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REACTION OF SULPHUR TETRAFLUORIDE WITH 1,3-DIHALOACETONES. FLUOROALKYLATION OF BENZENE AS EVIDENCE OF PARTICIPATION OF FLUOROCARBOCATIONS IN THE REACTION

J. WIELGAT, Z. DOMAGAŁA and R. KOLIŃSKI

Institute of Organic Chemistry, Polish Academy of Sciences,
00-961 Warsaw (Poland)

SUMMARY

Reaction of sulphur tetrafluoride with 1,3-dihaloacetones to give 1,3-dihalo-2,2-difluoropropanes (1, 2, 3), bis(1,3-dihalo-2-fluoroisopropyl)ethers (4, 5, 6) and 1,3-dihalo-2-fluoropropanes (7, 8) has been investigated. Formation of ethers, propanes and propenes as well as 1,3-dihalo-2-fluoro-2-phenylpropane (9) (electrophilic benzene substitution) was observed in the reactions in benzene solution. This confirms the proposed reaction mechanism involving participation of fluorocarbocations.

INTRODUCTION

Sulphur tetrafluoride reacts with carboxylic acids, carboxylic acid chlorides and fluorides, aldehydes and ketones appropriately changing the carbonyl group to the trifluoromethyl group, difluoromethyl group or difluoromethylene group [1], respectively. The formation of α-fluorinated dialkylethers was also described in these reactions [2]. This observation suggested an investigation of the reaction of sulphur tetrafluoride with 1,3-dihaloacetones in order to confirm whether fluoroethers are formed. Also it allowed confirmation of the proposed reaction mechanism with the participation of fluorocarbocations [3, 4].

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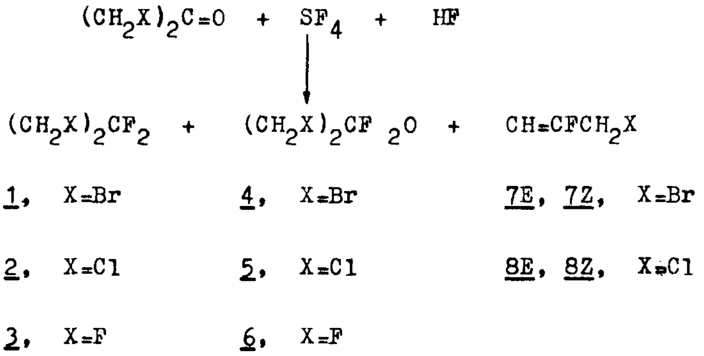
RESULTS

Reactions of 1,3-dihaloacetones with sulphur tetrafluoride were carried out in a steel autoclave at temperatures 120-130^{o}, in the presence of very small amounts of hydrogen fluoride, present as impurities in the sulphur fluoride or arising from the hydrolysis of sulphur tetrafluoride by trace amounts of water contained in the apparatus or in the ketone. The main reaction products were 1,3-dihalo-2,2-difluoropropanes (1, 2, 3) and bis(1,3-dihalo-2-fluoroisopropyl)ethers (4, 5, 6). Besides the compounds mentioned above, 1,3-dibromoacetone gave a mixture of 1,3-dibromo-2-fluoropropenes (7, isomer ratio E:Z 1:2). Only isomer 7Z was isolated. 1,3-Dichloroacetone gave a mixture of 1,3-dichloro-2-fluoropropenes (8, isomer ratio E:Z 1:2) and here both isomers were isolated. In the products of the 1,3-difluoroacetone reaction no trifluoropropene was found. However unindentified polymers were found which were probably formed from 1,3-difluoroacetone. Their presence made the isolation of analytically pure compound 3 impracticable.



$$(CH_2X)_2C{=}O \;+\; SF_4 \;+\; HF \;\longrightarrow\; (CH_2X)_2CF_2 \;+\; (CH_2X)_2CF\;_2O \;+\; CH{=}CFCH_2X$$

1, X=Br   4, X=Br   7E, 7Z, X=Br

2, X=Cl   5, X=Cl   8E, 8Z, X=Cl

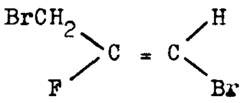
3, X=F   6, X=F

Under analogous conditions, a reaction of 1,3-dichloroacetone with sulphur tetrafluoride in the presence of benzene (molar ratio 1:2:1) was carried out. As a result, compounds 2, 5, 8 and 1,3-dichloro-2-fluoro-2-phenylpropane (9) were obtained.

$$(CH_2Cl)_2C{=}O + SF_4 + C_6H_6 \xrightarrow{HF} \underset{\underline{9}}{C_6H_5CF(CH_2Cl)_2} + \underline{2},\ \underline{5},\ \underline{8}$$

Isolated compounds were identified by the usual methods: elementary analysis, analytical gas chromatography (GLC), ^{1}H and ^{19}F N.M.R. spectrometry and mass spectrometry. Compounds 1 and 2 had physical constants in accordance with those described in the literature for 1,3-dihalo-2,2-difluoropropane [5, 6]. Compound 3 was not obtained analytically pure. N.M.R. data of these compounds are given in Table 1 and their mass spectra (molecular peaks) in the Experimental. Fluoroethers 4, 5 and 6 had correct elemental analyses and their N.M.R. spectra were similar to those obtained for fluoroethers described earlier [2]. These spectra are very complex and they do not allow first order analysis.

Fluoroethers 4, 5 and 6 do not give molecular peaks in their mass spectra but isotope peaks characteristic for fragments containing Br and Cl atoms are observed. The most characteristic peaks are $M^{+}-CH_2X$ and $(CH_2X)_2CF^{+}$. Halofluoroalkenes 7 and 8 appear in the form of mixture of isomers E and Z as observed by GLC. The N.M.R. spectra of these compounds (Table 1) showed that an isolated single isomer 7 has a configuration Z $-J_{HF\ \underline{trans}}$ is 25.5 Hz.



7Z

Compounds 8 have a configuration: 8Z $-J_{HF\ \underline{trans}}$ 21.8 Hz, b.p. 117-118° and low boiling 8E $-J_{HF\ \underline{cis}}$ 9.0 Hz. Compound 7Z shows molecular isotope peaks M^{+} 216, 218, 220 (ratio 1:2:) in mass spectra and this proved the presence of two atoms of bromine. Peaks of the fragment M^{+} - Br m/e 137, 139 were also observed.

TABLE 1

^{1}H and ^{19}F N.M.R. data for compounds 1-9

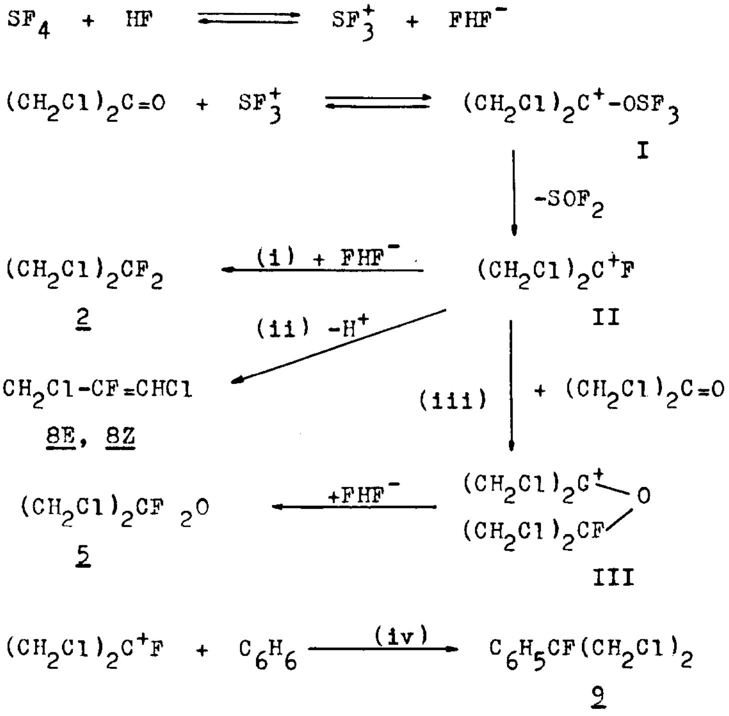
Compound		δ(TMS) ppm	ϕ(CCl_3F) ppm	^3J H-Z Hz
1	$CH_2Br-CF_2-CH_2Br$	3.73 t	99.7 t	12.0
2	$CH_2Cl-CF_2-CH_2Cl$	3.79 t	108.2 t	11.0
4	$[(CH_2Br)_2CF]_2O$	3.88 dm	112.3 m	
5	$[(CH_2Cl)_2CF]_2O$	3.90 dm	117.9 m	
6	$[(CH_2F)_2CF]_2O$	4.52 dm	129.8 m	
7Z	$CH_2Br-CF = CHBr$	3.92 d(a)	99.0 dt	17.7 (a)
	a b	5.73 d(b)		25.5 (b)
8E	$CH_2Cl-CF = CHCl$	4.25 d(a)	113.4 dt	20.6 (a)
	a b	6.08 d(b)		9.0 (b)
8Z	$CH_2Cl-CF = CHCl$	4.11 d(a)	112.2 dt	16.8 (a)
	a b	5.80 d(b)		21.8 (b)
9	$C_6H_5-CF(CH_2Cl)_2$	7.28 m(a)	156.5 t	
	a b	3.92 d(b)		17.3 (b)

d-doublet, t-triplet, m-multiplet

The N.M.R. spectra of compound 9 (Table 1) are as expected for 1,3-dichloro-2-fluoro-2-phenylpropane and together with the mass spectra containing peaks M^+ 206, 208, 210 and $M^+ - CH_2Cl$ 157, 159 (ratio 3:1) enable unequivocal determination of its structure.

DISCUSSION

Formation of the bis(fluoroalkyl)ethers has been described for the reaction of sulphur tetrafluoride with carboxylic acids and aldehydes [1, 2, 7, 8]. The proposed mechanism with the participation of carbocations RC^+F_2, obtained from the acids, has been confirmed by the electrophilic benzene substitution reaction with this cation [4]. Assuming an analogous reaction mechanism of sulphur tetrafluoride with 1,3-dichloroacetone in the presence of catalytic amounts of hydrogen fluoride we can explain the formation of all reaction products.



The reaction is started by generation of the SF_3^+ cation, which reacting with an oxygen atom of the carbonyl group forms complex I, which undergoes inter- or intramolecular fluorination with elimination of thionyl fluoride and the formation of fluorocarbocation II. Fluorocarbocation II is the main intermediate product. Cation II reacts further in a way typical for carbocations:

(i) by addition of F^- anion difluoroalkanes 2 are formed,
(ii) by elimination of a proton alkenes 8Z and 8E are formed,
(iii) by the attack of cation II on a ketone molecule cation III is formed, which reacts further with F^- anion to generate ether 5,
(iv) in the presence of benzene, cation II substitutes hydrogen in the benzene ring with generation of compound 9.

The proposed reaction mechanism explains why the well known reaction of sulphur tetrafluoride with ketones (acetone) in the presence of excess hydrogen fluoride led only to the formation of difluoroalkanes [1]: fluorocarbocation reacted most quickly with FHF^- ion and a big concentration of this anion made the reaction i predominant. In our conditions, in the presence of trace amounts of HF, reaction i is limited and fluorocarbocation II also reacts with formation of ii and iii: fluoroalkenes 8 and ether 5 are formed.

Some fluorinated ethers decompose under the influence of HF, with the formation of fluorocarbocations [3, 9, 10]. Therefore, we tested whether fluoroalkylation of benzene proceeded under the influence of ether 5, sulphur tetrafluoride and HF; or alkenes 8, sulphur tetrafluoride and HF. These reactions were however not observed: compound 9 was not obtained. This experiment shows that carbocation II is formed solely from the starting ketone and SF_3^+.

Reaction of the fluorocarbocation with benzene is a typical electrophilic benzene substitution and reaction of ketone with sulphur tetrafluoride and benzene can be defined as an electrophilic benzene fluoroalkylation.

EXPERIMENTAL

Sulphur tetrafluoride was obtained as described previously [9]. 1,3-Dibromoacetone was obtained from acetone by modification of Hughes method [11]. 1,3-Difluoroacetone was obtained as by Bergmann [12] with the purity exceeding 98%.

The remaining reagents were of commercial origin. Reagents for synthesis and compounds obtained were analysed by GLC-chromatography using a Giede 18.3 apparatus with chromatography column SE-52 (3% SE-52 on Chromosorb G, 60/80 mesh, 3.5 m). Gas-liquid preparative chromatography was carried out in Giede 18.3 apparatus (column as above, 1 cm^{2}x 4 m). Mass spectra were measured by an LKB-2091 spectrometer with chromatography column SE-52 as for Giede 18.3. ^{1}H and ^{19}F N.M.R. spectra were recorded on JEOL-JNM-4H spectrometer at 100 MHz and 94.07 MHz using TMS and CCl_3F as internal standards, respectively.

1,3-Dibromoacetone

Acetone (40.0 g, 0.69 mol), hydrochloric acid (80.0 ml) and water were heated at 26-30°. Bromine (135.0 g, 0.84 mol) was added dropwise keeping the temp. at 32-35° and then the reaction mixture was heated for 1 h at 30-35°. Water (200 ml) was added, the organic layer was separated and the water layer was extracted with ether (2 x 150 ml). Ethereal extracts were combined with the organic layer and dried over $CaCl_2$. Ether was distilled off under vacuum and the following fractions were collected: (i) monobromoacetone (18.0 g) b.p. 60-70°/50 mm Hg, (ii) mixture of 1,3- and 1,1-dibromoacetone (28.0 g, 9.5: 0.5 GLC) b.p. 120-130°/50 mm Hg. Fraction ii was distilled on Fisher's column (60 theoretical plates) and 1,3-dibromoacetone obtained (18.0 g, 98% GLC) b.p. 109-110°/35 mm Hg (cited [11] 57-58°/4 mm Hg).

Reactions of 1,3-dihaloacetones with sulphur tetrafluoride

1,3-Dihaloacetone was placed in an autoclave (100 ml capacity). The autoclave was closed and cooled to -80° and evacuated to 1-2 mm Hg. Sulphur tetrafluoride was condensed (appropriate amounts) and then the autoclave was heated at 120-130° for 3 h. After the reaction was complete the autoclave was cooled to room temperature, gases were vented and liquid products were poured into water and ice (100 ml).

The organic fraction was separated out, dried ($CaCl_2$) and distilled.

Reaction of sulphur tetrafluoride with 1,3-dibromoacetone

1,3-Dibromoacetone (15.0 g, 0.07 mol) and sulphur tetrafluoride (50.0 g, 0.46 mol) were reacted in an autoclave and the products isolated as described above. A mixture of obtained compounds (12.5 g) gave fraction i (9.0 g) with b.p. 60-80°/60 mm Hg. Fraction i contained compounds 1, 7E and 7Z (GLC analysis) which were isolated by preparative gas-liquid chromatography at 160°. The following compounds were obtained: 1,3-dibromo-2-2-difluoropropane (1, 2.0 g) b.p. 70°/85 mm Hg (cited [5] 136°) and 1,3-dibromo-2-fluoropropane (7Z, 0.3 g) b.p. 142-143° (Sivolobov), n_D^{21}1.5328, MS: m/e 216, 218, 220 (8, 14, 6%) two Br atoms, M^+; m/e 137, 139 (100, 98%) one Br atom, M^+-Br; m/e 111, 113 (47, 46%) one Br atom, C^+HBrF. IR film: 3300w, 1720m, 1440m, 1330s, 1275m, 1180s, 945s, 895s, 830s. Analysis: Found: C, 16.7; H, 1.4; Br, 73.3; F, 8.4%. $C_3H_3Br_2F$ requires C, 16.5; H, 1.4; Br, 73.4; F, 8.7%. Compound 7E was not obtained analytically pure. After fraction i was distilled off the residue (2.4g) was distilled in vacuum and bis(1,3-dibromo-2-fluoroisopropyl)ether (4) was obtained (1.7 g) b.p. 137-139°/3 mm Hg, n_D^{26}1.5317. MS: m/e 217, 219, 221 (49, 100, 54%) two Br atoms, $(CH_2Br)_2C^+F$; m/e 171, 173, 175 (8, 14, 7%) two Br atoms, C^+HBr_2; m/e 137, 139 (36, 35%) one Br atom, C^+H_2-CF=CHBr. Analysis: Found: C, 16.1; H, 1.7; Br, 70.5; F, 8.2. $C_6H_8Br_4F_2O$ requires C, 15.9; H, 1.8; Br, 70.4; F, 8.4%.

Reaction of sulphur tetrafluoride with 1,3-dichloroacetone

Reaction of 1,3-dichloroacetone (20.0 g, 0.16 mol) with sulphur tetrafluoride (50.0 g, 0.46 mol) was carried out in an autoclave and products were isolated as above. The mixture of compounds (20.0 g) was separated by distillation and gave fraction i with b.p. up to 120°. This fraction contained compounds 2, 8Z and 8E (GLC). Fraction i was separated by preparative gas chromatography at 130°. The following compounds were isolated: 1,3-dichloro-2,2-difluoropropane (2, 3.0 g) b.p. 93-94° (cited [6] b.p. 96.69°); 1,3-dichloro-2-fluoropropene (8E, 0.15 g) contains 5% of compound 2 (GLC) b.p. 106-107° (Sivolobov), (cited [13] b.p. 41.7°/100 mm Hg); 1,3-dichloro-2-fluoropropane (8Z, 0.4 g) b.p. 117-118° (Sivolobov) (cited [13] b.p. 46°/44 mm Hg). The residue was distilled under higher vacuum and the bis(1,3-dichloro-2-fluoroisopropyl)ether (5) was obtained (4.0 g) b.p. 128-130°/25 mm Hg, n_D^{20}1.4633. MS: m/e 225, 227 (6, 7%), M^+-CH_2Cl; m/e 189 (16%), $M^+-CH_2Cl-HCl$; m/e 129 (43%), $(CH_2Cl)_2C^+F$; m/e 93 (50%), $C^+H{=}CF-CH_2Cl$; m/e 49 (37%), C^+H_2Cl. Analysis: Found: C, 26.2; H, 2.9; Cl, 51.3; F, 13.7%. $C_6H_8Cl_4F_2O$ requires C, 26.1; H, 2.9; Cl, 51.4; F, 13.8%.

Reaction of sulphur tetrafluoride with 1,3-difluoroacetone

Reaction of 1,3-difluoroacetone (15.0 g, 0.16 mol) with sulphur tetrafluoride (40.0 g, 0.37 mol) was carried out in an autoclave and products (8.4 g) were isolated as above. Fraction i b.p. 30-35°/130 mm Hg was not collected due to its volatility. The following compound was isolated by distillation from the residue: bis(1,2,3-trifluoroisopropyl)ether (6, 1.6 g) b.p. 30-31°/5 mm Hg, n_D^{22}1.3495. MS: m/e 177 (1%), M^+-CH_2F; m/e 157 (8%), M^+-CH_2F-HF; m/e 97 (48%), $(CH_2F)_2C^+F$. Analysis: Found: C, 33.9; H, 3.9; F, 54.3. $C_6H_8F_6O$ requires C, 34.2; H, 3.8; F, 54.3%.

1,3-Dichloro-2-fluoro-2-phenylopropane (9)

Reaction of 1,3-dichloroacetone (20.0 g, 0.16 mol) with sulphur tetrafluoride (40.0 g, 0.3 mol) in the presence of benzene (15 ml) was carried out in an autoclave and the products were isolated as above. A mixture of compounds (29.0 g) was obtained. Fraction i was distilled off (b.p.

75-125°/20 mm Hg) and contained benzene and compounds 2, 5, 8E and 8Z (GLC). The residue gave fraction ii (4.8 g) b.p. 85-88°/3 mm Hg. Fraction ii was cooled to -20° and after 24 h the solid ether 5 was filtered off. Compounds 5 and 9 were found to be present in the filtrate (ratio 1:1 GLC). These compounds were separated by preparative gas chromatography at 180° and compound 9 was isolated b.p. 245° (Sivolobov), n_D^{21} 1.5325. MS: m/e 206, 208 (17, 10%), M^+; m/e 157, 159 (100, 30%), M^+-CH_2Cl; m/e 137 (14%), M^+-CH_2Cl-HF; m/e 126 (46%), M^+-CH_2Cl-CF. Analysis: Found: C, 51.9; H, 4.2; Cl, 34.0; F, 9.4. $C_9H_9Cl_2F$ requires C, 52.2; H, 4.4; Cl, 34.2; F, 9.2%.

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