Preparation of Arylimidobis(sulfates)[1]

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(Received October 18, 1985)

Synopsis. Seven arylimidobis(sulfates), six of which are new compounds, have been prepared by the *N*-sulfonation of the corresponding primary aromatic amines with 2-methylpyridine-sulfur trioxide in 60—92% yields.

In our previous work[1] we isolated (2,4,6-trimethylphenylimido)bis(sulfate) from the thermal reaction of 2,4,6-trimethylanilinium butylamidosulfate. Mechanistic consideration of this reaction led us to the successful preparation of this imidobis(sulfate) by fusion of an equimolar mixture of butylamidosulfuric acid and butylammonium (2,4,6-trimethylphenylamido)sulfate. Recently, considerable attention has been given to the mechanism of the sulfonation of aniline with excess concentrated and fuming sulfuric acid,[2,3] and the intermediacy of phenylimidobis(sulfuric) acid[4] as well as (2- and 4-sulfophenylamido)sulfuric acid,[2,5] has been suggested. In this context, we have become interested in the chemistry of arylimidobis(sulfuric) acids and their salts. In this paper we report the preparation of arylimidobis(sulfates).

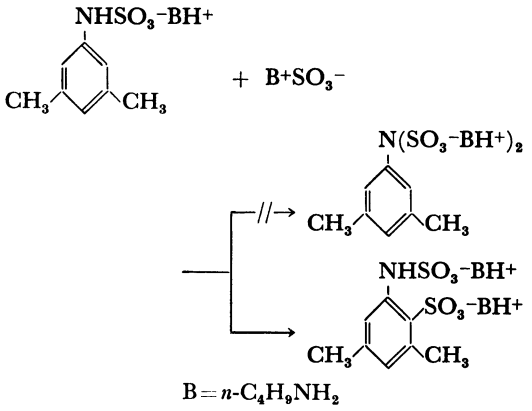
Results and Discussion

The standard method for the preparation of unsubstituted imidobis(sulfate) on a laboratory scale involves the fusion of ammonium amidosulfate itself[6] or the fusion of an equimolar mixture of ammonium amidosulfate and amidosulfuric acid.[7]

$$2\,NH_2SO_3NH_4 \xrightarrow[290-305\,^\circ C]{\Delta} HN(SO_3NH_4)_2 + NH_3$$

$$NH_2SO_3NH_4 + NH_3{}^+SO_3{}^- \xrightarrow[145-150\,^\circ C]{\Delta} HN(SO_3NH_4)_2$$

This method, however, cannot be applied to the synthesis of arylimidobis(sulfates) except (2,4,6-trimethylphenylimido)bis(sulfate), because their *N*-sulfonate group tends to thermally migrate to position(s) ortho and/or para relative to the amino group. In fact, the fusion of an intimate mixture of butylammonium (3,5-dimethylphenylamido)sulfate and butylamidosulfuric acid gave, in a 69% yield, (3,5-dimethyl-2-sulfonatophenylamido)sulfate instead of the desired (3,5-dimethylphenylimido)bis(sulfate) (see Experimental section).



Previously,[8] we reported a one-step method for the preparation of *N*-substituted imidobis(sulfates). This method involving the *N*-sulfonation of an appropriate amine with triethylamine-sulfur trioxide works well with aliphatic and alicyclic amines, but with aromatic amines gives only poor yields (see Ref. 8 and Table 1).

Vrba and Allan[9] have prepared disodium phenylimidobis(sulfate) by the *N*-sulfonation of aniline with 2-methylpyridine-sulfur trioxide. Unfortunately, this work was limited to the preparation of phenylimidobis(sulfate) itself and published only in a short communication. In addition, the yield of the isolated product was not given (presumably much less than 50%). Accordingly, we examined this reaction in some detail and found optimal conditions giving arylimidobis(sulfates) in good yields (Table 1).

Table 1. Preparation of Phenylimidobis(sulfate)[a]
$C_6H_5NH_2 + 2B\cdot SO_3 \longrightarrow C_6H_5N(SO_3{}^-BH^+)_2$

B	Mr[b]	Solv.	Reaction temp/°C	Reaction time/h	Yield/%[c]
$(C_2H_5)_3N$	2.19	2-MePy	25—30	71	17[e]
$(C_2H_5)_3N$	2.06	2-MePy	88—91	8	7
2-MePy[d]	2.42	2-MePy	17—18	71	84
2-MePy	2.34	2-MePy	88—92	1	78[f]

a) The imidobis(sulfate) was isolated as a sodium salt. b) Molar ratio of $B\cdot SO_3$ to aniline. c) Yields refer to the yield of isolated product based on aniline. d) 2-Methylpyridine. e) Data cited from: F. Kanetani and H. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **47**, 2713 (1974). f) Isolated as the potassium salt.

Thus the *N*-sulfonation of aniline with a slight excess of 2-methylpyridine-sulfur trioxide at room temperature for 71 h gave phenylimidobis(sulfate) in a 84% yield, together with a small amount of phenylamidosulfate. The use of higher temperature accelerated the reaction without significant lowering of the yield; i.e., the reaction at 88—91 °C for 1 h produced the imidobis(sulfate) in a 77% yield. TLC analysis of the reaction mixture revealed the formation of (4-sulfonatophenylamido)sulfate[1] as a by-product. This compound may arise either from the para sulfonation of the phenylamidosulfate or from the thermal rearrangement of phenylimidobis(sulfate) formed.

Table 2. Preparation of Arylimidobis(sulfates)[a]
$ArNH_2 + 2(2\text{-}MePy \cdot SO_3^{b)}) \longrightarrow ArN(SO_3^-\ 2\text{-}MePyH^+)_2$

$ArNH_2$	Mr[c]	Reaction temp/°C	Reaction time/h	Yield/%[d]
2-Methyl-aniline	2.14	89—91	2	67
3-Methyl-aniline	2.09	20—21	71	71
		88—92	2	trace[e]
4-Methyl-aniline	2.16	89—91	2	63
2-Chloro-aniline	1.99	22—23	142	60
3-Chloro-aniline	2.08	21—22	71	70
4-Chloro-aniline	2.05	22—23	120	92

a) All imidobis(sulfates) were isolated as potassium salts and characterized by IR spectroscopy and elemental analysis. b) 2-Methylpyridine-sulfur trioxide addition compound. c) Molar ratio of 2-MePy·SO_3 to substrate amine. d) Yields refer to the yield of isolated product based on amine. e) TLC analysis revealed the formation of (3-methylphenylimido)bis(sulfate) but in a trace; the chief product was (3-methyl-4-sulfonatophenylamido)sulfate.

Table 2 summarizes the results of the *N*-sulfonation of some other primary aromatic amines with 2-methylpyridine-sulfur trioxide. As can be seen from the table, the reaction at room temperature for 2—6 d or at 90 °C for 1—2 h gives arylimidobis(sulfates) in yields of 60—92%. 3-Methylaniline provided an exception; thus the reaction at 88—92 °C for 2 h failed to yield (3-methylphenylimido)bis(sulfate) and resulted in the formation of a new compound, which is identified as (3-methyl-4-sulfonatophenylamido)sulfate.[10] On the contrary, at room temperature the reaction proceeded in an expected manner to afford (3-methylphenylimido)bis(sulfate) in a 71% yield. Our results suggest that the use of the reaction conditions of Vrba and Allan (0 °C, 1 h) would lead to much lower yields of arylimidobis(sulfates).

The IR spectra of all the arylimidobis(sulfates) prepared, as well as alkylimidobis(sulfates),[11] showed two to four strong absorption peaks in the range of 1220—1298 cm^{-1}, and two strong peaks at 1029±3 and 1080±4 cm^{-1}. The former peaks are attributable to antisymmetric and the latter to symmetric vibrations of the SO_3^- groups. The imidobis(sulfates) were soluble in water, sparingly soluble in methanol, and insoluble in other ordinary organic solvents. All the arylimidobis(sulfates) are very liable to acid hydrolysis, which leads to the formation of sulfate ion by way of the corresponding arylamidosulfate ions.

$$ArN(SO_3^-)_2 \longrightarrow ArNHSO_3^- + HSO_4^-$$
$$\longrightarrow ArNH_3^+ + 2HSO_4^-$$

Experimental

Pyridine, 2-methylpyridine and triethylamine were dried

Table 3. Analytical Data for Arylimidobis(sulfates)

Ar	Formula	C(%) (Calcd)	H(%) (Calcd)	N(%) (Calcd)	IR spectra ($\tilde{\nu}$/cm^{-1})			
					$\nu_{as}SO_3^-$		$\nu_sSO_3^-$	Other prominent peaks
C_6H_5	$C_6H_5NO_6S_2Na_2$ (297.21)	24.18	1.58	4.70	1287	1250	1081	952 902 756 714 700
		(24.25)	(1.70)	(4.71)	1229	1193	1029	
2-$CH_3C_6H_4$	$C_7H_7NO_6S_2K_2$ (343.46)	24.20	2.13	4.01	1284	1250	1081	956 912 862 171 704
		(24.48)	(2.05)	(4.08)	1219		1029	
3-$CH_3C_6H_4$	$C_7H_7NO_6S_2K_2$ (343.46)	24.40	2.08	4.13	1285		1076	947 895 817 790 705
		(24.48)	(2.05)	(4.08)	1230	1195	1026	695
4-$CH_3C_6H_4$	$C_7H_7NO_6S_2K_2$ (343.46)	24.32	2.01	4.08	1298	1255	1078	956 917 816 685
		(24.48)	(2.05)	(4.08)	1245	1193	1027	
2-ClC_6H_4	$C_6H_4NClO_6S_2K_2$ (363.88)	19.50	1.03	3.81	1277		1084	971 937 867 757 735
		(19.80)	(1.11)	(3.85)	1225		1029	718 682
3-ClC_6H_4	$C_6H_4NClO_6S_2K_2$ (363.88)	19.69	1.20	3.73	1291	1256	1078	966 945 903 880 796
		(19.80)	(1.11)	(3.85)	1236	1197	1030	759 695 680
4-ClC_6H_4	$C_6H_4NClO_6S_2K_2$ (363.88)	19.82	1.17	3.82	1287	1260	1078	960 928 824 745 713
		(19.80)	(1.11)	(3.85)	1235	1205	1032	670

over KOH pellets, distilled, and stored over molecular sieves 4A. 1,2-Dichloroethane was dried over $CaCl_2$, distilled and stored over molecular sieves 4A. Sulfur trioxide was obtained by distillation of 60% fuming sulfuric acid. IR spectra were recorded on a JASCO IR-S spectrophotometer. Thin-layer chromatography was performed on 0.25 mm-thick cellulose plates (Cellulose Mikrokristallin, E. Merck). Compounds were visualized by UV fluorescence or by placing the plates in a container filled with nitrous gases, followed by spraying with sodium 1-naphthol-4-sulfonate and subsequent exposure to ammonia gas. All the reactions were carried out under anhydrous conditions.

General Procedure for the Preparation of Arylimidobis(sulfates). Sulfur trioxide was distilled into 10 ml of cooled (5—10 °C) 1,2-dichloroethane. To this solution was added 30 ml of 2-methylpyridine drop by drop. After stirring for 10 min at 10 °C, a substrate amine in 10 ml of 2-methylpyridine was added and the mixture was then stirred at room temperature or at 90 °C. After the reaction had been complete, the solvent was removed in vacuo at a bath temperature below 30 °C. The residue was dissolved in aqueous potassium hydroxide. The solution was warmed for 30 min at 50 °C while its pH being kept at 8—9. The mixture was then treated with a 5% barium acetate solution until no more precipitate was formed. The filtered solution was concentrated to about 5 ml. To this solution was added a few drops of 10% aqueous KOH and 100 ml of hot ethanol. The mixture was allowed to stand overnight. The crystals were collected by filtration, washed with 90% ethanol, and dried in a vacuum desiccator.

Reaction of Butylammonium (3,5-Dimethylphenylamido)sulfate with Butylamidosulfuric Acid. An intimate mixture of butylammonium (3,5-dimethylphenylamido)sulfate (0.548 g, 2.00 mmol) and butylamidosulfuric acid (0.303 g, 1.98 mmol) was heated at 120 °C for 4 h. After cooling to room temperature, the glass-like product was dissolved in 10% aqueous KOH and the solution was evaporated to dryness. The residual solid was dissolved in a little hot water. This solution was then added, with vigorous stirring, to hot ethanol (90 ml) containing a few drops of 10% aqueous KOH. The mixture was allowed to cool to room temperature to give colorless crystals (0.491 g). Recrystallization gave the pure dipotassium N, 2-disulfonate; IR (KBr) 3280 (NH), 1201 (SO_3^-), 1149, 1086, 1050 (SO_3^-), 1015, 874, 856 (1H), and 755 cm^{-1}. This disulfonate furnished 2-amino-4,6-dimethylbenzenesulfonic acid when heated with dil. HCl.[1)]

The author thanks Professor Richard N. Butler and Dr. William J. Spillane for the laboratory facilities during his stay at University College, Galway (Republic of Ireland) on sabbatical leave.

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