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Behavior of Sulfinic Acid toward *N*-Chloramines and Related Compounds

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Amination of *p*-toluenesulfinic acid with *O*-mesitylenesulfonylhydroxylamine in dichloromethane gave *p*-toluenesulfonamide (**4**) together with mesitylenesulfonic anhydride (**6**). Similarly, the reactions with *N*-chloramines and *N*-chlorimines afforded the corresponding *N*-substituted *p*-toluenesulfonamides (**7**) and *p*-toluenesulfonyl chloride (**8**).

Keywords——amination; electrophilic aminating reagent; *O*-mesitylenesulfonylhydroxylamine; *N*-chloramine; sulfinic acid; sulfonamide; mesitylenesulfonic anhydride

In the previous paper,[1] we reported that sulfinic acids reacted with *N*-chlorosuccinimide to give the corresponding sulfonyl chlorides. A similar result was obtained in the reactions of sulfinic acids with *tert*-butylhypochlorite and chloramine-T, and consequently these reactions were presumed to proceed through the direct attack of sulfinate *S*-nucleophile on the chloro cations. These results led us to examine the reactivity of sulfinate anion toward another cationic species instead of the chloro cation. We now describe aminations of *p*-toluenesulfinic acid (**1**) with *O*-mesitylenesulfonylhydroxylamine (**2**) and with *N*-chloramine (**3**).

The compound **2** is synthetically important as an electrophilic aminating reagent.[2] When **1** was treated with an equimolar amount of **2** in dichloromethane at room temperature, *p*-toluenesulfonamide (**4**) was obtained in 65% yield. Mesitylenesulfonic anhydride (**6**) was also unexpectedly isolated in 27% yield.

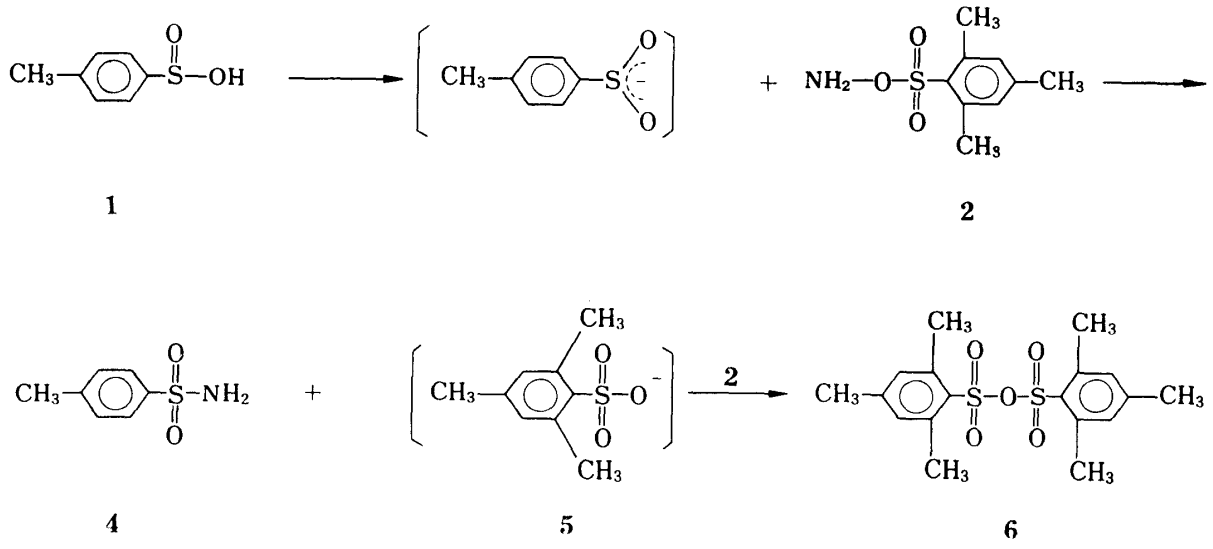


Chart 1

It is known that the sulfinate anions generally behave as ambident *S*- and *O*-nucleophiles.[3] The reaction of **1** with **2** is presumed to be initiated by the nucleophilic attack of *p*-toluenesulfinate *S*-nucleophile on the cationic amino group of **2**, resulting in the formation of **4** and mesitylenesulfonate anion (**5**). The anion **5** immediately reacts with **2**. The hard sulfonate anion **5** reacts preferentially with the hard sulfonyl sulfur rather than the comparatively soft

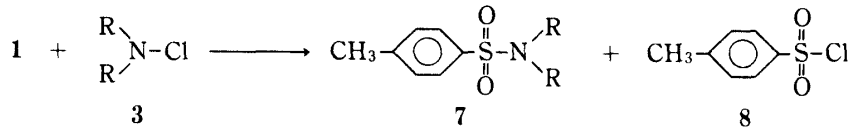


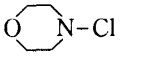
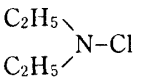
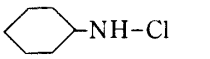
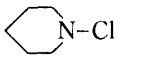
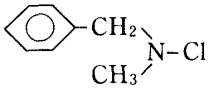
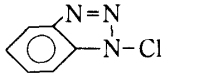
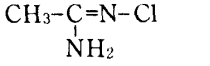
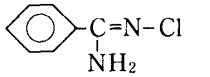
Chart 2

amino nitrogen of **2** to afford **6**.

The structure of **6** was assigned based on the spectral and elementary analysis data. In the IR spectrum of **6**, absorptions assignable to the sulfonyl group were seen at 1380 and 1180 cm^{-1}. The mass spectrum showed the molecular ion peak (M^+) corresponding to **6** at *m/e* 382.

When **1** was allowed to react with a small excess of *N*-chloromorpholine (**3a**) in dichloromethane at room temperature for 30 min, *N*-(*p*-toluenesulfonyl)morpholine (**7a**) and *p*-toluenesulfonyl chloride (**8**) were obtained in 76 and 10% yields, respectively. The reactions with other several *N*-chloramines (**3b**—**f**) and *N*-chlorimines (**3g** and **3h**) provided similar results. The yields of **7** and **8** are listed in Table I.

TABLE I. The Yields of *p*-Toluenesulfonamide (**7**) and *p*-Toluenesulfonyl Chloride (**8**)

	Reactant	Yield (%) 7	8
a		76	10
b		50	41
c		46	42
d		50	36
e		60	32
f		31	43
g		39	40
h		57	36

Generally amines represented by the generalized structure RR'NX are known to possess both electrophilic and nucleophilic properties.[4] *N*-Chloramines **3** show more complicated chemical behavior. The chlorine atom in **3** also has dual nature, exhibiting either anionic or cationic character.[5] The fact that the reaction of **1** with **3** gave **8** suggests that **3** behaves as a chloro cation. When the reaction of **1** with *N*-chlorodiethylamine (**3b**) wascarried out in the presence of an equimolar amount of morpholine under similar conditions, *N*,*N*-diethyl-*p*-toluenesulfonamide (**7b**) and **7a** were obtained in 28 and 67% yields, respectively. When the same reaction was carried out after **3b** had been treated with morpholine in dichloromethane at room temperature, an increased yield (over 90%) of

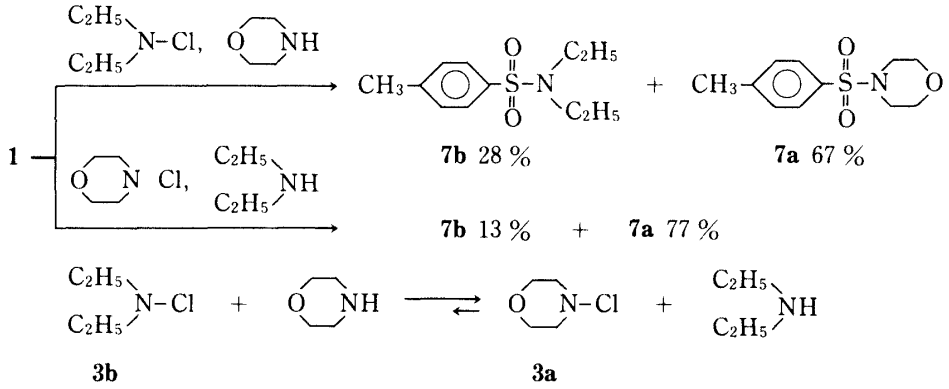


Chart 3

7a was obtained, together with a trace of **7b**. Compound **3b** may be converted to **3a** prior to the reaction. On the other hand, the reaction of **1** with **3a** in the presence of an excess of diethylamine under similar conditions provided **7a** and **7b** in 77 and 13% yields, respectively, and no influence of the added amine on the yield of **7a** was observed.

The transfer of the chlorine atom probably occurs on the basis of the relative basicities of the amine components in *N*-chloramine and the added amine.

Experimental

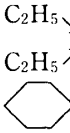
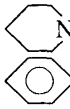
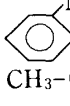
All melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were measured on a JASCO IRA-1 grating infrared spectrometer. Mass spectra were determined at 75 eV on a JEOL OISG mass spectrometer.

Reaction of *p*-Toluenesulfinic Acid (1) with *O*-Mesitylenesulfonylhydroxylamine (2)——Compound **1** (5 mmol) was added to a solution of **2** (5 mmol) in dichloromethane (30 ml) with stirring and ice water cooling. The mixture was stirred at room temperature for 5 h, and washed with H_2O (20 ml), 1% $NaHCO_3$ (20 ml), and H_2O (20 ml). Then Et_2O was added, and the resulting precipitates were collected by filtration to give mesitylenesulfonic anhydride (27%). mp 132—135°C. *Anal.* Calcd for $C_{18}H_{22}O_5S_2$: C, 56.52; H, 5.80. Found: C, 56.42; H, 5.70. IR ν_{max}^{KBr} cm^{-1}: 1380, 1180 (SO_2). MS *m/e*: 382 (M^+), 199, 183, 119. The filtrate was concentrated to dryness, and the residue was recrystallized from EtOH to give *p*-toluenesulfonamide (65%). mp 135—137°C. IR ν_{max}^{KBr} cm^{-1}: 1308, 1165 (SO_2), 3340, 3250 (NH_2).

Reaction of *p*-Toluenesulfinic Acid (1) with *N*-Chloramine (3): General Procedure——Compound **1** (10 mmol) was added slowly to a stirred solution of **3** (10 mmol) in dichloromethane (30 ml) at room temperature under a nitrogen atmosphere, and stirring was continued for 30 min. Then the mixture was washed successively with H_2O (20 ml), 0.5 N HCl (20 ml), 1% $NaHCO_3$ (20 ml), and H_2O (20 ml), dried over Na_2SO_4, and concentrated under reduced pressure. *n*-Hexane was added to the residue, and the insoluble part was collected by filtration and recrystallized from EtOH to give the corresponding *p*-toluenesulfonamide (**7**). The filtrate was concentrated, and the residue was chromatographed over silica gel. By using *n*-hexane–benzene (1: 2) as the eluent, *p*-toluenesulfonyl chloride (**8**) was separated from **7**. The melting points, elementary analyses, and IR data for **7** are listed in TableII.

Reaction of *p*-Toluenesulfinic Acid (1) with *N*-Chlorodiethylamine (3b) in the Presence of Morpholine——1) Compound **1** (10 mmol) and morpholine (10 mmol) were added successively with stirring to a solution of **3b** (10 mmol) in dichloromethane (30 ml) with ice-water cooling. The solution was stirred for 30 min

TABLE II. The Melting Points, Elementary Analyses, and IR Spectral Data of the *p*-Toluenesulfonamides (**7**)

	$\begin{matrix}R\\N\\R\end{matrix}$	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N	IR ν_{max}^{KBr} cm^{-1} SO_2
a		147—148	$C_{11}H_{15}NO_3S$	54.75 (54.57)	6.26 (6.14)	5.81 (5.63)	1345, 1165
b		58—59	$C_{11}H_{17}NO_2S$	58.12 (57.94)	7.54 (7.54)	6.16 (6.04)	1335; 1160
c		83—85	$C_{13}H_{19}NO_2S$	61.63 (61.82)	7.56 (7.68)	5.53 (5.53)	1325, 1160
d		97—98	$C_{12}H_{17}NO_2S$	60.22 (60.36)	7.20 (7.16)	5.85 (5.88)	1340, 1160
e		92—93	$C_{15}H_{17}NO_2S$	65.43 (65.27)	6.22 (6.21)	5.08 (5.04)	1340, 1165
f		136—137	$C_{13}H_{11}N_3O_2S$	57.13 (57.71)	4.06 (4.09)	15.37 (15.68)	1385, 1180
g		144—145	$C_9H_{10}N_2O_2S$	50.92 (50.87)	5.70 (5.89)	13.20 (13.23)	1275, 1145
h		146—147	$C_{14}H_{14}N_2O_2S$	61.29 (61.65)	5.14 (5.15)	10.21 (10.06)	1280, 1155

at room temperature, washed with H_2O (20 ml), 0.5 N HCl (20 ml), 1% $NaHCO_3$ (20 ml), and finally with H_2O (20 ml), and dried over Na_2SO_4. The solvent was distilled off under reduced pressure, and the residue was dissolved in benzene. The insoluble part was collected by filtration to give **7a**. The filtrate was concentrated and chromatographed on silica gel, and elution with benzene and benzene–AcOEt (10: 1) gave **7a** and **7b**. The yields of **7a** and **7b** were 67 and 28%, respectively.

2) *N*-Chlorodiethylamine (**3b**) (10 mmol)was stirred with a solution of morpholine (10 mmol) in dichloromethane (30 ml) for 10 min. Then **1** (10 mmol) was added with ice-water cooling, and stirring was continued for 30 min at room temperature. The mixture was washed successively with H_2O (20 ml), 0.5 N HCl (20 ml), and H_2O (20 ml), and dried over Na_2SO_4. After removal of the solvent by evaporation, the residue was dissolved in benzene. The insoluble part was collected by filtration to give **7a**. The filtrate was concentrated, and the residue was chromatographed on silica gel and eluted with benzene and benzene–AcOEt (10: 1). By this procedure, **7a** was obtained in more than 90% yield, along with a trace of **7b**.

Reaction of *p*-Toluenesulfinic Acid (1) with *N*-Chloromorpholine (3a) in the Presence of Diethylamine——Compound **1** (10 mmol) and diethylamine (10 mmol) were added to a stirred solution of **3a** (10 mmol) in dichloromethane (30 ml) with ice-water cooling. The mixture was stirred at room temperature for 30 min, washed successively with H_2O (20 ml), 0.5 N HCl (20 ml), 1% $NaHCO_3$ (20 ml), and H_2O (20 ml), then dried over Na_2SO_4, and concentrated under reduced pressure. Benzene was added to the residue, and the insoluble part was collected by filtration to give **7a**. The filtrate was concentrated and the residue was chromatographed on silica gel. Elution with benzene and benzene–AcOEt (10: 1) gave **7a** and **7b** in 77 and 13% yields, respectively.

References

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