Journal of Fluorine Chemistry, 16 (1980) 479–482

Received: March 21, 1980

SHORT COMMUNICATION

An Unexpected Reaction with 2,3,4,5,6-Pentafluoroformanilide

ROLF KOPPANG

Department of Dental Technology, University of Oslo,
Geitmyrsveien 69, Oslo (Norway)

There has recently been paid some attention to the preparation of 2,3,4,5,6-pentafluorophenylcarbonimidoyl dichloride, 1 [1]. As this compound would be an interesting intermediate for further reactions [2], the well-known route for preparing analogous compounds by reacting formanilides with a mixture of thionyl chloride and sulfuryl chloride was tried [2,3]. The yield of 1 was normally low (∿5%), but could be improved somewhat (∿15%) by cycling the temperature of the reaction mixture for some days. The results, however, were not reproducible. Addition of dimethylformamide [4] or silica gel [5,6] did not improve the yield of 1. Spectroscopic data for 1 were in accordance with published data [1], and 2,3,4,5,6-pentafluoroacetanilide was formed when 1 was boiled together with glacial acetic acid [1].

In the reactions described above N,N'-bis(N-2,3,4,5,6-pentafluoroimidoyl)pentafluoroaniline, 2, was formed in good yield together with a minor amount of 1 and N,N'-bis(2,3,4,5,6-pentafluorophenyl)formamidine, 3 [7]:

$$C_6F_5NHCHO + 2SO_2Cl_2 \xrightarrow{SOCl_2} \underset{1}{C_6F_5N=CCl_2} + \underset{2}{C_6F_5N(CH=NC_6F_5)_2} + \underset{3}{C_6F_5NHCH=NC_6F_5}$$

The structure of 2 has been confirmed by elemental analysis, IR and ^{1}H NMR spectra, and by comparing the MS spectrum of 2 with the one for 3. Compound 3 was the only reaction product when pentafluoroformanilide was treated with thionyl or sulfuryl chloride alone.

Infrared and NMR spectra were obtained by use of Perkin-Elmer 457 IR and 60 MHz NMR instruments. Mass spectra were recorded on a V.G. Micromass 7070F instrument attached to a V.G. 2200 data system.

Reaction with thionyl chloride

Pentafluoroformanilide 6.33 g (0.03 mol) was added to 15 ml thionyl chloride at ambient temperature. The mixture was warmed up slowly and refluxed for 7 h and the thionyl chloride distilled off. The residue was chromatographed on a silica gel column with a mixture of light petroleum and ether. In addition to the starting material one reaction product was isolated, viz. N,N'-bis(2,3,4,5,6-pentafluorophenyl)formamidine, 3, 2.60 g (46.5%) m.p. 162-163 °C. (The compound was identical with an authentic sample [7]).

Reaction with sulfuryl chloride

Pentafluoroformanilide 6.33 g (0.03 mol) was added to 15 ml sulfuryl chloride. The reaction and work up was performed as in the reaction with thionyl chloride and gave one reaction product, viz. N,N'-bis(2,3,4,5,6-pentafluorophenyl)formamidine, 3 0.46 (8.2%) m.p. 162-163 °C.

Reaction with a mixture of sulfuryl and thionyl chloride

Pentafluoroformanilide 6.33 g (0.03 ml) was added to a mixture of 8.1 g (0.06 mol) sulfuryl chloride dissolved in 20 ml thionyl chloride at ambient temperature. The mixture was stirred for 2 h, then slowly heated for 4.5 h, until the mixture started to reflux, whereupon unreacted sulfuryl and thionyl

chloride were distilled off. The remaining reaction mixture was chromatographed on neutral alumina (Woelm) with light petroleum mixed up with increasing amounts of ether. The first eluted compound, pentafluorophenylcarbonimidoyl dichloride, 1, was further purified by slow distillation under vacuum onto a cold finger. This gave 2,3,4,5,6-pentafluorophenylcarbonimidoyl dichloride, 0.41 g (5.2%). MS [Electron energy 70 eV; m/e (% rel.int.)]: 267(2.7, M^+), 265(17.0, M^+), 263(26.5, M^+), 230(30.3), 228(100), 193(41.1), 167(34.5), 117(31.5), 71(17.9), 69(20.5). IR (cm^{-1}) neat: 1663s, 1647sh, 1510s, 1138m, 1001s, 985s, 923s, 729w, 644m, 579w.

A sample treated with glacial acetic acid gave pentafluorophenylacetamide, m.p. 133-135 °C [1]. (IR, NMR and MS were in accordance with what should be expected from pentafluorophenylacetamide.)

The next compound eluted from the column was N,N'-bis-(N-2,3,4,5,6-pentafluoroimidoyl)pentafluoroaniline, 2, (n.c.) 3.42 g (60.1%) m.p. 137-138.5 °C. Found: C, 42.53; H, 0.48. Calc. for $C_{20}H_2F_{15}N_3$: C, 42.20; H, 0.35. MS [Electron energy 70 eV; m/e (% rel.int.)]: 569(5.2,M^+), 377(3.8), 376(21.7), 357(6.1), 285(1.4), 195(2.8), 194(30.0), 184(6.1), 183(100), 174(5.8), 167(9.7). ^1H NMR (60 MHz, $CDCl_3$): δ8.50(CH). IR (cm^{-1}) in KBr: 1630s, 1520s, 1502s, 1450m, 1377w, 1368w, 1300w, 1286w, 1245m, 1237m, 1102m, series of bands from 1015 to 932 (1015, 1002, 990, 977, 962, and 932).

Finally N,N'-bis(2,3,4,5,6-pentafluorophenyl)formamidine, 3, 0.38 g (6.7%) m.p. 162-163 °C, was eluted from the column.

1 T.I. Savchenko, T.D. Petrova, V.E. Platonov and G.G. Yakobson, J. Fluorine Chem., 9 (1977) 505, and J. Org. Chem. of U.S.S.R., 15 (1979) 909.

2 E. Kühle, Angew. Chem., 74 (1962) 861.

3 E. Kühle, B. Anders and G. Zumach, Angew. Chem., 79 (1967) 663.

4 R.C. De Selms, C.J. Fox and R.C. Riordan, Tetrahedron Lett. (1970) 781.

5 M. Hojo and R. Masuda, Synth. Commun., 5 (1975) 169, 173.

6 H. Hart, J.L. Reilly and J. Bau-Chien Jiang, J. Org. Chem., 42 (1977) 2684.

7 R. Koppang and K. Schaumburg, J. Fluorine Chem., 12 (1978) 169.