Journal of Fluorine Chemistry, 19 (1981/82) 85–88

Received: April 6, 1981

Synthesis of trichlorophosphazo-trifluoromethane and -pentafluoroethane

WALTER LEIDINGER and WOLFGANG SUNDERMEYER[+]

Department of Inorganic Chemistry, University of Heidelberg,
D-69oo Heidelberg, Im Neuenheimer Feld 27o,(Federal Republic
of Germany)

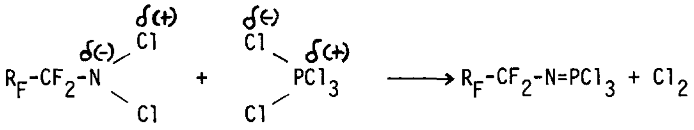
SUMMARY

The trichlorophosphazo compounds $CF_3\text{-}N{=}PCl_3$ and $C_2F_5\text{-}N{=}PCl_3$ could be obtained by reacting the corresponding perfluoroalkyl dichloroamines and phosphorous trichloride.

INTRODUCTION AND RESULTS

Trichlorophosphazo compounds have been studied for a long time. However, the smallest perfluorinated monomer compounds, $CF_3\text{-}NPCl_3$ (1) and $C_2F_5\text{-}NPCl_3$ (2) with fluorine in the α-position relative to nitrogen, have not yet been prepared. A probable reason for this may have been the difficulty in obtaining the free amines, which are the usual starting materials for preparing trichlorophosphazo compounds. As is known from the literature [1,2], $CF_3\text{-}NH_2$ as well as $CF_3\text{-}CF_2\text{-}NH_2$ easily lose HF to give the corresponding nitriles.

It seemed reasonable to use the dichloroamines instead. Because of the different polarities of N-Cl and P-Cl bonds [3], we decided to react the dichloroamines with phosphorous pentachloride when chloride should be eliminated.



$$R_F\text{-}CF_2\text{-}\overset{\delta(-)}{N}\!\!\begin{array}{l}\overset{\delta(+)}{Cl}\\ Cl\end{array} + \begin{array}{l}\overset{\delta(-)}{Cl}\\ Cl\end{array}\!\!\overset{\delta(+)}{PCl_3} \longrightarrow R_F\text{-}CF_2\text{-}N{=}PCl_3 + Cl_2$$

R_F = F, CF_3 1, 2

[+] Author to whom correspondence should be addressed.

It has been reported [3] that no reaction was observed between $FC(O)NCl_2$ and chlorinating agents (PCl_3, PCl_5, Al_2Cl_6); however, during our experiments we observed a side reaction between $CF_3\text{-}NCl_2$ and PCl_5, which was catalysed by UV-light. The yields obtained were poor. The main reaction was the reduction of the dichloroamine to form the azocompound, $CF_3\text{-}N{=}N\text{-}CF_3$ [4].

Accordingly, it was thought convenient to allow the dichloroamine to interact with a reagent susceptible to oxidation. Thus using PCl_3 we obtained the trichlorophosphazo-trifluoromethane and -pentafluoroethane in high yields.

$$R_F\text{-}CF_2\text{-}NCl_2 \;+\; 2\,PCl_3 \longrightarrow R_F\text{-}CF_2\text{-}N{=}PCl_3 \;+\; PCl_5$$

$$R_F = F,\ CF_3 \qquad\qquad \mathbf{1},\ \mathbf{2}$$

Both compounds are colourless liquids under normal conditions. They hydrolyse very rapidly and decompose above 105°C. Structures **1** and **2** were confirmed by IR, ^{19}F-NMR, ^{31}P-NMR and mass spectrometry.

EXPERIMENTAL

The IR-spectra were recorded on a Perkin-Elmer 457 spctrometer; the ^{19}F-NMR on a JEOL C 60 HL; the ^{31}P-NMR on a BRUKER HFX-90 spectrometer and the mass spectra on a VARIAN MAT CH7.

The dichloroamines were obtained by the reaction of the imidosulfurdifluorides $R_F\text{-}CF_2\text{-}NSF_2$ with Cl-F in CF_3Cl. They must be extremely pure, since traces of SF_4 (from their preparation) gave $R_F\text{-}\ CF_2\text{-}NSCl_2$, which was difficult to separate by 'trap to trap' distillation. Therefore the crude dichloroamines were shaken with PCl_5 at -40°C and afterwards with mercury. Other starting materials were obtained from commercial sources and purified by drying or distillation.

General procedure:

0.05 mol dichloroamine was condensed in a glass bulb containing 0.1 mol phosphorous trichloride. The reaction mixture was warmed slowly from -196^{0}C to -100^{0}C and stirred at this temperature for 1/2 h until a precipitate was formed. The solid was separated by filtering in the absence of air while cooling the filtrate with dry ice. The crude product (filtrate) amounted to a yield of about 75 %. The pure compounds were obtained after separation by GLC on a 400 x 0.2 cm column packed with 30% FS 1265 on chromosorb P-AW 80-100 mesh.

The ^{19}F-NMR of 1 shows a doublet at +41.8 ppm ($CFCl_3$ external standard) with a coupling constant of J(F—P) = 33.8 cps.

The ^{31}P-NMR shows a quartet at +4.4 ppm; +5.3 ppm; +6.3 ppm and + 7.3 ppm (H_3PO_4 external standard) with a coupling constant of J(P—CF_3)= 32.9 cps. The IR-spectrum shows absorptions at (cm^{-1}): 1490 m, 1415 vs, 1330 m, 1195 vs, 1145 vs, 820 m, 650 m, 600 s and 580 s.

The mass spectrum (70eV; m/e; % rel.int.): 219 (M^+) 43.8; 200 (M—F) 100; 184 (M—Cl) 28.8; 114 (CF_3NP) 10.6; 101 (PCl_2) 15.4; 95 (CF_2NP) 18.3; 85 (PFCl) 8.7; 69 (CF_3) 11.5. It shows metastable peaks at: m/e 42, 92.5 and 105.5 for the transitions: m/e 114 ⟶ 69; 155 ⟶ 120 and 184 ⟶ 139.

The ^{19}F-NMR of 2 shows two doublets, their intensities correspond to an a:b = 2:3 ratio; δ_a = +78.6 ppm; J(CF_2—P) = 33.3 cps and δ_b = +86.6 ppm with a coupling constant of J(CF_3—P) = 5 cps. ($CFCl_3$ external standard). No CF_3-CF_2 coupling was observed; this curious fact has already been described in the literature for C_2F_5NX (X = SF_2, SCl_2, SO) compounds [5]. The ^{31}P-NMR shows a complex triplet, consisting of three quartets at +0.6 ppm,+1.5 ppm and +2.4 ppm; the coupling constant for them is 5 cps. The coupling constant for the basic triplet ist 34.1 cps. The IR-spectrum shows absorptions at (cm^{-1}): 1475 m, 1450 s, 1420 m, 1335 vs, 1235 vs, 1145 m, 1110 m, 1050 m, 705 w, 630 sh, 600 s.

The mass spectrum (70eV; m/e; % rel.int.): 250 $(M-F)^+$ 4.9; 234 (M—Cl) 13.5; 200 (M—CF_3) 100; 184 (CF_3NPCl_2) 36.8; 130 (CF_2NPCl) 7.1; 101 (PCl_2) 8.5;85(PFCl)12.8; 69 (CF_3) 12.8. It shows metastable peaks at: m/e 55.8, 92.5, 120, 145 and 160 for the transitions: m/e 130 ⟶ 85, 200 ⟶ 136, 200 ⟶ 155, 234 ⟶ 184 and 250 ⟶ 200.

ACKNOWLEDGEMENTS

We thank the Fonds der Chemischen Industrie, the Alcoa Foundation and the Deutsche Forschungsgemeinschaft for financial support in this work. W. Leidinger has a DAAD scholarship. - We also thank Dr. R. Geist for the GLC-MS-coupling measurements as well as Dr. G. Schilling for the ^{31}P-NMR-spectra.

REFERENCES

1 G. Klöter, W. Lutz, K. Seppelt and W. Sundermeyer, Angew. Chem. 89 (1977) 754; Angew.Chem.Int.Ed.Engl., 16 (1977) 7o7.

2 R.C. Kumar, J.M. Shreeve, J.Am.Chem.Soc., 1o2 (198o) 4958.

3 R.A. De Marco, J.M. Shreeve, J. Fluorine Chem., 1 (1971/72) 269 - 276.

4 J.B. Hynes, B.C. Bishop and L.A. Bigelow, Inorg. Chem. 6 (1967) 417.

5 M. Lustig, Inorg. Chem. 5 (1966) 1317.