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Preliminary Note

A Direct Preparation of Fluorinated Imides

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SUMMARY

N-Fluorosulfuryltrifluoroacetimide and N-chlorosulfuryltrifluoroacetimide have been prepared in high yield by a one-step reaction of trifluorothiolacetic acid with the corresponding fluoro- and chlorosulfuryl isocyanates. The trifluoroacetimides are easily purified by vacuum sublimation from the crude product mixture.

Perfluoroalkyl-, perfluoroacyl-, and perfluoroalkanesulfonyl imides have desirable electrochemical properties which make them potentially useful as electrolytes in fuel cells [1-4]. Such materials are not particularly easy to prepare and synthetic schemes often involve several steps [5-8]. As part of a program involving the preparation and study of fluorinated substances of electrochemical interest, we have developed a simple one-step synthesis of N-halosulfuryltrifluoroacetimides. In this preliminary note, we provide details for the synthesis of the known N-fluorosulfuryltrifluoroacetimide, I, [7] and the new compound, N-chlorosulfuryltrifluoroacetimide, II. We are in the process of extending this reaction to other fluorinated isocyanate systems and will report on these reactions in a forthcoming paper.

Fluorosulfuryl isocyanate was synthesized by the method of Hoff and Roesky [9]. Chlorosulfuryl isocyanate was purchased from Aldrich and trifluorothiolacetic acid was obtained from PCR, Inc. Purities were checked by IR and ^{19}F NMR [9, 10, 11].

Proton (TMS ref.) and fluorine (CCl_3F int. ref.) spectra were recorded on a Varian VXR-200 NMR spectrometer. Molecular weights were measured by the vapor density method. Elemental analyses were performed by Beller Mikroanalytisches Lab., Gottingen and Atlantic Microlab, Atlanta. Infrared spectra were recorded on Perkin-Elmer Model 1330 (dispersive) and Model 1620 (FT) IR spectrophotometers.

In a typical reaction, about 3 mmol of each reagent was condensed in a 30 mL bulb equipped with a stirbar. The mixture was stirred in the dark, and COS was removed at regular intervals. The product, a volatile solid, was sublimed under high vacuum at room temperature into a distillation condenser cooled to -20° . Samples for analysis and NMR were prepared in a dry-bag. Small amounts of SO_2 and $\text{CF}_3\text{C}(\text{O})\text{X}$ ($\text{X}=\text{F}$ or Cl) were

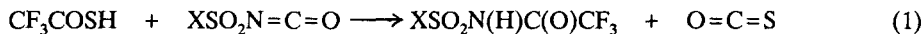
found to be present in the volatile fraction and these were separated from COS by fractional condensation. The COS was then weighed and analyzed by IR spectroscopy and molecular weight measurements.

Preparation of FSO₂N(H)C(O)CF₃. Reactants: FSO₂NCO, 3.0 mmol; CF₃C(O)SH, 3.0 mmol. Products: COS, 3.0 mmol, *M*, calcd. 60.0, found. 60.4 g mol⁻¹; CF₃C(O)F, SO₂, trace. FSO₂N(H)C(O)CF₃, *Anal*: calcd. C, 12.31; H, 0.52; N, 7.18; F, 38.95; S, 16.43. found. C, 12.29; H, 0.43; N, 7.29; F, 38.6; S, 16.6. *NMR*: ¹⁹F; CF₃, -75.5 (s); SF, 55.5 (s). ¹H; NH, 8.70 (s,b) ppm.

Preparation of ClSO₂N(H)C(O)CF₃. Reactants; ClSO₂NCO, 3.0 mmol; CF₃C(O)SH, 3.04 mmol. Products: COS, 2.0 mmol, calcd. from obs. *M* (67.2 g mol⁻¹) assuming equimolar production of CF₃C(O)Cl and SO₂ which were observed to be present in small amounts by infrared spectroscopy. ClSO₂N(H)C(O)CF₃, *Anal*: calcd. C, 11.36; H, 0.48; N, 6.62; Cl, 16.76. found. C, 11.44; H, 0.74; N, 6.75; Cl, 17.0. *NMR*: ¹⁹F; CF₃, -76.0 (s). ¹H; NH, 9.78 (s,b) ppm. *MP*: 54-56° C. *IR* (solid): 3248 (m, b), 1778 (vs), 1472 (s), 1408 (m), 1299 (m), 1232 (s), 1190 (vs), 1176 (sh), 1114 (s), 1049 (vw), 891 (m), 760 (m), 732 (w), 607 (s), 584 (m), 514 (m) cm⁻¹.

N-Fluorosulfuryltrifluoroacetimide was first prepared by Heinze [6], and some of its properties were reported by Roesky *et al.* [7]. The latter group synthesized the compound by the reaction of trifluoroacetic acid with FSO₂N=PCl₃, a substance which is prepared from N-fluorosulfurylamide and PCl₅. It was pointed out that this method was employed because the strong acid, CF₃COOH, did not react with FSO₂ N=C=O, although weaker acids such as acetic acid did. It occurred to us that the relatively weaker trifluorothiolacetic acid should undergo this reaction smoothly and this proved to be the case.

N-Fluorosulfuryltrifluoroacetimide and N-chlorosulfuryltrifluoroacetimide were prepared by the reaction of trifluorothiolacetic acid, CF₃COSH, with the corresponding isocyanate according to the reaction:



The reaction takes place readily at room temperature in glass and goes nearly to completion in the case of I and to the extent of 66% in the case of II as monitored by the evolution of carbonyl sulfide which is vacuum transferred from the reaction vessel at regular intervals. The products can be purified easily by vacuum sublimation and are obtained analytically pure in one step.

The analytical data are in accord with those required for the compositions of I and II; the value for hydrogen is high in the case of II probably owing to its greater affinity for water. The NMR data for I are in good agreement with those reported earlier; the position of the N-H resonance is strongly dependent on the amount of water in the

sample, and our value is slightly upfield of the literature value [7]. The resonances observed for II are consistent with the presence of the $\text{CF}_3\text{C}(\text{O})$ - group (-76.0 ppm) and N-H (9.78 ppm). Attempts to record the infrared spectrum of II as a KBr pellet or in a vapor phase cell were unsuccessful owing to rapid reaction of II with KBr. A solid-phase spectrum of II was obtained by pressing the ground material between AgCl plates and showed the expected symmetric and antisymmetric stretching modes associated with the sulfuryl group and the carbonyl stretching mode for the trifluoroacetyl group. The carbonyl stretching frequency is in the range normally found for trifluoroacetyl compounds ($\text{HN}(\text{C}(\text{O})\text{CF}_3)_2$ 1802, 1748 cm^{-1} [5], I, 1800 cm^{-1} [7]). The reaction involving the formation of I produces higher yields than that involving II as evidenced in the latter case by the production of larger amounts of the corresponding trifluoroacetyl chloride and SO_2 which were detected by infrared analysis and vapor density measurements. However, the yield of pure material is still quite high (over 50%).

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