148-149		-	<u>31,88</u> <u>32,19</u>	$\frac{21,14}{20.86}$	C <sub>9</sub> H <sub>7</sub> ClFN <sub>5</sub> O <sub>6</sub>
(XVIII)	63,0	109-111	-	-	<u>33,89</u> <u>34,33</u>	20,15	C10H9ClFN5O6
(XIX)	60,0	85-87	-	-	<u>35,75</u> 36,31	19,03 19,26	C11H11ClFN5O6

TABLE 2. Physicochemical Indices of the Compounds Synthesized

Products (VI)-(XIX) are stable yellow crystalline compounds. The spectral and physicochemical indices of the compounds prepared are given in Tables 1 and 2.

## EXPERIMENTAL

The IR spectra were taken neat on a Specord IR-75 spectrometer. The <sup>1</sup>H and <sup>19</sup>F NMR spectra were taken on a Bruker CXP-200 spectrometer at 200 and 188 MHz, respectively. TMS served as the internal standard for the <sup>1</sup>H NMR spectra, while  $CF_3CO_2H$  served as the external standard for the <sup>19</sup>F NMR spectra.

<u>Bis(1-fluoro-1-chloro-1-nitroethyl)</u> Sulfite (VI). A sample of 5.7 g (0.04 mole) (I) was mixed with 3.2 g (0.04 mole) pyridine in 30 ml ether. The mixture was cooled to  $-10^{\circ}$ C and 1.2 g (0.02 mole) SOCl<sub>2</sub> in 10 ml ether was added slowly with stirring. Then, the mixture was brought to room temperature and maintained for 2 h. After filtration, the solution was evaporated and distilled in vacuum to give 4.2 g (63.8 g) (VI), bp 120-121 (2 mm). Products (VII)-(IX) were obtained by analogy to (VI).

<u>1-Fluoro-1-chloro-1-nitroethyl Formate (X)</u>. A sample of 7.3 g (0.61 mole) DMF was added with stirring to 11.9 g (0.1 mole)  $SOC1_2$  at -15°C such that the temperature did not rise above -5°C. A solution of 14.4 g (0.1 mole) (I) in 25 ml chloroform was added to this mixture. The reaction mixture was brought to room temperature and then maintained for 2 h at 50°C, washed with water until the washings were neutral, and dried over CaCl<sub>2</sub>. Distillation gave 5.9 g (36.7%) (X), bp 102°C (80 mm). Products (XI) and (XII) were obtained by analogy to (X).

<u>1-Fluoro-1-chloro-1-nitro-2-pentanone (XV)</u>. A sample of 5.6 g (0.03 mole) (IV) was mixed with 10 g (0.035 mole)  $K_2Cr_2O_7$  and 14 ml water. Then, 16.5 ml concentrated sulfuric acid was added dropwise. The mixture was stirred for 0.5 h at 90°C, cooled, poured into 60 ml ice water, and extracted thrice with ether. The ethereal extracts were dried over MgSO<sub>4</sub> and distilled to give 3.2 g (58.2%) (XV).

Products (XIII), (XIV), and (XVI) were obtained by analogy to (XV). Hydrazones (XVII)-(XIX) were obtained from 2,4-dinitrophenylhydrazine according to a standard procedure [10].

## CONCLUSIONS

Previously unreported bis(fluorochloronitroalkyl) sulfites were obtained upon carrying out the reactions with flushing of hydrogen chloride by an inert gas or using an amine acceptor, while the reaction with  $SOCl_2 + DMF$  (the Weismeier-Haake reagent) gives O-formylation. Fluorochloronitromethyl ketones were obtained for the first time upon the oxidation of secondary fluorochloronitroalcohols using potassium dichromate.

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OXIDATION OF BIS(TRIMETHYLSILYL)AMIDODIFLUOROPHOSPHITE

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Bis(trimethylsilyl)amidodifluorophosphite, which is readily obtained from  $PF_3$  and the lithium derivatives of hexamethyldisilazane, is very resistant to oxidation and does not react with atmospheric oxygen even at 155°C [1].

We carried out the oxidation of this compound using tert-butyl hypochlorite. The reaction of alkyl hypochlorites with phosphites was described in the case of a series of trialkyl phosphites and proceeds through an Arbuzov-type reaction mechanism [2]. Such a reaction was not carried out for bis(trimethylsilyl)amidophosphites.

We have discovered that the reaction of bis(trimethylsilyl)amidodifluorophosphite (I) with tert-butyl hypochlorite gives quasiphosphonium salt (II) in the first step, which decomposes, losing the tert-butyl or Me<sub>3</sub>Si group with equal probability.



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