Organic compounds containing a pentafluorothio group

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The addition of sulfur chloride pentafluoride to various terminal olefins, including those containing functional substituents, was studied. Possible side processes in these reactions are oligomerization and fluorination of the starting olefin.

Key words: sulfur chloride pentafluoride, terminal olefins, radical addition, organic pentafluorothio derivatives.

The addition of sulfur chloride pentafluoride (SF_5Cl) (**1**) at the multiple bond of olefins has been studied for a wide range of compounds.[1–6] Among them, unsubstituted and halogen-substituted olefins have predominated. It is of obvious interest to extend this reaction to other types of unsaturated compounds, including those containing functional substituents.

We studied reactions of compound **1** with methyl methacrylate (**2a**), methyl acrylate (**2b**), vinyl chloride (**2c**), allyl chloride (**2d**), allyl bromide (**2e**), acrylonitrile (**2f**), allyl alcohol (**2g**), and mesityl oxide (**2h**). It was established that the reactions yield predominantly products of the addition of chloride **1** at the C=C bond of the initial compounds **2a–f** (Scheme 1). Olefins **2a–e** enter into this reaction most smoothly. In the case of nitrile **2f**, the yield of the corresponding pentafluorothio derivative is low.[7] In the reactions of functionalized olefins **2g** and **2h**, we failed to isolate the desired products.

Scheme 1

$$\underset{\mathbf{2a-f}}{CH_2{=}CRR^1} + \underset{\mathbf{1}}{SF_5Cl} \longrightarrow \underset{\mathbf{3a-f}}{SF_5CH_2CClRR^1}$$

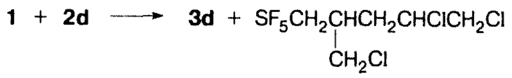
R = Me, R^1 = COOMe (**a**); R = H, R^1 = COOMe (**b**), Cl (**c**), CH_2Cl (**d**), CH_2Br (**e**), CN (**f**)

The reactions were initiated thermally and carried out in an autoclave with the use of Khladon-113 (Freon) as the solvent. The optimum reaction temperatures were in the range of 100—150 °C. Heating the reaction mixture to higher temperatures resulted in substantial resinification and a decrease in the yields of the target compounds. The use of initiators of radical reactions (benzoyl peroxide or bromine) increases the yields of pentafluorothio derivatives, whereas the use of inhibitors (for example, hydroquinone) sharply decreases their yields. All these facts agree well with the present view that the reactions with SF_5Cl are of a radical nature.[1,8]

Note that compounds **3a–f** are the products of the addition of the $^{\cdot}SF_5$ radical to the terminal CH_2 group of the initial olefins **2a–f**. This agrees with the previous suggestion[9] that the direction of the addition of chloride **1** at the multiple bond of terminal olefins is sterically controlled owing to the bulkiness of the $^{\cdot}SF_5$ radical. However, the reaction of **2b** with a large excess of compound **1** yielded a small amount of a product of the addition of two SF_5 groups at the C=C bond.

$$\mathbf{1} + \mathbf{2b} \longrightarrow \mathbf{3b} + \underset{\mathbf{4}}{SF_5CH_2CH(SF_5)COOMe}$$

Oligomerization and fluorination are alternative transformations of the intermediates of these reactions. Resinification was observed to a greater or lesser extent in all the cases under consideration. The suggestion that oligomerization of the initial olefin is the basis for this process was confirmed by isolation of dimer **5** in the reaction of compound **1** with allyl chloride **2d**.



$$\mathbf{1} + \mathbf{2d} \longrightarrow \mathbf{3d} + SF_5CH_2\underset{\displaystyle CH_2Cl}{\underset{|}{C}}HCH_2CHClCH_2Cl$$

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The formation of the product of the fluorination of the starting substrate rather than the pentafluorothio derivative was observed in the reaction of compound **1** with allyl alcohol **2g**. This reaction carried out under drastic conditions gave 2-chloro-3-fluoropropan-1-ol (**6**) in moderate yield.

$$\mathbf{1} + \mathbf{2g} \longrightarrow \underset{\mathbf{6}}{FCH_2CHClCH_2OH}$$

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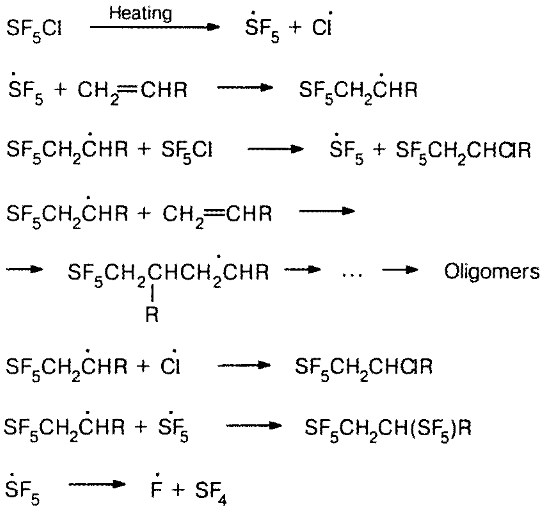
There is evidence in the literature that SF_5Cl can act as a fluorinating agent as, for example, in the reaction with cyclohexene in which 2-chloro-1-fluorocyclohexane is the major product.[1] This behavior of compound **1** is attributable to the fact that the $^{\cdot}SF_5$ radical decomposes rather readily, with the elimination of the fluorine radical and the formation of a molecule of sulfur tetrafluoride. No unambiguous evidence is available that only chlorination products form. On the whole, the experimental results make it possible to present the following scheme of the elementary reactions of compound **1** with the olefins under study (Scheme 2, fluorination is not considered).

Scheme 2



In addition to the reactions with substituted olefins considered above, we attempted to extend the reaction with SF_5Cl to aromatic compounds using anthracene and toluene as examples. According to the ^{19}F NMR data, in the first case a product containing the SF_5 group was obtained even under rather mild conditions (heating at 60—80 °C). However, the reaction of toluene carried out under rather drastic conditions gave only a fluorination product. The structures of the compounds obtained are currently under examination.

Some possibilities of the use of pentafluorothio derivatives for further synthesis were investigated using compounds **3d** and **3e**. Thus, these compounds react with KOH in polar solvents to form 3-pentafluorothioprop-1-yne (**7**) in high yield, which is a new representative of acetylenes containing the pentafluorothio group.[9]

$$\textbf{3d} \text{ or } \textbf{3e} + KOH \longrightarrow SF_5CH_2C{\equiv}CH$$

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Under very mild conditions, these compounds react with fluorosulfonyl hypochlorite $ClOSO_2F$. The reaction starts at temperatures < 0 °C and ends with the formation of the corresponding bisfluorosulfonate (**8**) in high yield as a result of the replacement of chlorine atoms (or bromine and chlorine atoms) by the fluorosulfonyloxy group.

$$\textbf{3d} \text{ or } \textbf{3e} + 2\,ClOSO_2F \longrightarrow SF_5CH_2\underset{\displaystyle OSO_2F}{\underset{|}{C}}HCH_2OSO_2F$$

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The above-mentioned reactions demonstrate the stability of the pentafluorothio group to such drastic reagent as a strong alkali (KOH) and a strong oxidizing agent ($ClOSO_2F$).

Experimental

The ^{19}F NMR (188.31 MHz, CF_3COOH as the external standard) and ^1H NMR (200.13 MHz, Me_4Si as the internal standard) spectra were recorded on a Bruker WR-200 instrument.

The purity of compounds was monitored by GLC on a LKhM-8MD instrument (3 m×4 mm column, 20% FS-T-5 on Chromosorb P (80—100 mesh), helium as the carrier gas) and by TLC on Silufol UV-254 plates. Preparation of methyl 2-chloro-3-pentafluorothiopropionate (**3b**) and 2-chloro-3-pentafluorothiopropionitrile (**3f**) has been described previously.[7]

Methyl 2-chloro-2-methyl-3-pentafluorothiopropionate (3a). A mixture of chloride **1** (29 g, 0.18 mol) and ester **2a** (18 g, 0.18 mol) in Khladon-113 (60 mL) was heated with periodic shaking in a metal autoclave at 120—130 °C for 10 h. The mixture was cooled, and the solvent was removed. Fractionation of the residue gave product **3a** in a yield of 18 g (38%), b.p. 85—88 °C (20 Torr). Found (%): C, 23.4; H, 3.6. $C_5H_8ClF_5O_2S$. Calculated (%): C, 22.9; H, 3.0. ^{19}F NMR, δ: −144.0 (m, SF_A); −141.0 (quintet, SF_B). ^1H NMR, δ: 1.35 and 1.45 (both s, CH_3); 3.60 (s, OCH_3); 3.70 (m, CH_2).

Reaction of ester 2b with excess chloride 1. The reaction of compound **1** (16 g, 0.10 mol) with **2b** (4 g, 0.033 mol) in Khladon-113 (20 mL) was carried out at 120 °C for 20 h under the conditions of the above-described experiment and gave product **3b** in a yield of 1.8 g (43%), b.p. 70—72 °C (90 Torr), n_D^{20} 1.4401 (*cf.* Ref. 7), and methyl 2,3-bis(pentafluorothio)propionate (**4**) in a yield of 1.27 g (31%), b.p. 81 °C (8 Torr), n_D^{20} 1.4451. Found (%): C, 14.6; H, 1.4; F, 54.3. $C_4H_6F_{10}O_2S_2$. Calculated (%): C, 14.1; H, 1.3; F, 55.8. ^{19}F NMR, δ: −143.4 (d, SF_A); −143.6 (d, $SF_{A'}$); −161.6 (quintet, SF_B); $J_{F(A,A')-F(B)}$ = 144 Hz.

1,1-Dichloro-2-pentafluorothioethane (3c). The reaction of compound **1** (8.5 g, 0.052 mol) with vinyl chloride **2c** (2.5 g, 0.040 mol) in Khladon-113 (20 mL) carried out at 100—120 °C for 8 h gave product **3c** in a yield of 5.7 g (62.9%), b.p. 108—110 °C, n_D^{20} 1.3841 (*cf.* Ref. 1). ^{19}F NMR, δ: −134.0 (quintet, SF_B); −165.0 (d, SF_A). ^1H NMR, δ: 3.1 (d, CH_2); 5.9 (CH).

2,3-Dichloro-1-pentafluorothiopropane (3d). The reaction of compound **1** (12 g, 0.074 mol) with allyl chloride **2d** (5.3 g, 0.070 mol) in the presence of bromine (0.5 g) at 80—100 °C for 8 h gave 11.3 g (68%) of **3d**, b.p. 35—38 °C (3 Torr). Found (%): C, 15.0; H, 2.3. $C_3H_5Cl_2F_5S$. Calculated (%): C, 15.1; H, 2.1. ^{19}F NMR, δ: −144.0 (d.m, SF_A);

−159.2 (quintet, SF_B); $J_{F(A)-F(B)}$ = 146 Hz, intensity ratio A : B = 4 : 1. 4,5-Dichloro-2-chloromethyl-1-pentafluorothiopentane (**5**) was also isolated in a yield of 0.5 g (5%), b.p. 90—100 °C (3 Torr). Found (%): C, 21.5; H, 3.5; Cl, 31.1. $C_6H_{10}Cl_3F_5S$. Calculated (%): C, 22.9; H, 3.1; Cl, 33.4. ^{19}F NMR, δ: −138.2 (d.m, SF_A); −176.0 (quint.d, SF_B); $J_{F(A)-F(B)}$ = 145 Hz, intensity ratio A : B = 4 : 1. ^1H NMR, δ: 2.07 (m, CH); 2.85 (m, CH_2); 2.8 (m, 2 CH_2Cl, CH_2SF_5); 4.20 (m, CHCl).

In the absence of a catalyst, the reaction of **1** (3.2 g, 0.020 mol) with **2d** (2.7 g, 0.036 mol) gave **3d** and **5** in yields of 0.8 g (18%) and 4.0 g (64%), respectively.

1-Bromo-2-chloro-3-pentafluorothiopropane (3e). The reaction of compound **1** (22.7 g, 0.14 mol) with **2e** (17.0 g, 0.14 mol) in Khladon-113 (40 mL) carried out at 80—100 °C for 8 h gave product **3e** in a yield of 17.0 g (43%), b.p. 55—56 °C (3 Torr), n_D^{20} 1.5441, d_4^{20} 2.03. Found (%): C, 13.5; H, 2.0. $C_3H_5BrClF_5S$. Calculated (%): C, 12.7; H, 1.8. ^{19}F NMR, δ: −141.8 (d, SF_A); −161.8 (quintet, SF_B); $J_{F(A)-F(B)}$ = 142 Hz, intensity ratio A : B = 4 : 1. ^1H NMR, δ: 3.75 (t, CH_2Br); 3.95 (d, CH_2SF_5); 4.25 (m, CHCl), intensity ratio was 2 : 2 : 1.

Under analogous conditions, the reaction of **1** (2.5 g, 0.0154 mol) with **2e** (2.4 g, 0.020 mol) in the presence of benzoyl peroxide (0.3 g) gave compound **3e** in a yield of 3.1 g (72%).

Reaction of compound 1 with allyl alcohol (2g). Under the above-described conditions, the reaction of compound **1** (10 g, 0.062 mol) with **2g** (2 g, 0.034 mol) in the presence of catalytic amounts of bromine at 80—100 °C for 8 h gave 2-chloro-3-fluoropropan-1-ol **6** in a yield of 2.3 g (60%), b.p. 130—132 °C. Found (%): C, 32.9; H, 6.1. C_3H_6ClFO. Calculated (%): C, 32.1; H, 5.3. ^1H NMR, δ: 4.11 (d, CH_2O, J_{H-H} = 5 Hz); 5.25 (d.d, CH_2F, J_{H-F} = 30 Hz, J_{H-H} = 21 Hz); 5.85 (t.t.d, CHCl), intensity ratio was 2 : 2 : 1; 6.85 (OH). ^{19}F NMR, δ: 55.1 (br.s, CF).

Dehydrohalogenation of 3d and 3e.[10] A mixture of **3e** (15 g, 0.053 mol) and KOH (17 g, 0.30 mol) in diglyme (10 mL) was heated to 80 °C. The products that formed were collected in a trap (−78 °C). The fractionation of the products gave 3-pentafluorothioprop-1-yne (**7**) in a yield of 5.4 g (61%), b.p. 45—50 °C (120 Torr), n_D^{20} 1.3512, d_4^{20} 1.59. Found (%): C, 21.4; H, 2.1; F, 56.9. $C_3H_3F_5S$. Calculated (%): C, 21.7; H, 1.8; F, 57.2. ^{19}F NMR, δ: −140.8 and −144.5 (both d, SF_A); −161.4 and −161.7 (both quintet, SF_B); $J_{F(A)-F(B)}$ = 145 Hz, intensity ratio was A : B = 4 : 1. ^1H NMR, δ: 3.2 (s, CH); 3.52 and 3.55 (CH_2), intensity ratio was 1 : 2.

Under analogous conditions, the reaction of **3d** (38 g, 0.162 mol) with KOH (34 g, 0.60 mol) gave compound **7** in a yield of 21 g (79%).

Reactions of 3d and 3e with $ClOSO_2F$. $ClOSO_2F$ (1.9 g, 0.0143 mol) was added slowly with stirring to a solution of **3e** (2 g, 0.0071 mol) in perfluorotriethylamine (10 mL) at −15—0 °C. The mixture was kept at room temperature for 0.5 h. The solvent was removed *in vacuo* to give 1,2-bis(fluorosulfonyloxy)-3-pentafluorothiopropane (**8**) in a yield of 2.3 g (92%) as a yellowish oily liquid stable below 50 °C. ^{19}F NMR, δ: −118.8 and −119.2 (both s, 2 OSO_2F); −144.3 (d, SF_A); −160.7 (quintet, SF_B). ^1H NMR, δ: 3.40 (m, CH_2OSO_2F); 3.42 and 3.60 (m, CH_2SF_5); 4.2 (m, $CHOSO_2F$).

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