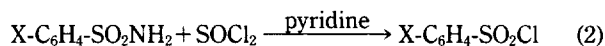
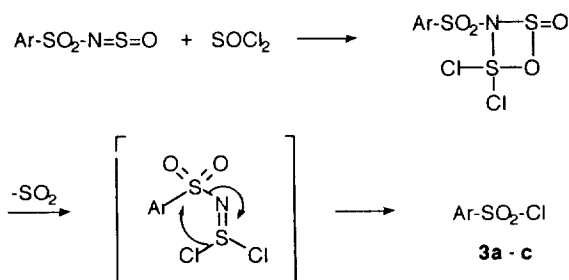


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**Table 1.** Formation of Arenesulfonyl Chloride (**3a-c**) from Arenesulfonamide (**1a-c**) and SOCl<sub>2</sub> (3 equiv) with pyridine (1 equiv)

Substrate	Time (hrs)	Product	Yield <sup>a</sup>
<b>1a</b>	6	<b>3a</b>	48
<b>1b</b>	6	<b>3b</b>	55
<b>1c</b>	6	<b>3c</b>	32

<sup>a</sup> Isolated yield.



- |                                |                                |
|--------------------------------|--------------------------------|
| <b>1a</b> ; X=H                | <b>3a</b> ; X=H                |
| <b>b</b> ; X=p-Me              | <b>b</b> ; X=p-Me              |
| <b>c</b> ; X=m-NO <sub>2</sub> | <b>c</b> ; X=m-NO <sub>2</sub> |

a flask containing benzene (20 mL). The reaction mixture was refluxed for 6 hrs, followed by evaporation of benzene and excess of thionyl chloride. Kugelrohr distillation of remaining residue gave **3b**. Yield: 0.61 g (55%) mp. 68-69°C (Ref.<sup>8</sup> mp. 71°C). The structure of product was identified by comparison of its GC retention time and IR spectra with those of the commercially available authentic sample.

As is shown in Table 1, it can be supposed that the formation of arenesulfonyl chloride (**3a-c**) is a common reaction for arenesulfonamide.

In order to study in more detail, compound **1b** was chosen as a prototype and was reacted with thionyl chloride in various conditions and the results are shown in Table 2. Several points are noteworthy in Table 2. First of all, it can be seen that both thionyl chloride of at least 2 equivalent (entry 9) and refluxing temperature are required for the formation of **3a-c**, which suggests obviously that the reaction of equation 2 might proceed *via* the intermediacy of N-sulfonyl compound. In fact, N-sulfonyl *p*-toluenesulfonamide gave **3b** in reaction with 1 mole of thionyl chloride (entry 14). Though the reaction of equation 2 did not proceed at all without pyridine (entry 4), it gave slowly **3b** both in the presence of large excess of thionyl chloride and under longer period of reflux (entry 8). Also seen in Table 2 is that the reaction of equation 2 proceeded faster in more polar solvent (entry 5-7). This suggests that **3b** would be formed *via* a polar intermediate made between -N=S=O and thionyl chloride.

We then turned to study whether other compounds having an amino group behave similarly as **1a-c**. Among the substrates employed, derivatives of benzamides, Ar-C(O)NH<sub>2</sub>, were responsive to give a mixture of benzonitrile (~70%)

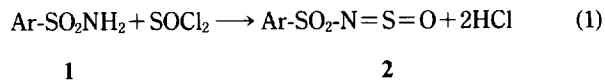
## Deaminative Chlorination of Arenesulfonamide with Thionyl Chloride: Formation of Arenesulfonyl Chloride

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Arenesulfonamide (**1**) is well known to react with thionyl chloride to give corresponding N-sulfonyl compound (**2**), a reactive intermediate,<sup>1,3</sup> as shown in equation 1.



The chemistry of N-sulfonyl compound (**2**) has been extensively investigated in connection with synthetic applications such as in the synthesis of pyridine derivatives *via* Diels-Alder reaction,<sup>4</sup>  $\alpha$ -amino acids *via* ene reactions,<sup>5,6</sup> and derivatives of arylsulfonamides.<sup>7</sup> We report herein that arenesulfonyl chloride (**3**) is produced from the reaction of arenesulfonamide with more than 2 equivalents of thionyl chloride under refluxing condition in inert solvents (equation 2).

General procedure for the formation of arenesulfonyl chloride using *p*-toluenesulfonamide (**1b**) as a prototype is as follows: **1b** (1 g, 5.8 mmol), pyridine (0.05 mL, 0.62 mmol), thionyl chloride (1.3 mL, 17.8 mmol) were introduced into

**Table 2.** Formation of *p*-Toluenesulfonyl Chloride (**3b**) from *p*-Toluenesulfonamide (**1b**) and Thionyl Chloride in Various Reaction Conditions

Entry	SOCl <sub>2</sub> (equiv)	Pyridine (equiv)	Temp	Time (hrs)	Yield <sup>a</sup> of <b>3b</b> (%)
1	3	10 mol%	reflux	9	55
2	3	2	reflux	9	59
3	3	2	RT	42	—
4	3	— <sup>b</sup>	reflux	9	—
5 <sup>c</sup>	3	2	reflux	9	77
6 <sup>d</sup>	3	2	reflux	9	49
7 <sup>e</sup>	3	2	reflux	9	87
8	47	—	reflux	24	52
9	2	2	reflux	9	53
10	1	10 mol%	reflux	9	trace
11	1	2	reflux	9	trace
12	1	2	RT	24	—
13	1	—	reflux	9	—
14 <sup>f</sup>	1	—	reflux	9	47

<sup>a</sup> Isolated yied. <sup>b</sup> Denotes absence. <sup>c</sup> In THF. <sup>d</sup> In hexane. <sup>e</sup> In 1,4-dioxane. <sup>f</sup> Starting material is N-sulfinyl *p*-toluenesulfonamide.

and benzoyl chloride (~30%) derivatives. Other compounds such as toluidines, *o*-anisidine, *m*-nitroaniline, and 2,4-dinitroaniline gave only the corresponding N-sulfinyl compounds. These results indicate that only the substrates having carbonyl- or sulfonyl group adjacent to -N=S=O, react with thionyl chloride. Therefore, carbonyl group of the benzamides and the sulfonyl group of arenesulfonamides seem to exert influences to make the sulfur in -N=S=O group more electrophilic enough to be able to react with thionyl chloride. In conclusion, this method can be utilized to deaminatively chlorinate the arenesulfonamide to give arenesulfonyl chloride.

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## The Electrochemical Activation of Amino Acid 4-(Methylthio)phenyl Ester and Its Application in Peptide Synthesis

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The 4-(methylthio)phenyl (MTP) group has been utilized as a carboxyl protecting group in peptide synthesis, and revealed several advantages.<sup>2</sup> Thus, the MTP group can serve as a safety-catch type protecting group during peptide coupling reactions, and later the resulting peptide fragment can be oxidized by common oxidizing agents to sulfone ester, which is an active ester to be coupled with other N-free peptide fragments to form a new peptide bond.

In our previous reports, we have reported that the charge transfer (CT) interaction between Kaiser's oxime resin<sup>3</sup> and the MTP group accelerated the coupling reaction between the resin bound N-protected amino acid or peptide and the amino acid MTP ester, yielding the N-protected peptide MTP ester.<sup>4</sup> The released peptide fragment was oxidized to 4-(methylsulfonyl)phenyl (MSO<sub>2</sub>P) ester and used in cyclization