The Preparation of *N*-Alkyl-*O*-arenesulfonylhydroxylamines

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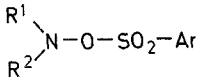
While unsubstituted *O*-arylsulfonylhydroxylamines (**1**; R^1, R^2 = H) are useful and well-known reagents[1], reports of the corresponding *N*-substituted compounds (**1**; R^1 = H, R^2 = alkyl; R^1, R^2 = alkyl) are rare[2]. Only one report of their isolation is available[3].



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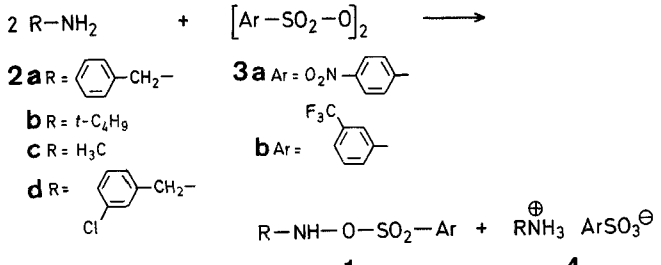
In connection with our studies of amine oxidations with sulfonyl peroxides[4], we have developed a new, general method for the preparation and isolation of these materials (Scheme **A**).

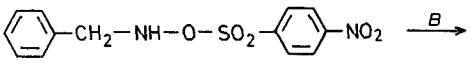


Scheme **A**

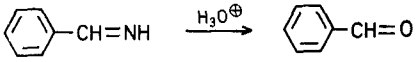
When primary amines **2** (2 equiv.) are treated with arylsulfonyl peroxides[5] **3** at −78 °C in ether, dichloromethane, or ethyl acetate, immediate precipitation of the ammonium arenesulfonate salt **4** commences. After being stirred for 2 h, the solution is filtered, and evaporated at low temperature. Low temperature chromatography (−20 °C) on silica gel gives the crystalline hydroxylamine derivatives **1** in high yields (Table). It is necessary to use two equivalents of the starting amine, one of which forms the adduct **1** the other of which forms the salt **4**. If more than two equivalents of the amine are used, base-promoted elimination in **1** leads to decreased yields.

The products **1** were shown to be homogeneous by T.L.C. and were characterized by ^{1}H-N.M.R. spectroscopy at low temperature (−40 °C). The results are reported in the Table. In addition to a four proton aromatic sulfonate multiplet, the products **1** all have a broad one proton singlet at δ = 4.8–5.2 ppm (exchangeable with D_2O) assigned to the N—H proton, and have alkyl group resonances different in chemical shift than either the starting amine **2** or the ammonium salt **4**, but with the same multiplicities. The instability of these materials precluded other spectral characterization and microanalysis. They can, however, be stored for several days at −20 °C without extensive decomposition.

The chemical behavior of products **1** is in accord with their structure. Thus, the benzylamine product **1aa** undergoes base-promoted elimination to benzaldimine **(5)** and thence benzaldehyde[6] **(6)** in 83% yield (Scheme **B**), and the second order rate constant for elimination using the isolated products and benzylamine as the promoting base, 8.10×10^{-3} M^{-1} s^{-1}, is the same as for **1aa** generated and studied *in situ*, 8.6×10^{-3} M^{-1} s^{-1}.[4]

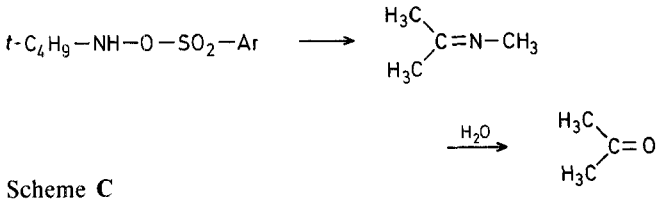


1aa



Scheme **B** **5** **6** (83%)

The *t*-butylamine products **1ba** and **1bb** in chloroform solution at room temperature rearrange to *N*-isopropylidenemethylamine and then give acetone by hydrolysis[8] (Scheme **C**). This is similar to the Stieglitz rearrangement of *N*-arylsulfonyloxy compounds reported earlier[10].



Scheme **C**

This new method offers two distinct advantages in the preparation of *N*-alkyl-*O*-arylsulfonylhydroxylamines, **1**. The first is that amines are converted directly to these derivatives; the corresponding hydroxylamine is not a required precursor[2,3]. Secondly, a wide range of arylsulfonate groups can be attached to nitrogen including the more reactive ones (*p*-NO_2, *m*-CF_3) not heretofore possible. Thus, it is potentially possible to convert any amine to an active aminating agent by this method.

N-*t*-Butyl-*O*-*m*-trifluoromethylbenzenesulfonylhydroxylamine, (1bb); Typical Procedure:

A solution of **3b** (0.995 g, 2.2 mmol)[5] in ether (40 ml) is flushed with nitrogen, sealed with a serum stopper, and cooled to −78 °C in a Dry Ice bath. *t*-Butylamine (**2b**; 0.3220 g, 4.4 mmol) is added via a syringe and precipitation of the ammonium salt starts immediately. After stirring for 2 h, the mixture is filtered and the solvent removed under vacuum at −40 °C. The pale yellow residue is dissolved in chloroform (20 ml) and chromatographed on a silica gel column (1.5 × 20 cm) with chloroform. The column is maintained at −20 °C by a cooled jacket. The first 50 ml of eluate contains the product **1bb** as determined by the T.L.C. (Eastman silica gel plates, chloroform eluent). Removal of solvent gives **1bb** as a white solid; yield: 0.52 g (90%); m.p. 105–108 °C (dec).

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Table. *N*-Alkyl-*O*-arenesulfonylhydroxylamines **1**

Product No.	R	Ar	Yield[a] [%]	m.p. (dec) [°C]	Molecular formula[b]	^{1}H-N.M.R. ($CDCl_3$/TMS, −40 °C) δ [ppm]
1ab	$C_6H_5CH_2$	3-F_3C—C_6H_4	83	40–43°	$C_{14}H_{12}F_3NO_3S$ (331.3)	4.98 (s, 2H); 5.3 (br. s, 1H); 7.2 (m, 5H_{arom}); 8.2 (m, 4H_{arom})[c]
1ba	*t*-C_4H_9	4-O_2N—C_6H_4	87	112–115°	$C_{10}H_{14}N_2O_5S$ (274.3)	0.96 (s, 9H); 4.8 (br. s, 1H); 8.19, 8.40 (AB q, 4H_{arom}, J=6 Hz)
1bb	*t*-C_4H_9	3-F_3C—C_6H_4	90	105–108°	$C_{11}H_{14}F_3NO_3S$ (297.3)	0.95 (s, 9H); 4.5 (br. s, 1H); 8.2 (m, 4H_{arom})
1ca	H_3C	4-O_2N—C_6H_4	96	83–85°	$C_7H_8N_2O_5S$ (232.2)	2.80 (s, 3H); 4.8 (br. s, 1H); 8.18, 8.40 (AB q, 4H_{arom}, J=6 Hz)
1da	3-Cl—$C_6H_4CH_2$	4-O_2N—C_6H_4	63	—[d]	$C_{13}H_{11}ClN_2O_5S$ (342.8)	4.22 (s, 2H); 5.2 (br. s, 1H); 7.8 (m, 4H_{arom}); 8.19, 8.40 (AB q, 4H_{arom}, J=6 Hz)

[a] Yield of product isolated by chromatography. In all cases the ammonium salt **4** was isolated in ~100% yield and identified by comparison with an authentic sample.

[b] All products are new, microanalyses could not be obtained due to instability.

[c] In acetone-d_6.

[d] This material was stable at −20 °C for short periods but began to decompose at 25 °C, so no melting point could be measured.

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[1] Y. Tamura, J. Minamikawa, M. Ikeda, *Synthesis* **1977**, 1.

[2] For attempts to prepare these materials see:
A. Y. Berlin, M. N. Shchukina, E. D. Sayonova, *Zh. Obshch. Khim.* **14**, 249 (1944).
P. G. Gassman, G. D. Hartman, *J. Am. Chem. Soc.* **95**, 449 (1973).

[3] G. Boche, N. Mayer, M. Bernheim, K. Wagner, *Angew. Chem.* **90**, 733 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 687 (1978).

[4] R. V. Hoffman, E. L. Belfoure, *J. Am. Chem. Soc.* **104**, 2183 (1982) and references therein.

[5] Arylsulfonyl peroxides were prepared as follows:
3b: R. L. Dannley, P. K. Tornstorm, *J. Org. Chem.* **40**, 2278 (1975).
3a: R. L. Dannley, J. E. Gagen, O. J. Stewart, *J. Org. Chem.* **35**, 3076 (1970).

[6] Benzaldehyde was quantitated by gas chromatography (2 m, QF-1, 80 °C) and identified by conversion to its 2,4-DNP derivative; m.p. 234–236 °C (Ref.[7], m.p. 237 °C).

[7] R. L. Shriner, R. C. Fuson, D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, New York, 1964, p. 320.

[8] Acetone was identified by conversion to its 2,4-DNP derivative; m.p. 123–124 °C (Ref.[9], m.p. 126 °C).

[9] Ref.[7], p. 362.

[10] R. V. Hoffman, D. J. Poelker, *J. Org. Chem.* **44**, 2464 (1979).

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