

Friedel-Crafts Reaction of Tosylamide Derivatives: A Useful Source of Carbocationic Species

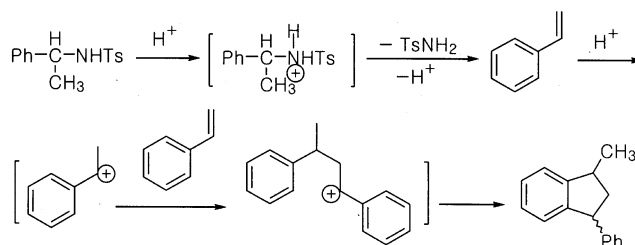
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Friedel-Crafts alkylation reactions are important in organic synthesis. These and related reactions have been well studied and reviewed in many reports and monographs.¹ Various kinds of electrophile source have been used in the Friedel-Crafts alkylations including alkyl halides, alkenes, alkynes, alcohols, esters, ethers, alkanes, mercaptans, and thiocyanates. All of the compounds could generate carbocation or carbocationic species in the presence of acid catalyst. However, there were known little on the Friedel-Crafts reaction of nitrogen containing compounds.² As a carbocation source in the Friedel-Crafts alkylations, nitroalkanes,^{2a-b} strained cyclic sulfonamide systems,^{2c-e} and some other cases^{2f-i} have been reported. Recently, we have reported that certain nitrogen containing compounds such as carbodiimides, amides, sulfonamides, and ureas could generate a carbocationic species in the presence of sulfuric acid or aluminum chloride.³ Among the substrates we examined, sulfonamide derivatives have some advantages such as ease of preparation of starting materials, highest yields of Friedel-Crafts products in most cases. Thus, we examined on the synthetic applications of sulfonamides, and wish to report herein the preliminary results for the preparation of mixed triarylmethane derivatives.

Tosylamide derivatives **2** could be prepared easily from *N*-tosylimine derivatives **1** by addition of organometallic compounds. The reaction of **2** in benzene or *p*-xylene as representative arene nucleophiles in the presence of sulfuric acid



Scheme 1

(0.5 equiv) gave diaryl- or triarylmethane derivatives **3** in moderate yields (Table 1).

However, the use of chlorobenzene did not afford the corresponding product. 1-Methyl-3-phenylindane⁴ as a *cis/trans* (1 : 1) mixture was obtained as shown in Scheme 1.

N-Tosylimines **1** can be used directly in the Friedel-Crafts alkylation as shown in Table 2. *N*-Tosylimines **1** in the presence of sulfuric acid (5 equiv) in arenes gave the corresponding tosylamide derivatives **2** *in situ*, and successive Friedel-Crafts alkylation gave **3** in good yields.

Finally, we examined the possibility of obtaining triarylmethanes from the reaction of aldehydes and *p*-toluenesulfonamide in arenes as shown in Table 3. We could isolate the corresponding **3** in good yields. There was reported on the reaction of benzaldehyde and benzene in the presence of trifluoromethanesulfonic acid, which gave complex compound mixtures including triphenylmethane.⁵ However, our



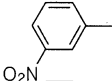

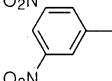

Table 1. Synthesis of **3** from tosylamides **2**

Entry	R ₁	R ₂ M	ArH	Yield (%)	
1		MeLi		61	
2		MeLi		59	
3		MeLi			43
4		PhMgBr		53	
5		PhMgBr		87	

Table 2. Synthesis of **3** from *in situ* generated tosylamides **2**

Entry	R ₁	ArH	Yield (%)
1			75
2			61
3			57
4			89
5			29

Table 3. Synthesis of **3** from aldehydes and *p*-toluenesulfonamide
$$R_1\text{-CHO} + \text{TsNH}_2 \xrightarrow[60-80\text{ }^\circ\text{C, 24 h}]{\text{ArH, H}_2\text{SO}_4 (5 \text{ eq})} \begin{array}{c} \text{H} \\ | \\ \text{R}-\text{C}-\text{Ar} \\ | \\ \text{Ar} \\ \mathbf{3} \end{array}$$

Entry	R ₁	ArH	Yield (%)
1			70
2			87
3			65

methods have some merits for the formation of **3** in respect of yields and its simplicity. We could isolate the corresponding tosylimine derivatives in the reaction mixtures. However, we could not exclude completely the possibility that **3** was formed from direct Friedel-Crafts alkylation of benzaldehyde as reported.⁵

In summary, we demonstrate in this communication the usefulness of tosylamide derivatives as a source of carbocationic species in Friedel-Crafts reaction conditions as a isolated form or a *in situ* generated entity.

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