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DIHALOGENOFORMALS*

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Until recently, the dihalogenoformals in the literature were represented exclusively by the difluoro derivatives of the type $ROCF_2OR'$, where $R = R' = CH_2CF(NO_2)_2$ [2-4] and $R = CH_2CF(NO_2)_2$, where $R' = CH_2CF_2NO_2$ or CH_2CF_3 [5]. The compounds were obtained by the reaction of the carbonates of alcohols with sulfur tetrafluoride in an autoclave at the temperature >100°C for a prolonged time (up to several days); according to their properties, the compounds are fairly inert.

From a chemical viewpoint, the dichloroformals, the reactivity of which should be significantly higher than that of the corresponding difluoro analogs, may present great interest.

We found that the dihalogenoformals, including the dichloro derivatives, can be obtained by the halogenation of the central carbon atom of the symm.-thionocarbonates. The initial thionocarbonates have been intensively studied in recent years, and methods to synthesize them have been described in detail [6-8]. The attempt to obtain the dichloroformals from the corresponding thionocarbonates by the chlorination using PCl_5 and $SOCl_2$ was unsuccessful.

The first example of the dichloroformals – bis(2-fluoro-2,2-dinitroethyl)dichloroformal – was obtained by boiling bis(2-fluoro-2,2-dinitroethyl)thionocarbonate in sulfuryl chloride

$$[(NO_2)_2CFCH_2O]_2C{=}S \xrightarrow{SO_2Cl_2} [(NO_2)_2CFCH_2O]CCl_2 \qquad \text{(I)}$$

The chlorine atoms in (I) are available, and are substituted by fluorine with the formation of bis(2-fluoro-2,2-dinitroethyl)difluoroformal (II). Metal fluorides – AgF in CH_3CN and SbF_3 or SbF_5 in SO_2Cl_2 – were utilized as fluorinating agents.

Even more simple proved to be the halogenation reaction of the thionocarbonates with elemental chlorine or fluorine (a fluorine–nitrogen mixture was utilized in the case of the fluorination)

$$(RCH_2O)_2C{=}S \xrightarrow{X_2} (RCH_2O)_2CX_2$$
$$X{=}Cl,\ R{=}CF_2NO_2\,(III);\ X{=}F,\ R{=}CF_2NO_2\,(IV);\ X{=}Cl,\ R{=}CF_3\,(V);$$
$$X{=}F,\ R{=}CF_3\,(VI).$$

The halogenation reactions were performed at −20 to +50°C in solutions of CH_2Cl_2 or CH_3CN; some physical constants and the analytical data of the compounds (I)-(VI) are presented in Table 1. The dibromo- and diiodoformals could not be obtained from the investigated thiocarbonates. The spectral characteristics are presented in Table 2.

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*For previous communication, see [1].

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TABLE 1. Some Physical Constants and the Elemental Analysis of the Dihalogenoformals

Compound	Formula	Bp, °C (p, mm Hg) or mp, °C	n_D^{20}	Found, %					Empirical formula	Calculated, %				
				C	H	N	F	Cl		C	H	N	F	Cl
(I)	$[(O_2N)_2CFCH_2O]_2CCl_2$	54–55	–	15,3	1,1	14,7	10,0	18,3	$C_5H_4N_4O_{10}F_2Cl_2$	15,44	1,04	14,40	9,77	18,23
(II)	$[(O_2N)_2CFCH_2O]_2CF_2$	100–105(2)	1,4160	16,9	1,2	15,8	21,3		$C_5H_4N_4O_{10}F_4$	16,86	1,13	15,73	21,34	–
(III)	$(O_2NCF_2CH_2O)_2CCl_2$	115–117(2)	1,4230	18,0	1,1	8,7	23,0	20,9	$C_5H_4N_2O_6F_4Cl_2$	17,93	1,20	8,36	22,69	21,17
(IV)	$(O_2NCF_2CH_2O)_2CF_2$	110–112(18)	1,3625	20,1	1,2	9,5	37,5		$C_5H_4N_2O_6F_6$	19,88	1,33	9,27	37,74	
(V)	$(CF_3CH_2O)_2CCl_2$	127–128(750)	1,3518					24,8 *	$C_5H_4O_2F_6Cl_2$					25,24
(VI)	$(CF_3CH_2O)_2CF_2$	81–82(750)	1,2837				61,1 *		$C_5H_4O_2F_8$				61,27	

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*The analysis of the other elements was not performed due to the high volatility of the compound.

TABLE 2. ^{1}H and ^{19}F NMR Spectra of the Dihalogenoformals

Compound	PMR spectrum			^{19}F NMR spectrum*		
	group	δ, ppm	J, Hz	group	δ, ppm	J, Hz
(I)	CH_2	5,06 d	16,0			
(II)	CH_2	5,15 d	15,5	$(O_2N)_2CF$	−34,78 s	
				$O-CF_2-O$	13,37 t	3,85
(III)	CH_2	4,67 q	9,0			
(IV)	CH_2	4,71 t	9,0	O_2NCF_2	−17,60 s	
				$O-CF_2-O$	12,57 qu	2,25
(V)	CH_2	4,60 q	8,0			
(VI)	CH_2	4,20 q	7,7	CF_3	1,78 s	
				$O-CF_2-O$	11,80 sep	

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*Quintet is indicated by qu; septet is indicated by sep.

EXPERIMENTAL

The PMR spectra were obtained on the NMR spectrometer developed and produced in the Section of the Institute of Chemical Physics, Academy of Sciences of the USSR with a superconducting magnet (294 MHz) and the internal standard of TMS. The ^{19}F NMR spectra were taken on a "Bruker CXP-200" spectrometer with the working frequency of 188 MHz and the internal standard of CF_3COOH. The IR spectra were taken on the UR-20 instrument.

Bis(2-fluoro-2,2-dinitroethyl)dichloroformal (I). The solution of 3.5 g (0.01 mole) of bis(2-fluoro-2,2-dinitroethyl)thionocarbonate in 10 ml of SO_2Cl_2 was boiled under a reflux condenser. After the distillation of the excess SO_2Cl_2, the residue was crystallized from CCl_4. The yield of 2.5 g (65%) of (I) was obtained. The IR spectrum (ν, cm^{-1}) was as follows: 1086, 1131, 1169, 1182, 1260 (CO, CF), 1332, and 1612 (NO_2).

Bis(2-fluoro-2,2-dinitroethyl)difluoroformal (II). a. To the solution of 3.9 g (0.01 mole of (I) in 15 ml of absolute CH_3CN are added 3.8 g (0.03 mole) of AgF at 0-5°C with energetic stirring. After 30 min, the reaction mass was filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in 15 ml of CH_2Cl_2, washed with a 1% aqueous solution of NaOH (5 portions of 20 ml) and water, and dried with $MgSO_4$. Distillation led to the isolation of 2.3 g (65%) of (II). The IR spectrum (ν, cm^{-1}) was as follows: 790 w, 812 med, 830 s, 871 med, 1028 w, 1143 s, 1221 s, 1259 s, 1332 s, 1415 s, 1462 med, 1500 w, 1610 s, 1719 w, 2392 med, 2700 med, 2950 med, 3020 med, and 3060 med.

b. To the solution of 3.9 g (0.01 mole) of (I) in 10 ml of SO_2Cl_2 were added 4.4 g (0.02 mole) of SbF_5 at −5 to 0°C with stirring. The solution was stirred at the temperature indicated for 2 h prior to its dilution with 50 ml of CH_2Cl_2 and washing with water; the solvent was removed in vacuo. The residue was repeatedly dissolved in 20 ml of CH_2Cl_2, washed with a 1% aqueous solution of NaOH (5 portions of 20 ml) and water, and dried with $MgSO_4$. After the removal of the solvent, distillation was carried out. The yield of 2.5 g (70%) of (II) was obtained.

Bis(2,2-difluoro-2-nitroethyl)dichloroformal (III). Into the solution of 3.0 g (0.01 mole) of bis(2,2-difluoro-2-nitroethyl)thionocarbonate in 20 ml of dry CH_2Cl_2 at 0-5°C was passed 0.34 liters (0.015 mole) of dry Cl_2 in the course of 1.5 h. After the distillation of the solvent and the double distillation of the residue, 2.1 g (62%) of (III) were isolated. The IR spectrum (ν, cm^{-1}) was as follows: 708 med, 781 med, 792 med, 850 med, 869 med, 965 w, 1045 w, 1078 med, 1130 s, 1180 s, 1219 s, 1316 s, 1367 med, 1423 med, 1460 w, 1600 s, 1648 w, and 2980 w.

Bis(2,2,2-trifluoroethyl)dichloroformal (V). Under the conditions of the preceding experiment, 2.4 g (0.01 mole) of bis(2,2,2-trifluoroethyl)thionocarbonate gave 1.5 g (53%) of (V). The IR spectrum (ν, cm^{-1}) was as follows: 560 med, 628 s, 672 med, 698 med, 740 s, 804 s, 844 med, 868 med, 947 s, 1007 s, 1056 s, 1104 s, 1139 v.s., 1156 v.s., 1171 v.s., 1228 w, 1284 v.s., 1415 s, 1448 med, 2883 w, and 2959 w.

Bis(2,2-difluoro-2-nitroethyl)difluoroformal (IV). Into the solution of 3.0 g (0.01 mole) of bis(2,2-difluoro-2-nitroethyl)thionocarbonate in 10 ml of absolute CH_3CN at −20 to −15°C was passed the 1:10 fluorine–nitrogen mixture, containing 0.34 liters (0.015 mole) of elemental fluorine, for 30 min. The reaction mixture was poured into water. The product was separated and washed with a 1% aqueous solution of NaOH (5 portions of 10 ml) and water prior to being dried with $MgSO_4$. Double distillation led to the isolation of 2.5 g (83%) of (IV). The IR spectrum (ν, cm^{-1}) was as follows: 802 w, 871 med, 960 w, 1000 w, 1038 w, 1118 s, 1160 med, 1215 v.s., 1306 med, 1328 s, 1377 med, 1419 med, 1450 w, 1602 v.s., 1628 w, 2392 med, 2960 w, 2990 w, and 3040 w.

Bis(2,2,2-trifluoroethyl)difluoroformal (VI). Under the conditions of the preceding experiment, 2.4 g (0.01 mole) of bis(2,2,2-trifluoroethyl)thionocarbonate gave 1.5 g (60%) of (VI). The IR spectrum (ν, cm^{-1}) was as follows: 609 med, 617 med, 668 med, 690 sh, 752 med, 773 w, 840 med, 958 med, 990 med, 1024 med, 1069 s, 1092 s, 1115 s, 1170 v.s., 1218 v.s., 1235 sh, 1242 v.s., 1296 v.s., 1305 v.s., 1320 v.s., 1333 med, 1394 w, 1423 s, 1456 w, and 2974 med.

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CONCLUSIONS

The interaction of the thionocarbonates of fluoro- and nitro-containing alcohols with chlorinating (Cl_2, SO_2Cl_2) and fluorinating (F_2, AgF, SbF_5) agents gave the dichloro- and difluorohalogenoformals of the corresponding alcohols.

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REACTION OF POLYHALODISULFIDES WITH HEXAETHYLPHOSPHORUS TRIAMIDE

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Until recently, trifluoromethylthiirane (I) was the sole representative of the perfluoroalkyl-containing thiiranes which are of interest as starting materials for the preparation of perfluoroalkyl-containing polyethylene sulfides, sulfonic acids, functionally substituted mercaptans, etc.

We have previously prepared (I) from bis(1-trifluoromethyl-2-chloroethyl)disulfide (II) in two stages by successive reaction with Cl_2 and H_2S in N-methylpyrrolidone (NMP) [1].

In the present work, with the object of preparing fluorothiiranes directly from disulfides in one stage, we have studied the reaction of polyhalogen derivatives of disulfides with $P(NEt_2)_3$.

It has been found that reaction of the disulfides (II) and (III) with $P(NEt_2)_3$ yields trifluoromethyl- and pentafluoroethylthiiranes (I) and (IV), respectively

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