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A Novel Method for Sulfinylation Reaction of Lithioamines Using Sulfur Dioxide

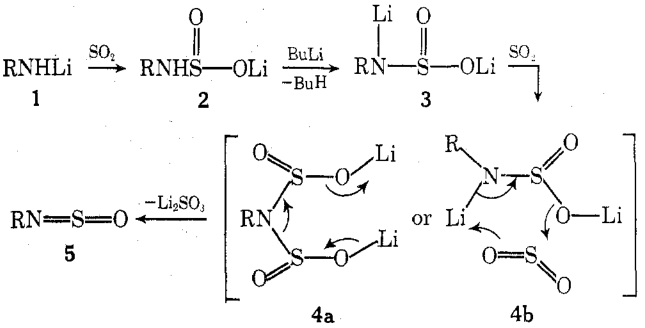
Shizuyoshi Sakai,* Tatsuo Fujinami, and Kazunaga Komizo

Department of Industrial Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu, 432 Japan

Received May 14, 1975

Thionyl chloride is usually used as a sulfinylating reagent of amines or amides in the presence of base such as pyridine or trimethylsilyl amide.[1-9] In connection with a utilization of sulfur dioxide, we have found a novel and direct sulfinylation reaction of lithioamines with sulfur dioxide to afford *N*-sulfinylamines.

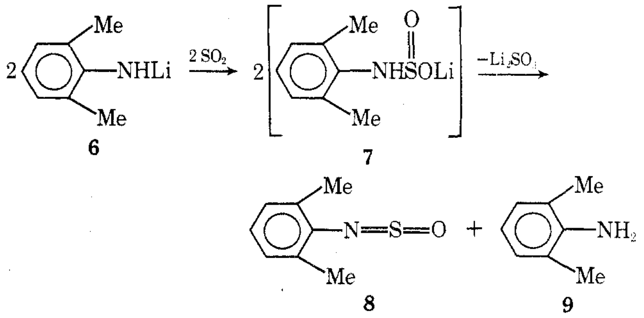
The lithioamine **1** prepared in situ from primary amine and butyllithium in tetrahydrofuran was treated with an equimolar amount of sulfur dioxide to form lithium aminosulfinate **2**. The A_2B_2 signals in the NMR spectra were shifted downfield from δ 6.07 and 6.47 for **1** to 6.39 and 6.59 for **2** (R = p-$CH_3C_6H_4$). Lithium *N*-(*p*-tolyl)aminosulfinate (**2**) was allowed to react with butyllithium to afford butane and the *N*-lithio-*N*-tolylaminosulfinate **3** (R = p-$CH_3C_6H_4$), which showed a new broad singlet at δ 6.66 in the NMR spectrum. Subsequently, introduction of a second mole of sulfur dioxide caused exothermic reaction and the characteristic bands of ν_{NSO} appeared at 1280 and 1157 cm^{-1} in the ir spectrum of the reaction mixture. After refluxing, the reaction mixture was distilled to separate *N*-sulfinyltoluidine **5** (R = $CH_3C_6H_4$).



The formation of *N*-sulfinyltoluidine by heating the intermediate **2** or **3** could not be observed even in the ir and NMR spectra of the reaction mixture, so the role of the second mole of sulfur dioxide is essential in the preparation reaction for *N*-sulfinylamine **5**. On the other hand, in the presence of the second mole of sulfur dioxide, **3** was easily decomposed to afford **5** and lithium sulfite which was detected by the $\nu_{SO_3{}^{2-}}$ bands of inorganic sulfite at 1010 and 960 cm^{-1} in the ir spectrum of solid mass in a distillation residue. Although the intermediate or transition state, **4a** or **4b**, could not be identified even by spectroscopic method such as ir or NMR, it will be postulated to explain the observed accelerating effect of the second mole of sulfur dioxide in the decomposition reaction of **3**. The same phenomena have also reported in the cases of the reaction of lithium *N*-lithiocarbamate with carbon disulfide to give isothiocyanate[10] and of the exchange reaction of heterocumulenes using organostannyl compounds.[11]

In usual cases for preparation of sulfinylamines, 2 mol each of butyllithium and sulfur dioxide per 1 mol of amine were used stepwise. The NMR data for the product mixtures indicated the complete and selective conversion of amines to sulfinylamines, but the yields shown in Table I were rather low, probably owing to hydrolysis of *N*-sulfinylamines.

The behavior of *N*-lithio-2,6-xylidine (**6**) was different from those of other *N*-lithioamines: it reacted exothermically with an equimolar amount of sulfur dioxide to afford an equimolar mixture of free xylidine and *N*-sulfinylxylidine in the absence of the second mole of sulfur dioxide, the latter being characterized by the comparisons of the ir and NMR spectra of the reaction products with those of the mixture of the authentic **8** and **9**.



The abnormal behavior of *N*-lithio-2,6-xylidine was assumed to be due to the steric effect of two *o*-methyl groups on the stability of **7** or **8**, although detailed investigations are now in progress.

Table I
Sulfinylamines Prepared by the Reaction of Primary Amines with 2 Mol Each of Butyllithium and Sulfur Dioxide

		RNSO			
Amine used (RNH_2)	Registry no.	Bp, °C (mm)	Yield, %	ν_{NSO}	Lit.
$C_6H_5NH_2$	62-53-3	55–60 (10)	46	1280, 1160	1
2-$MeC_6H_4NH_2$	95-53-4	83–85 (13)	59	1285, 1167	2
4-$MeC_6H_4NH_2$	106-49-0	75–80 (10)	58	1280, 1157	3
2,6-$Me_2C_6H_3NH_2$	87-62-7	97–100 (15)	52	1280, 1178	4
2-$MeOC_6H_4NH_2$	90-04-0	75–80 (0.2)	60	1286, 1156	2
3-$MeOC_6H_4NH_2$	536-90-3	66–72 (0.2)	50	1292, 1154	5
4-$MeOC_6H_4NH_2$	104-94-9	80–84 (0.5)	47	1305, 1157	6, 7
4-$ClC_6H_4NH_2$	106-47-8	100–105 (12)	45	1292, 1166	1
n-$C_3H_7NH_2$	107-10-8	80–90	30	1230, 1140	1
n-$C_4H_9NH_2$	109-73-9	80–90	20	1240, 1115	1
c-$C_6H_{11}NH_2$	108-91-8	55–60 (16)	14	1245, 1120	1

Experimental Section

All melting and boiling points were uncorrected. The ir and NMR spectra were determined with a Jasco Model IRA-1 spectrometer and a Hitachi Perkin-Elmer Model R-24 spectrometer, respectively. Solvents, amines, and sulfur dioxide were dried by common methods. Reactions were performed under dry nitrogen atmosphere. Identification of the products isolated was carried out by comparisons of boiling point, ir, and NMR spectra of authentic samples prepared by published methods.[1-9]

Standard Method for Preparation of *N*-Sulfinylamines. A. *N*-Sulfinyltoluidine. Under dry nitrogen atmosphere, *p*-toluidine (5.3 g, 50 mmol) was dissolved in dry tetrahydrofuran (50 ml) in a flask equipped with a mechanical stirrer, a condenser, a drying tube, a dropping funnel, and a nitrogen inlet, and treated with butyllithium (55 mmol in 40 ml of petroleum ether) at room temperature. After stirring for 30 min, sulfur dioxide gas was slowly introduced to the solution of *N*-lithiotoluidine (**1**, R = *p*-$CH_3C_6H_4$; δ 6.07, 6.47, dd, in tetrahydrofuran). Lithium *N*-tolylaminosulfinate (**2**, R = *p*-$CH_3C_6H_4$; δ 6.39, 6.59, dd) was formed exothermically. The muddy solution of **2** thus prepared in situ was treated again with butyllithium (55 mmol) with cooling to give a pale yellow suspension of lithium *N*-lithio-*N*-tolylaminosulfinate (**3**, R = *p*-$CH_3C_6H_4$; δ 6.66, br s). Sulfur dioxide (57 mmol) was allowed to react slowly with **3**, to give the reddish-orange solution of *N*-sulfinyltoluidine (**5**, R = *p*-$CH_3C_6H_4$), containing insoluble powders of lithium sulfite. The NMR spectrum of the solution was nearly the same as that of pure **5**. After refluxing for 2 hr, separation of insoluble materials by decantation method, and evaporation of solvent, the liquid layer was distilled in vacuo to afford *N*-sulfinyltoluidine: yield 3.2 g (40%); bp 85–90° (11 mm); ir (neat) ν_{NSO} 1280 and 1156 cm^{-1}. The ir and NMR spectra were in good agreement with those of the authentic sample prepared by the published method.[3] The solid mass obtained from the residue in the decantation or in the distillation showed the ir bands at 1010 and 960 cm^{-1} which were ascribable to $\nu_{SO_3{}^{2-}}$ bands of lithium sulfite.

Other aromatic *N*-sulfinylamines were also prepared and isolated in the same manner described above, and the structure of **5** obtained was identified by the comparison of ir and NMR spectra with those of authentic samples.[1-9]

In a separate experiment, the suspension of **2** or **3** (R = *p*-$CH_3C_6H_4$) was heated at 180° under reduced pressure (20 mm), but *N*-sulfinylamine (R = *p*-$CH_3C_6H_4$) was never obtained. The residue was hydrolyzed by dilute acid to recover toluidine in good yield (80–90%).

B. Aliphatic *N*-Sulfinylamines. Aliphatic *N*-sulfinylamines were prepared in the same procedure mentioned above. However, aliphatic *N*-sulfinylamine is readily hydrolyzed by moisture, so the suspension containing **5** and lithium salt in tetrahydrofuran was directly distilled in vacuo, and the distillate was trapped by cooling using liquid nitrogen. The distillate was fractionally redistilled to separate **5** (R = alkyl).

Equimolar Reaction of *N*-Lithio-2,6-xylidine with Sulfur Dioxide. Sulfur dioxide (50 mmol) was introduced slowly into the solution of *N*-lithio-2,6-xylidine (50 mmol) prepared in situ in tetrahydrofuran with cooling. The NMR and ir spectra of the reaction mixture coincided well with those of an equimolar mixture of free 2,6-xylidine (**6**) (multiplet at δ 6.2–6.8; ν_{NH_2} at 3380 and 3450 cm^{-1}) and *N*-sulfinyl-2,6-xylidine (**8**) (br singlet at δ 6.94; ν_{NSO} at 1280 and 1178 cm^{-1}). Isolation of *N*-sulfinylxylidine from the mixture failed by distillation.

Registry No.—**5** (R = Ph), 1122-83-4; **5** (R = 2-MeC_6H_4), 15182-74-8; **5** (R = 4-MeC_6H_4), 15795-42-3; **5** (R = 2,6-$Me_2C_6H_4$), 17420-02-9; **5** (R = 2-$MeOC_6H_4$), 17419-98-6; **5** (R = 3-$MeOC_6H_4$), 17420-00-7; **5** (R = 4-$MeOC_6H_4$), 13165-69-0; **5** (R = 4-ClC_6H_4), 13165-68-9; **5** (R = C_3H_7), 53437-16-4; **5** (R = C_4H_9), 13165-70-3; **5** (R = c-C_6H_{11}), 30980-11-1.

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Solvolysis of Covalent Arylsulfonylmethyl Perchlorates. General Base Catalysis by Dipolar, Aprotic Solvents

L. Menninga, W. D. E. Steenge, and Jan B. F. N. Engberts*

Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands

Received May 13, 1975

Dimethyl sulfoxide (Me_2SO) as well as the Me_2SO–H_2O binary system are valuable reaction media for many organic reactions. The solvation properties of Me_2SO are characteristic of those of dipolar, aprotic (DPA) solvents and have been reviewed in detail.[1-3] In Me_2SO–H_2O strong intermolecular interactions occur between the components and recent studies indicate that the behavior of these mixtures may be rationalized by assuming the formation of thermolabile, nonstoichiometric 1:2 complexes and by considering the effect of Me_2SO on the diffusionally averaged water structure.[4-6]

In this paper we focus our attention on the dynamic basicity (also referred to as "kinetic basicity") of Me_2SO and Me_2SO–H_2O mixtures employing the rates of irreversible deprotonation of two carbon acids as a kinetic probe. The carbon acids are the covalent arylsulfonylmethyl perchlorates **1** and **2** which hydrolyze via a mechanism involving general base catalysis (Brönsted β ca. 0.5, primary kinetic