

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

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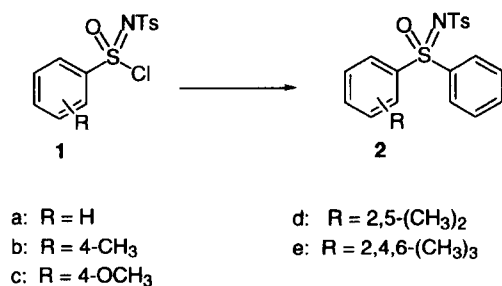
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In the presence of an equimolar amount of FeCl_3 , sulfonimidoyl chlorides were allowed to react with aromatic compounds to give the corresponding sulfoximines. Structure of the sulfonimidoyl chlorides and the aromatic compounds had considerable influence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



Scheme 1.

phenyl-*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).

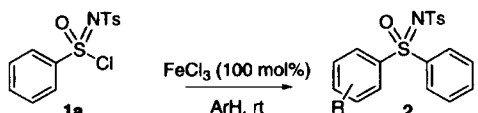
Several aromatic hydrocarbons were examined as nucleophiles; the results are shown in Table 2. These reactions were very sensitive to the structure of aromatic hydrocarbons. Toluene and *p*-xylene smoothly reacted with **1a** to give the corresponding sulfoximines **2b** and **2d** in high yields. In 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

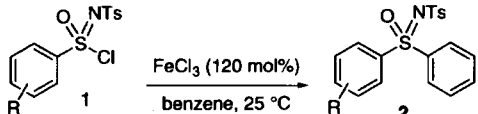
Table 1. Synthesis of **2a**: Effects of Lewis Acid, Temperature, and Solvent

Entry	L. A. (mol%)	T/°C	Solvent	Time/h	Yield/(%) ^a
1	AlCl_3 (120)	25	none	140	0
2	$\text{BF}_3 \cdot \text{OEt}_2$ (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	<i>p</i> -xylene	2d	2	67

a) only the *p*-isomer was obtained.Table 3. Synthesis of **2**: Effect of the Substituents of Arenesulfonyl Chloride


Entry	Sulfonyl 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 sulfonyl group completely prevented the Friedel–Crafts reaction (entry 4).

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

Experimental

Materials. The sulfonyl chlorides **1a–c** and **1e** were syn-

thesized from the corresponding sulfonyl chlorides and chloramine-T in a method similar to that from the literature.^{4,5} The spectroscopic data of the sulfoximines **2a**, **2b**, and **2c** were identical with those reported previously.

A Typical Procedure for the Friedel–Crafts Reaction of Sulfonyl Chloride. A mixture of *N*-tosylbenzenesulfonyl 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. NaHCO₃ aq and extracted with CH₂Cl₂ (×3). The extract was washed with sat. NaHCO₃ aq (×2) and brine (×1), dried (MgSO₄), and evaporated to dryness. The residue was chromatographed over silica gel (eluent: CH₂Cl₂ : 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, CDCl₃) 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 C₂₁H₂₁NO₃S₂: C, 63.13; H, 5.30; N, 3.51%. Found: C, 63.07; H, 5.37; N, 3.51%.

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