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Unusual reactivity of 3-chloro-1-pentafluorosulfanylpropene in nucleophilic substitution reactions

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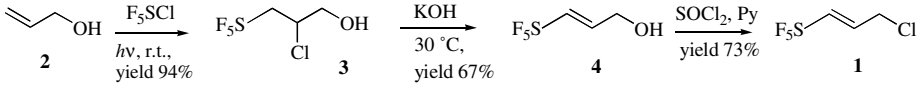
Abstract—Treatment of 3-chloro-1-pentafluorosulfanylprop-1-ene **1** with KCN yielded the product of prototropic rearrangement $ClCH{=}CHCH_2SF_5$, whereas reactions with NaN_3 and KSCN gave the S_N2 products. Ab initio calculations at MP2/6-311++G** level are used to explain the unusual behaviour of cyanide. It was found that proton transfers from both **1** to CN^- and from HCN to the anion of **1** are exothermic. In contrast, azide and thiocyanate ions are too weakly basic to deprotonate **1**.

The introduction of a pentafluorosulfanyl group, SF_5, into organic molecules brings about substantial changes with regard to their physical, chemical and biological behaviour. Compounds containing this group often possess advantageous properties due to the electronegativity, high hydrolytic stability and steric effect of the SF_5-substituent. These properties are manifested in various potential applications such as solvents for polymers, surfactants, fumigants, rocket fuels and others.[1–4] Therefore, the preparation of new organic molecules with an SF_5-group as well as the investigation of their properties, is very important for both theoretical and applied chemistry.

Allylic systems have a broad scope in organic synthesis due to their high reactivity and ability to form different kinds of products with or without allylic rearrangement depending on their structure, the nature of reagent and reaction conditions. In the course of our investigations of the synthesis and reactivity of pentafluorosulfanyl-containing organic compounds, we synthesized 3-chloro-1-pentafluorosulfanylpropene **1** by a three-step sequence (Scheme 1). The pentafluorosulfanyl group was introduced into allyl alcohol **2** by gas-phase radical addition of F_5SCl and subsequent alkali treatment, following a known method of synthesis of pentafluorosulfanylethene.[5] Standard treatment of the resulting alcohol **4** with thionyl chloride gave the corresponding allyl chloride **1**.

With the intention of preparing some heteroaromatic compounds containing the F_5S-moiety (thiazoles, triazoles, tetrazoles, etc.), we studied the reactions of **1** with different nucleophiles. It was found that this substrate reacted smoothly at 40–50 °C with sodium azide yielding **5**, the product of nucleophilic substitution in ca. 83% yield. Similarly, treatment with potassium thiocyanate gave rise to the corresponding product of S_N2 reaction (Scheme 2).

However, reaction of **1** with KCN failed to give the nucleophilic substitution product. Instead of the nitrile, we isolated 1-chloro-3-pentafluorosulfanylpropene **7** (Scheme 3).



Scheme 1.

Keywords: Pentafluorosulfanyl group; Nucleophilic substitution; Rearrangements.
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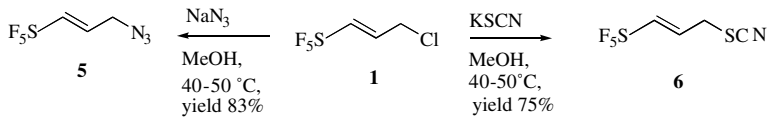
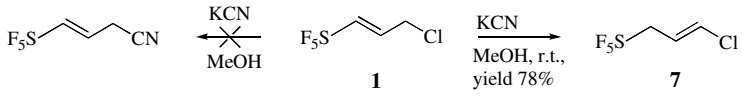
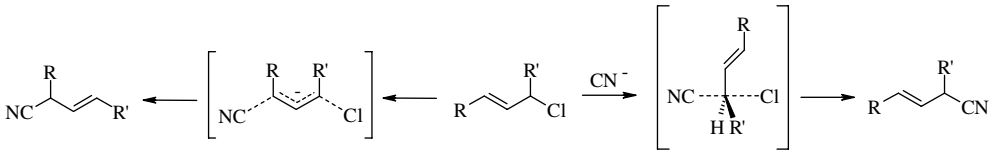


Scheme 2.



Scheme 3.



Scheme 4.

This result was unexpected since allyl chlorides are normally very good substrates for nucleophilic substitution reactions. We have found a single example of a similar nucleophile-induced double bond migration in substituted allyl chlorides: treatment of 3-chloro-3-(4-nitrophenyl)propene with triethylamine gave rise to the corresponding styrene derivative.[6] Moreover, cyanide is usually considered to be a good nucleophile with relatively low basicity.[7] Therefore, S_N2 or S_N2' reactions are expected between cyanide and allylic substrates (Scheme 4).

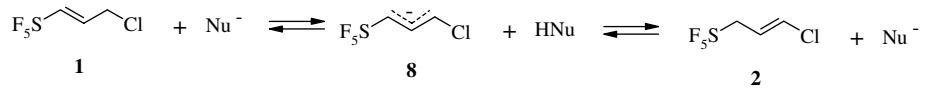
We have calculated[8] the structure and properties of **1** to understand the effect of the SF_5-substituent on the chemical behaviour of the allyl chloride (Table 1). The results obtained showed that a charge-controlled reaction would proceed on an α carbon atom but orbital control moves the nucleophilic attack to the γ carbon. However, the bulkiness of the pentafluorosulfanyl group prevents an S_N2' reaction. As a result, even soft nucleophiles react with **1** by an S_N2 mechanism. All three studied anions (N_3^-, SCN^-, CN^-) are good nucleophiles but weak bases.[7] Cyanide is the most basic of them. Earlier, we showed[9] that the basicity of the nucleophile is an important factor in S_N2/S_N2' competition: the higher the basicity of the nucleophile, the more preferable is attack on the γ carbon atom. Electron-withdrawing groups in the substrate also favour the S_N2' mechanism. This is why the energy barrier for the S_N2 reaction of a cyanide ion with **1** is large. At the same time, steric effects prevent S_N2' reaction. However, the basicity of cyanide also has another effect: cyanide can deprotonate an appropriate substrate. The base-catalyzed nature of isomerization of **1**–**7** is supported by the fact that treatment of **1** with the slightly more basic potassium carbonate leads to the same result.

Table 1. The contributions of α and γ carbon atoms of **1** to LUMO, ξ, and charges on atom, *Q*, calculated at MP2/6-311G** levels

ξCα	ξCγ	*Q*Cα	*Q*Cγ	*Q*CH_2	*Q*CH
0.18	0.42	−0.20	−0.31	0.13	−0.12

Proton transfer is a fast process for exothermic reactions between O-, N- and S-atoms but is relatively slow for CH-acids. This has been explained by non-perfect synchronization between the extent of proton transfer and the extent of delocalization of a negative charge in the developing carbanion.[10] The more efficient is the mesomeric stabilization of the carbanion, the slower is proton transfer from a CH-acid with the same acidity. However, the electron-withdrawing effect exerted by the pentafluorosulfanyl group is believed to be inductive rather than a mesomeric effect. Therefore, proton transfer from **1** must be fast for an exothermic process. We have calculated the reaction energy for the deprotonation of **1** by different anions as well as for the overall transformation of **1** into **7** (Table 2). The isomerization process is exo-

Table 2. Reaction energies for processes **1** + Nu^- ⇆ **8** + HNu and **8** + HNu ⇆ **2** + Nu^- calculated at MP2/6-311++G** level, kcal/mol



Nu	**1** + Nu^- ⇆ **8** + HNu	**8** + HNu ⇆ **2** + Nu^-
CN^-	−2.9	−1.4
N_3^-	11.0	−15.3
SCN^-	32.6	−36.9

thermic: calculations by HF/6-31G, MP2/6-311G** and MP2/6-311++G** gave reaction energies of −5.5, −3.8 and −4.3 kcal/mol, respectively. The data in Table 2 demonstrates that both azide and thiocyanate ions are too weak to deprotonate **1** or **7**. In the case of cyanide, both deprotonation of **1** and reprotonation of the allyl anion **8** leading to **7** are exothermic processes. The low reactivity of **1** in nucleophilic substitution reactions, explains the unusual behaviour of cyanide but 'normal' reactivity of azide and thiocyanate ions. In the case of cyanide, the exothermic proton transfer predominates. Deprotonation is impossible for azide and thiocyanate ions due to high endothermicity. So, for azide and thiocyanate, an S_N2 reaction is the only possible process.

It was found that N_3^- and SCN^- react with 3-chloro-1-pentafluorosulfanylprop-1-ene by S_N2 reaction but treatment of this substrate with CN^- leads to 1-chloro-3-pentafluorosulfanylprop-1-ene by base-catalyzed double bond migration. These results have been interpreted using ab initio calculations at the MP2/6-311++G** level. It was shown that proton transfer from **1** to a cyanide ion is an exothermic process, in contrast to the other studied nucleophiles. At the same time, **1** is an unreactive substrate in S_N2' processes and has low reactivity in S_N2 reactions. The structures of **1**, **4**–**7** were proved by ^1H, ^{19}F and ^{13}C NMR spectroscopy.[11]

Acknowledgements

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11. Compound **1**: liquid, bp 64–65 °C (60 mm). ^1H NMR (200 MHz, $CDCl_3$): δ = 4.18–4.21 (m, 2H), 6.51–6.86 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 40.95 (s), 133.0 (pent, J_{C-F} = 7.4 Hz), 143.55 (d pent, J_{C-F} = 1.6 Hz, J_{C-F} = 21.3 Hz); ^{19}F NMR (188 MHz, $CDCl_3$): δ = 140.56 (m, incl. app. d, J_{F-F} = 148.0 Hz, 4F), 157.67–160.86 (m, 1F). Elemental analysis: % calcd for $C_3H_4ClF_5S$: C, 17.79; H, 1.99; S, 15.83%; found: C, 17.94; H, 2.07; S, 15.67%. Compound **4**: liquid, bp 83 °C (20 mm). ^1H NMR (200 MHz, $CDCl_3$): δ = 4.26 (t, br, J_{H-H} = 5.6 Hz, 1H), 4.31–4.41 (m, 2H), 6.53–6.83 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 59.97 (s), 137.36 (pent, J_{C-F} = 7.0 Hz), 140.22 (d pent, J_{C-F} = 1.7 Hz, J_{C-F} = 20.7 Hz); ^{19}F NMR (188 MHz, $CDCl_3$): δ = 141.30 (m, incl. app. d, J_{F-F} = 150.9 Hz, 4F), 159.68–162.88 (m, 1F). Elemental analysis: % calcd for $C_3H_5F_5OS$: C, 19.57; H, 2.74; S, 17.40%; found: C, 19.42; H, 2.82; S, 17.57%. Compound **5**: oil. ^1H NMR (200 MHz, $CDCl_3$): δ = 4.09 (d pent, J_{H-H} = 2.4 Hz, J_{H-H} = 2.0 Hz, 2H), 6.47–6.59 (m, 1H), 6.74 (d pent t, J_{H-H} = 8.4 Hz, J_{H-F} = 6.2 Hz, J_{H-H} = 1.8 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 49.97 (s), 132.71 (pent, J_{C-F} = 7.1 Hz), 142.90 (d pent, J_{C-F} = 1.7 Hz, J_{C-F} = 21.3 Hz); ^{19}F NMR (188 MHz, $CDCl_3$): δ = 140.39 (m, incl. app. d, J_{F-F} = 150.5 Hz, 4F), 157.94–161.13 (m, 1F). Elemental analysis: % calcd for $C_3H_4F_5N_3S$: C, 17.23; H, 1.93; S, 15.32%; found: C, 17.48; H, 2.12; S, 15.60%. Compound **6**: oil. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.65–3.66 (m, 1H), 3.67–3.69 (m, 1H), 6.54–6.86 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 33.24 (s), 110.49 (s), 131.41 (pent, J_{C-F} = 7.0 Hz), 145.12 (d pent, J_{C-F} = 1.5 Hz, J_{C-F} = 20.1 Hz); ^{19}F NMR (188 MHz, $CDCl_3$): δ = 140.51 (m, incl. app. d, J_{F-F} = 150.4 Hz, 4F), 156.61–159.81 (m, 1F). Elemental analysis: % calcd for $C_4H_4F_5NS_2$: C, 21.33; H, 1.79; S, 28.48%; found: C, 21.47; H, 1.84; S, 28.56%. Compound **7**: liquid, bp 72 °C (65 mm). ^1H NMR (200 MHz, $CDCl_3$): δ = 4.55 (dd pent, J_{H-H} = 7.2 Hz, J_{H-H} = 0.5 Hz, J_{H-F} = 7.6 Hz, 2H), 6.12 (dd, J_{H-H} = 7.2 Hz, J_{H-H} = 7.6 Hz, 1H), 6.50 (dt, J_{H-H} = 7.2 Hz, J_{H-H} = 1.0 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 67.05 (dt pent, J_{C-F} = 1.0 Hz, J_{C-F} = 16.5 Hz), 120.91 (pent, J_{C-F} = 4.1 Hz), 126.58 (pent, J_{C-F} = 1.0 Hz); ^{19}F NMR (188 MHz, $CDCl_3$): δ = 143.72 (m, incl. app. d, J_{F-F} = 145.0 Hz, 4F), 157.50–161.23 (m, 1F). Elemental analysis: % calcd for $C_3H_4ClF_5S$: C, 17.79; H, 1.99; S, 15.83%; found: C, 17.84; H, 2.05; S, 15.97%.