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Synthesis of Diarylsulfoximines by the Friedel–Crafts Reaction of Sulfonimidoyl Chlorides

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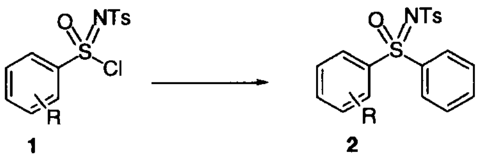
In the presence of an equimolar amount of $FeCl_3$, sulfonimidoyl chlorides were allowed to react with aromatic compounds to give the corresponding sulfoximines. Structure of the sulfonimidoyl chlorides and the aromatic compounds had considerable influence on the yield of the sulfoximines.

Sulfoximines are teracoordinate organosulfur compounds which are of great utility in organic synthesis.[1] Synthesis of sulfoximine is performed mainly by imination of sulfoxide and oxidation of sulfilimine.[1] Although the Friedel–Crafts reaction of sulfonimidoyl halide is regarded as one of the methods for sulfoximine synthesis from a viewpoint of accessibility of sulfonimidoyl halides, only two examples, to our knowledge, have been reported to date, both by Johnson et al.[2] It was reported that use of sulfonimidoyl fluoride derived from the corresponding chloride was indispensable to obtain *S*,*S*-diarylsulfoximine in a reasonable yield. Recently, we have reported that the Friedel–Crafts-type polycondensation of *N*-tosyl-4-phenoxybenzenesulfonimidoyl chloride afforded poly(sulfoximine) in a good yield.[3] We have thus examined the reactivity of sulfonimidoyl chlorides as precursors of diarylsulfoximines. In this paper, we report synthesis of *S*,*S*-diarylsulfoximines by the Friedel–Crafts reaction of sulfonimidoyl chlorides with aromatic compounds (Scheme 1).

At first, the Friedel–Crafts reaction of *N*-tosylbenzenesulfonimidoyl chloride **1a** with benzene affording *S*,*S*-diphenyl-*N*-tosylsulfoximine **2a** was chosen as a model reaction. The effects of Lewis acids, solvents, concentration, temperature, and so on were examined (Table 1). Among several Lewis acids screened, the best yield was obtained when $FeCl_3$ was employed (entry 1—5). In the Friedel–Crafts reaction with $FeCl_3$, yield of **2a** increased as temperature was lowered (entry 6—7). Among the solvents tested, nitromethane gave the best result (entry 8—11). This reaction needed an equimolar amount of Lewis acid, as in the case of the typical Friedel–Crafts acylation. When a catalytic amount of $FeCl_3$ was used, the yield of **2a** was less than the amount of $FeCl_3$ (entry 12—15).



1 **2**

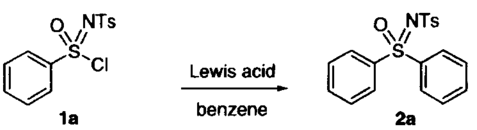
a: R = H
b: R = 4-CH_3
c: R = 4-OCH_3
d: R = 2,5-$(CH_3)_2$
e: R = 2,4,6-$(CH_3)_3$

Scheme 1.

Several aromatic hydrocarbons were examined as nucleophiles; the results are shown in Table 2. These reactions were very sensitive to the structure of aromatic hydrocarbons. Toluene and *p*-xylene smoothly reacted with **1a** to give the corresponding sulfoximines **2b** and **2d** in high yields. In the reaction of toluene with **1a**, no isomer (*o*- or *m*-) was formed. It is reasonable that toluene leads to a higher yield than that of benzene, since toluene has a higher nucleophilicity than benzene. **2d** was obtained in the lower yield than that of **2b**; this difference is attributed to the steric hindrance of methyl group at *ortho* to the reacting position of *p*-xylene. Anisole also reacted with **1a** in the presence of 100 mol% of $FeCl_3$ to give the corresponding sulfoximine **2c**, but the yield was lower. The low yield of **2c** might be attributed to the high reactivity of anisole, which leads to further side reactions.

The effect of the structure of sulfonimidoyl chloride (**1**) was also examined. The results are listed in Table 3. Introduction of an electron-donating group such as methyl or

Table 1. Synthesis of **2a**: Effects of Lewis Acid, Temperature, and Solvent

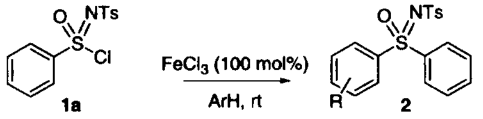


1a **2a**

Entry	L. A. (mol%)	T/°C	Solvent	Time/h	Yield/%[a]
1	$AlCl_3$ (120)	25	none	140	0
2	$BF_3·OEt_2$ (120)	25	none	170	0
3	$SnCl_4$ (120)	25	none	340	4
4	$TiCl_4$ (120)	25	none	190	0
5	$FeCl_3$ (120)	25	none	2	74
6	$FeCl_3$ (120)	70	none	2	54
7	$FeCl_3$ (120)	0	none	17	72
8	$FeCl_3$ (120)	25	CH_3NO_2	2	78
9	$FeCl_3$ (120)	25	$PhNO_2$	2	58
10	$FeCl_3$ (120)	25	CS_2	48	43
11	$FeCl_3$ (120)	25	CH_2Cl_2	2	60
12	$FeCl_3$ (10)	25	none	96	6
13	$FeCl_3$ (50)	25	none	48	50
14	$FeCl_3$ (100)	25	none	4	69
15	$FeCl_3$ (300)	25	none	0.5	79

a) Isolated yield.

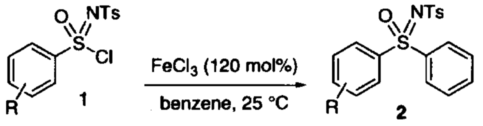
Table 2. Synthesis of **2a**—**d** from **1a** and Several Aromatic Hydrocarbons



Entry	ArH	Product	Time/h	Yield/%
1	benzene	**2a**	4	69
2	toluene	**2b**	1	80[a)]
3	anisole	**2c**	1	31[a)]
4	*p*-xylene	**2d**	2	67

a) only the *p*-isomer was obtained.

Table 3. Synthesis of **2**: Effect of the Substituents of Arenesulfonimidoyl Chloride



Entry	Sulfonimidoyl Chloride	Time/h	Yield/%
1	**1a**	2	78
2	**1b**	2	60
3	**1c**	24	10
4	**1e**	24	0

methoxy group on the benzene ring of **1** decreased the yield of sulfoximines (**2**). This is presumably due to the stabilization of cationic intermediates by the substituents lowering the reactivity of **1** (entry 2 and 3). Two substituents at *ortho* to the sulfonimidoyl group completely prevented the Friedel–Crafts reaction (entry 4).

In summary, we have demonstrated that the Friedel–Crafts reaction of sulfonimidoyl chlorides with aromatic nucleophiles readily yielded sulfoximines, where substituents on the sulfonimidoyl chlorides or aromatic nucleophiles had considerable influence on their reactivity.

Experimental

Materials. The sulfonimidoyl chlorides **1a**—**c** and **1e** were synthesized from the corresponding sulfinyl chlorides and chloramine-T in a method similar to that from the literature.[4,5] The spectroscopic data of the sulfoximines **2a**[6], **2b**[6], and **2c**[7] were identical with those reported previously.

A Typical Procedure for the Friedel–Crafts Reaction of Sulfonimidoyl Chloride. A mixture of *N*-tosylbenzenesulfonimidoyl chloride **1a** (330 mg, 1.00 mmol), iron(III) chloride (194 mg, 1.20 mmol) in benzene (2.0 mL) was stirred at 25 °C for 2 h under Ar. The reaction mixture was poured into sat. $NaHCO_3$aq and extracted with CH_2Cl_2 (×3). The extract was washed with sat. $NaHCO_3$aq (×2) and brine (×1), dried ($MgSO_4$), and evaporated to dryness. The residue was chromatographed over silica gel (eluent: CH_2Cl_2, then $CH_2Cl_2 : MeOH = 9 : 1$) to afford *S*,*S*-diphenyl-*N*-tosylsulfoximine **2a** in 69% yield.

***S*-phenyl-*S*-xylyl-*N*-tosylsulfoximine (2d).** White solid; mp 127—128 °C; IR (KBr) 1305, 1232, 1153, 1092 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ = 8.09 (1H, s), 7.99 (2H, dd, *J* = 7.3 and 1.8 Hz), 7.80 (2H, dd, *J* = 7.9 Hz), 7.62—7.46 (3H, m), 7.30 (1H, d, *J* = 7.9 Hz), 7.20 (2H, d, *J* = 7.9 Hz), 7.09 (1H, d, *J* = 7.3 Hz), 2.42 (3H, s), 2.37 (3H, s), 2.26 (3H, s). Calcd for $C_{21}H_{21}NO_3S_2$: C, 63.13; H, 5.30; N, 3.51%. Found: C, 63.07; H, 5.37; N, 3.51%.

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