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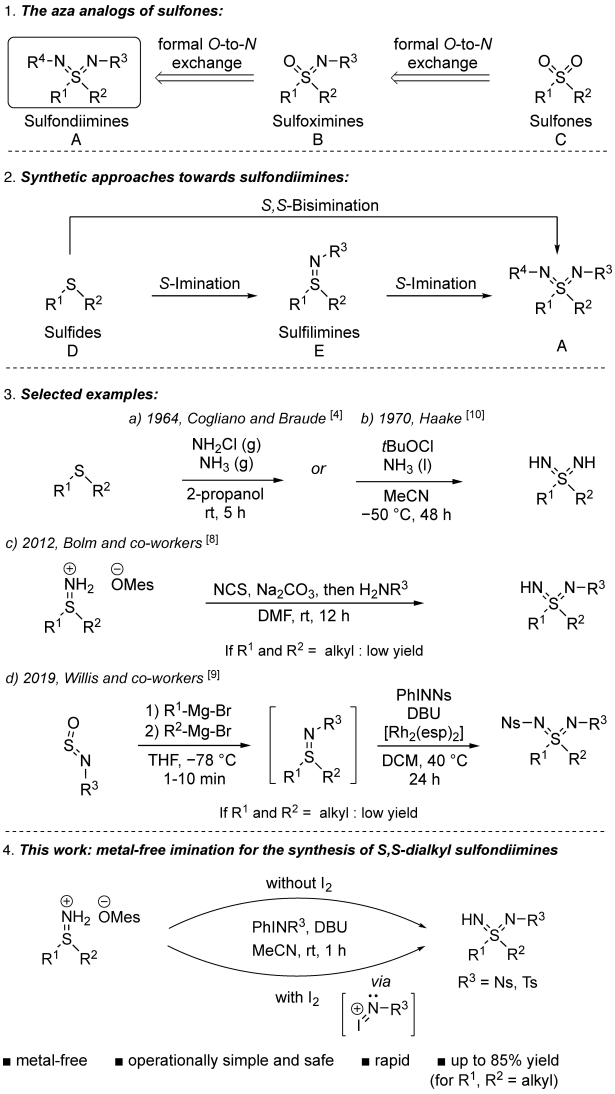
Synthesis of *N*-Monosubstituted Sulfondiimines by Metal-free Iminations of Sulfilimium Salts

*Marco T. Passia, Niklas Bormann, Jas S. Ward, Kari Rissanen, and Carsten Bolm**

Abstract: Sulfondiimines are marginalized entities among nitrogen-containing organosulfur compounds, despite offering promising properties for applications in various fields including medicinal and agrochemical. Herein, we present a metal-free and rapid synthetic procedure for the synthesis of *N*-monosubstituted sulfondiimines that overcomes current limitations in their synthetic accessibility. Particularly, *S*,*S*-dialkyl substrates, which are commonly difficult to convert by existing methods, react well with a combination of iodine, 1,8-diazabicyclo[5.4.0]undec-7-en (DBU), and iminoiodinanes (PhINR) in acetonitrile (MeCN) to furnish the corresponding sulfondiimines in yields up to 85 % (25 examples). Valuable "free" *N*H-*N'*H-sulfondiimines can then be accessed by *N*-deprotection under mild reaction conditions. Several experimental observations suggest a mechanistic pathway diverging from the common radical-based iodine/iminoiodinane mechanism. Based on the experimental results in combination with data obtained by ^{1}H NMR spectroscopy, ESI mass spectrometry, and crystallographic analysis we propose a direct amination from PhINNs and a reaction path via a cationic iodonitrene.

Introduction

Sulfondiimines **A**, the mono- and di-aza analogues of sulfoximines **B** and sulfones **C**, respectively, are underrepresented organosulfur compounds with potential bioactivities (Scheme 1, part 1).[1] In contrast to sulfones, sulfoximines and sulfondiimines can be stereogenic at sulfur and they have further sites for structural modifications that can be important for medicinal[1c,2] and agrochemical[3] applications.



Scheme 1. Overview on the aza analogues of sulfones and synthetic approaches towards sulfondiimines including selected examples for their preparation.

Since their inadvertently discovery by Cogliano and Braude in 1964,[4] several methods for their preparation, *N*-functionalization, and application as building blocks in *S*,*N*-heterocycle syntheses have been developed.[5] However, even today, significant preparative limitations exist and despite various recent investigations,[6] the application of sulfondiimines is hampered by the restricted understanding of their chemical and physiochemical behaviour.

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Usually, sulfondiimines are prepared from organosulfur compounds in lower oxidation states (i.e. sulfides **D** or sulfilimines **E**) by means of *S*-imination reactions to either *N*,*N*′-disubstituted, *N*-monosubstituted, or *N*-unsubstituted products (Scheme 1, part 2). The efficiency of the synthetic procedure is strongly dependent on the substitution pattern of the substrate as *S*,*S*-dialkyl-, *S*-alkyl-*S*-aryl-, and *S*,*S*-diaryl-substituted substrates show very different reactivity.[5] In the case of *S*,*S*-diaryl and *S*-alkyl-*S*-aryl sulfondiimines, effective methods are available, for instance, by applying chloramine T as shown by Oae and co-workers[7] or using a combination of *N*-chlorosuccinimide (NCS) and primary amines as demonstrated by Bolm and co-workers[8] (Scheme 1, part 3). Additionally, Willis and co-workers utilized a combination of hypervalent iodine(III) compounds [i.e. *N*-(*p*-nitrophenylsulfonyl)-imino phenyliodinane (PhINNs)] and a rhodium catalyst in a modular synthetic approach starting from sulfinylamines (R-NSO).[9]

However, for the preparation of *S*,*S*-dialkyl sulfondiimines, the aforementioned synthetic pathways are characterized by long reaction times and poor to moderate yields (<46 %) with only very few examples of the corresponding products,[7–9] which is most likely due to the inherent instability of the intermediate *N*-unsubstituted *S*,*S*-dialkyl sulfilimines.[8] Thus up to date, bisiminations of sulfides with toxic and reactive gas mixtures of monochloramine and ammonia (introduced by Cogliano and Braude)[4] and an evolved procedure with *tert*-butyl hypochlorite and liquid ammonia (reported by Haake)[10] are still the most effective methods for the preparation of *S*,*S*-dialkyl sulfondiimines (with yields <56 %, except for benzylic products).[5]

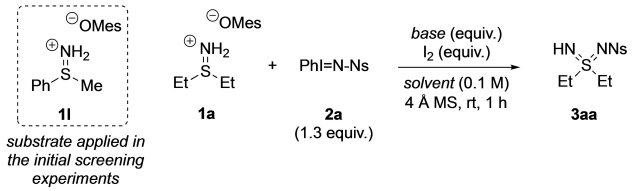
With the aim to address and overcome the present limitations in the accessibility of sulfondiimines, in particular those with two *S*-alkyl substituents, we searched for an alternative synthetic procedure. In light of our previous work,[8] sulfiliminium mesitylenesulfonates **1** appeared as suitable substrates. Although their preparation involves the potentially hazardous *O*-mesitylsulfonylhydroxylamine (MSH),[11] the salts themselves are convenient reagents with practical stability for an extensive period of time (up to months) when stored under argon at low temperature. Single-step iminations of **1** with a suitable nitrogen carrier agent can then directly lead to (*N*-monosubstituted) sulfondiimines. The results of our study (Scheme 1, part 4) are presented herein.

Results and Discussion

In the very first screening experiment with *S*-methyl *S*-phenyl sulfiliminium mesitylenesulfonates (**1l**) and PhINNs (**2a**) we had found that the substrates reacted with [Rh_2-$(esp)_2$] as catalyst and DBU (2.0 equiv) in DCM at 40 °C for 24 h under conditions reported by Willis and co-workers,[9] to give sulfondiimine **3al** in 38 % yield (for details of this part of the investigation, see the Supporting Information).[12] Unfortunately, all attempts to optimize this system or to advance the protocol by applying other metal-containing or metal-free catalysts did not result in a significant improvement of the product formation, furnishing sulfondiimine **3al** in yields of only 17–48 % after a reaction time of 1 h at room temperature. However, this initial screening led to an important discovery: simple molecular iodine had a catalytic effect. Thus, stirring substrates **1l** and **2b** in the presence of 20 mol % of iodine and 2 equiv of DBU in acetonitrile (0.1 M) for 1 h at room temperature gave **3al** in 50 % yield. This initial positive result with *S*-alkyl *S*-aryl-substituted sulfiliminium salt **1l** served as guide in the subsequent development of a protocol for conversions of more challenging *S*,*S*-dialkyl-substituted substrates.

For studying this substrate class, *S*,*S*-diethyl sulfiliminium mesitylenesulfonate (**1a**) was selected as starting material. Knowing of the strong influence of the *S*-substituents in other sulfondiimine syntheses,[5a] the aforementioned iodine catalysis was re-evaluated. The results are shown in Table 1. To our delight, the conversion of **1a**

Table 1: Optimization of the reaction parameters for the synthesis of *N*H,-*N*′Ns-*S*,*S*-diethyl sulfondiimine (**3aa**).[a]



Entry	Cat. (equiv.)	Base (equiv.)	Solvent	Yield [%] of **3aa**[b]
1	I_2 (**0.20**)	DBU (2.0)	MeCN	53
2	I_2 (**0.10**)	DBU (2.0)	MeCN	**85** (80)[c]
3	I_2 (**0.05**)	DBU (2.0)	MeCN	31
4	–	DBU (2.0)	MeCN	51
5	**TEMPO (0.10)**	DBU (2.0)	MeCN	30
6	**NCS (0.10)**	DBU (2.0)	MeCN	32
7	**NBS (0.10)**	DBU (2.0)	MeCN	36
8	**NIS (0.10)**	DBU (2.0)	MeCN	60
9	I_2 (0.10)	DBU (2.0)	**DCM**	61
10	I_2 (0.10)	DBU (2.0)	**PhCN**	62
11	I_2 (0.10)	DBU (2.0)	**1,4-dioxane**	74
12	I_2 (0.10)	DBU (2.0)	**benzene**	70
13[d]	I_2 (0.10)	DBU (2.0)	–	45
14	I_2 (0.10)	**pyridine** (2.0)	MeCN	16
15	I_2 (0.10)	**Cs_2CO_3** (2.0)	MeCN	17
16	I_2 (0.10)	–	MeCN	12
17[e]	I_2 (0.10)	DBU (2.0)	MeCN	69
18[f]	I_2 (0.10)	DBU (2.0)	MeCN	67
19[g]	I_2 (0.10)	DBU (2.0)	MeCN	47
20[h]	I_2 (0.10)	DBU (2.0)	MeCN	82

[a] Reaction conditions: 0.1 mmol of **1a**, added to a stirred solution (5 min) of PhINNs (**2a**, 1.3 equiv), 4 Å MS (40 mg), I_2 (0.1 equiv), and base (2.0 equiv) diluted in the solvent (0.1 M) under argon. Then the reaction mixture was stirred for 1 h at room temperature. [b] After purification by column chromatography on silica gel. [c] Reaction time of 5 min. [d] The reaction (0.2 mmol of **1a**) was conducted under solvent-free mechanochemical conditions in a mixer mill using a stainless-steel milling vessel (V=5 mL) with two stainless-steel milling balls (d=7 mm) at 25 Hz for 90 min with the addition of silica (1 mg per 1 mg of reactants). [e] The reaction was performed in an atmosphere of air. [f] The reaction was performed without 4 Å MS. [g] The reaction was performed with PhINNs generated in situ from PIDA (1.3 equiv) and nosylamide (1.3 equiv). [h] The reaction was conducted with 2.0 equiv of PhINNs for 3 h.

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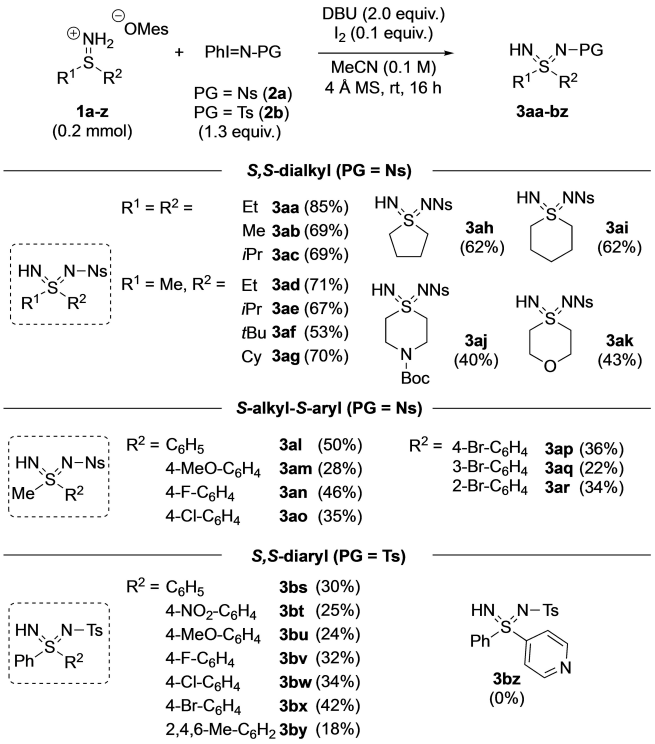
required even less iodine than the one of **1l**. Thus now, only 10 mol % of iodine (instead of 20 mol % as for **1l**) was sufficient to give product **3aa** in 85 % yield (Table 1, entry 2). Already after 5 min of reaction time, **3aa** could be obtained in 80 % yield.[13] With more (20 mol %) or less (5 mol %) of iodine, the yield of **3aa** was lower (Table 1, entries 1 and 3). We assume that an equilibrium between different *N*-iodo species may explain these inconclusive observations (Scheme 4). Expecting to see a further decrease in product yield, we were surprised to obtain **3aa** in 51 % yield when the reaction was carried out in the absence of iodine (Table 1, entry 4). Apparently, the role of iodine was complex, and PhINNs itself (in combination with DBU in MeCN) was also able to iminate **1a** leading to **3aa** in good yield.[14] Experiments with other potential oxidants and electrophilic halogen sources (i.e. TEMPO, NCS etc., Table 1, entries 5–8) provided lower yields of sulfondiimine **3aa** (Table 1, entries 5–8). In the series of the halosuccinimides NCS, NBS, and NIS (10 mol % each), the latter showed the best activity providing **3aa** in 60 % yield, which reinforced our hypothesis that iodine played an important role in the reaction progress (Table 1, entry 8). Hence, the subsequent screenings were performed with iodine (10 mol %). Solvents other than MeCN were tolerated but the efficiency of the product formation was reduced (Table 1, entry 2 versus entries 9–12). Also solvent-free mechanochemical conditions proved applicable.[15] Hence, with silica (1 mg per 1 mg of all reactants) as solid grinding auxiliary, sulfondiimine **3aa** was obtained in up to 45 % yield (Table 1, entry 13; for more details and the full optimization of the mechanochemical system, see the Supporting Information). In MeCN, negative effects on the product formation were observed when DBU was substituted by pyridine or Cs_2CO_3. In those case, the yield of **3aa** dropped to only 16 % and 17 %, respectively (Table 1, entries 14 and 15). Those results were similar to the one observed in an experiment without base, which led to **3aa** in 12 % yield (Table 1, entry 16).

Until this stage, all data showed that the combination of DBU and iodine with MeCN as solvent was crucial for achieving a high yield of **3aa**. If one of the two reagents was missing, the yield dropped. Furthermore, the experimental details were important. For example, a high reactivity was only observed when DBU was added to the reaction mixture as solution in MeCN. Using undiluted DBU led to a black reaction mixture, and the substrate imination proceeded with a lower efficiency.

Finally, other factors were evaluated. Conducting the reaction in an atmosphere of air or in the absence of 4 Å MS furnished the corresponding sulfondiimine **3aa** in yields of 69 % and 67 %, respectively (Table 1, entries 17 and 18), demonstrating a high tolerance of the reaction system against moisture and oxygen in air. In situ generated PhINNs from (diacetoxyiodo)benzene (PIDA, 1.3 equiv) and nosylamide (1.3 equiv) gave **3aa** in 47 % yield (Table 1, entry 19). Increasing the amount of PhINNs from 1.3 equiv to 2.0 equiv and extending the reaction time from 1 h to 3 h had only a minor effect, leading to a yield of 82 % for **3aa** (Table 1, entry 20). In summary, the best conditions for the conversion of **1a** (on a 0.1 mmol scale) involved the use of 1.3 equiv of PhINNs (**2a**), 0.1 equiv of iodine, 2.0 equiv of DBU, and 40 mg of 4 Å MS in anhydrous MeCN under argon, which provided **3aa** after 1 h at room temperature in 85 % yield.

With the optimized reaction conditions in hand, the substrate scope was evaluated (Scheme 2). Due to the strong ionic character of both starting material **1** and iminoiodinane **2**, a reaction monitoring by TLC was not effective and thus, to ensure maximum conversion, the reaction time was increased to 16 h. *S*,*S*-Dialkyl-substituted sulfiliminium mesitylenesulfonates **1a–k** reacted well under the optimized reaction conditions leading to products in up to 85 % yield. Among them, acyclic products **3aa–ag** (53–85 %) were obtained in slightly higher yields compared to their cyclic counterparts **3ah–ak** (40–62 %). Both, bulky substituents (i.e. **3af**, $R^2 = t$Bu, 53 %) and heteroatom-containing substrates (**3aj** and **3ak**, 40 % and 43 %, respectively) allowed reactivity, but hampered the reaction to the corresponding sulfondiimines.

Attempts to iminate *S*-aryl *S*-methyl-substituted substrates **1l–r** under the optimized reaction conditions for the conversions of dialkyl-substituted substrates remained unsatisfying, and the corresponding sulfondiimines **3al–ar** were obtained in only poor to moderate yields (up to 50 %). In more detail, product **3am** with an electron-donating methoxy group bound to the aryl was isolated in a lower yield (28 %) compared to *S*-methyl *S*-phenyl-substituted sulfondii-



Scheme 2. Reaction scope of *S*,*S*-dialkyl-, *S*-alkyl-*S*-aryl- and *S*,*S*-diaryl-substituted substrates **1a–z** and *N*-nosyl- or *N*-tosyl substituted iminoiodinanes **2a** or **2b** for the synthesis of *N*-monosubstituted sulfondiimines **3aa–bz**.

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mine **3al** (50 %). The reaction with halo-containing substrates **1n–r** worked better for smaller halogens [**3an**: *p*-F (46 %) > **3ao**: *p*-Cl (35 %) ≈ **3ap**: *p*-Br (36 %)] and, pleasingly, also sulfondiimines with *ortho*-substituents were formed in comparable yields as their *para*-substituted counterparts [**3ar**: *o*-Br (34 %) > **3aq**: *m*-Br (22 %) < **3ap**: *p*-Br (36 %)], suggesting a minor steric impact.

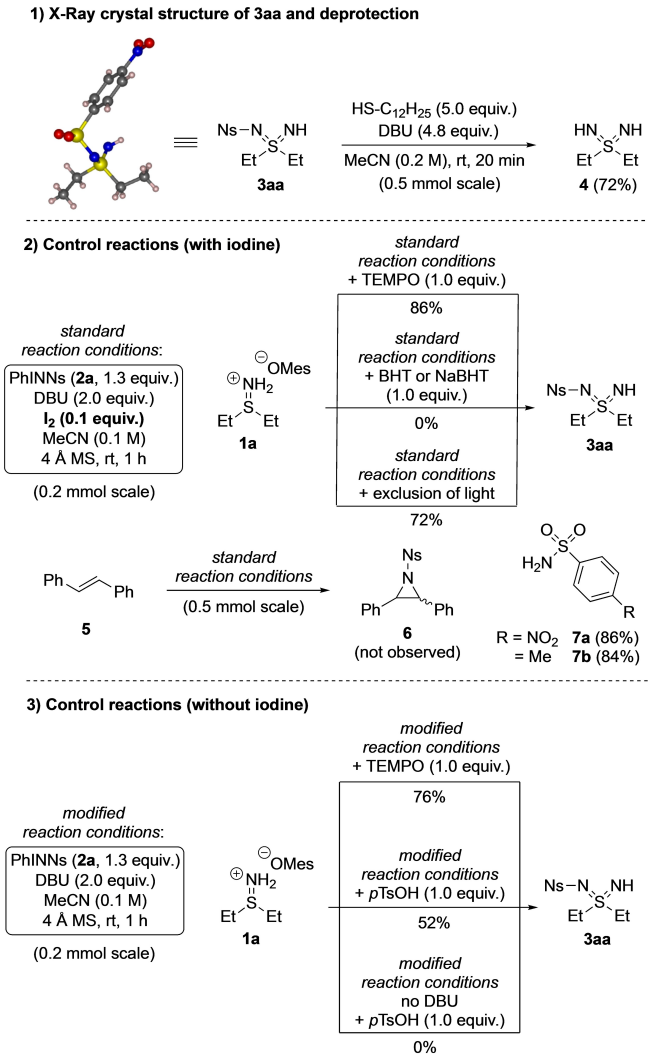
With *S*,*S*-diaryl sulfiliminium mesitylenesulfonates **1s–y** iminations by PhINNs led to complex reaction mixtures without the indication of product formation. Interestingly, iminations with PhINTs were effective for these substrates, albeit diminishing the yield of the corresponding sulfondiimines **3bs–3by** to 18–42 %. *S*- Pyridyl-substituted sulfondiimine **3bz** was not obtained under those reaction conditions with PhINTs (**2b**), presumably due to the coordinative lone pair of the pyridine nitrogen or a decreased electron density at the sulfur atom.[16]

In general, for most substrates the iminations were fast,[13] and if the yields remained moderate, numerous unidentified side-products were detected (by TLC) that indicate degradation pathways of labile intermediates.

An X-ray crystal structure[22] confirmed the identity of compound **3aa** (Scheme 3, part 1), which packed head-to-tail as dimers featuring a pair of (S)NH···O(NOR) hydrogen bonds. The cleavage of the *N*-nosyl group of **3aa** was achieved by following a modified procedure from Willis and co-workers,[9] which led to *N*,*N′*-unsubstituted sulfondiimine **4** in 72 % yield after treatment of **3aa** with dodecanethiol (5 equiv) and DBU (5 equiv) in MeCN and stirring at room temperature for 20 min (Scheme 3, part 1). This approach is of interest because *N*H-*N′*H-sulfondiimines are versatile precursors for the synthesis of a range of *S*,*N*-heterocycles.[5a]

With the goal to get insights into the mechanistic pathway of the process, several control experiments were performed. Primarily, those studies focused on the optimized reaction conditions with iodine. However, in light of the aforementioned good results achieved in the imination of **1a** without iodine, also those (modified) conditions were briefly investigated.

The first set of experiments involved iodine (Scheme 3, part 2). In two separate reactions, the effect of adding 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO, 1.0 equiv) and 2,6-di-*tert*-butyl-4-methylphenol (BHT, 1.0 equiv) as radical scavengers was tested. In the presence of TEMPO, the reaction remained unaffected, and product **3aa** was obtained in a similar yield (86 %) as under standard conditions. In contrast, BHT showed a very pronounced effect. Immediately, the colour of the reaction mixture changed to deep black, and the formation of sulfondiimine **3aa** was inhibited. While we regard the first result with TEMPO as indication for a non-radical pathway, the second appears less conclusive as the phenolic OH of BHT might have been deprotonated by the excess of base (DBU) leading to a phenolate which underwent degradation. In order to test this hypothesis, the sodium salt of BHT (NaBHT) was prepared and added to the standard reaction mixture instead of BHT. As observed before, **3aa** was not formed, and only sulfonamide **7a** was obtained in high yield supporting the suggestion that the phenolate decomposed the iodine(III) compound.



Scheme 3. X-ray crystal structure of sulfondiimine **3aa**, deprotection strategy for the *N*-Ns group and mechanism-related control reactions.[22]

Excluding light in the reaction under the optimized conditions furnished **3aa** in a yield of 72 %. Finally, two typical nitrene trapping experiments with **2a** and **2b** as potential nitrene precursors and *trans*-stilbene (**5**) as a trapping agent were conducted.[17] Both reactions were performed under the standard optimized reaction conditions with (10 mol % of iodine and) **1a** as the substrate, and in neither of them the corresponding aziridine **6** was observed. Instead, the expected sulfonamides **7** (**a** with R = NO_2 and **b** with R = Me) were obtained in high yields (86 % and 84 %, respectively). Thus, intermediate nitrenes or nitrene radicals were not evidenced.

The second set of experiments was conducted without iodine (Scheme 3, part 3). As described earlier, the benchmark for this reaction was the yield of 51 % in the formation of **3aa** from **1a** and **2a** (Table 1, entry 4). First, the influence of TEMPO (1 equiv) as radical scavenger was studied. To

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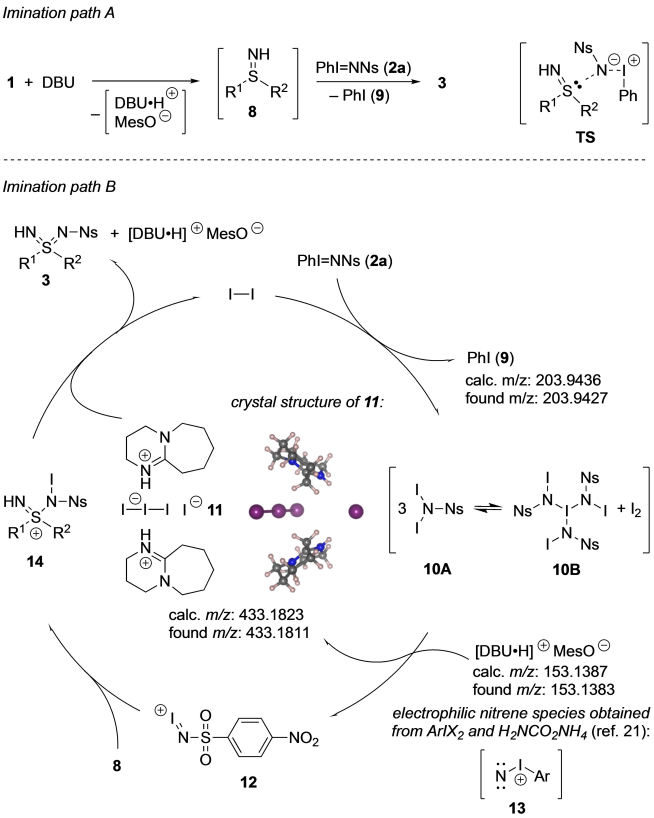
our surprise, and in contrast to our expectations, the yield of **3aa** did not drop but increased to 76 %. Apparently, also in the absence of iodine, radicals were most likely not involved in the imination of **1a** with PhINNs, and probably, the process benefited from the oxidative power of the N-oxide resulting in an improved product formation. This assumption is supported by the observation that with 10 % of TEMPO, **3aa** was only formed in 30 % yield (Table 1, entry 5). Adding 1 equiv of *p*-toluenesulfonic acid to the reaction mixture to investigate the equilibrium of the DBU/sulfonate salt had no effect, and **3aa** was formed in 52 % yield. The crucial effect of DBU was shown in the last control experiment. Thus, performing the same reaction as before but without DBU inhibited the process, and **3aa** was not formed.

Based on the experimental results, literature precedence on iminoiodinane/iodine and related systems,[17–21] as well as further studies by ^{1}H NMR spectroscopy and ESI mass spectrometry (for more details, see the Supporting Information), we propose reaction pathways as shown in Scheme 4.

Two mechanistic scenarios (imination paths A and B) can be discerned depending on the absence and presence of iodine. In both cases, the use of DBU as base is important. Furthermore, the sulfondiimine formation with PhINNs (as depicted in Scheme 4 for simplicity and being representative for imino phenyl-iodinanes in general) is supported by MeCN as the solvent and 4 Å MS as the drying agent. The



Scheme 4. Proposed reaction mechanism for the DBU/iodine-mediated imination of sulfiliminium mesitylenesulfonates **1** with PhINNs (**2a**) via electrophilic nitrene species **12** as reactive intermediate.[22]

control reactions with TEMPO reveal that the involvement of radical species is unlikely in both imination paths.

In the absence of iodine (imination path A), DBU deprotonates sulfiliminium salt **1** generating a "free" sulfilimine **8** and the mesitylenesulfonate salt of DBU. Product **8** then directly reacts with PhINNs yielding sulfondiimine **3** (and phenyliodide, **9**) as known for analogous iminations of sulfoxides and sulfides.[12] The transformation itself probably proceeds via a transition state like **TS**, which is deduced from work by Ochiai et al., who applied a sulfonylimino-λ^3-bromane as nitrenoid in aziridinations of olefins.[17]

The results of the three control reactions shown in Scheme 3 (part 3) are in agreement with this mechanistic proposal and they provide further insights. As discussed before, the positive effect of TEMPO on the product formation could be due to its oxidative mediator strength as also observed in other applications of combinations of $ArIX_2$ reagents and TEMPO.[18] Here, however, mechanistic details remain to be uncovered. The addition of 1 equiv of *p*-toluenesulfonic acid to the reaction mixture did not affect the product formation because a sufficient quantity of DBU (2 equiv) was present, which could trap this additional acidic reagent. The role of DBU proved instrumental as it is needed to "liberate" free sulfilimine **8** from its sulfiliminium salt (here **1**), which does not react in the imination. Overall, imination path A is effective in providing a significant amount of product **3**, but as shown, the process can be improved by adding iodine. Probably, both pathways proceed in parallel as long as the reagent quantities allow.

Imination path B (Scheme 4, bottom) involves literature precedence related to iminoiodinane/iodine systems[19–21] and starts from elemental iodine (I_2), which reacts with iminoiodinane **2** (here again depicted as the nosyl derivative **2a**). From this combination, a monomeric *N*,*N*-diiodo species **10A** results, which is in equilibrium with an oligomeric compound represented by formular **10B**, as first described by Lamar and Nicholas in 2010.[19a] Unfortunately, attempts to obtain crystals suitable for X-ray diffraction analysis proved unsuccessful. Phenyliodide (**9**) is expelled here as well (as confirmed by ESI MS). Under these conditions, neither **10**[20] nor PhINNs generate intermediates with nitrene reactivity as revealed by the result of the control experiment with stilbene where no aziridination was observed (Scheme 3, part 2). Notably, in all of the aforementioned literature, radical pathways are proposed as evidenced by the process inhibition upon addition of TEMPO or BHT.[19,20] Apparently, those pathways are different to the one reported here, where the presence of TEMPO has no inhibitory effect (Scheme 3).

As detailed for imination path A (and not depicted here), DBU deprotonates sulfiliminium salt **1** on path B as well, leading to "free" sulfilimine **8** and the mesitylenesulfonate salt of DBU. Both of those compounds are important for the success of the subsequent transformations. While **8** is needed as "free" reagent to be iminated, the protonated DBU {in the form of $[DBU{\cdot}H]^+{\cdot}MesO^-$, as also detected by ESI MS} serves as trap for I_3^- and I^- ions to give **11**, thereby providing the driving force for the generation of electro-

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philic *N*-iodo nitrene cation **12**, which is the key to product formation. As proven by X-ray crystal structure (obtained from a sample prepared by mixing DBU and I_2 in a 1:1 ratio, see the Supporting Information) and confirmed by ESI MS, **11** consists of two $[DBU{\cdot}H]^+$, an I_3^-, and an I^- species.[22] Intermediate **12** is unusual but analogous to other cationic iodo nitrene species such as **13** which were identified by Luisi and Bull, and utilized by Morandi and co-workers.[21] The reaction of **12** with **8** gives intermediate **14**, which loses I^+ (likely by the reaction with an I_3^- species) leading to product **3** and molecular iodine, which closes the catalytic loop.

At the present stage, our mechanistic hypothesis is based on experimental observations and literature reports on combinations of iminoiodinanes and iodine.[19–21] Further experiments and a theoretical validation by computational studies shall substantiate or disprove the present catalytic cycle.

Conclusion

In summary, we describe an operationally simple and convenient method for the synthesis of *N*-monosubstituted sulfondiimines starting from stable and crystalline sulfiliminium mesitylenesulfonates in combination with molecular iodine, DBU, and an iminoiodinane in anhydrous acetonitrile. The process is particularly effective for accessing cyclic and acyclic *S*,*S*-dialkyl sulfondiimines, which are difficult to prepare in high yields by existing technology. Deprotection of the *N*-Ns moiety under mild reactions conditions leads to valuable *N*H-*N*′H-sulfondiimines. The experimental results and control experiments suggest two concomitant pathways with one proceeding via an electrophilic nitrene cation as intermediates. With future computational studies we plan to elucidate more details of the relevant reaction steps.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Imination · Iodine · Nitrene · Sulfondiimine · Sulfur

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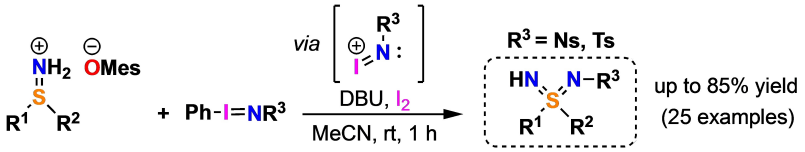
Research Articles

Sulfur Chemistry

M. T. Passia, N. Bormann, J. S. Ward, K. Rissanen, C. Bolm* e202305703

Synthesis of *N*-Monosubstituted Sulfondiimines by Metal-free Iminations of Sulfiliminium Salts



√ stable starting materials √ metal-free √ operationally simple and safe √ rapid

We report an operationally simple and safe method for the synthesis of *N*-monosubstituted sulfondiimines starting from stable sulfiliminium salts. This metal-free procedure employs a combination of iodine(III) reagents with iodine and 1,8-diazabicyclo[5.4.0]undec-7-en (DBU), providing particularly, *S*,*S*-dialkyl-substituted sulfondiimines in up to 85 % yield. Mechanistically, electrophilic nitrene cations are suggested as the reactive intermediates.

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