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Brønsted Base-Mediated Aziridination of 2-Alkyl-Substituted-1,3-Dicarbonyl Compounds and 2-Acyl-Substituted-1,4-Dicarbonyl Compounds by Iminoiodanes

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The synthesis of α,α-diacylaziridines and α,α,β-triacylaziridines from reaction of 2-alkyl-substituted-1,3-dicarbonyl compounds and 2-acyl-substituted-1,4-dicarbonyl compounds with arylsulfonyliminoiodinanes ($ArSO_2N{=}IPh$) under Brønsted base-mediated atmospheric conditions is described. The reaction mechanism is thought to involve the formal oxidation of the substrate followed by aziridination of the ensuing α,β-unsaturated intermediate by the hypervalent iodine(III) reagent.

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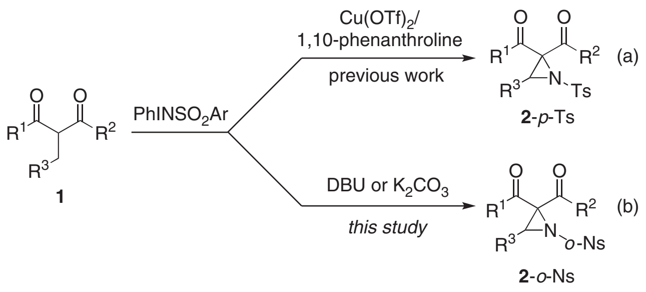
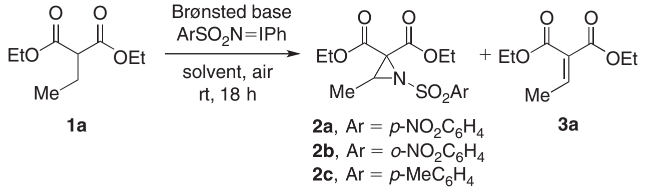
Aziridines are versatile building blocks in organic synthesis as well as a structural motif found in many bioactive natural products and compounds of pharmaceutical interest.[1–23] As a consequence, this has prompted a significant amount of effort towards the development of a myriad of synthetic methods to efficiently and selectively prepare the three-membered nitrogen-containing heterocycle.[24–38] For example, as part of an ongoing program exploring the reaction chemistry of iminoiodanes,[39–70] we recently reported a facile synthetic approach to prepare α,α-diacylaziridines involving Cu^{II}-catalyzed aziridination of 2-alkyl-substituted-1,3-dicarbonyl compounds with *p*-TsN=IPh (where *p*-Ts = *p*-toluenesulfonyl; Scheme 1a).[38] Building on this initial work, we queried whether the construction of the aziridine motif in this manner could be achieved in analogous reactions under transition metal-free-mediated conditions (Scheme 1b).[64–66,71–81] Herein, we report the aziridination of 2-alkyl-substituted diethyl malonates and β-ketoesters in the presence of a Brønsted base and *o*-NsN=IPh (where *o*-Ns = *o*-nitrobenzenesulfonyl) under atmospheric conditions to give the corresponding α,α-diacylaziridine products in moderate-to-excellent yields. Under similar reaction conditions, the aziridination of 2-acyl-substituted succinates and dimethyl 2-(2-oxo-substituted)malonates by *o*-NsN=IPh to produce α,α,β-triacylaziridines in good yields is also presented.

We first examined the Brønsted base-mediated aziridination of diethyl ethylmalonate (**1a**) by *p*-NsN=IPh to establish the optimum conditions for this reaction (Table 1). These results revealed that treating the substrate with 2.2 equiv. of *p*-NsN=IPh and 1.1 equiv. of K_2CO_3 in acetonitrile at room temperature under atmospheric conditions gave the 1,1-diacylaziridine **2a** and α,β-unsaturated 1,3-dicarbonyl compound **3a** in 70 % and 23 % yields, respectively (Table 1, entry 1). Changing the base to other inorganic bases such as *t*-BuOK or Na_2CO_3 led to the recovery of the starting material (Table 1, entries 2 and 3). On the other hand, replacing K_2CO_3 with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base in reactions using 3.3 or 2.2 equiv. of *p*-NsN=IPh led to the formation of aziridine adduct as the only product in 71 % and 72 % yields, respectively (Table 1, entries 4 and 5). Lower product yields of 29 % and 21 % were observed when the amount of DBU was reduced from 2.2 equiv. to 0.2 equiv. and 0.1 equiv. (Table 1, entries 6 and 7). On the other hand, increasing the concentration of the reaction mixture from 0.1 M to 0.2 M at the Brønsted base catalyst loading of 0.2 equiv. was found to give a product yield of 71 % (Table 1, entry 8). Replacing the Brønsted base catalyst with other organic bases such as 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) and 1,4-diazabicyclo[2.2.2]octane (DABCO) gave either a lower product yield of 58 % or no



Scheme 1. Aziridination of 2-alkyl-substituted-1,3-dicarbonyl compounds with arylsulfonylphenyliodinanes

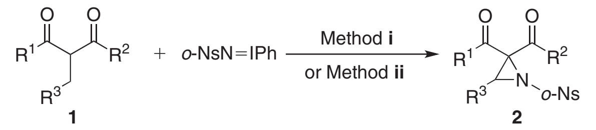
Table 1. Optimization of the reaction conditions[A]

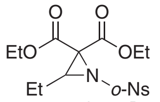


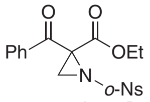
Entry	Brønsted base [equiv.]	$ArSO_2N{=}IPh$ [equiv.]	Solvent	Yield [%][B]
1	K_2CO_3 (1.1)	p-NsN=IPh (3)	MeCN	70[C]
2	t-BuOK (1.1)	p-NsN=IPh (3)	MeCN	–
3	Na_2CO_3 (1.1)	p-NsN=IPh (3)	MeCN	–
4	DBU (1.1)	p-NsN=IPh (2.2)	MeCN	71
5	DBU (1.1)	p-NsN=IPh (2.2)	MeCN	72
6[D]	DBU (0.2)	p-NsN=IPh (2.2)	MeCN	29
7[D]	DBU (0.1)	p-NsN=IPh (2.2)	MeCN	21
8[D]	DBU (0.2)	p-NsN=IPh (2.2)	MeCN	71
9[D]	MTBD (0.2)	p-NsN=IPh (2.2)	MeCN	58
10[D]	DABCO (0.2)	p-NsN=IPh (2.2)	MeCN	–
11[D]	DBU (0.2)	p-NsN=IPh (2.2)	THF	–
12[D]	DBU (0.2)	p-NsN=IPh (2.2)	Toluene	–
13[D]	DBU (0.2)	p-NsN=IPh (2.2)	CH_2Cl_2	74
14[D]	DBU (0.2)	o-NsN=IPh (2.2)	MeCN	97[E]
15[D]	DBU (0.2)	p-TsN=IPh (2.2)	MeCN	12 (81)[F]

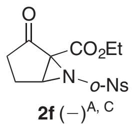
[A] All reactions were performed with **1a** (1 equiv.) at a concentration of 0.1 M at room temperature under atmospheric conditions for 18 h.
[B] Product yield of **2** was determined by ^1H NMR analysis of the crude mixture with CH_2Br_2 as the internal standard.
[C] Isolated yield of **2a**. Compound **3a** was also obtained in 23 % yield.
[D] Reaction was performed with **1a** at a concentration of 0.2 M.
[E] Isolated product yield.
[F] Value in parentheses denotes the yield of **2c** obtained from the analogous reaction catalyzed by $Cu(OTf)_2$/1,10-phenanthroline under the conditions described in ref. [38].

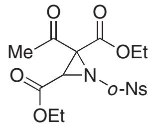
Table 2. Brønsted base-mediated aziridination of 1d–1l

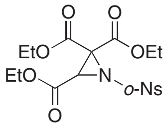


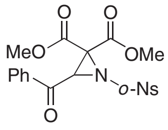

2d (80),[A] [89][B]

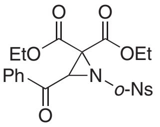

2e (25),[A] [98][B]

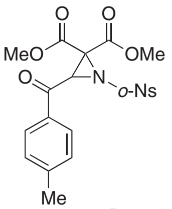

2f (–)[A, C]

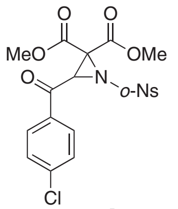

2g (61),[D] [99][B]


2h (45)[D]


2i (56)[D]


2j (58)[D]


2k (50)[D]


2l (41)[D]

[A] Method **i**: reaction performed in 0.2 M MeCN at a o-NsN=IPh/**1**/DBU ratio of 11 : 5 : 1 at room temperature under atmospheric conditions for 18 h; values in parentheses denote isolated product yields.
[B] Values in square brackets denote product yields obtained from the analogous reactions of **1d**, **1e**, and **1g** with p-TsN=IPh and catalyzed by Cu $(OTf)_2$/1,10-phenanthroline under the conditions described in ref. [38].
[C] Unidentifiable decomposition products obtained.
[D] Method **ii**: reaction carried out in 0.2 M CH_2Cl_2 at a o-NsN=IPh/K_2CO_3/**1** ratio of 3 : 1.1 : 1 at 40°C under atmospheric conditions for 18 h; values in parentheses denote isolated product yields.

product formation, respectively (Table 1, entries 9 and 10). Examination of the solvent effect on the aziridination reaction revealed that with using THF or toluene instead of acetonitrile (MeCN) as the solvent resulted in no reaction based on thin layer chromatography analysis and ^1H NMR measurements of the crude mixtures. In contrast, a product yield of 74 % was obtained when CH_2Cl_2 was used as solvent (Table 1, entries 11–13). At a catalyst loading of 20 mol-%, our subsequent studies revealed that changing the arylsulfonyl-substituted iminoiodane source from p-NsN=IPh to o-NsN=IPh gave the best result, affording **2b** in 97 % yield (Table 1, entry 14). In a final control experiment, performing the DBU-mediated reaction using p-TsN=IPh instead of p-NsN=IPh gave **2c** in a 12 % yield (Table 1, entry 15). In comparison, the analogous reaction catalyzed by Cu $(OTf)_2$/1,10-phenanthroline gave a product yield of 81 %.[38]

A survey of the present DBU-catalyzed procedure involving other 2-alkyl-substituted-1,3-dicarbonyl compounds showed that reaction of the diethyl malonate (**1d**), containing a n-Pr group at the C2 position, afforded **2d** in 80 % yield (Table 2). Under similar reaction conditions, the aziridination of the 2-methyl-substituted β-keto ester **1e** was found to furnish the corresponding product **2e** in 25 % yield. However, the analogous experiment with the cyclopentanone derivative **1f** led to a complex concoction of unidentifiable by-products based on ^1H NMR analysis of the crude reaction mixture. Reactions of the 2-acyl-substituted-1,4-dicarbonyl compounds **1g**–**1l** afforded higher product yields using the K_2CO_3-mediated conditions described in entry 1 of Table 1 at 40°C. The application of this second set of conditions to the reactions of diethyl succinates with a pendant methyl ketone (**1g**) or ethyl ester (**1h**) group gave the corresponding aziridines **2g** and **2h** in respective yields of 61 % and 45 %. Likewise, the use of methyl and ethyl 4-oxo-4-arylbutanoates containing a methyl ester (**1i**, **1k**, **1l**) or an ethyl ester (**1j**) moiety gave favourable results. In these experiments, the corresponding α,α,β-triacylaziridine adducts **2i**–**2l** were obtained in 37–58 % yield with the structure of **2i** being

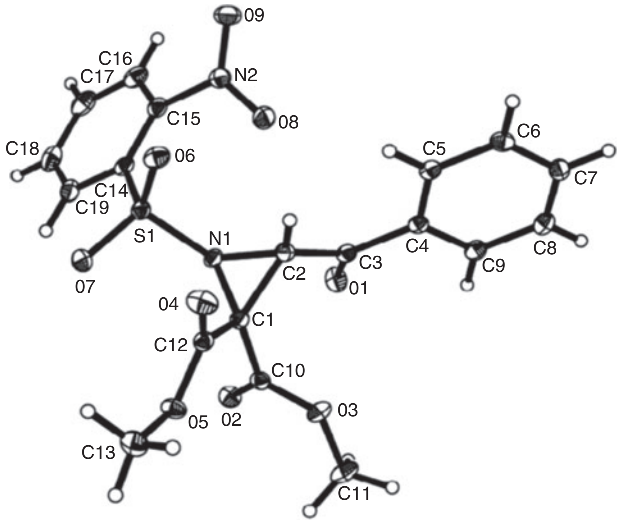
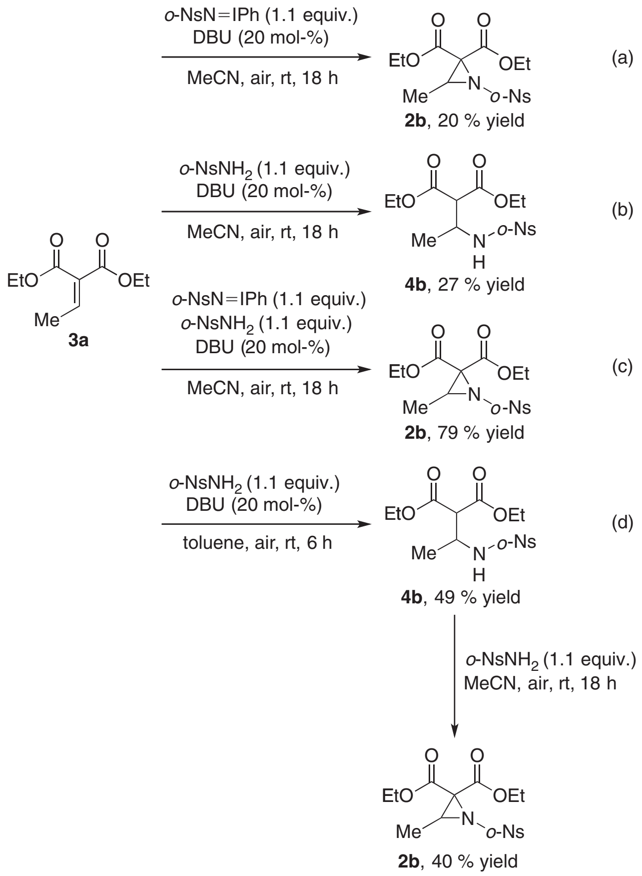


Fig. 1. *ORTEP* drawing of **2i** with thermal ellipsoids at 50 % probability levels.[82]

confirmed by X-ray crystallography (Fig. 1).[82] The reactions involving **1d** and **1g** were also found to give product yields that were either comparable or slightly lower than those obtained from analogous experiments involving the same substrates and *p*-TsN=IPh and catalyzed by Cu(OTf)$_2$/1,10-phenanthroline.[38] The only exception was the reaction involving **1e**, which was found to give a low product yield of 25 % under the present Brønsted base-mediated conditions.

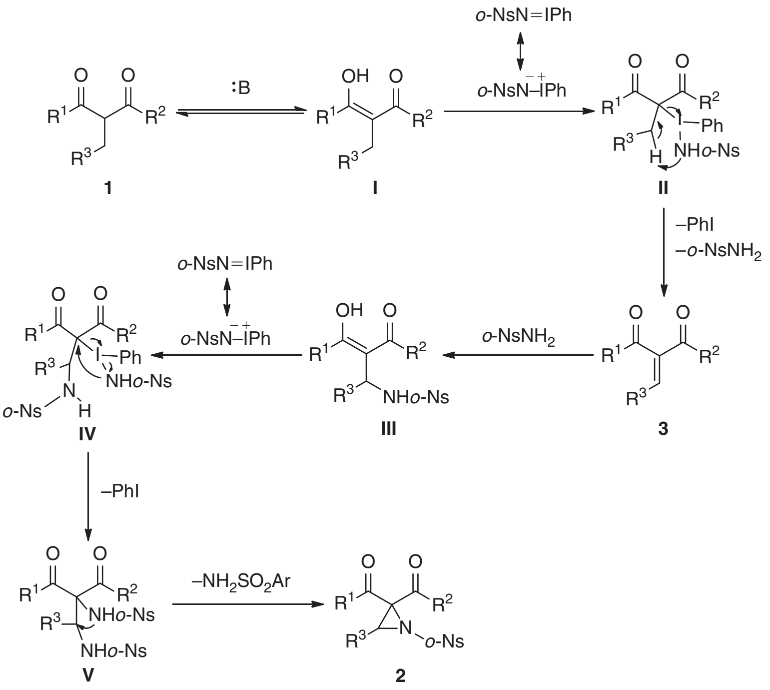
Though fortuitous, the isolation of the α,β-unsaturated 1,3-dicarbonyl compound **3a** led us to speculate its possible involvement in the reaction mechanism of the present transformation. It would also imply the decomposition of *o*-NsN=IPh to *o*-NsNH$_2$ and PhI with the in situ formed sulfonamide subsequently initiating a iminoiodane-mediated Michael-initiated ring closure (MIRC) reaction and product formation.[83–88] To verify this hypothesis as well as gain a better understanding of how the present aziridination process might proceed, we next conducted a series of control reactions involving **3a** (Scheme 2). In an initial control reaction, subjecting **3a** to 20 mol-% of DBU and 1.1 equiv. of *o*-NsN=IPh in acetonitrile at room temperature for 18 h afforded **2b** in 20 % yield (Scheme 2a). Conducting this control experiment again using *o*-NsNH$_2$ instead of *o*-NsN=IPh afforded the sulfonamide compound **4b** in 27 % yield (Scheme 2b). In a third control reaction, the *N*-heterocyclic product was then furnished in 79 % yield when the α,β-unsaturated 1,3-dicarbonyl compound was treated under the DBU-catalyzed conditions in the presence of equimolar amounts of the iminoiodane and sulfonamide (Scheme 2c). The possibility of a pathway involving compound **4b** was further supported by reacting **3a** with 0.2 equiv. of DBU and 1.1 equiv. of *o*-NsNH$_2$ in toluene at room temperature for 6 h (Scheme 2d). Subsequent addition of 1.1 equiv. of *o*-NsN=IPh to the ensuing crude reaction mixture containing the sulfonamide in 49 % yield (as determined by ^{1}H NMR analysis using CH$_2$Br$_2$ as the internal standard) in acetonitrile at room temperature for 18 h afforded aziridine **2b** in 40 % yield. In a final set of control experiments involving **3a**, the recovery of the substrate only was detected when each of the above control reactions were repeated under the conditions described in Scheme 2 and in the absence of the Brønsted base.



Scheme 2. Control experiments using **3a**. The yield of **4b** was determined by ^{1}H NMR analysis using CH$_2$Br$_2$ as the internal standard.

Based on the above results, a tentative mechanism for the present Brønsted base-mediated aziridination reactions is illustrated in Scheme 3. The mechanism could initially involve the Brønsted base-promoted tautomerization of substrate **1** to give the enol isomer **I**. Nucleophilic attack of this tautomer at the iodine centre in *o*-NsN=IPh might then produce the putative iodinated species **II**.[89–100] Intramolecular deprotonation of the β-methylene centre by the sulfonamide motif and deiodination in this newly formed adduct would afford intermediate **3** along with the release of *o*-NsNH$_2$ and iodobenzene. At this juncture, an iminoiodane-mediated MIRC may now come into play upon the 1,4-conjugate addition of *o*-NsNH$_2$ to the Michael acceptor site of **3** to furnish the posited 1,3-amino enol **III**.[83–88] A second nucleophilic addition step involving this adduct and another molecule of *o*-NsN=IPh could occur to give the iodinated 1,3-dicarbonyl compound **IV**. Subsequent deiodination of this hypervalent iodine(III) adduct followed by deaminative cyclization of the ensuing disulfonamide adduct **V** might then deliver the aziridine product **2**.[89–100]

In conclusion, we have developed a transition metal-free synthetic strategy to access α,α-diacylaziridines and α,α,β-triacylaziridines. The nitrogen ring-forming process relies on the aziridination of the respective 2-alkyl-substituted-1,3-dicarbonyl compounds and 2-acyl-substituted-1,4-dicarbonyl compounds by *o*-NsN=IPh under Brønsted base-mediated reaction conditions. Though the substrate scope of the present methodology is less broad than the analogous Cu^{II}-catalyzed approach,[38] the present methodology was shown to be more practical as it did not require



Scheme 3. Proposed mechanism of the present Brønsted base-mediated aziridination reaction.

the need for inert reaction conditions. Efforts to explore the synthetic applications of the present reactions are currently underway and will be reported in due course.

Supplementary Material

Detailed experiment procedures, characterization data, and ^{1}H and ^{13}C NMR spectra for compounds **2**, **3a**, and **4a** are available on the Journal's website.

Acknowledgements

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