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Reactions of N-Pentafluorosulfanylurethanes and Thiolurethanes with Phosphorus Pentachloride

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SUMMARY

Urethanes of the type $SF_5NHC(O)OR$ react with PCl_5 to give primarily SF_5NCO. In only one case, where R = C_6H_5, was any evidence for an imine product observed. The corresponding reactions of $SF_5NHC(O)SR$ compounds give both SF_5NCO and the imine product. The new compounds $SF_5N{=}C(Cl)SCH_3$ and $SF_5N{=}C(Cl)SC_6H_5$ were identified by IR, NMR, and mass spectrometry.

INTRODUCTION

In studying the reactions between various halo-sulfonyl urethanes and PCl_5 [1], Roesky found that the corresponding sulfonylchloroimines could be isolated in varying yields. Contrary to his results, we recently found that reaction of $SF_5NHC(O)OCH_3$ with PCl_5 gave only the isocyanate, SF_5NCO [2]. We have now studied this reaction with other N-pentafluorosulfanylurethanes and thiolurethanes and have found several systems where both reaction pathways are followed.

$$FSO_2NHC(O)OCH_3 + PCl_5 \rightarrow FSO_2N{=}C(Cl)OCH_3 + HCl + POCl_3$$

$$SF_5NHC(O)OCH_3 + PCl_5 \rightarrow SF_5NCO + HCl + CH_3Cl + POCl_3$$

The reaction of $SF_5NHC(O)OC_6H_5$ [3] with PCl_5 gave evidence for the formation of the imine $SF_5N{=}C(Cl)OC_6H_5$ [2], but again the major product was SF_5NCO. The low yield of material, which was stopped in a -20°C

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TABLE 1

Reactions of $SF_5NHC(O)XR$ (X=O,S) compounds with PCl_5[a]

XR(amt,mmol)/PCl_5	Conditions[b]	Products(amt,mmol)[c]
OCH_3 (3.8)/(5)	3 days at 60-70°C	SF_5NCO, HCl(2.5), CH_3Cl, $POCl_3$
OCH_2CH_2O (5.0)/(15)	5 days at 70-80°C	SF_5NCO(5), HCl(3), $POCl_3$, $ClCH_2CH_2Cl$, Cl_2CHCH_2Cl
OC_6H_5 (4.4)/(4.4)	33 h at 60°C	SF_5NCO and HCl(7 total), $POCl_3$, C_6H_5Cl, $C_6H_4Cl_2$, $SF_5N{=}C(Cl)OC_6H_5$
SCH_3 (3.46)/(3.5)	33 h at 60°C	HCl and SiF_4(3.2 total), SF_5NCO and POF_3(0.9 total), POF_2Cl, CH_3SSCH_3 and other poly(methylsulfides), $SF_5N{=}C(Cl)SCH_3$(0.3)
SC_6H_5 (3.6)/(5)	4 h at 60-70°C	HCl and SiF_4(2.5 total), SF_5NCO and POF_3(2.5 total), C_6H_5Cl, $POCl_3$, $C_6H_5SSC_6H_5$, $SF_5N{=}C(Cl)SC_6H_5$(0.4)

[a]Gas chromatography-mass spectrometry (utilizing an SP-1000 column) was used along with IR and NMR spectroscopy to identify components of the product mixtures.

[b]All reactions were carried out in glass reaction cylinders using CCl_4 as the solvent.

[c]Amounts were not determined in all cases.

trap during vacuum fractionation, was found to be a mixture of $SF_5N{=}C(Cl)OC_6H_5$, C_6H_5Cl, and $C_6H_4Cl_2$. As with $SF_5NHC(O)OCH_3$, the reaction with $[SF_5NHC(O)OCH_2]_2$ [3] led strictly to the isocyanate and gave no evidence for the formation of $[SF_5N{=}C(Cl)OCH_2]_2$. However, both $SF_5NHC(O)SCH_3$ and $SF_5NHC(O)SC_6H_5$ [3] gave approximately 10% yield of the corresponding chloroimine when reacted with PCl_5. The new chloroimines were characterized by infrared, NMR, and mass spectrometry and were found to be extremely air sensitive when compared to the marked stability of other known N-pentafluorosulfanylchloroimines [2,4].

$SF_5N{=}C(Cl)SCH_3$ (nc) IR (gas): 2945 (w), 1625 (m) [ν(N=C)], 945 (m), 898 (s), 872 (vs), 797 (vs), 770 (vs), 721 (m), 594 (vs), 545 (vs) cm^{-1}; ^1H NMR: $\delta(SCH_3) \sim 2.5$ (s); ^{19}F NMR: δ(SF) 75.7 (m), $\delta(SF_4)$ 66.6 (d of m) (J_{SF-SF_4} = 156.0 Hz); mass spectrum (70 eV) m/e (rel intensity): 237, 235 M^+ (2.5, 6.4), 200 $[M-Cl]^+$ (39.7), 190, 188 $[M-SCH_3]^+$ (3.1, 8,3), 127 $[SF_5]^+$ (100.0), 110, 108 $[M-SF_5]^+$ (8.9, 25.9), and smaller fragments.

$SF_5N{=}C(Cl)SC_6H_5$ (nc) IR (capillary film): 3070 (m), 1640 (s) [ν(N=C)], 1600 (sb), 1497 (m), 1467 (m), 1435 (m), 1365 (m), 1263 (m), 1210 (m), 1065 (m), 915 (s), 870 (vsb), 840 (vsb), 745 (s), 680 (m), 660 (m), 580 (vs) cm^{-1}; ^1H NMR: $\delta(C_6H_5)$ 7.50 (bm); ^{19}F NMR: δ(SF) 77.2 (m), $\delta(SF_4)$ 66.8 (d of m) (J_{SF-SF_4} = 156.4 Hz); mass spectrum (70 eV) m/e (rel intensity): 299, 297 M^+ (4.6, 10.8), 262 $[M-Cl]^+$ (16.7), 190, 188 $[M-SC_6H_5]^+$ (7.5, 20.8), 172, 170 $[M-SF_5]^+$ (32.5, 100.0), 135 $[C_6H_5SCN]^+$ (87.5), 127 $[SF_5]^+$ (66.7), 109 $[C_6H_5S]^+$ (95.8), and smaller fragments.

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