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Preparation of fluorinated imides

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Abstract

A direct method for the preparation of trifluoroacetimides has been extended to the preparation of trifluoroacetyl trifluoracetimide and the new compound trifluoromethylsulfuryl trifluoroacetimide. Points concerning previously reported syntheses of trifluoroacetyl isocyanate have also been clarified.

Keywords: Trifluoroacetimides; Fluorinated isocyanates; Trifluoroacetyl isocyanate; Trifluorothiolacetic acid; Synthesis

1. Introduction

Recently it has been reported that fluorinated imides have great potential as additives to or replacements for phosphoric acid electrolytes currently employed in fuel cells [1–3]. In general, the fluorinated imides are very stable and have pK_a values comparable with that of phosphoric acid; the volatility of these substances can be controlled by lengthening the perfluoroalkyl chains attached to the nitrogen atom [1,2]. In addition, the lithium salts of fluorinated imides can be prepared and offer exciting possibilities for use as electrolytes in lithium batteries [4–7].

In a recent article by Folk et al. [8], a simple direct method for the preparation of trifluoroacetimides was reported which utilized fluorinated isocyanates as precursors. In this paper, we report on the generality of the method which has been extended to the preparation of the new compound trifluoromethylsulfuryltrifluoro-acetimide (DesMarteau has prepared this compound by a different method as yet unpublished [9]) and the previously known trifluoroacetyl trifluoroacetimide. In the course of these studies, we obtained some new data which are relevant to the original syntheses of trifluoroacetyl isocyanate and allow its preparation in high yield.

2. Experimental

2.1. Materials

Trifluoromethanesulfonamide, $CF_3SO_2NH_2$, was prepared by the method given by Burdon et al. [10] and was purified by vacuum sublimation. The proton NMR (5.3 ppm, s, br) and the MP (118.5–120.5 °C) were in agreement with the literature [10]. Trifluoromethylsulfuryl isocyanate, CF_3SO_2NCO, was prepared after Behrend and Haas [11]. The IR spectrum was in agreement with that published [11] and the molecular weight by vapor density was 175 g/gmv (Calc. 175.08). Silver isocyanate, AgNCO, was freshly prepared according to Holtzclaw [12] and was dried and stored in a vacuum desiccator. Trifluoroacetyl chloride, $CF_3C(O)Cl$, and trifluorothiolacetic acid, $CF_3C(O)SH$, were obtained from PCR, Inc. Trifluoroacetamide, $CF_3C(O)NH_2$, and chlorosulfuryl isocyanate, $ClSO_2NCO$, were obtained from Aldrich Chemical Co., Inc.

2.2. Methods

^{1}H and ^{19}F NMR spectra were obtained using a Varian VXR-200 FT-NMR Spectrometer (TMS and $CFCl_3$ ref.). Infrared spectra were recorded on a Perkin-Elmer Model 1330 Infrared Spectrophotometer using KBr or AgCl windows.

2.3. Preparation of trifluoromethylsulfuryl trifluoroacetimide

CF_3SO_2NCO (0.84 g, 4.8 mmol) was transferred to a 100 ml Pyrex reaction vessel under high vacuum in a scrupulously dried vacuum line. An equimolar amount of $CF_3C(O)SH$ was condensed into the vessel, and the mixture was stirred overnight in the dark. Periodically the vessel was cooled with dry ice and the gaseous COS was removed and measured (PVT) to monitor the course of the reaction. In one experiment, the conversion monitored in this way was

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67%; in another trial it was close to quantitative. The crude product, $CF_3SO_2N(H)C(O)CF_3$, sublimed under vacuum to give large needlelike and very hygroscopic crystals. Anal: calcd. C, 14.70; H, 0.41; N, 5.72; S, 13.08. found. C, 14.02; H, 0.73; N, 5.48; S, 12.63%. IR (AgCl pellet): 3285 (ms), 2917 (w), 1786 (ms), 1617 (ms), 1609 (w), 1473 (ms), 1413 (m), 1221 (vs), 1189 (s, sh), 1133 (m), 886 (w), 853 (w), 792 (w), 590 (m) cm^{-1}. The ^1H NMR spectrum showed a single broad peak at 8.5 ppm (TMS). The ^{19}F NMR spectrum showed two singlet peaks at −76.0 and −73.5 ppm (CCl_3F) and the ^{13}C spectrum exhibited three quartets at 153.7 ppm, $^2J_{CF}=47.0$ Hz, 118.8 ppm, $^1J_{CF}=321$ Hz, and 114.0 ppm, $^1J_{CF}=288$ Hz. A sample of $CF_3SO_2N(H)C(O)CF_3$ (0.490 g) was dissolved in deionized water, and an aliquot (10.0 ml) was titrated with 0.09854 M NaOH. The sample consumed two equivalents of base; the first endpoint appeared at a pH of 4.0 and the second at a pH of 9.4. The molecular weight of the substance calculated from the titration data is 250 g/gmw (theor. 245).

2.4. *Preparation of trifluoroacetyl trifluoroacetimide*

$CF_3C(O)NCO$ (0.22 g, 1.6 mmol) was condensed in a 100 ml reactor and an equimolar amount of $CF_3C(O)SH$ was added. The reaction mixture was stirred in the dark overnight. White crystals formed in the reaction vessel and 1.5 mmol of COS was removed (94% yield of $CF_3C(O)N(H)C(O)CF_3$ based on COS). The crystals were sublimed under vacuum into a column cooled to −20 °C. However, ^1HNMR analysis revealed the presence of some $CF_3C(O)NH_2$ (6.38 ppm, s,br; 6.38 ppm, authentic sample) as well as that of $CF_3C(O)N(H)C(O)CF_3$ (9.15 ppm, s, br). The crystal mixture was placed in a 100 ml bulb and allowed to vaporize and recondense for two weeks. Large needlelike crystals formed on the walls of the bulb and a small amount of white residue was left at the bottom. The needles were collected in a dry bag and found to be pure $CF_3C(O)N(H)C(O)CF_3$ by ^1H NMR (9.15 ppm, s, br), ^{19}F NMR (−76.2 ppm, s) and ^{13}C NMR (113.9 ppm, q, $^1J_{CF}=289$ Hz; 153.4 ppm, q, $^2J_{CF}=41$ Hz). The infrared spectrum agreed with that reported in the literature [12] and the MP was 84.5–85.5 °C (Lit. 85 °C [14] and 86.4–87 °C [13]).

2.5. *Preparation of trifluoroacetyl isocyanate*

2.5.1. *Method I [11]*

$CF_3C(O)NH_2$ (2.83 g, 25 mmol) was placed in a Pyrex reaction vessel connected to a vacuum line through a reflux condenser. The system was evacuated and $ClSO_2NCO$ (7.08 g, 50 mmol) was condensed into the reaction vessel. Dry nitrogen was bled into the system to a pressure of 400 torr after which the reaction mixture was heated to reflux (110–120 °C) with stirring overnight. The nitrogen was then removed and the reaction mixture was separated by fractional condensation at −23, −132, and −196 °C. Infrared analysis of the −196 °C fraction, which constituted the bulk of the product mixture, revealed the presence of CO_2 [15], CF_3CN [15], some SO_2 [15], HCl [14], and a small amount of $CF_3C(O)NCO$ [13,14]. The greenish solution in the trap at −132 °C was identified as Cl_2 and a small amount of $CF_3C(O)NCO$. The trap at −23 °C contained mostly unreacted starting materials.

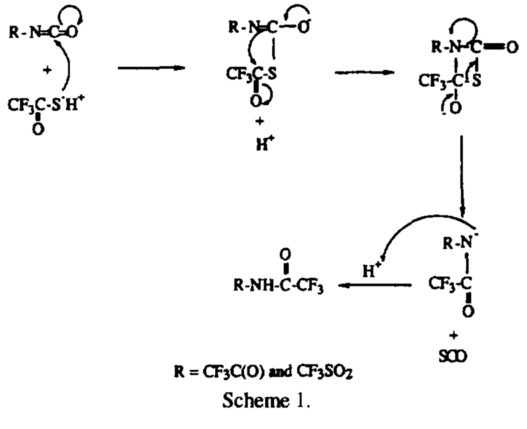
2.5.2. *Method II [17]*

Freshly prepared, dry AgNCO (3.0 g, 20 mmol) was placed in a 30 ml stainless steel Hoke bomb under dry nitrogen. The bomb, which contained three nickel stirring rings, was evacuated and $CF_3C(O)Cl$ (1.32 g, 10 mmol) was added by vacuum transfer. The bomb was rotated in a furnace held at 110–120 °C for 12 h and the contents were quickly condensed into a trap while the reaction mixture was still hot. The mixture was passed through traps held at −78 and −196 °C. The bulk of the material was in the trap held at −196 °C and infrared analysis showed that it consisted mainly of CO_2 and CF_3CN [16] along with traces of $CF_3C(O)NCO$. The trap held at −78 °C contained a small amount of $CF_3C(O)NCO$ and an as yet unidentified material. The solid left in the bomb gave a positive test for AgCl indicating that reaction between AgNCO and $CF_3C(O)Cl$ had taken place.

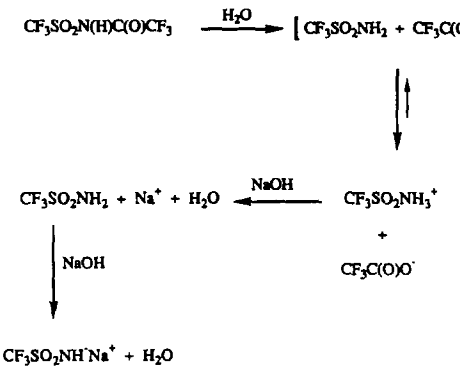
In another attempt based on information gleaned in the preceding experiment, Method II was employed under the same conditions as stated above, but the reaction was carried out at a much lower temperature (AgNCO (1.5 g, 10 mmol), $CF_3C(O)Cl$ (0.66 g, 5.0 mmol) 50 °C for 15 h). The product mixture was condensed in a trap and found to consist of $CF_3C(O)NCO$ (0.43 g recovered, 61% yield based on $CF_3C(O)Cl$) with traces of CO_2 and CF_3CN.

3. Discussion

The new compound, trifluoromethylsulfuryl trifluoroacetimide [9], and the previously known trifluoroacetyl trifluoroacetimide are easily prepared in high yields by the reaction of the corresponding isocyanate with trifluorothiolacetic acid. A plausible route to the products is shown below (Scheme 1). Nucleophilic attack by sulfur on the carbon atom of the iso-



Scheme 1.



Scheme 2.

cyanate is followed by cyclization to give a four-membered ring intermediate which eliminates carbonyl sulfide. Protonation of the imide anion then occurs to give the final product.

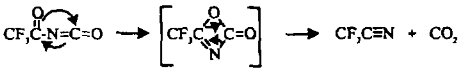
The products were characterized by the usual spectroscopic methods and, in the case of $CF_3SO_2N(H)C(O)CF_3$, by elemental analysis as well. ^1H, ^{19}F, and ^{13}C NMR spectra are in agreement with the proposed structures; the infrared spectra showed the presence of the carbonyl stretching mode at 1786, the N–H stretching mode at 3285, and the SO_2 modes at 1473 and 1221 cm^{-1} for $CF_3SO_2N(H)C(O)CF_3$.

$CF_3SO_2N(H)C(O)CF_3$ is unstable in water as shown by the titration data; the compound slowly hydrolyzes to species which consume two moles of base per mole of $CF_3SO_2N(H)C(O)CF_3$. This behavior can be explained as in Scheme 2. In the first step, $CF_3SO_2N(H)C(O)CF_3$ hydrolyzes to $CF_3SO_2NH_2$ and $CF_3C(O)OH$; the very weak acid, $CF_3SO_2NH_2$ is protonated by $CF_3C(O)OH$ forming the acid $CF_3SO_2NH_3^+$. Titration of $CF_3SO_2NH_3^+$ consumes one equivalent of base to reach an endpoint at a pH of 4.0 at which point $CF_3SO_2NH_2$ and CF_3COO^- are present. The pK_a of $CF_3SO_2NH_3^+$ is estimated to be 2.2 from the midpoint on the titration curve for the first neutralization. Further addition of base results in the neutralization of $CF_3SO_2NH_2$ ($pK_a = 6.2$; Lit. 6.3 [18]) at a pH of about 9.4. An alternative scheme involving hydrolysis of $CF_3SO_2N(H)C(O)CF_3$ to $CF_3C(O)NH_2$ and CF_3SO_2OH was considered; however, the pK_a of $CF_3C(O)NH_2$ is 10.4 [19] which is inconsistent with the second endpoint. The hydrolysis of $CF_3SO_2N(H)C(O)CF_3$ is probably slow enough to allow study of its electrochemical properties but too rapid for use as an electrolyte in fuel cells.

Trifluoroacetyl trifluoroacetimide, $CF_3C(O)N(H)C(O)CF_3$, was first reported by Smith [20] who prepared it by the reaction of trifluoroacetamide with trifluoroacetic anhydride. Young et al. [14] have cast doubt on this by observing that trifluoroacetyl trifluoroacetimide prepared by the reaction of trifluoroacetic acid with trifluoro-acetonitrile is a solid with a clean melting point at 85 °C rather than a liquid as observed by Smith [20]. Other methods involved the reaction of barium trifluoroacetate with phosphonitrilic trimer [21] and the reaction of isocyanic acid with excess trifluoroacetic anhydride [13]. Our analytical results agree with those of Young et al. [14] and Firth [13]. Both of their methods can give high yields of the product; however, the first suffers from the fact that the volatile mixture must be heated to 150 °C for 3 h to give a 93% yield while the second, although run at room temperature, requires the preparation and handling of HNCO. Our method gives close to quantitative conversion at room temperature but requires care in the purification by sublimation because of an impurity of trifluoroacetamide presumably resulting from trace hydrolysis of the extremely hygroscopic trifluoroacetyl isocyanate.

The preparation of trifluoroacetyl isocyanate revealed some interesting facts concerning the stability of this substance. The first preparation of $CF_3C(O)NCO$ was reported by Firth [13] who allowed trifluoroacetic anhydride to react with an excess of HNCO. $CF_3C(O)NCO$ was formed in about 37% yield along with other unidentified products. Sprenger et al. were able to prepare useful amounts of the compound by the reaction of $CF_3C(O)Cl$ with AgNCO at 120 °C in a stainless steel bomb for 12 h [17] but cautioned that long reaction times resulted in increased production of CO_2 and that polymerization resulted if the product mixture was allowed to cool before removing it from the bomb. Behrend and Haas [11] reported that chlorosulfuryl isocyanate reacted with trifluoroacetamide at reflux temperatures over a period of 30 h to give a 12.6% yield of $CF_3C(O)NCO$; we also observed a very low yield when we employed this method. The method providing the highest yield of the compound has been reported by Lidy and Sundermeyer [22] who found that an 89% yield resulted from the reaction of $CF_3C(O)Cl$ with KOCN in a molten salt mixture of LiCl and KCl at 400 °C. Since the most convenient method seemed to be the reaction of AgNCO with $CF_3C(O)Cl$ [17], we carried out the reaction under the literature conditions and found that $CF_3C(O)NCO$ resulted but the yield was too low for our purposes. Further investigation revealed that CF_3CN was one of the gaseous products that formed along with CO_2 during the reaction. Our prior experience with isocyanates suggested to us that decomposition of $CF_3C(O)NCO$ to CF_3CN and CO_2 was occurring at high temperature possibly via a concerted electrocyclic mechanism such as that shown in Scheme 3.

Such four-membered intermediates have been invoked by Durrell et al. [23] to explain the synthesis of nitriles from the reaction of aldehydes with *O*,*N*-bis(trifluoroacetyl)-hydroxylamine first observed by Pomeroy and Craig [24] as well as their synthesis of $CF_3C(O)N(H)C(O)CF_3$ from trifluoroacetonitrile and trifluoroacetic acid. When the reaction of $CF_3C(O)Cl$ with AgNCO was carried out at much lower temperature (50 °C), the yield of $CF_3C(O)NCO$ increased to 61% and only very small amounts of CF_3CN and CO_2 were formed.



Scheme 3.

Acknowledgements

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