Trifluoromethylsulfide Anion: Generation and Reaction with Pentafluoropyridine

Wojciech Dmowski and Alois Haas***

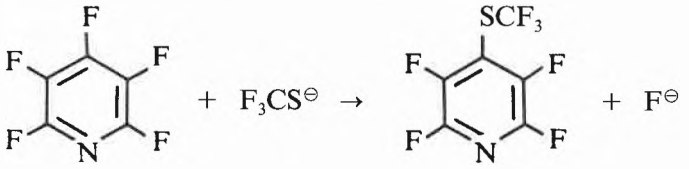
Abstract: The anion $F_3CS^{\ominus}$, generated from thiocarbonyl difluoride **1** and alkali metal fluorides, reacts with pentafluoropyridine **2** to give high yield of 2,3,5,6-tetrafluoro-4-trifluoromethylthiopyridine **3**.

Thiocarbonyl difluoride **1** has been long time ago reported to react with alkali metal fluorides at −80 °C to give a colourless voluminous powder which for the reaction with CsF was presumed to be caesium trifluoromethyl sulfide, F_3CSCs[1]. This salt when warmed to ambient temperature decomposes to give an orange-red liquid consisting of trifluoromethyl-fluorodithioformate, $F_3CS(F)C{=}S$, and bis(trifluoromethyl)-trithiocarbonate, $(F_3CS)_2C{=}S$, and a solid polymer of general formula $(F_2CS)_x$. Formation of these products has been postulated to involve the trifluoromethylsulfide anion, $F_3CS^{\ominus}$, as an intermediate[1]. Since then no other reactions of $F_3CS^{\ominus}$ have been reported, probably, because of the unusual ease with which its precursor, i.e. thiocarbonyl difluoride **1**, undergoes either anionic or cationic or free-radical polymerisation and co-polymerisation[2].

We have proved that the anion $F_3CS^{\ominus}$ can be generated from **1** and alkali metal fluorides in an aprotic solvent, and that it is stable enough to be trapped by sufficiently electrophilic substrates having suitable leaving groups, e.g. perfluoroheterocycles, to give trifluoromethylthio-substituted derivatives. For example, gaseous thiocarbonyl difluoride **1** was enabled to react under an initial pressure of ca. 700 Torr with a stirred solution of pentafluoropyridine **2** (2.46 g, 14.5 mmole) in dry acetonitrile (8 mL) containing caesium fluoride (0.65 g, 4.3 mmole) at −10 to 5 °C. A spontaneous pressure drop occured until nearly equimolar amounts of **1** (13.8 mmole) were absorbed. A pale-yellow solution was formed which, as shown by gas liquid chromatography (GLC), besides the solvent contained a sole compound. The crystal structure of CsF evidently changed during the reaction such that a light fine powder was formed. Distillation of the solution gave a colourless liquid (*b.p.* 133–134 °C, GLC purity > 98%) identified as 2,3,5,6-tetrafluoro-4-trifluorothiopyridine **3**; the yield of isolated product was 84% (2,9 g, 11.6 mmole) as related to **1**.

$$F_2C{=}S + F^{\ominus} \rightleftharpoons F_3CS^{\ominus}$$

1



2 **3**

2,3,5,6-Tetrafluoro-4-trifluorothiopyridine **3** is a new compound with the structure having been elucidated from elemental analysis and spectral data. The mass spectrum indicates a high intensity molecular ion, m/z 251, ions with m/z 232, 182, and 150 formed by elimination of fluorine, the CF_3, and the CF_3S fragments, respectively, ions with m/z 138, 105, 100, and 93 which are characteristic for the fragmentation of pentafluoropyridine and its derivatives[3], and the base peak resulting from $CF_3^{\oplus}$. The ^{19}F-NMR spectrum ($CDCl_3$, CCl_3F) exhibits three signals with relative intensities 3:2:2, $\delta = -40.7$ (t, CF_3), −87.8 (m, 2F at ring positions 2,6), and −131.8 (m, 2F at ring positions 3,5). The coupling-pattern for the signals is identical with that reported for 2,3,5,6-tetrafluoro-4-trifluoromethylpyridine[4]. The CF_3-group signal splitting ($J = 5.80$ Hz) is due to a coupling to the F-atoms at the 3 and 5 ring positions. The ^{13}C-NMR spectrum of **3** ($CDCl_3$, TMS) is consistent with that reported for 4-chloro-2,3,5,6-tetrafluoropyridine[5]. Signals of the C-2, C-3, C-5, and C-6 ring atoms form a complex system centered at $\delta = 143.5$. The C-4 signal, $\delta = 118.14$ (tq), exhibits coupling to the F-atoms at the 3 and 5 ring positions ($J = 17.65$ Hz) and to the CF_3-group ($J = 2.94$ Hz). The CF_3-group carbon atom gives a characteristic strong quartet at $\delta = 127.60$ ($J = 311.8$ Hz).

The reaction of pentafluoropyridine **2** with thiocarbonyl difluoride **1** is also promoted by catalytic amounts of CsF or by KF; however, in these cases, the reaction mixture readily turns dark-brown and the product is contaminated with tar-like by-products. No reaction occurs in the absence of a solvent. When using an excess of **1** and more extreme reaction conditions subsequent substitution of compound **3** with the anion $F_3CS^{\ominus}$ occurs.

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* *Correspondence:* Prof. Dr. A. Haas
Lehrstuhl für Anorganische Chemie II
Ruhr-Universität Bochum
Postfach 102148, D-4630 Bochum I
(Bundesrepublik Deutschland)

** On leave of absence from the Institute of Organic Chemistry, Polish Academy of Science, 00-961 Warsaw (Poland).

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