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Divergent amine-catalyzed [2+2] annulation of allenoates with azodicarboxylates: facile synthesis of 1,2-diazetidines

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ABSTRACT

In this Letter, we described a distinct DABCO-catalyzed [2+2] annulation reaction of allenoates with azodicarboxylates which affords 3-alkylidene-1,2-diazetidines in moderate yields with excellent stereo- and regioselectivity. This reaction constitutes the first example of Lewis base-catalyzed annulation of allenoates with azodicarboxylates, and showcases a divergent reactivity between phosphines and amines.

1,2-Diazetidines, which contain two adjacent nitrogen atoms within a four-membered ring, exhibit promising biological and pharmacological effects[1] because of their structural similarity to β-lactams. However, effective synthetic approaches to 1,2-diazetidines have been lacking for several decades probably due to the intrinsic ring strain. It is until recently that Ma[2] and Shipman[3] have reported effective synthesis of 1,2-diazetidines via 4-*exo*-tet ring closure of substituted hydrazines. Chen and Ma[4] have also disclosed Pd-catalyzed cyclizations of 2,3-allenyl hydrazines with aryl halides for accessing 1,2-diazetidines. On the other hand, intermolecular [2+2] cycloadditions between diazenes and alkenes provide a straightforward approach to 1,2-diazetidines. In this respect, Fu[5] and Ye[6] have reported efficient Lewis base-catalyzed [2+2] cycloadditions of azodicarboxylates with ketenes for the enantioselective synthesis of 1,2-diazetidines. Despite these progresses, developing new and effective methods for the assembly of functionalized 1,2-diazetidines from readily available starting materials is still of current interest.

Lewis base-catalyzed annulation reactions of allenoates using phosphines and amines as nucleophiles have been established as a powerful toolbox for the construction of carbo- and heterocycles.[7] Since Lu's pioneer work[8] on PPh_3-catalyzed formal [3+2] cycloaddition of allenoates with activated alkenes or imines, a vast array of annulation reactions between allenoates and polarized C=X bonds (X = C, N, O) have been disclosed, such as [1+4],[9] [2+1],[10] [2+2],[11] [2+3],[12] [2+4],[13] [2+2+2],[14] [2+8],[15] [3+2],[16] [3+3],[17] [3+4],[18] [4+1],[19] [4+2],[20] [4+3][21] and sequential/domino annulations.[22] Among various electrophiles participated in annulations with allenoates, however, the use of electrophilic N=N bonds as building blocks has been seldom investigated.[23]

In 2006, Nair and co-workers[23a] reported a reductive annulation of allenoates with azodicarboxylates using a stoichiometric amount of PPh_3 as the mediator (Scheme 1, Eq. 1). The reluctance of PPh_3 to promote a catalytic annulation is reasoned that PPh_3 attacks preferentially on azodicarboxylates to form the Huisgen zwitterion **A**[24] which facilitates the reductive annulation with the concomitant formation of $O{=}PPh_3$. As part of our interest in exploiting divergent reactivities between phosphines and amines,[25] we envisaged the employment of amines as a trigger would circumvent the Huisgen type intermediate and may favor the formation of zwitterion **B**, which could possibly lead to a catalytic annulation between allenoates and azodicarboxylates (Scheme 1, Eq. 2). Herein, we report a divergent DABCO-catalyzed [2+2] annulation of allenoates with azodicarboxylates which provides an easy access to 3-alkylidene-1,2-diazetidines. Furthermore, an interesting cooperative DABCO/PPh_3-catalyzed formal [3+2] annulation of allenoate with azodicarboxylate for the formation of pyrazoline is also presented (vide infra).

In an initial experiment, benzyl allenoate **1a** (0.5 mmol), diisopropyl azodicarboxylate **2a** (0.5 mmol), and catalytic amount of

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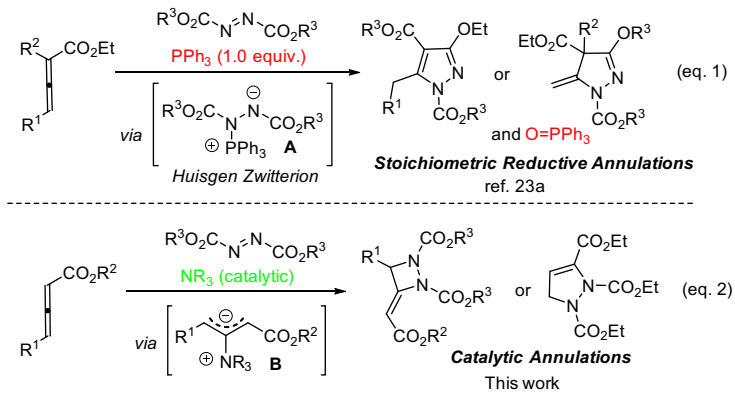


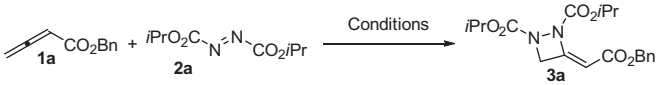
Scheme 1. Divergent annulations between allenoates and azodicarboxylates promoted by phosphines and amines.

DABCO (20 mol %) were taken up in dichloromethane (2.0 mL) at room temperature (Table 1, entry 1). The reaction was completed in 1 hour and afforded a [2+2] annulation product 1,2-diazetidine **3a** in 48% isolated yield with excellent *Z*-selectivity (*Z*/*E* > 20:1) (Table 1, entry 1). The alkenyl proton (=CH) of **3a** is observed at δ 5.81 ppm as a triplet (J = 2.3 Hz) in the ^{1}H NMR spectrum, and the methylene protons of the 1,2-diazetidine core appears at δ 4.94 ppm as a doublet (J = 2.3 Hz). In the ^{13}C NMR, the signal at δ 95.9 ppm indicates the olefinic carbon (=CH) adjacent to the ester group, and resonance at δ 59.5 ppm corresponds to the methylene carbon of the 1,2-diazetidine ring. All the other signals are in good agreement with the assigned structure. The *Z*-configuration of the C=C bond is well supported by a NOESY spectrum of an analogous compound **3e** (see Supplementary data). To our knowledge, this [2+2] annulation represents the first Lewis base-catalyzed annulation of allenoates with azodicarboxylates,[26] and showcases a divergent reactivity between amines and phosphines with regard to the previous phosphine-mediated reductive annulation.[23a]

In view of the pleasing result, the reaction conditions were optimized using the above reaction as a probe (Table 1). Several common amine catalysts were examined. It was found that triethylamine as the catalyst only gave **3a** in 11% yield (entry 2). DMAP led to a complex reaction, while diisopropylethylamine, pyridine, DBU, or DBN as the catalysts all gave trace amount of the product (entries 3–7). With DABCO as the catalyst, several common solvents were tested. $CHCl_3$ gave a comparable 46% yield, whereas DMF, DMSO, toluene, and THF delivered lowered yields (24–43%) (entries 8–12). Protic solvent ethanol was completely ineffective (entry 13); however, ethyl acetate and CH_3CN could upgrade the yield to 57% and 58%, respectively (entries 14 and 15). Finally it was revealed that 1,4-dioxane was the best, affording the [2+2] product **3a** in 68% yield (entry 16). Reducing the catalyst loading to 10 mol % did not deteriorate the yield, but 5 mol % of that resulted in a substantial decrease in the yield (entries 17 and 18). A lower temperature showed little influence on the reaction, but a higher one proved detrimental (entries 19 and 20). Interestingly, introducing an acid additive, for example, benzoic acid, to the reaction completely shut down the [2+2] annulation and led to the formation of the aza-Morita–Baylis–Hillman product (for more information, see Scheme 2).[27,28]

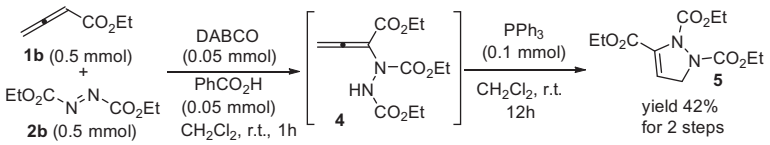
Subsequent studies focused on the scope of the [2+2] annulation under the optimized conditions (Table 2). It was found that variation in the ester alkyl groups of both azodicarboxylates and allenoates had little influence on the reaction (entries 1–6); the corresponding 1,2-diazetidines with different ester alkyl groups were generated in 47–68% yields and excellent stereoselectivity. A discernible trend is the bulky *tert*-butyl azodicarboxylate **2c** giving lowered yields (entries 3 and 6). Notably, γ-substituted allenoates are well compatible with the [2+2] annulation, which greatly enhances the synthetic potential of the reaction. For example, γ-substituted allenoates containing methyl, ethyl, benzyl, and hexyl substituents (**1c**–**f**) readily reacted with azodicarboxylates **1a** or **1b**, producing the corresponding 1,2-diazetidines endowed with an alkyl chain in 34–64% yields with high stereo- and regioselectivity (entries 7–15). However, *tert*-butyl azodicarboxylate **2c** failed in the reaction with γ-substituted allenoates probably due to the steric hindrance (entry 9). It was found that α-substituted allenoates, for example, α-methyl allenoate **1g** and α-ethoxycarbonylmethyl allenoate **1h**, however, were inert toward the [2+2] annulation. It is noteworthy that the above [2+2] annulation is fast;

Table 1
Optimization on amine-catalyzed [2+2] annulation of benzyl allenoate **1a** with diisopropyl azodicarboxylate **2a**[a]



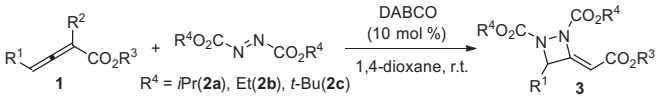
Entry	Catalyst	Solvent	Time (h)	Yield of **3a**[b] (%)
1	DABCO	CH_2Cl_2	1	48
2	NEt_3	CH_2Cl_2	12	11
3	DMAP	CH_2Cl_2	1	Complex
4	NEt*i*Pr$_2$	CH_2Cl_2	12	Trace
5	Pyridine	CH_2Cl_2	12	Trace
6	DBU	CH_2Cl_2	12	Trace
7	DBN	CH_2Cl_2	12	Trace
8	DABCO	$CHCl_3$	1.5	46
9	DABCO	DMF	1.8	43
10	DABCO	DMSO	8	39
11	DABCO	Toluene	8	36
12	DABCO	THF	1	24
13	DABCO	EtOH	12	/
14	DABCO	CH_3CN	3	57
15	DABCO	EtOAc	2	58
16	DABCO	1,4-Dioxane	1	68
17[c]	DABCO	1,4-Dioxane	1	68
18[d]	DABCO	1,4-Dioxane	1	59
19[c,e]	DABCO	1,4-Dioxane	1	66
20[c,f]	DABCO	1,4-Dioxane	1	44
21[c,g]	DABCO	1,4-Dioxane	1	Trace

[a] At room temperature and under N_2, allenoate **1a** (0.5 mmol) was added to a solution of diethyl azodicarboxylate **2a** (0.5 mmol) and catalyst (0.1 mmol, 20 mol %) in the specified solvent (2.0 mL).
[b] Isolated yield.
[c] 10 mol % DABCO was used.
[d] 5 mol % DABCO was adopted.
[e] The reaction was conducted at 0 °C.
[f] The reaction was run under reflux.
[g] 10 mol % benzoic acid was used as an additive.



Scheme 2. Cooperative DABCO/PPh_3-catalyzed formal [3+2] annulation between allenoate **1b** and azodicarboxylate **2b**.

Table 2
Investigation on the scope of DABCO-catalyzed [2+2] annulation of allenoates **1** with azodicarboxylates **2**[a]

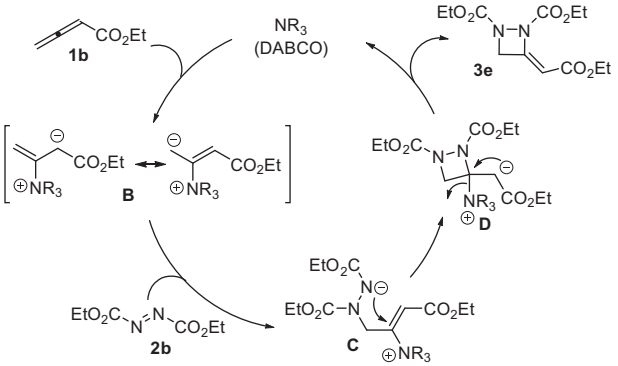


Entry	R^1, R^2, R^3 in **1**	**2**	Time (h)	**3**, yield[b] (%)	*Z*/*E*[c]
1	H, H, Bn (**1a**)	**2a**	1	**3a**, 68	20:1
2	H, H, Bn (**1a**)	**2b**	1.2	**3b**, 64	20:1
3	H, H, Bn (**1a**)	**2c**	4	**3c**, 54	20:1
4	H, H, Et (**1b**)	**2a**	3	**3d**, 57	20:1
5	H, H, Et (**1b**)	**2b**	3	**3e**, 47	20:1
6	H, H, Et (**1b**)	**2c**	3	**3f**, 21	20:1
7	Me, H, Et (**1c**)	**2a**	1.5	**3g**, 64	20:1
8	Me, H, Et (**1c**)	**2b**	1.3	**3h**, 62	20:1
9	Me, H, Et (**1c**)	**2c**	12	Trace	/
10	Et, H, Et (**1d**)	**2a**	1.8	**3i**, 59	20:1
11	Et, H, Et (**1d**)	**2b**	1.6	**3j**, 62	20:1
12	Bn, H, Et (**1e**)	**2a**	3	**3k**, 60	20:1
13	Bn, H, Et (**1e**)	**2b**	2.5	**3l**, 63	20:1
14	n-C_6H_{13}, H, Et (**1f**)	**2a**	5	**3m**, 36	8:1
15	n-C_6H_{13}, H, Et (**1f**)	**2b**	5	**3n**, 34	10:1
16	H, Me, Et (**1g**)	**2a**	12	/	/
17	H, CH_2CO_2Et, Et (**1h**)	**2a**	12	/	/

[a] Under N_2 atmosphere and at room temperature, to a solution of azodicarboxylates **2** (0.5 mmol) and DABCO (0.05 mmol) in 1,4-dioxane (2.0 mL) was slowly added allenoates **1** (0.5 mmol), and the mixture was stirred and monitored by TLC.
[b] Isolated yield.
[c] Determined by ^{1}H NMR assay.

all the reactions were completed in a few hours. The reaction also exhibits high stereoselectivity (*Z*/*E* = 8:1 to 20:1) and exclusive regioselectivity, with β,γ-carbon of allenoates involved in ring formation. The structure and stereochemistry of 1,2-diazetidines **3** were well identified by ^{1}H, ^{13}C NMR, HRMS analysis, and by COSEY, HMQC, HMBC, and NOESY spectra for a representative product **3e** (for characterization data, see Supplementary data).

Interestingly, it was found that an acid additive was able to direct the DABCO-catalyzed [2+2] annulation toward the aza-Morita–Baylis–Hillman reaction, producing unstable α-hydrazino allenoate **4** (Scheme 2). It occurs to us that a follow-up phosphine-catalyzed umpolung cyclization[11h,29] of intermediate **4** would accomplish a formal [3+2] annulation between allenoates and azodicarboxylates. Noteworthy is that the direct phosphine-catalyzed [3+2] annulation between allenoates and azodicarboxylates has proved unsuccessful.[23a] Delightfully, running the reaction of allenoate **1b**, azodicarboxylate **2b**, DABCO (10 mol %), and benzoic acid (10 mol %) in dichloromethane for 1 h, and followed by the addition of catalytic amount of PPh_3 (20 mol %) in one-pot for 12 h, the desired [3+2] product **5** was obtained in overall 42% yield (Scheme 2). A possible mechanism for the formation of **5** is outlined in Supplementary data. This preliminary result illustrates the potential synthetic utility of cooperative catalysis with amines and phosphines. Further investigations along this line are currently underway in our laboratory.



Scheme 3. Proposed mechanism for DABCO-catalyzed [2+2] annulation between allenoates and azodicarboxylates.

Based on the related mechanistic investigations[30] and closely related amine-catalyzed [2+2] annulations of allenoates,[11] a plausible mechanism for the DABCO-catalyzed [2+2] annulation of allenoates with azodicarboxylates is depicted in Scheme 3. Initially, the nucleophilic attack of DABCO on the β carbon of allenoate **1b** generates a resonance-stabilized zwitterionic intermediate **B**. Addition of **B** to the azodicarboxylate **2b** through its γ-carbanion produces **C**, which converts into species **D** via a favorable 4-*exo*-trig cyclization. 1,2-Elimination of the amine catalyst finally completes the catalytic cycle and produces the 1,2-diazetidine **3e**. In contrast with the previous stoichiometric PPh_3-mediated reductive annulation of allenoates with azodicarboxylates,[23] this distinct amine-catalyzed [2+2] process presumably attributes to the lower affinity of amines toward azodicarboxylates.[31] The amine prefers to attack allenoates over azodicarboxylates to form intermediate **B** leading to a divergent catalytic [2+2] annulation.

In conclusion, a distinct DABCO-catalyzed [2+2] annulation of allenoates with azodicarboxylates is developed under very mild conditions, which provides a facile access to 3-alkylidene-1,2-diazetidines in moderate yields with excellent *Z*/*E*- and regioselectivity. A cooperative DABCO/PPh_3-catalyzed formal [3+2] annulation of allenoate and azodicarboxylate for the formation of pyrazoline is also demonstrated. These reactions showcase divergent reactivities between amines and phosphines, and constitute the first examples of Lewis base-catalyzed annulations of allenoates with azodicarboxylate. Future efforts in our laboratory will focus on expanding the scope and developing the asymmetric version of these annulations.

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Supplementary data

Supplementary data (general experimental procedures, analytical data and NMR spectroscopic copies for compounds **3** and **5**, and a proposed mechanism for the formation of **5**) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.09.151. These data include MOL files and InChiKeys of the most important compounds described in this article.

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