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N-FLUORO-BIS(TRIFLUOROMETHANESULFONYL)IMIDE. AN IMPROVED SYNTHESIS

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SUMMARY

An improved synthesis of $(CF_3SO_2)_2NH$ and its conversion to the very useful fluorination reagent $(CF_3SO_2)_2NF$ is described. The five-step synthesis yields $(CF_3SO_2)_2NF$ in 76% yield based on the starting CF_3SO_2F.

INTRODUCTION

N-fluoro compounds recently gained much attention as selective fluorinating agents for organic compounds. Well known examples are 1-fluoro-2-pyridone [1], N-fluoro-N-alkylsulfonamides [2] and N-fluoropyridinium triflates [3]. In a recent paper we introduced the group of N-fluoro-perfluoroalkanesulfonyl imides [4].

N-fluoro-bis(trifluoromethanesulfonyl) imide is clearly the most remarkable member of this group since it combines several useful chemical and physical properties. It exhibits high reactivity towards olefins [5], carbanionic [5] and activated aromatic [4] compounds. It is, however, so inert

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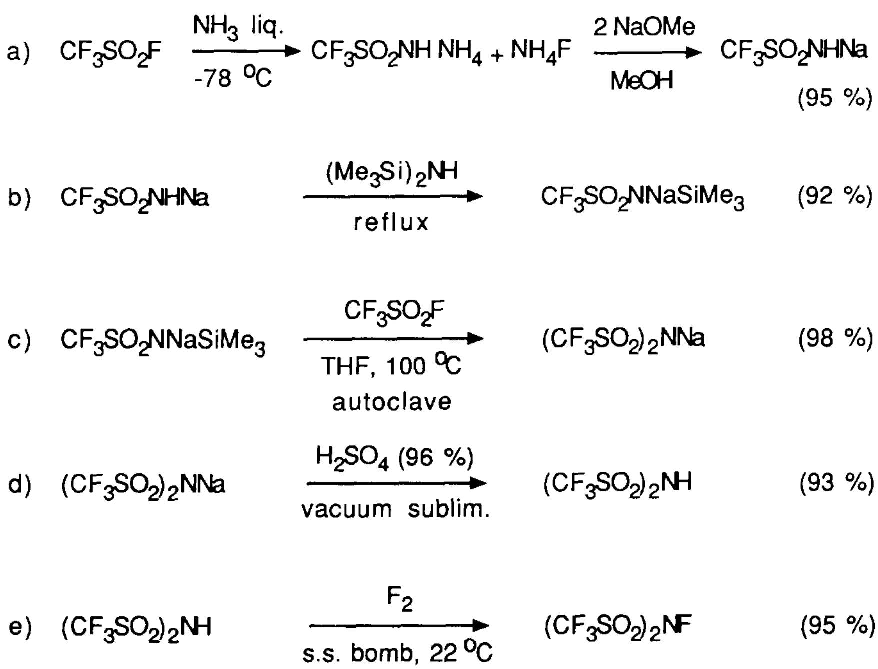
against water that fluorinations can be carried out in a two-phase-system containing water [6]. The shelf-lifetime of $(CF_3SO_2)_2NF$ is indefinite when stored properly. Its volatility is moderate, b.p. 90-91°C. Therefore, it can be handled in vacuum lines, in flow systems or in traditional glassware. The low melting point of -69.8° C [4] and the low-temperature solubility of this compound in many solvents increase the range of possible reaction conditions even more.

$(CF_3SO_2)_2NF$ is obtained from bis(trifluoromethanesulfonyl) imide by direct fluorination [4]. Our first synthesis of $(CF_3SO_2)_2NH$ however, was rather complicated and had an overall yield of only 48 % [7]. We wish to report about improvements in the syntheses of both compounds (Scheme 1).



Scheme I

CF_3SO_2NHNa can be synthesized directly from CF_3SO_2F and liq. ammonia (a). NaOMe is used to transform the intermediate ammonium salts into sodium salts. Since NaF is insoluble in methanol it can be removed easily. Procedure (a) avoids the isolation of $CF_3SO_2NH_2$, which was accomplished by treating the ammonium salts with HCl in 1,4-dioxane [7]. The purification of $CF_3SO_2NH_2$ was complicated due to partial decomposition of the solvent.

It is important to synthesize and handle $CF_3SO_2NNaSiMe_3$ under strictly anhydrous conditions. The progress of reaction (b) should be monitored by the formation of ammonia. Purification of the silyl salt can be avoided since the purification of $(CF_3SO_2)_2NNa$ is very easy.

The synthesis of $(CF_3SO_2)_2NNa$ (c) has been improved by changing several factors. THF is used instead of 1,4-dioxane since it dissolves the starting material better. The reaction is carried out in a stirrable autoclave. A very effective way of cleaning the product is the extraction of $(CF_3SO_2)_2NNa$ in aqueous solution with CH_2Cl_2.

$(CF_3SO_2)_2NH$ is generated from $(CF_3SO_2)_2NNa$ by means of concentrated sulfuric acid (d). Due to the improvements in the previous steps no further purification is required.The overall yield for $(CF_3SO_2)_2NH$ is 80 %.

The fluorination of $(CF_3SO_2)_2NH$ (e) is a crucial step. A scale of 10 g in a 500 ml stainless steel bomb and a fluorine pressure of 1600 torr should not be exceeded. The bomb must be clean and thoroughly prefluorinated. Slow pressurization of $(CF_3SO_2)_2NH$ with a small excess of F_2 at room temperature reduces the incidence of uncontrollable reactions compared with our previous method [4]. The work-up procedure did not have to be changed. This fluorination usually yields 95 % $(CF_3SO_2)_2NF$.

EXPERIMENTAL

CF_3SO_2F (76 g) was bubbled into 600 ml of semi-frozen NH_3 within 0.5 h (1000 ml three-neck flask with mechanical stirrer/ slow flow of dry N_2 to exclude moisture). The melting of ammonia and later some external cooling maintained a constant temperature of -78 °C. The excess of ammonia was removed by allowing the mixture to warm up to 22 °C under N_2-flow. NaOMe (54 g) in 500 g MeOH was added and the mixture was heated to 60 °C for a short time. The NaF was removed by filtration through a glassfrit. The solution was rotary evaporated and the remaining solid was dried under high vacuum. 81 g (95 %) CF_3SO_2NHNa.

Powdered CF_3SO_2NHNa (81 g) was refluxed with hexamethyldisilazane (HMDS, 500 g) in a 1000 ml three-neck flask under dry N_2. The oil-bath temperature never exceeded 145 °C to avoid excessive darkening of the product. The mixture was stirred with a strong mechanical stirrer since it tends to become very viscous, making stirring progressively difficult. After the NH_3-production had stopped the excess HMDS was removed by distillation (starting at normal pressure and using vacuum at the end). The remaining moisture-sensitive solid was dried under high vacuum at 100 °C in the same flask. 106 g (92 %) $CF_3SO_2NNaSiMe_3$.

A concentrated solution of $CF_3SO_2NNaSiMe_3$ (106 g) in tetrahydrofuran (ca. 370 ml solution) was transferred to an evacuated 600 ml stainless steel stirrable autoclave. CF_3SO_2F (67 g, 26 % excess) was added by transfer under pressure through a metal vacuum system since it was not possible to cool the autoclave much below -50°C, due to the sealing type. The mixture was stirred overnight at 100 °C. At 22 °C the volatile products were vented in the hood. The autoclave was washed out with 500 ml water. The combined H_2O/THF solution was washed with CH_2Cl_2, rotary evaporated and the remaining solid was dried under high vacuum at 110 °C. 129 g (98 %) $(CF_3SO_2)_2NNa$.

$(CF_3SO_2)_2NNa$ (129 g) and H_2SO_4 (96 %, 150 ml) were heated in a 500 ml single-neck flask under high vacuum to 60-90 °C. The product sublimed through an ascending glasstube and was collected at -22 °C. 111 g (93 %) $(CF_3SO_2)_2NH$. No further purification was necessary. The product was handled under dry nitrogen.

$(CF_3SO_2)_2NH$ (10 g) was filled in a clean prefluorinated stainless steel bomb under dry N_2. The bomb was evacuated at -196 °C and warmed up to 22 °C. Fluorine was introduced up to a total pressure of 1570 torr over a time period of about 10 min. The bomb was then closed off and allowed to stand overnight at room temperature. The excess of fluorine was pumped through a soda-lime tube keeping the reactor at -196 °C. The remaining volatile materials were condensed into another bomb containing 10 g NaF and then kept at 22 °C for 1 h with occasional shaking. The remaining product was cleaned by trap to trap distillation (22 °C/-55 °C/-196 °C). It stopped in the -55 °C trap. 10.1 g (95 %) $(CF_3SO_2)_2NF$.

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