## A General Method for the Preparation of *N*-Sulfonyl Aldimines and Ketimines<sup>†</sup>

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## ABSTRACT

 $R^{3} = \text{Ar, Akyl, vinyl} \\ R^{2} = \text{H, Ar, Akyl}$   $\begin{array}{c} a)R^{1}SONH_{2} \\ b) \text{ m-CPBA} \\ R^{1}=p\text{-Tol, t-Bu} \\ R^{3} = A^{2} \\ 43\text{-96 \% yield} \\ \end{array}$ 

A simple procedure to obtain *N*-sulfonyl imines involving the condensation of carbonyl compounds with *p*-tolyl or *tert*-butyl sulfinamides followed by oxidation with *m*-CPBA of the resulting *N*-sulfinylimines is reported. The method is applicable to aldehydes (aliphatics and aromatics) and ketones (diaryl, dialkyl, and aryl alkyl), even those containing enolizable protons. It also does not affect C=N or C=C double bonds and does not epimerize  $\alpha$ -stereogenic centers.

The sulfonyl moiety has proven to be a powerful activating group of imine derivatives. As a consequence, *N*-sulfonyl imines have been widely used in organic synthesis.<sup>1</sup> They are excellent substrates in aza Diels–Alder reactions,<sup>2</sup> nucleophilic additions,<sup>3</sup> and reductions,<sup>4</sup> as well as in radical<sup>5</sup> or ene<sup>6</sup> reactions. They have been also applied in the synthesis of aziridines.<sup>7</sup>

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A plethora of methods exists for obtaining *N*-sulfonyl imines,<sup>8–16</sup> from aromatic or nonenolizable aldehydes.<sup>9,10,15</sup> Notwithstanding this, *N*-sulfonylimines derived from aliphatic aldehydes and ketones remain difficult to prepare because of their kinetic instability and ease of enolization. As a consequence, only a few of the existing published methods can be applied. Some of the problems encountered with existing methodology are summarized below. Although *N*-sulfonylimines from enolizable aldehydes can be formed by using Trost's method, epimerization at the  $\alpha$ -chiral center

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 $<sup>^\</sup>dagger\,\text{Dedicated}$  to Professor Jose Elguero on the occasion of his 70th birthday.

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is often observed.8 Likewise, although aliphatic aldehydes can be transformed into their corresponding N-sulfonylimines by formation of the sulfonamidosulfone intermediates and sulfonyl elimination,<sup>11</sup> this two-step procedure cannot be extended to hindered or  $\alpha,\beta$ -unsaturated aldehydes or to ketones. The Hudson reaction of oximes with sulfinyl chlorides has been used to form  $\beta$ -trimethylsilyl ethanesulfonyl and tert-butyl ketimines in moderate yields.12 N-Sulfonyl derivatives of ketimines and  $\alpha,\beta$ -unsaturated aldimines can be formed by the condensation of oximes with sulfonyl cyanides, but this is an expensive method and generates toxic byproducts.<sup>13</sup> More recently, a new method for the preparation of N-tosyl ketimines via palladiumcatalyzed isomerization of N-tosyl aziridines has been reported.<sup>14</sup> This method does, however, require prior preparation of the precursor aziridine and is limited to methyl ketimines.

Therefore it seems highly desirable to find a simple, efficient, economical, and general protocol for *N*-sulfonyl aldimines and ketimines synthesis, even those containing enolizable  $\alpha$ -hydrogens.

In theory, the ideal procedure for obtaining N-sulfonylimines would involve the condensation of carbonyl compounds with sulfonamides. However, the low nucleophilicity of the latter generally requires harsh acidic conditions to activate the carbonyl, conditions that are usually incompatible with the resulting unstable sulfonyl imines.<sup>9</sup> In light of this, we decided to focus our attention on preparing N-sulfonylimines from N-sulfinylaldimines and ketimines using technologies recently introduced by the Davis and Ellman groups, in a variety of other contexts.<sup>17</sup> The latter compounds can easily formed by condensation of the optically pure sulfinamides  $2^{18}$  and  $3^{19}$  with carbonyl compounds. Additionally, they are stable enough to be chromatographed and stored without significant hydrolysis. Thus, we reasoned that finding a reagent capable of oxidizing N-sulfinyl into N-sulfonyl imines without affecting the C=N bond could provide a general method for the synthesis of the latter species.

We present herein a simple and general two-step procedure for synthesizing *N*-sulfonylimines through the condensation of racemic sulfinylamides with aldehydes and ketones and oxidation with *m*-CPBA (Scheme 1). We have used **2** and **3** as sulfinamides because the resulting *N*-sulfonylimines contain the *p*-Tol and *t*-Bu residues, which are the most widely used in the literature.



Our preliminary studies were carried out with the more common p-tolyl substituent. The racemic sulfinylamide 2 was

prepared from disulfide **8** on a multigram scale as outlined in Scheme 2. Compound **8** was transformed into the methyl sulfinate **9** using the procedure reported by Brownbridge and Jowett.<sup>20</sup> Treatment of **9** with LiHMDS<sup>21</sup> followed by precipitation from hexane afforded the pure sulfinamide **2** in 92% overall yield.<sup>22</sup>

Scheme 2. Mul	tigram Scale Pro Sulfinylamide 2	cedure To Obtain
Tol-S-S-Tol i) MeOl 8 NBS (1.5e rt, (100%	O <sup>II</sup> sq) ToI-S-OMe <u>i</u> ₀) <b>9</b>	LiHMDS ToI-SNH <sub>2</sub> THF <b>2</b> (92%)

The condensation of aldehydes and ketones 1a-o with *p*-tolylsulfinylamide **2** was accomplished using Ti(OEt)<sub>4</sub> protocol of Davis,<sup>18</sup> with slight modifications in the workup (see Table 1).<sup>23</sup> With these adjustments the desired *N*-sulfinylimines 4a-o were obtained in high yields.



entr

1

 $\mathbf{2}$ 

3

4

5

6

$R^{1} \xrightarrow{P}{} R^{2} \xrightarrow{A) p-\text{TolSONH}_{2}} \xrightarrow{R^{1} p-\text{TolSONH}_{2}} \xrightarrow{R^{2} p-\text{Tol}} \xrightarrow{R^{2} p-\text{Tol}} \xrightarrow{B) p-\text{TolSONH}_{2}} \xrightarrow{R^{2} p-\text{Tol}} \xrightarrow{R^{2} p$							
				react	tion yield	ds (%)	
7	$\mathbb{R}^1$	$\mathbb{R}^2$	s.m./prod.	step a	step b	overall	
	Ph	Н	1a/6a	93(99) <sup>18</sup>	100	93(100)8	
	$3-MeOC_6H_4$	Н	1b/6b	$(92)^{18a}$	100	92()	
	2-Napht	Н	1c/6c	94()	95	89(88)10	
	$2\text{-BrC}_6\text{H}_4$	Н	1d/6d	$91(65)^{30}$	100	91()	
	$4\text{-}\mathrm{CNC_6H_4}$	Н	1e/6e	$81(60)^{30}$	$85^b$	69()	
	$PhCH=CH_2$	Н	1f/6f	$(80)^{31a}$	95	$76(73)^{32}$	
	$n ext{-}\Pr$	н	1g/6g	$78(87)^{18}$	96 <sup>c</sup>	$75(78)^{11}$	

7	$n ext{-}\Pr$	н	1g/6g	$78(87)^{18}$	<b>96</b> <sup>c</sup>	$75(78)^{11}$
8	<i>i</i> -Pr	н	1h/6h	$65(90)^{18}$	$100^{c}$	$65(53)^{11}$
9	<i>t</i> -Bu	н	1i/6i	$79(89)^{18}$	96	$76(90)^8$
10	Ph	Ph	1j/6j	79 (70)33	88	$69(100)^{15}$
11	Ph	$\mathbf{Me}$	1k/6k	$78(65)^{34}$	96	$75(79)^{35}$
12	$4-MeOC_6H_4$	$\mathbf{Me}$	11/61	$73(53)^{34}$	84	61()
13	$4\text{-}\mathrm{CNC_6H_4}$	$\mathbf{Me}$	1m/6m	77()	90	69()
14	<i>t</i> -Bu	$\mathbf{Me}$	1n/6n	$48(42)^{34}$	90	$43(51)^{36}$
15	<i>i</i> -Pr	Me	<b>10/60</b>	64()	90	58()

 $^a$  Yield not recorded.  $^b$  In this case the reaction time was 15 min.  $^c$  To avoid oxaziridine formation, this reaction was carried out at 45 °C.

*m*-CPBA has previously been used to oxidize arene *N*-sulfenylimines into the corresponding *N*-sulfinylimines<sup>24</sup> and *N*-sulfonylimines.<sup>16</sup> Nevertheless, the conditions used

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in the latter transformation (a two-phase system, involving m-CPBA and aqueous NaHCO<sub>3</sub>) invariably resulted in the formation of complex mixtures containing oxaziridines<sup>25</sup> when this method was applied to such imines derived from aliphatic aldehydes and ketones. On the basis of research recently developed in our group, we suspected that these failures and deficiencies could be related to the use of *m*-CPBA in aqueous basic media.<sup>26</sup> Therefore, we examined the oxidation of compounds 4a-o using an equimolecular amount of dry m-CPBA. Under these conditions S-oxidation occurred readily at room temperature in excellent yield to afford the pure *N*-sulfonylimines 6a - o without any need for chromatography.<sup>27</sup> The scope of the oxidation reaction can be deduced from the results summarized in Table 1. For comparison purposes, the yields of the N-sulfinylimines we obtained are presented, alongside yields so far described for *N*-sulfonylimines prepared by other methods.

Aromatic aldehydes containing both electron-withdrawing and -donating substituents 1a-e (entries 1-5, Table 1) afforded the corresponding sulforylimines 6a - e in very high yields, comparable with those of other methods; the latter vields are shown in brackets. The lower reactivity of the arylaldehydes containing electron-withdrawing substituents (entry 5) generally necessitates longer reaction times in the first step. The more challenging  $\alpha,\beta$ -unsaturated and enolizable sulfonyl aldimines 6f-i (entries 6–9, Table 1) are also easily obtained following the same protocol. It is also posisible to prepare N-sulfinylimines derived from ketones. Thus, benzophenone (1j, entry 10) and different enolizable arylmethyl ketones 1k-o (entries 11-14) were easily transformed into their corresponding N-sulfonylimines 6j-o. In these reactions, the overall yields are not as high as those obtained from the aldehydes as a result of the lower efficiency of the condensation step, which in the case of the bulky pinacolone is only 48% (entry 14).

The high chemoselectivity of the present oxidation method is noteworthy, the imine and olefinic double bonds usually being left intact. Only for aliphatic aldehydes containing the *n*-butyl and isopropyl substituents (entries 7 and 8), traces

(20) Brownbridge, P.; Jowett, I. C. Synthesis 1987, 252.

(21) This procedure had been used by Davis for the synthesis of the (S)-*p*-tolylsulfinamide from (S)-menthyl sulfinate.<sup>18</sup>

(22) We have checked that this procedure is also appropriate to prepare other aliphatic or aromatic sulfinamides.

(23) The reaction mixture was treated with MeOH and some drops of NaHCO<sub>3</sub> until precipitation of the titanium salts. Then it was filtered through a short pad of anhydrous  $Na_2SO_4$ , the solvent was evaporated, and the residue was purified by flash chromatography.

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(27) General Procedure for the Oxidation of Sulfinylimines 4 to Sulfonylimines 6. Dry *m*-CPBA (0.4 mmol) was added in one portion to a solution of the corresponding sulfinylimine 4 or 5 (0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at room temperature. Once the reaction was complete (less than 1 min), the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (8 mL) and washed with a saturated solution of NaHCO<sub>3</sub> (3 × 5 mL). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated to yield pure sulfonylimines 6 or 7.

of the sulfonyl oxaziridine, resulting from the oxidation of **6g** and **6h**, were observed. This side reaction can be easily avoided by carrying out the reaction at 45 °C. Therefore, our method to prepare *N*-*p*-tolylsulfinylimines **6** is applicable to any kind of aldehyde or ketone, even those containing enolizable protons and bulky substituents.

We next studied the application of our protocol to the synthesis of the *N-tert*-butylsulfonyl derivatives **7** because they have shown behavior similar to that of **6** in different reactions and because they offer some advantages in removal of the protecting group.<sup>28</sup> Condensation of the commercially available racemic *N-tert*-butylsulfinamide **3**<sup>29</sup> with carbonyl compounds was accomplished using the method reported by Ellman<sup>19</sup> but using the workup indicated in ref 23. The resulting compounds **5** were then oxidized into **7** with *m*-CPBA as previously indicated; the results are summarized in Table 2.

Table	2.	Preparation	of N-tert-hi	itylsulfony	limines 7	7
Lanc	<i>_</i>	1 ICparation	OI IV - ie I i - OU	itvisunonv	minines /	ε.

0		,,∠SO₂ <sup>t</sup> Bu
Ŭ	a) 'BuSONH <sub>2</sub>	N -
	b) <i>m</i> -CPBA	
1	CH <sub>2</sub> Cl <sub>2</sub> , 1 min	R' <b>7</b> R <sup>-</sup>

				reaction yields (%)		
entry	$\mathbb{R}^1$	$\mathbb{R}^2$	s.m./prod.	step a	step b	overall
1	Ph	Н	1a/7a	96(91) <sup>19</sup>	100	$96(64^a)^{12}$
<b>2</b>	2-furyl	Н	1p/7p	$63(82)^{19}$	100	63()
3	<i>n</i> -Pr	Н	1g/7g	100(100) <sup>39</sup>	$84^c$	84()
4	Ph	Ph	1j/7j	75()	100	$75(61^a)^{12}$
<b>5</b>	Ph	Me	1k/7k	$63(89)^{19}$	100	$63(d)^{4c}$
6	$4-MeOC_6H_4$	Me	11/71	62()	100	62()
7	$4\text{-}\mathrm{CNC_6H_4}$	Me	1m/7m	73()	100	73()
8	-(CH <sub>2</sub> ) <sub>5</sub> -		1q/7q	$65(91)^{19}$	90	$59(48^a)^{12}$
9	Et	Me	1r/7r	$73^{b}()$	78	57()
10	2-pyridyl	Me	1s/7s	$59^{c}()$	80	47()
9 10	Et 2-pyridyl	Me Me	1r/7r 1s/7s	73 <sup>b</sup> () 59 <sup>c</sup> ()	78 80	57() 47()

<sup>*a*</sup> Yields given are calculated from the corresponding oxime. <sup>*b*</sup> A 4:1 mixture of the E/Z isomers was formed. <sup>*c*</sup> In this case the reaction time was 15 min. <sup>*d*</sup> Yield not reported.

As was the case for the *p*-tolyl derivatives, the *N*-tertbutylsulfinylimine **5g** (derived from the aliphatic aldehyde **1g**) was prone to overoxidation into the *N*-sulfonyloxaziridine, and so the amount of *m*-CPBA had to be precisely measured to avoid this complication.<sup>37</sup> It is noteworthy that

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(29) Racemic sulfonamide 3 can be obtained according to the method of ref 28b and references therein.

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(31) Davis, F. A.; Reddy, R. E.; Szewczyk, J. M.; Reddy, G. V.; Portonovo, P. S.; Zhang, H.; Fanelli, D.; Reddy, R. T.; Zhou, P.; Carroll, P. J. J. Org. Chem. **1997**, 62, 2555.

(32) Raghavan, S.; Rajender, A. Tetrahedron 2004, 60, 5059.

(33) Annunziata, R.; Cinquini, M.; Cozzi, F. J. Chem. Soc., Perkin Trans. 1 1982, 2, 339.

(34) Davis, F. A.; Lee, S.; Zhang, H.; Fanelli, D. L. J. Org. Chem. 2000, 65, 8704.

other *N*-sulfonylimines were completely stable to overoxidation in the presence of a slight excess of *m*-CPBA. This result clearly demonstrates that this procedure is applicable to a wide variety of carbonyl compounds, even those containing substituents that are prone to oxidation, such as pyridine<sup>38</sup> (entry 10), or those sensitive to acidic media, such as furan (entry 2).

A general concern in the preparation of *N*-sulfonylimines is epimerization of the stereocenter at the  $\alpha$ -position.<sup>8</sup> Nevertheless, no  $\alpha$ -epimerization has been observed in the formation of sulfinylimines.<sup>40</sup> The smooth oxidation conditions involved in our synthetic sequence to prepare *N*sulfonylimines prompted us to investigate the stability of stereogenic centers joined to the carbonyl group. In Scheme 3 are indicated the two studied examples. Aldehyde **1t**, a



*cis*-disubstituted cyclopropane, was transformed exclusively into its corresponding *N*-sulfonylimine **6t**, without detection of the thermodynamically more stable *trans* isomer. In the second experiment, the commercially available optically pure ketone 1u was converted into a mixture of sulfinylimines 5u and 5u' when treated with racemic sulfonamide 3. This mixture was oxidized to the *N*-sulfonyl derivative 7u with complete regioselectivity without affecting the stereogenic center and, remarkably, with no epoxidation of the disubstituted double bond, which demonstrates the high chemoselectivity of *m*-CPBA toward sulfur.

In conclusion, we have developed a simple and efficient two-step process for obtaining *N*-sulfonylaldimines and *N*-sulfonylketimines by reaction of the corresponding aldehydes or ketones with sulfinamides and further oxidation of the resulting *N*-sulfinylimines with *m*-CPBA. The method is applicable to aromatic and aliphatic carbonyl compounds, even those containing enolizable protons. Additionally, it does not affect the configuration of  $\alpha$ -stereogenic centers and is highly selective in the presence of C=N and C=C (deactivated or not) double bonds.

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**Supporting Information Available:** Experimental procedures and spectroscopic data for compounds **2**, **4**–**7**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(37)</sup> The use of a deficiency of m-CPBA produced mixtures of 7g and 5g, whereas an excess of the reagent afforded 7g and the correponding oxaziridine.

<sup>(38)</sup> In the oxidation reaction of **5s** a slight excess of *m*-CPBA highly favored the formation of the sulfonyl oxaziridine. This is probably due to the pyridine ring, which makes easier the dissociation of the peracid, increasing the concentration of the R-CO<sub>2</sub>O<sup>-</sup> that is acting as a nucleophile at the C=N bond. This could be the reason Davis obtained large amounts of oxaziridines in the oxidation of aliphatic sulfenylimines with the system *m*-CPBA/NaHCO<sub>3</sub> (see ref 16).

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 G. J. Org. Chem. 2002, 67, 8276.

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