2-Chloro-3-(dimethylamino)prop-2-enoyl Fluoride, a Stable Acyl Fluoride

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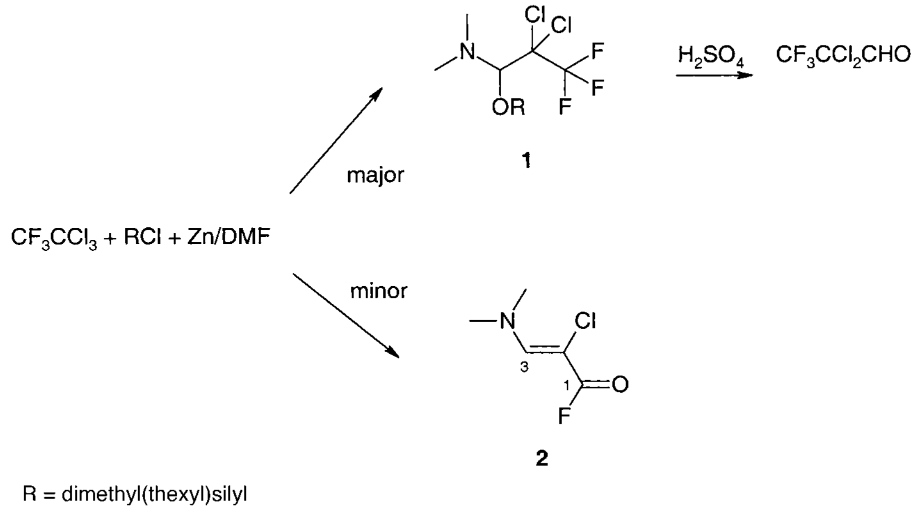
The title compound is formed as a side-product in the reaction of CF_3CCl_3 with Zn/DMF and dimethyl(thexyl)silyl chloride (=dimethyl(1,1,2-trimethylpropyl)silyl chloride). The structure and the double-bond configuration are deduced from its ^{13}C-NMR data. Its formation is discussed in terms of a *Vilsmeier*-type formylation and a reductive elimination.

Introduction. – In the context of a search for versatile and inexpensive CF_3-containing synthetic building blocks [1][2], a synthesis of polyhalogenated aldehydes has been described [2], which consists of two steps as shown in *Scheme 1* for the example of CF_3CCl_2CHO. Without cooling the reaction mixture during the markedly exothermic first step of the *Vilsmeier*-type formylation, a side-product **2** is formed in amounts that increase with the reaction temperature. The structure elucidation of the novel compound **2** with NMR and a discussion of its formation are the topics of this paper.

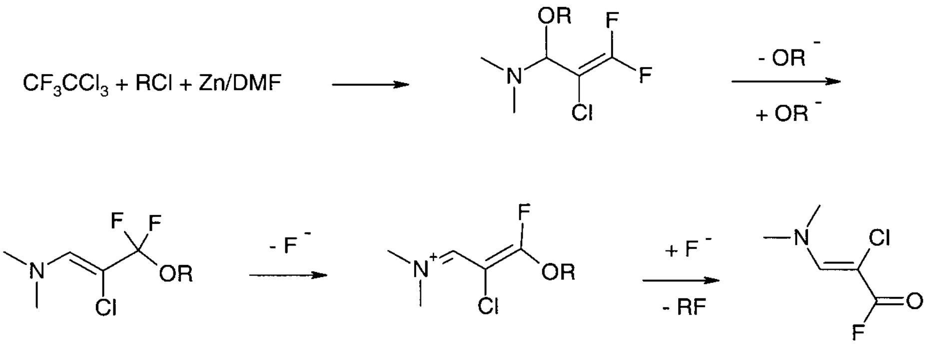
Scheme 1



Structure of the Acyl Fluoride 2. – Compound **2** has the elemental composition C_5H_7ClFNO and shows a C=O absorption in the IR spectrum at 1760 cm^{-1}. The structure of **2** was deduced from its ^{13}C-NMR data (*cf. Exper. Part*). In detail, the ^{13}C signal at 156.6 ppm has a ^1J(C,F) value of 317 Hz. The size of this coupling constant shows that the F-atom is directly bound to a C=O C-atom (*cf.* the C=O signal of AcF [3]: 162.7 ppm, $^1J = 356$ Hz, or of PhCOF [4]: 158.0 ppm, $^1J = 343.5$ Hz). Likewise, the large coupling constant of 77 Hz (^2J(C,F)) of the signal at 80.4 ppm requires the corresponding C-atom to be in β-position to the F-atom [3][4]. The chemical shift of this C-atom and the absence of a coupling to the Me protons indicate that it must be substituted by the Cl-atom and not by the Me_2N group. The C-atom at 150.1 ppm, on the other hand, is coupled to the Me protons and is, therefore, substituted by the Me_2N group. This C-atom carries also a proton as shown by a ^1J(C,H) coupling of 169 Hz. Finally, the vicinal coupling between the C=O C-atom and the vinyl proton is 3.5 Hz, thereby establishing a (*Z*)-configuration of the C=C bond. At room temperature, two MeN signals are observed in (D_6)DMSO solution due to hindered rotation about the N–C(3) bond. Consequently, the C(1)–C(2) bond has appreciable double-bond character. This explains the decrease of ^1J(C,F) and the increase of ^2J(C,F) as compared with the same values in PhCOF [4] (317 *vs.* 343.5 Hz, and 77 *vs.* 61.3 Hz).

Discussion. – The formation of **2** as a side-product in the reaction of CF_3CCl_3 with Zn/DMF and dimethyl(thexyl)silyl chloride (thexyl = 1,1,2-trimethylpropyl) can be rationalized as a *Vilsmeier*-type formylation and a reductive elimination (*cf.* [5]). A possible reaction sequence is depicted in *Scheme 2*. The first step is based upon the following observations: CF_3CCl_2ZnCl/DMF does not react with DMF in the absence of the silyl chloride [6], the formation of the analogous 2-chloro-1,1-difluoroalk-1-en-3-ols by reductive elimination is a known side reaction of CF_3CCl_3 with Zn/DMF and aldehydes [6][7], and **2** is not formed from **1** under the reaction conditions applied, not even at elevated temperatures. The reaction sequence also explains the origin of the acyl fluoride moiety in the absence of H_2O, *i.e.*, by working under rigorously anhydrous

Scheme 2



2

R = dimethyl(thexyl)silyl

conditions. Compound **2** may be regarded as a vinylogous *N*-formyl fluoride: *N*-formyl fluorides are known to form from the corresponding *N*-(trifluoromethyl) amines by hydrolysis [8].

Compound **2** has been stored for years at room temperature without recognizable degradation. Even though acyl fluorides undergo hydrolysis much slower than acyl chlorides [9], this stability is remarkable and is due to the electron donation of the amino substituent in agreement with the amide-type hindered rotation observed by NMR spectroscopy.

Experimental Part1)

General. See [1]. The reaction was carried out under Ar. Zn Powder from *Riedel-de Haen* was activated as mentioned in [10]. The solvents used were dried over molecular sieves.

2-Chloro-3-(dimethylamino)prop-2-enoyl Fluoride (**2**). Zn Powder (6.6 g) was mixed with 70 ml of DMF and cooled to 0–3°. A mixture of dimethylthexylsilyl chloride (36 g) and 1,1,1-trichloro-2,2,2-trifluoroethane (20 g) was slowly added within 1 h, and the temp. of the exothermic reaction was held at max. 10° for 1 further h. After addition of 100 ml of hexane, the hexane layer was separated, and the DMF layer was extracted again with hexane. The combined hexane layers were filtered, and the solvent was evaporated. The residue (20.2 g) was distilled at 80–82°/0.15 mbar to afford 10.2 g of **1** as a yellow oil [2] and 0.9 g of white crystalline **2**, which is removed as sublimate from the cooler. M.p. after sublimation 44–45°. IR (CH$_2$Cl$_2$): 1760, 1630. ^{1}H-NMR (CDCl$_3$): 7.50 (*d*, *J*(H,F) = 2, vinyl H); 3.26 (br. *s*, Me). ^{13}C-NMR ((D$_6$)DMSO, 25°, multiplicities of the signals in the proton coupled spectrum): 156.6 (*dd*, *J*(C,F) = 317, *J*(C,H) = 3.5, C(1)); 150.1 (*ddsept.*, ^1J(C,H) = 169, *J*(C,F) = 4, C(3)); 80.4 (*dd*, *J*(C,F) = 77, *J*(C,H) = 9, C(2)); 47.5 (*qm*, MeN *anti*); 38.2 (*qm*, MeN *syn*). At 120°, the two Me groups form a single broad peak at 42.3 ppm. MS: 151 (M^+). Anal. calc. for C$_5$H$_7$ClFNO (151.57): C 39.62, H 4.65, Cl 23.39, F 12.53, N 9.24; found: C 39.6, H 4.6, Cl 23.4, F 12.6, N 9.3.

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Received August 25, 2001

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1) This work was carried out at the Central Research Laboratories of *CIBA-GEIGY AG*, Basel.