



Convenient method for preparation of aryl sulfinates from arenes and DABSO as the SO₂ surrogates

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ARTICLE INFO

Article history:

Received 13 November 2017

Revised 24 January 2018

Accepted 26 January 2018

Available online 3 February 2018

Keywords:

Aryl sulfinates

DABSO

Sulfination

In situ IR

Synthetic methods

ABSTRACT

A safe and efficient protocol for the synthesis of aryl sulfinates from arenes and 1,4-diazabicyclo[2,2,2]octane bis(sulfur dioxide) (DABSO) under mild conditions is described. Through *in situ* infrared spectroscopic studies, a plausible mechanism for the sulfination reaction is proposed as well.

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Introduction

As the valuable and pivotal intermediates for the preparation of sulfoxides, sulfonamides and other organic compounds which have sulfonyl motifs (-SO₂-), sulfinic acids and their salts should not be ignored. They were first reported in the 1860s¹ and started to be extensively developed over the last decade. The commonly used method is the reduction of the corresponding sulfonyl chlorides.² Other strategies for the preparation of sulfinates include the reaction between organometallic agent and SO₂,³ Pd-catalyzed coupling of diazonium tetrafluoroborates with SO₂ and H₂,⁴ and the oxidation of thiols.⁵ In recent years, some new advances have been made in the synthesis of sulfinates, such as iron-catalyzed reaction of diphenyliodonium salts and rongalite (HOCH₂SO₂Na·2H₂O),⁶ palladium-catalyzed sulfination of aryl halides and K₂S₂O₅,⁷ gold (I)-catalyzed synthesis of sulfinates from aryl boronic acid derivatives and K₂S₂O₅⁸ and so on.^{9,10}

The most straightforward approach to sulfinates is the Friedel-Crafts sulfination.¹¹ However, the use of toxic and irritative SO₂ gas and HCl gas is cumbersome and it requires careful handling. Therefore, we were attracted to use the SO₂ surrogates for the Friedel-Crafts sulfination reaction. DABSO (1,4-diazabicyclo [2.2.2] octane bis (sulfur dioxide) adduct), as a bench-stable colorless solid, has been proved that it can be applied to various reactions instead of SO₂ gas. It was first found and characterized by Santos in 1987.¹²

Willis et al. reported the palladium-catalyzed aminosulfonylation process with DABSO,¹³ the synthesis of sulfinates from DABSO and organometallic agent,¹⁴ and another way to access sulfinates is from DABSO and boronic acids.¹⁵ Wu et al. studied the formation of sulfonamides with DABSO and arylboronic acids,¹⁶ metal-free aminosulfonylation of aryldiazonium tetrafluoroborates with DABSO and hydrazines¹⁷ and other related reactions with insertion of sulfur dioxide.¹⁸ Furthermore, there have been many other researches on the use of DABSO in the synthesis of related substances in the recent years.¹⁹ Considering the wide application of DABSO in organosulfur chemistry, we envisioned that DABSO might be employed in the Friedel-Crafts sulfination as well. Herein, we report the simple preparation of aryl sulfinates from arenes and DABSO as the SO₂ surrogates.

Results and discussion

We started our initial studies with acetanilide (**1a**), which could be the starting material for parabase ester [2-(*p*-aminophenylsulfonyl)ethyl hydrogen sulfate] (Fig. 1). Initially, we performed the reaction between acetanilide (**1a**) and DABSO (1.0 equiv) at 20 °C, using AlCl₃ (4 equiv) as the catalyst and DCE as the solvent, respectively. However, only a trace amount of the desired product was obtained (Table 1, entry 1). Then we increased the amount of catalyst. To our delight, the reaction occurred smoothly to give the desired product with 83% yield when the amount of AlCl₃ was increased to 8 equiv (Table 1, entry 3). Further investigation on the effect of reaction temperature was conducted and at 25 °C

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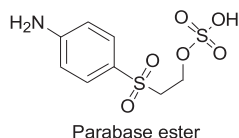


Fig. 1. A key intermediate of reactive dyes.

the reaction produced the highest yield (91%, Table 1, entry 6). The use of different solvents also strongly influenced the reaction. When the reaction was carried out in DCM, MeNO₂, CS₂ or PhNO₂, the yield of the desired product decreased dramatically (Table 1, entries 7–10). Reaction was not observed when using FeCl₃, ZnCl₂ and TiCl₄ as catalyst (Table 1, entries 11–13). The “SO₂” precursor also played a vital role in this reaction. We tried another two tertiary amine-SO₂ complexes. The SO₂ adduct of quinuclidine (ABSO) gave a low yield (Table 1, entry 14), and the SO₂ adduct of hexamethylenetetramine (HMTA·2SO₂) gave a moderate yield (Table 1, entry 15), while DABSO gave the best result in terms of yield. Therefore, the optimal conditions were established as: using AlCl₃ (8 equiv) as the catalyst and DABSO as the “SO₂” precursor to perform the reaction in DCE at 25 °C.

Then we investigated the scope of our reaction, and the results were summarized in Table 2. Interestingly, compared to acetanilide, using only 4 equiv of AlCl₃, the reaction could be carried out with a series of substituted arenes, affording the corresponding products in good yields (75–98%) in several hours.

As shown in detail in Table 2, the introduction of electron-donating groups, such as alkyl and alkoxy group (1b–e) could cause high yields. While the presence of electron-withdrawing groups could lead to different results: the halides (1g–i) gave good to excellent yields (70–98%), but the nitro group (1j) failed. It was noteworthy that for anisole (1d), nitrobenzene was more appropriate than DCE or DCM as the solvent in this reaction. But for other substrates listed in Table 2, the corresponding product could not be observed when the nitrobenzene was used as solvent. Presumably due to the interaction of AlCl₃ and nitrobenzene, which weakened its catalytic effect, however, the extremely elec-

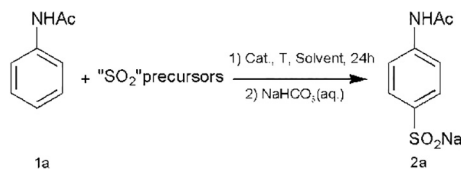
tron-donating effect of methoxyl group made the reaction proceed smoothly.

Various methods including *in situ* IR were used to study the possible mechanisms.²⁰ But to our knowledge, no detailed mechanistic study of Friedel–Crafts sulfonation was reported. We established the possible mechanism of Friedel–Crafts sulfonation that acetanilide reacted with DABSO using AlCl₃ as catalyst in DCE.

The FTIR spectra in the 1800–1400 cm⁻¹ range of acetanilide and addition of different amounts of AlCl₃ in DCE were compared in Fig. 2, which showed the interaction of acetamido group with AlCl₃. The spectrum of acetanilide (Fig. 2a) gave band at 1700 cm⁻¹ from the band amide I ν (C=O), and the band amide II, involving δ (NH), appeared at 1525 cm⁻¹, and at 1603 cm⁻¹ from the ν (C=C) of the aromatic ring.²¹ When different amounts of AlCl₃ were added (Fig. 2b–e), the two bands at 1700 cm⁻¹ and 1525 cm⁻¹ were almost disappeared, whereas the band at 1625 cm⁻¹ was observed, indicating the disappearance of the N–H and that the vibration frequency of the C=O was obviously changed.²¹ It would be taken as the evidence of the interaction of acetamido group with AlCl₃. Besides, the absorption peak of aromatic ring appeared red shift, decreasing from 1603 cm⁻¹ to 1592 cm⁻¹.²² Therefore, these five bands would indicate the formation of the AlCl₃ adduct of acetanilide. It also suggested why acetanilide required much more AlCl₃ than other substrates. The possible structure was shown in Scheme 1.

Next, *in situ* infrared experiment of acetanilide with AlCl₃ and DABSO was carried out (Fig. 3). Careful analysis of these spectra revealed that after the addition of DABSO, five new bands appeared in the range of 1400–800 cm⁻¹ and the absorption intensity gradually increased as the reaction went on. Three new peaks appeared immediately at 1208 cm⁻¹(B), 1048 cm⁻¹(E) and 846 cm⁻¹(F). Band B was due to DABSO; bands E and F were assigned to product (the AlCl₃ adduct of 4-acetamidobenzenesulfonic acid), indicating a very fast sulfonation reaction. Band E could be attributed to the symmetric S–O stretching vibrations of product.^{23,24} Band F was the characteristic absorption peak of para substitution of benzene ring. In the next 30 min two new bands appeared at 1324 cm⁻¹(A) and 1130 cm⁻¹(C), which were assigned to the antisymmetric and

Table 1
Optimization of reaction conditions.^a



Entry	“SO ₂ ”	Cat.[equiv]	Temp.[°C]	Solvent	Yield [%] ^b
1	DABSO	AlCl ₃ [4]	20	DCE	Trace
2	DABSO	AlCl ₃ [6]	20	DCE	64
3	DABSO	AlCl ₃ [8]	20	DCE	83
4	DABSO	AlCl ₃ [8]	40	DCE	85
5	DABSO	AlCl ₃ [8]	0	DCE	49
6	DABSO	AlCl ₃ [8]	25	DCE	91
7	DABSO	AlCl ₃ [8]	25	DCM	46
8	DABSO	AlCl ₃ [8]	25	MeNO ₂	<1
9	DABSO	AlCl ₃ [8]	25	PhNO ₂	Trace
10	DABSO	AlCl ₃ [8]	25	CS ₂	N.R.
11	DABSO	FeCl ₃ [8]	25	DCE	N.R.
12	DABSO	ZnCl ₂ [8]	25	DCE	N.R.
13	DABSO	TiCl ₄ [8]	25	DCE	N.R.
14	ABSO	AlCl ₃ [8]	25	DCE	<10
15	HMTA·2SO ₂	AlCl ₃ [8]	25	DCE	73

^a Reaction conditions: acetanilide (2.0 mmol), “SO₂” precursors (1.0 equiv), solvent (10 mL).

^b HPLC yields relative to an internal standard. N.R. = No reaction.

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