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Insertion of Sulfur Trioxide into the N–Si Bond of Anilinotrimethylsilane. An Improved Method for the Preparation of Free Phenylamidosulfuric Acid[1)]

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The reaction between anilinotrimethylsilane (**1**) and a variety of sulfonating agents [SO_3, $ClSO_3H$, trimethylsilyl chlorosulfate (**5**), dioxane-sulfur trioxide complex, ethyl chlorosulfate (**10**)] has been studied. With SO_3, **5**, or a dioxane-sulfur trioxide complex a sulfur trioxide molecule was inserted selectively into the N–Si bond of **1** to yield trimethylsilyl phenylamidosulfate (**2**), which on treatment with acetic acid, trifluoroacetic acid, or methanol gave free phenylamidosulfuric acid (**3**). The reaction of **1** with $ClSO_3H$ afforded **3** directly, but the product was contaminated with slight amounts of anilinium hydrogensulfate and anilinium chloride. The reaction of **1** with **10** yielded a mixture containing dianilinium (4-sulfonatophenylamido)sulfate, 4-aminobenzenesulfonic acid, and ethyl phenylamidosulfate as major products (after desilylation). The reaction of **1** with **5** has been found to provide an improved method for preparing **3**.

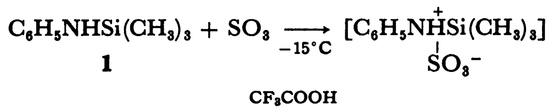
Arylamidosulfuric acids ($ArR^1R^2N^+SO_3^-$) have long been believed, but not yet proved, to be intermediates in the sulfonation of aromatic amines.[2—5)] In a previous paper,[6)] one of us (F. K.) has reported the first definite preparation and characterization of some arylamidosulfuric acids. The method of preparation used simply involves the addition of ice-cold concentrated hydrochloric acid to a saturated aqueous solution of an appropriate ammonium arylamidosulfate, followed by filtration and drying of the product. This method, however, rather requires technical skillfulness for obtaining the product of high purity; therefore, it is desirable to develop a more convenient method for preparing free arylamidosulfuric acids.

In view of their great tendency to undergo thermal rearrangement and reactions with Lewis bases, such as water, alcohols, amines, etc., it is highly desirable that arylamidosulfuric acids should be generated in an inert organic medium under mild conditions and isolated in a high purity without any purification. We considered that the silyl esters ($ArR^1NSO_3SiR_3{}^2$) would meet such requirements and be the most promising precursor of the free arylamidosulfuric acids.

To our knowledge, there is no report on the silyl esters of arylamidosulfuric acids, although several reports[7—9)] have appeared on the aliphatic counterparts. We, therefore, decided to examine the reation of anilinotrimethylsilane (**1**) with several sulfonating agents with the aim of preparing trimethylsilyl phenylamidsosulfate (**2**) and have found that a sulfur trioxide molecule is inserted into the N–Si bond of **1** to yield the desired silyl ester **2**, which, on treatment with an appropriate desilylating agent such as trifluoroacetic acid, directly gives pure phenylamidosulfuric acid (**3**) very easily.

Results and Discussion

Reaction of Anilinotrimethylsilane (1) with Sulfur Trioxide. The reaction of **1** with sulfur trioxide at −15 °C for 8 h, followed by the treatment with trifluoroacetic acid gave the desired phenylamidosulfuric acid (**3**). HPLC analysis revealed that sulfur trioxide was inserted exclusively into the N–Si bond; the ring-sulfonation products were detected but in traces. In contrast, the same reaction at room temperature (17 °C) for 4 h led to the formation of 4-aminobenzenesulfonic acid and (4-sulfophenylamido)sulfuric acid in addition to **3**.



$$\underset{\mathbf{1}}{C_6H_5NHSi(CH_3)_3} + SO_3 \xrightarrow[-15^\circ C]{} [C_6H_5\overset{+}{N}\underset{\underset{SO_3^-}{|}}{H}Si(CH_3)_3]$$

$$\underset{\mathbf{2}}{C_6H_5NHSO_3Si(CH_3)_3} \xrightarrow{CF_3COOH} \underset{\mathbf{3}}{C_6H_5NH_2{}^+SO_3^-}$$

Reaction of 1 with Chlorosulfuric Acid. When chlorosulfuric acid was added dropwise to a solution of **1** in 1,2-dichloroethane at −20 °C, **3** separated out directly. This product, however, was contaminated with slight amounts of anilinium hydrogensulfate and anilinium chloride as indicated by HPLC and IR spectroscopy, and also by tests for sulfate and chloride ions. The anilinium hydrogensulfate arose probably

$$\mathbf{1} + ClSO_3H \xrightarrow[-20^\circ C]{} \mathbf{3} + \underset{\mathbf{4}}{(CH_3)_3SiCl}$$

from aniline and sulfuric acid, which are commonly present as contaminants in **1** and chlorosulfuric acid, respectively. Great difficulty in obtaining very pure starting materials and the lack of methods for purifying **3** make this reaction less valuable for the preparation of pure **3**.

Reaction of 1 with Trimethylsilyl Chlorosulfate (5). Sundermeyer and his collaborators[10)] have prepared several trimethylsilyl esters of alkylamidosulfuric acids in yields of 70—90% by the reaction of (alkylamino)trimethylsilane with **5**. Our preliminary experiments showed that, with anilinotrimethylsilane (**1**), the use of much lower temperature is essential, or else

$$R^1R^2NSi(CH_3)_3 + \underset{\mathbf{5}}{ClSO_3Si(CH_3)_3} \xrightarrow[r.t.]{CH_2Cl_2} R^1R^2NSO_3Si(CH_3)_3 + \mathbf{4}$$

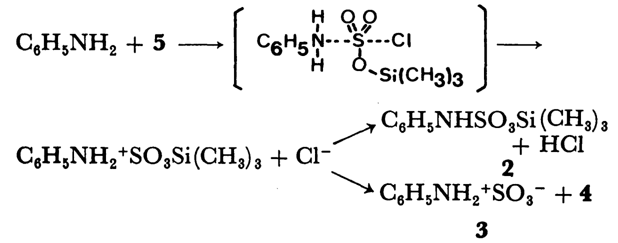
ring sulfonation occurs appreciably. Thus, a solution of **5** in dichloromethane was added dropwise to a solution of **1** in the same solvent at −10—−15 °C and the mixture was stirred at −10—−15 °C for 7 h; after removal of insoluble material,[11] the filtrate was treated with trifluoroacetic acid to give analytically pure phenylamidosulfuric acid (**3**) in yields of 62—71%. When the desilylating process was omitted, trimethylsilyl phenylamidosulfate (**2**)[12] was isolated from the reaction mixture.

$$\underset{\mathbf{1}}{C_6H_5NHSi(CH_3)_3} + \underset{\mathbf{5}}{ClSO_3Si(CH_3)_3} \xrightarrow[-10 - -15^\circ C]{} \underset{\mathbf{2}}{C_6H_5NHSO_3Si(CH_3)_3} + \mathbf{4}$$

Acetic acid and methanol, as well as trifluoroacetic acid, can be used as a desilylating agent. As for methanol, however, its use in excess must be avoided; otherwise phenylamidosulfuric acid first formed will react with the excess methanol at room temperature to yield anilinium methyl sulfate (**6**).

$$\underset{\mathbf{3}}{C_6H_5NH_2{}^+SO_3{}^-} + CH_3OH \xrightarrow[r.t.]{} \underset{\mathbf{6}}{C_6H_5NH_3{}^+CH_3OSO_3{}^-}$$

Reaction of Aniline with Trimethylsilyl Chlorosulfate (5). The reaction of aniline with **5** in a 1 : 1 molar ratio produced a mixture consisting of trimethylsilyl phenylamidosulfate (**2**) (16%), phenylamidosulfuric acid (**3**) (51%), anilinium hydrogensulfate, and anilinium chloride. The latter two anilinium salts arose probably from the hydrolysis of **5** by adventitious water during the reaction. Simchen and his collaborator have repoted[13] that the action of **5** on *N*,*N*-diethylaniline with ice-cooling gives an *N*,*N*-diethylanilinesulfur trioxide adduct (**7**), which rearranges to 4-(diethylamino)benzenesulfonic acid at room temperature.

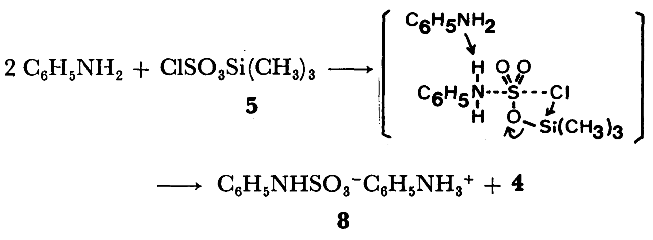


$$C_6H_5NH_2 + \mathbf{5} \longrightarrow [\ ] \longrightarrow C_6H_5NH_2{}^+SO_3Si(CH_3)_3 + Cl^- \longrightarrow \underset{\mathbf{2}}{C_6H_5NHSO_3Si(CH_3)_3} + HCl \quad / \quad \underset{\mathbf{3}}{C_6H_5NH_2{}^+SO_3{}^-} + \mathbf{4}$$

$$C_6H_5N(C_2H_5)_2 + \mathbf{5} \longrightarrow \underset{\mathbf{7}}{C_6H_5N(C_2H_5)_2{}^+SO_3{}^-} + \mathbf{4}$$

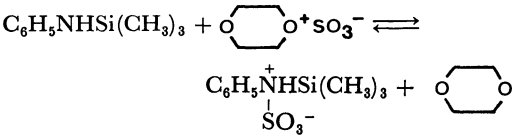
$$\mathbf{7} \xrightarrow[r.t.]{} 4\text{-}(C_2H_5)_2NH^+C_6H_4SO_3{}^-$$

The reaction of aniline with **5** in a 2:1 molar ratio at −10—−15 °C yielded anilinium phenylamidosulfate (**8**) in a 87% yield; the same result was obtained when the direction of addition of both reagents was inverted. HPLC analysis showed the absence of the ring sulfonation; in addition, tests with acidic aqueous silver nitrate and barium nitrate solutions were practically negative. These facts indicate that the reaction proceeds probably as follows.



$$2\,C_6H_5NH_2 + \underset{\mathbf{5}}{ClSO_3Si(CH_3)_3} \longrightarrow [\ ] \longrightarrow \underset{\mathbf{8}}{C_6H_5NHSO_3{}^-C_6H_5NH_3{}^+} + \mathbf{4}$$

Reaction of 1 with Dioxane–Sulfur Trioxide Complex. Kricheldorf and his collaborator[8] have prepared trimethylsilyl *N*-methylbenzylamidosulfate in 77% yield by reaction of *N*-methyl-*N*-(trimethylsilyl)-benzylamine[9] with dioxane-sulfur trioxide. In our case, the reaction of 1 with dioxane–sulfur trioxide (−20 °C, 2 h) in 1,2-dichloroethane and subsequent desilylation with trifluoroacetic acid gave a mixture consisting of the desired product **3**, 4-aminobenzenesulfonic acid, and anilinium hydrogensulfate. The sulfate salt arose undoubtedly from the hydrolysis of unconverted **1** and the dioxane–sulfur trioxide in the course of workup; therefore, lengthening of the reaction time would lead to an increase in the yield of **3**, and removal of the insoluble by-products from the reaction mixture before the desilylation would permit the isolation of **3** in a pure state without any additional purification.



$$\underset{\mathbf{2}}{C_6H_5NHSO_3Si(CH_3)_3} \xrightarrow{H^+} \underset{\mathbf{3}}{C_6H_5NH_2{}^+SO_3{}^-}$$

Reaction of 1 with Ethyl Chlorosulfate (10). The reactions between aromatic as well as aliphatic amines and alkyl chlorosulfates have been studied by several investigators.[14,15] It has been found that, for example, in the reaction of aniline with **10**, *N*-ethyl- and *N*,*N*-diethylaniline, phenylamidosulfate, *N*-ethylphenylamidosulfate, and 4-aminobenzenesulfonic acid are formed in varying proportions, which depend on the reaction conditions used. Yaguzhinskii and Berlin[15] have investigated the reaction of anilines with alkyl chlorosulfates in some detail and found that the corresponding alkyl *N*-alkylphenylamidosulfates were also formed.

By analogy with these findings, the reaction of anilinotrimethylsilane **1** with **10** had been expected to yield the desired product **3**; actually, however, **3** was formed in only a trace. Thus, treatment of **1** with **10** in dichloromethane at −10—−15 °C for 1 h and at reflux for 3 h yielded a solid product, which was identified as dianilinium (4-sulfonatophenylamido)sulfate; treatment of the filtrate with acetic acid gave another precipitate, which was found to be 4-aminobenzenesulfonic acid contaminated with slight amounts of 2-aminobenzenesulfonic acid and a disulfonic acid, and a trace of **3**. In addition, ethyl phenylamidosulfate and its *N*-ethyl derivative were isolated from the desilylation mixture.

Experimental

All reactions were carried out in oven-dried glassware under a dry nitrogen atmosphere by use of Schlenk-tube techniques. All solvents were dried over appropriate drying agents. Aniline was dried over KOH pellets and distilled under reduced pressure. Triethylamine was dried over KOH and distilled. Chlorotrimethylsilane was distilled (bp 57.0—57.5 °C). Trifluoroacetic acid and chlorosulfuric acid were of reagent grade and used as purchased. Sulfur trioxide was obtained from 60—65% fuming sulfuric acid by distillation. IR spectra were recorded on a Hitachi 215 spectrophotometer; ^{1}H NMR spectra were obtained on a JNM-PMX 60 instrument. High-performance liquid chromatography (HPLC) was carried out on a Toyo Soda HPLC-803D instrument by using a TSK-GEL ODS-120T (4.6 mm ×25 cm)column and a 0.05 M Na_2HPO_4 (pH 7.0) aqueous solution containing 1% of CH_3CN as the eluant; peaks were monitored at 240 nm on a UVIDEC-100-IV. TLC was performed on Cellulose mikrokristallin (E Merck) plates by using dioxane–water (3 : 1 v/v) as a developing solvent; spots were visualized by diazotization with nitrous gases and spraying with 1% sodium 1-naphthol-4-sulfonate and subsequent exposure to ammonia. Samples for HPLC and TLC analyses were prepared by dissolving the products in aqueous NaOH.

Preparation of Anilinotrimethylsilane (1). To a stirred solution of chlorotrimethylsilane (24.0 g, 0.220 mol) in cyclohexane (100 ml) was added at 5 °C over 10 min a solution of triethylamine (22.2 g, 0.220 mol) in cyclohexane (15 ml). After the mixture had been stirred for 1 h, aniline (20.5 g, 0.220 mol) was added at 5—6 °C over 30 min, and stirring was continued for further 7 h. The mixture was filtered and evaporated. The residue was fractionally distilled under reduced pressure to give **1** (23.5 g, 65%): Bp 103.7—104.5 °C/21 Torr† (lit, 106-107 °C/24 Torr);[16] 95% purity as determined by GLC;IR (neat) 3405, 1605, 1503, 1388, 1295, 1253, 900, 838, and 690 cm^{-1}.

Preparation of Trimethylsilyl Chlorosulfate (5). Sulfur trioxide (71.0 g, 0.89 mol) was added with stirring to chlorotrimethylsilane (96.3 g, 0.89 mol) at −35 °C. The mixture was then allowed to warm to room temperature, heated at 50 °C for 10 min, and distilled in vacuo to yield **5** (145.8 g, 87%): Bp 73.0—74.0 °C/18 Torr (lit, [17] 66 °C/12 Torr).

Reaction of 1 with Sulfur Trioxide. To a stirred solution of **1** (2.50 g, 15.1 mmol) in 1,2-dichloroethane (55 ml) was added at −15 °C over 30 min a solution of SO_3 (1.21 g, 15.1 mmol) in 1,2-dichloroethane (15 ml). After being stirred for 8 h at −15 °C, the mixture was filtered and the filtrate was treated with CF_3COOH (1.72 g, 15.1 mmol) at −15 °C for 2 h. The solid produced (1.19 g, 45.5%) was collected by filtration, washed with 1,2-dichloroethane, and dried in vacuo. The product was identified as phenylamidosulfuric acid (**3**) by comparison of its IR spectrum and HPLC data with those of the authentic sample prepared in previous work.[6]

Reaction of 1 with Chlorosulfuric Acid. To a stirred solution of **1** (2.56 g, 15.5 mmol) in 1,2-dichloroethane (55 ml) was added at −20 °C over 30 min chlorosulfuric acid (1.81 g, 15.5 mmol). The mixture was then stirred for 8 h at −20 °C. A precipitate produced was collected by filtration under dry nitrogen, washed with 1,2-dichloroethane, and dried in vacuo to give **3** (2.55 g, 95%). HPLC analysis and tests with acidic aqueous $Ba(NO_3)_2$ and 0.05 M $AgNO_3$ solutions indicated the contamination with slight amounts of anilinium hydrogensulfate and anilinium chloride.

Reaction of 1 with 5. Trimethylsilyl chlorosulfate (**5**) was redistilled directly into a dropping funnel under reduced pressure (bp 75.0—75.5 °C/23 Torr). A solution of this ester (3.43 g, 18 mmol) in CH_2Cl_2 (5 ml) was added with stirring to freshly distilled anilinotrimethylsilane (**1**) (bp 104.5—106.0 °C/22 Torr) (2.97 g, 18 mmol) in CH_2Cl_2 (20 ml) at −10—−15 °C over 30 min. The mixture was stirred at this temperature for further 7 h and filtered. The filtrate was then treated at −10—−15 °C for 3 h with CF_3COOH (2.00 g, 18 mmol) to give a white solid, which was collected by filtration, washed with CH_2Cl_2, and dried in vacuo to yield pure phenylamidosulfuric acid **3** (2.0 g, 64%); IR (KBr) 1545 (NH_2^+), 1497, 1480, 1360 (SO_3^-), 1302, 1256 (SO_3^-), 1050 (SO_3^-), 875, 765, and 685 cm^{-1}. Found: C, 41.63; H, 4.17; N, 8.26%. Calcd for $C_6H_7O_3NS$: C, 41.61; H, 4.07; N, 8.09%. This product gave no turbidity with aqueous $Ba(NO_3)_2$; its homogeneity was proved by HPLC analysis.

Isolation of Trimethylsilyl Phenylamidosulfate (2). The reaction of **1** with **5** was carried out as described above. The reaction mixture was filtered and evaporated in vacuo. Distillation of the residue yielded **2** as a colorless liquid boiling at 119 °C/ca. 1 Torr; IR (film) 3285 (NH), 2965, 2900, 1605, 1503, 1345 (SO_2), 1258 ($Si(CH_3)_3$), 1175 (SO_2), 950 (SiOSi), 845, 765, and 698 cm^{-1}; treatment of this compound with CF_3COOH yielded phenylamidosulfuric acid **3**.

Formation of Anilinium Methyl Sulfate (6) on Treatment of 2 with Excess of Methanol. The reaction between **1** (2.60 g, 15.7 mmol) and **5** (2.29 g, 15.7 mmol) was carried out as described above. After removal of a white precipitate (0.85 g), the filtrate was treated with methanol (1.00 g, 31.4 mmol) at −10—−15 °C. A white solid rapidly separated out, as the methanol was added.[18] While the mixture was stirred for further 1.5 h, the solid gradually disappeared and colorless crystals, in turn, separated out as thin plates; this compound (1.26 g, 39%) was identified as **6** by comparison of its melting point (130—131 °C) and IR spectrum with those of an authentic sample.[19] Found: C, 41.09; H, 5.04; N, 6.65%. Calcd for $C_7H_{11}O_4NS$: C, 40.97; H, 5.40; N, 6.83%.

Reaction of Aniline with 5 in a 1 : 1 Molar Ratio. To a stirred solution of **5** (2.14 g, 11.3 mmol) in CCl_4 (20 ml) was added a solution of aniline (1.06 g, 11.3 mmol) in CCl_4 (20 ml) at −10—−15 °C over 30 min. After the mixture had been stirred for 7 h at −10—−15 °C, a precipitate (**A**) thus formed (1.26 g) was collected by filtration. Treatment of the filtrate with acetic acid (0.68 g; 11.3 mmol) for 3 h at −10—−15 °C yielded another precipitate (**B**) (0.34 g).

Precipitate **A**: Neutralization of this material with aqueous NaOH gave sodium phenylamidosulfate; its identity was verified by HPLC analysis and by comparison of its IR

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†Torr=133.322Pa.

spectrum with that of an authentic sample; tests with aqueous $Ba(NO_3)_2$ and $AgNO_3$ indicated the contamination with anilinium hydrogensulfate and anilinium chloride.

Precipitate **B**: Its IR spectrum was identical with that of an authentic sample of **2** and its HPLC showed a single peak ascribable to **2**.

Reaction of Aniline with 5 in a 2:1 Molar Ratio. To a stirred solution of aniline (1.69 g, 18.2 mmol) in CCl_4 was added a solution of **5** (1.72 g, 9.1 mmol) in the same solvent (5 ml) over 30 min at −10—−15 °C. After the mixture had been stirred for 3 h at −10—−15 °C, the resulting precipitate was collected, washed with CCl_4, and dried in vacuo to give anilinium phenylamidosulfate (**8**) (2.12 g, 87%). Recrystallization from water gave the pure salt; its IR spectrum was identical with that of an authentic sample. Found: C, 54.33; H, 5.24; N, 10.27%. Calcd for $C_{12}H_{14}O_3N_2S$: C, 54.12; H, 5.30; N, 10.52%.

Reaction of 1 with Dioxane–Sulfur Trioxide. To a stirred solution of 1,4-dioxane (1.00 g, 11.4 mmol) in 1,2-dichloroethane (20 ml) was added a solution of SO_3 (0.78 g; 9.74 mmol) in 1,2-dichloroethane (20 ml) over 1 h at −10 °C. To this mixture was added with stirring a solution of **1** (1.61 g; 9.74 mmol) in 1,2-dichloroethane (20 ml) over 30 min at −20 °C. After having been stirred for an additional 2 h at −20 °C, the mixture was filtered. The filtrate was then treated with CF_3COOH (1.50 g, 13 mmol) at −5 °C for 3 h; the solid thus formed was collected, washed with 1,2-dichloroethane, and dried in vacuo, giving phenylamidosulfuric acid (**3**) (1.1 g; 65%).

Reaction of 1 with Ethyl Chlorosulfate (10). To a stirred solution of **1** (2.28 g; 13.8 mmol) in CH_2Cl_2 (20 ml) was added a solution of **10** (2.00 g; 13.8 mmol) in CH_2Cl_2 (10 ml) at −10—−15 °C over 30 min. After having been stirred for an additional 2 h, the mixture was allowed to warm to room temperature, and then refluxed for 3 h. A white solid (**A**) (0.45 g) was collected, washed with CH_2Cl_2, and dried; the combined filtrate and washings were treated with CH_3COOH at −10—−15 °C for 3 h to yield a solid (**B**). After the solid (**B**) had been filtered off, the filtrate was washed with water repeatedly, dried over Na_2SO_4, and evaporated to give a semi-solid (**C**), which probably is a mixture of ethyl phenylamidosulfate and ethyl *N*-ethyl-*N*-phenylamidosulfate.

Solid **A**: IR (KBr) 3270 (NH), 1601, 1501, 1230 (SO_3^-), 1162 (SO_3^-), 1125, 1033 (SO_3^-), 900, 835, 740, and 682 cm^{-1}; the IR spectrum of its sodium salt was identical with that of an authentic sample of disodium (4-sulfonatophenylamido)sulfate.[20]

Solid **B**: The IR and NMR spectra of its sodium salt agreed with those of an authentic sample of sodium 4-aminobenzenesulfonate; HPLC analysis revealed the contamination with slight amounts of 2-aminobenzenesulfonic acid and aminobenzenedisulfonic acid, and with a trace of **3**.

Residue **C**: IR (KBr) 1603, 1503, 1360 (SO_2), 1165 (SO_2), 1008, 915, 752, and 695 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ=1.0 (t, CH_3), 1.23 (t, CH_3), 3.65 (q, OCH_2), 4.08 (q, NCH_2), and 7.48 (m, ArH).

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