Diazo Compounds

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Metal-Free Ring-Expansion Reaction of Six-membered Sulfonylimines with Diazomethanes: An Approach toward Seven-Membered Enesulfonamides

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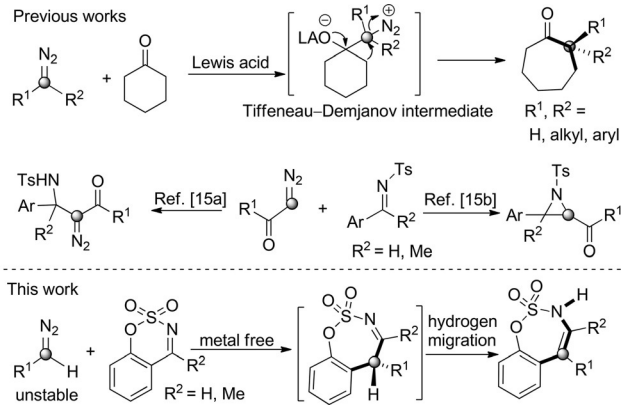
Abstract: *A new metal-free, ring-expansion reaction of six-membered N-sulfonylimines with unstable diazomethanes, generated in situ from the N-tosylhydrazones, has been developed. This reaction delivers valuable seven-membered enesulfonamides by a Tiffeneau–Demjanov rearrangement and intramolecular proton transfer tautomerization process. Moreover, this ring-expansion reaction can be carried out in a one-pot fashion and scaled up to the gram scale by using aryl aldehydes, without the need to isolate the N-tosylhydrazone.*

Seven-membered sulfonamides or sulfamates are found to possess prominent biological activities,[1] such as, calcium sensing receptor agonists,[1c] HIV-1 protease inhibiters,[1d] and ASBT inhibitors.[1e] In addition, they are also used as synthetic intermediates for the synthesis of biologically active molecules.[1c,2–5] Despite being appealing structural motifs, only few metal-catalyzed methods for the synthesis of these compounds have been reported.[1f,2–5] Major synthetic methods consist of: 1) Rhodium- or iron-catalyzed intramolecular allylic C–H amination;[2] 2) Rhodium-catalyzed intramolecular alkyne or allene amination;[3,4] 3) Copper-catalyzed intramolecular nucleophilic ring-opening of sulfamate-derived aziridines;[5] 4) Scandium- or lutetium-catalyzed haloaminocyclization of primary sulfamate ester derivatives.[1f] Despite great achievements in metal-catalyzed reactions, the discovery of efficient metal-free reactions will also be of great importance because of the reduced toxicity and elimination of the cost of the metal.[9a] For these reasons, the metal-free reaction is highly desirable, and indeed, significant progress has been made in the past years.[6,8–10] The metal-free coupling reactions of diazo compounds generated in situ from N-tosylhydrazones under basic reaction conditions (Bamford–Stevens reaction)[7] have appeared in the recent literature.[8] In pioneering studies, Barluenga, Valdés, and co-workers discovered metal-free reductive cross-coupling of boronic acids,[9a] phenols, and alcohols[9b] with N-tosylhydrazones. The group of Wang also reported a metal-free reaction to convert N-tosylhydrazones into pinacol boronates.[10]

The diazo carbon insertion into either a keto C–C bond or formyl C–H bond is a valuable tool in organic synthesis.[11,12] For example, the Lewis acid catalyzed ring-expansion reaction of cyclohexanones with diazo compounds have become a classical strategy for synthesis of seven-membered rings through the Tiffeneau–Demjanov rearrangement (Scheme 1 a).[13,14] Although it is clear that the reaction between acyclic N-tosylimines and acyldiazomethanes could afford N-tosyldiazoketamines[15a] or N-tosylaziridines[15b] under various reaction conditions (Scheme 1 b), we reasoned that if the ring-expansion reaction were conducted with a six-membered imine, the resulting product might form a seven-membered imine, based on a similar Tiffeneau–Demjanov rearrangement mechanism under certain reaction conditions (Scheme 1 c).



Scheme 1. The ring-expansion reaction of cyclohexanone or cyclic N-sulfonylimine. Ts = 4-toluenesulfonyl.

The ring-expansion reactions between cyclic ketones and diazo compounds have been widely used in organic synthesis.[16] However, to the best of our knowledge, there has been no systematic study on the ring-expansion reaction of

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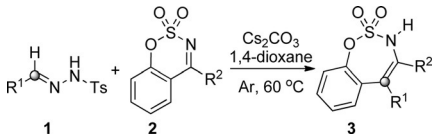
cyclic imines with diazo compounds so far. Herein, we report a metal-free ring-expansion reaction of six-membered imines with diazomethanes, thus providing a new and promising route to seven-membered enesulfonamides.

To test our hypothesis, we employed the N-tosylhydrazone **1a** and benzoxathiazine 2,2-dioxide **2a**[17] as model substrates (for structures see Table ; see Table S1 in the Supporting Information). After some optmization work (entries 1–12), it was found that the best yield of the expected seven-membered sulfonamide **3a** was achieved by employing Cs_2CO_3 as a base in 1,4-dioxane at 60 °C (entry 2). It should be noted that the diazoketamine and aziridine products were not found.

With the optimal reaction conditions established, a variety of N-tosylhydrazones (**1**) derived from aldehydes and benzoxathiazine 2,2-dioxides (**2**) were subjected to the ring-expansion reaction (Table 1). The electronic nature of substituents on the aryl ring attached on the α-position of N-tosylhydrazone had no apparent effects on the reaction. Aromatic groups bearing electron-donating and electron-withdrawing substituents were tolerated. The higher reactivity of the substrates containing an electron-withdrawing group at the 4-position of the aryl ring could lead to formation of the products in higher yields (**3b–g**). Steric hindrance had a slight effect on this transformation, both *ortho*- and *meta*-substituted phenyl N-tosylhydrazones presented lower reactivity and led to the formation of the products in moderate yields (**3j–o**). Notably, 1-naphthyl N-tosylhydrazone participated in the reaction to give the corresponding product **3p** in 81 % yield. The heteroaromatic 3-thiophenyl *N*-tosylhydrazone provided the expected products **3q** in 45 % yields (entry 17), but the 2-furanyl or 2-thiophenyl *N*-tosylhydrazones failed (entries 18–19). To our delight, when R^2 = methyl, the corresponding products **3r–t** were afforded in moderate yield (entries 20–22). Using an N-tosylhydrazone derived from an aliphatic aldehyde as a substrate resulted in no new products (entry 23). Considering that the alkyl diazomethane generated in situ from the corresponding N-tosylhydrazones at 60 °C are highly unstable, we turned to the direct utilization of alkyl diazomethanes. By using diazomethane as a substrate, the same seven-membered product **3u** was afforded at 0 °C in excellent yield, irrespective of R^2 being a hydrogen or methyl group (entries 24 and 25). The use of diazoethane gave the product **3v** at room temperature in 90 % yield (entry 26).

This reaction was not significantly affected by the substituents on the aromatic ring of the benzoxathiazine 2,2-dioxides **2** (Table 2). Although a slightly lower yield was observed when the substituent was 8-Me or 6,8-*t*Bu (**4h**, **4i**), both electron-donor and electron-withdrawing substituents were effective, thus giving the corresponding products **4** in moderate to good yield (**4a–j**). The reaction also worked well with a 1-naphthyl N-sulfonylimine (**4k**).

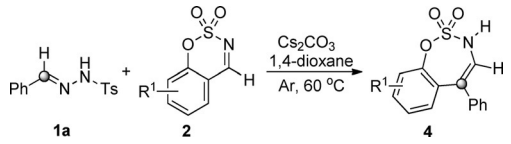
Table 1: Reaction scope of the N-tosylhydrazones.[a]

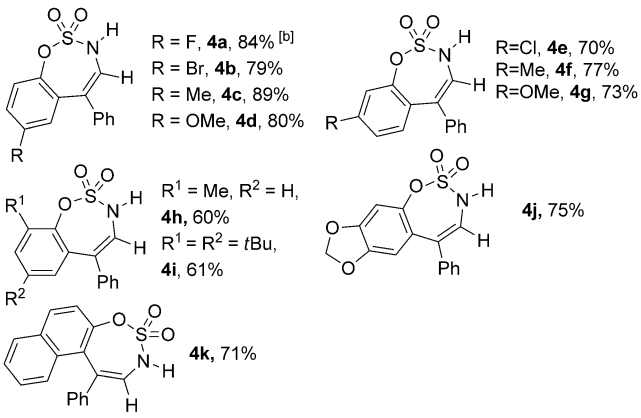


Entry	R^1	R^2	3	Yield [%][b]
1	Ph	H	**3a**	87
2	4-FC_6H_4	H	**3b**	95
3	4-ClC_6H_4	H	**3c**	94
4	4-BrC_6H_4	H	**3d**	92
5	4-$CF_3C_6H_4$	H	**3e**	89
6	4-CNC_6H_4	H	**3f**	90
7	4-$NO_2C_6H_4$	H	**3g**	88
8	4-MeC_6H_4	H	**3h**	70
9	4-$MeOC_6H_4$	H	**3i**	64
10	3-BrC_6H_4	H	**3j**	78
11	3-MeC_6H_4	H	**3k**	62
12	3-$MeOC_6H_4$	H	**3l**	60
13	2-ClC_6H_4	H	**3m**	68
14	2-BrC_6H_4	H	**3n**	65
15	2-$MeOC_6H_4$	H	**3o**	63
16	1-naphthyl	H	**3p**	81
17	3-thienyl	H	**3q**	45
18	2-thienyl	H	–	–[c]
19	2-furanyl	H	–	–[c]
20	Ph	Me	**3r**	64
21	4-BrC_6H_4	Me	**3s**	70
22	3-BrC_6H_4	Me	**3t**	67
23	*n*Bu	H	–	–[d]
24[e]	CH_2N_2	H	**3u**	99
25[e]	CH_2N_2	Me	**3u**	98
26[f]	CH_3CHN_2	Me	**3v**	90

[a] Reaction conditions: N-tosylhydrazone (**1**; 0.21 mmol), cyclic N-sulfonylimine (**2**; 0.2 mmol), and Cs_2CO_3 (75 mol %) in 0.5 mL of 1,4-dioxane at 60 °C for 8–16 h under argon. [b] Yield of isolated product. [c] Other products were obtained; see the Supporting Information. [d] No new products were detected. [e] The CH_2N_2 was used. See the Supporting Information for details. [f] The CH_3CHN_2 was used. See the Supporting Information for details.

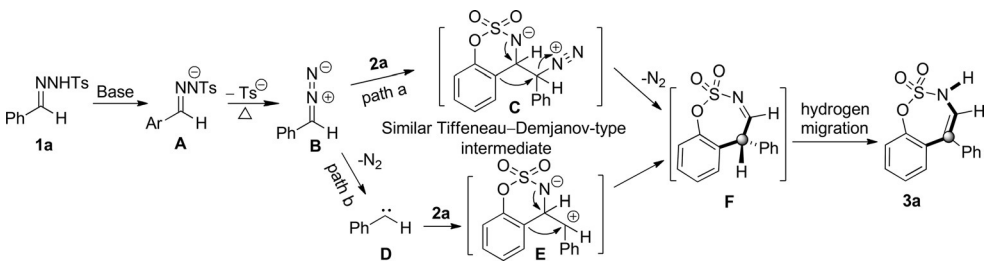
Table 2: Scope of the cyclic N-sulfonylimines.[a]





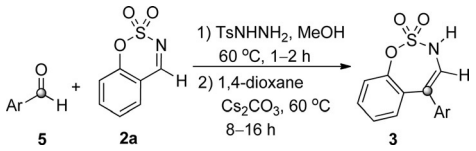
[a] Reaction conditions: N-tosylhydrazone **1a** (0.21 mmol), cyclic N-sulfonylimines **2** (0.2 mmol), Cs_2CO_3 (75 mol %) in 0.5 mL of 1,4-dioxane at 60 °C for 8–16 h in argon. [b] Yield of isolated product.

This ring-expansion reaction could be carried out in a one-pot fashion and scaled-up to a gram scale from the aryl aldehydes **5** without the need to isolate the tosylhydrazone, thus affording the enesulfonamides **3** in similar yield (see the Supporting Information for details; selected examples are shown in Table 3).



Scheme 2. Proposed mechanism for the ring-expansion reaction.

Table 3: One-pot reaction of the aryl aldehydes **5** with cyclic N-sulfonylimine **2a**.[a]



Entry	Ar	3	Yield [%][b]
1	Ph	**3a**	86
2	4-FC_6H_4	**3b**	90
3	3-BrC_6H_4	**3j**	75
4	2-ClC_6H_4	**3m**	65
5	2-$MeOC_6H_4$	**3o**	60
6	1-naphthyl	**3p**	75
7[c]	Ph (10.5 mmol)	**3a** (2.18 g)	80

[a] Reaction conditions: 1) aryl aldehyde **5** (0.21 mmol), tosylhydrazide (0.22 mmol) in MeOH (1 mL), at 60 °C for 1–2 h; 2) cyclic N-sulfonylimine **2a** (0.2 mmol) and Cs_2CO_3 (75 mol %) in 1,4-dioxane (1 mL), at 60 °C for 8–16 h under argon. [b] Yield of isolated product. [c] 10 mmol scale; see the Supporting Information for the reaction conditions.

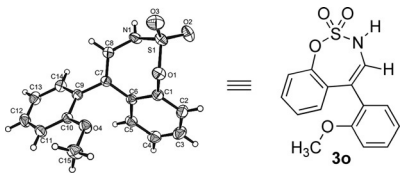
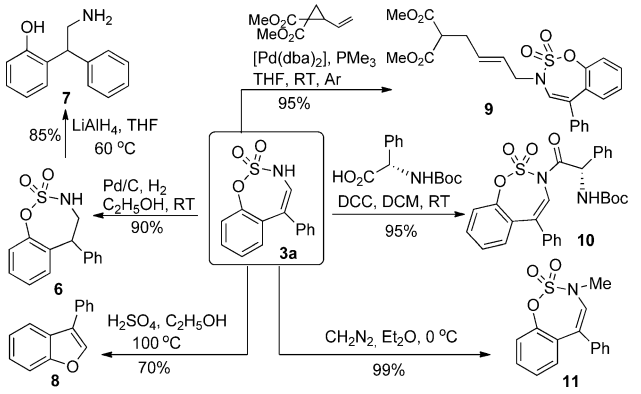


Figure 1. X-ray structure of **3o**; thermal ellipsoids shown at 30% probability.

The structure of **3o** was confirmed by X-ray crystal structure analysis (Figure 1).[18] Based on the Bamford–Stevens reaction[7] and the mechanistic study reported by the groups of Barluenga[9a] and Maruoka,[15] the formation of **3a** is rationalized by a ring-expansion reaction as outlined in Scheme 2. The compound **1a** undergoes deprotonation to form the tosylhydrazone salt **A**. And the diazo compound **B** is generated by decomposition of **A**. From **B**, two pathways are possible: a) **B** could react with **2a** via a similar Tiffeneau–Demjanov-type intermediate **C**, and a rearrangement of the carbon skeleton with release of N_2, subsequently affords **F**. b) The carbene **D**, generated by thermally induced N_2 release, reacts with **2a** via a zwitterionic intermediate **E**, thus smoothly affording **F** by a rearrangement of the carbon



Scheme 3. Transformations of **3a**. Boc = *tert*-butoxycarbonyl, dba = dibenzylideneacetone, DCC = dicyclohexylcarbodiimide, DCM = dichloromethane, THF = tetrahydrofuran.

skeleton. Finally, intramolecular proton transfer tautomerization of **F** leads to the expected product **3a**.

The synthetic versatility of the product **3a** is demonstrated by a series of transformations (Scheme 3). Hydrogenation of **3a** using Pd/C gave the cyclic sulfamate **6** in 90% yield. 2-(2-Amino-1-phenylethyl)phenol (**7**), which is an important structural unit in the agricultural and pharmaceutical agents,[19] was easily derived from the cyclic sulfonamide **6** in 85% yield. Acidic hydrolysis of **3a** produced the valuable 3-phenylbenzofuran (**8**) in 70% yield. Palladium-catalyzed hydroamination reaction between dimethyl 2-vinylcyclo-propane-1,1-dicarboxylate and **3a** produced the allylic sulfonamide **9** in 95% yield. This approach is an effective and valuable hydroamination protocol. The N-Boc-(*S*)-2-amino-2-phenylacetic acid reacting with **3a** afforded **10** in 95% yield. The diazo carbon atom could be selectively inserted into the N–H bond of **3a**, thus giving **11** in 99% yield.

In conclusion, we developed a new metal-free ring-expansion reaction of cyclic N-sulfonylimines with diazomethanes by a tandem reaction similar to a Tiffeneau–Demjanov rearrangement/proton-transfer tautomerization process. This transformation represents an extremely simple way to afford seven-membered enesulfonamides. Moreover, the reaction can be conducted in one pot and on gram scale using aryl aldehydes without isolation of the tosylhydrazones. We believe that this new ring-expansion reaction could become a widely used transformation in organic synthesis.

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[18] CCDC 1423532 (**3o**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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