JOC Note

Selective Synthesis of 4-Alkylidene-β-lactams and *N*,*N*′-Diarylamidines from Azides and Aryloxyacetyl Chlorides via a Ketenimine-Participating One-Pot Cascade Process

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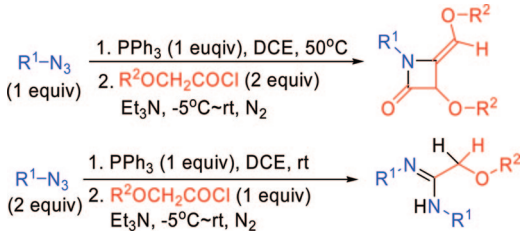
Received December 21, 2007



A one-pot cascade approach to 4-alkylidene-β-lactams and *N*,*N*′-diarylamidines from aryl azides and aryloxyacetyl chlorides has been developed. The chemical outcome of the reaction can be controlled selectively by an appropriate choice of the stoichiometric ratio of different substrates and reagents. The products should find use in pharmaceutical discovery, especially in the development of new antimicrobial agents against multidrug-resistant pathogens.

The β-lactams are an important class of heterocyclic compounds due to their antibiotic activity[1] and their utility as versatile building blocks in organic synthesis.[2] The Staudinger reaction[3] and the Gilman−Speeter reaction[4] are the classical methods for the construction of β-lactam rings. A number of modern synthetic methods have also been reported.[5] On the other hand, the problem of microbial resistance, related to the use of antibiotic agents over the last 50 years, is nowadays widely recognized, and treatment options in clinical practice are limited by multidrug-resistant bacteria. More recently, it was reported that some 4-alkylidene-β-lactams exhibited antibiotic activity against resistant bacteria.[6] However, very few examples of this new class of monocycle β-lactams have been reported in the literature.[6,7]

Ketenimines are nitrogenated heterocumulenes, which can account for the addition of a variety of nucleophiles[8] and radicals[9] to their central carbon atom, and participate in pericyclic reactions such as [2 + 2] and [2 + 4] cycloadditions[10] as well as sigmatropic rearrangements.[11] Previously, we developed an efficient synthesis of iminocoumarins, 5-arylidene-2-imino-3-pyrrolines, 2-imino-1,2-dihydroquinolines, and 2-iminothiochromenes, involving a ketenimine intermediate in situ generated from copper-catalyzed cycloaddition of sulfonyl azides and terminal alkynes.[12] Encouraged by these works, we are interested in the ketenimine-participating cascade reactions. Herein, we describe a one-pot cascade synthesis of 4-alkylidene-β-lactams and *N*,*N*′-diarylamidines from arylazides and aryloxyacetyl chlorides through a ketenimine intermediate.

We began our investigations by looking into the reaction of the triphenylphosphazene derived from (4-methyloxyphenyl)-azide (**1a**) and the ketene in situ generated from phenoxyacetyl chloride (**2a**) (Scheme 1). In a one-pot procedure, **1a** reacted with triphenylphosphine in 1,2-dichloroethane (DCE) to form triphenylphosphazene **3** via the Staudinger−Meyer reaction,[13a] which was immediately treated with 2 equiv of **2a** and triethylamine at −5 °C and then at room temperature to afford 4-phenoxymethylene-β-lactam **5a**. We believe that this cascade process involves an aza-Wittig reaction of triphenylphosp-

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10.1021/jo702733h CCC: $40.75
Published on Web 03/26/2008

SCHEME 1. Synthesis of 4-Alkylidene-β-lactam 5a from 4-Methyloxyphenyl Azide (1a) and Phenoxyacetyl Chloride (2a)

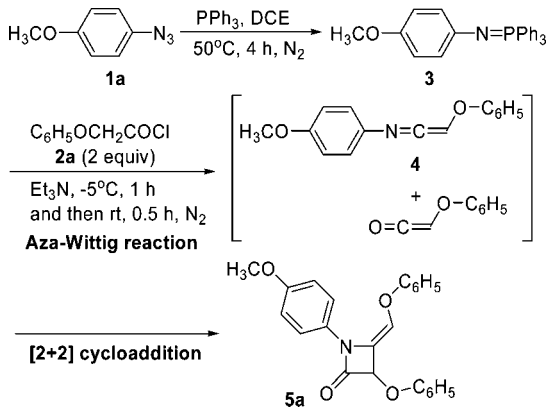
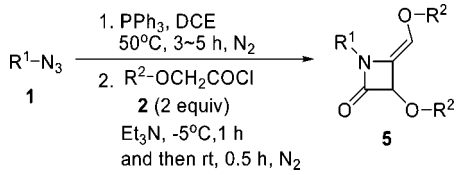


TABLE 1. Synthesis of 4-Alkylidene-β-lactams 5 from Aryl Azides 1 and Aryloxyacetyl Chlorides 2[a]



entry	R^1	R^2	product	yield[b] (%)
1	4-$MeOC_6H_4$ (**1a**)	C_6H_5 (**2a**)	**5a**	76
2	4-MeC_6H_4 (**1b**)	**2a**	**5b**	86
3	2-MeC_6H_4 (**1c**)	**2a**	**5c**	80
4	C_6H_5 (**1d**)	**2a**	**5d**	89
5	3,4-$Me_2C_6H_3$ (**1e**)	**2a**	**5e**	83
6	3-MeC_6H_4 (**1f**)	4-MeC_6H_4 (**2b**)	**5f**	85
7	4-$EtOC_6H_4$ (**1g**)	**2a**	**5g**	78
8	**1g**	**2b**	**5h**	75
9	**1d**	**2b**	**5i**	90
10	**1b**	3-MeC_6H_4 (**2c**)	**5j**	87
11	**1f**	**2c**	**5k**	91
12	**1f**	**2a**	**5l**	88
13	**1a**	2-Me,4-ClC_6H_3 (**2d**)	**5m**	79
14	**1b**	**2d**	**5n**	80
15	**1c**	**2d**	**5o**	87
16	**1d**	**2d**	**5p**	78
17	**1f**	**2d**	**5q**	81
18	**1g**	**2d**	**5r**	81
19	**1a**	**2b**	**5s**	77
20	**1d**	**2c**	**5t**	92
21	2-BrC_6H_4 (**1 h**)	**2a**	**5u**	51

[a] Reaction conditions: (1) **1** (1.25 mmol), PPh_3 (1.25 mmol) in DCE (8 mL), N_2, 50 °C, 3−5 h; (2) Et_3N (2.5 mmol), **2** (2.5 mmol), N_2, –5 °C, 1 h, then rt, 0.5 h. [b] Isolated yields.

hazenes **3** with ketene[13] and a [2 + 2] cycloaddtion reaction of ketenimine **4** with ketene. Although the formation of **3** could take place at room temperature, the reaction required longer reaction time (5 h) and gave **5a** in lower yield (72%). Heating could shorten the first step reaction time and increase the yield. Under the optimum reaction conditions for the first step (50 °C, 4 h), we obtained **5a** in 76% yield (Table 1, entry 1).

With this result in hand, we went on to study the scope of the methodology. Using the optimized reaction conditions, a

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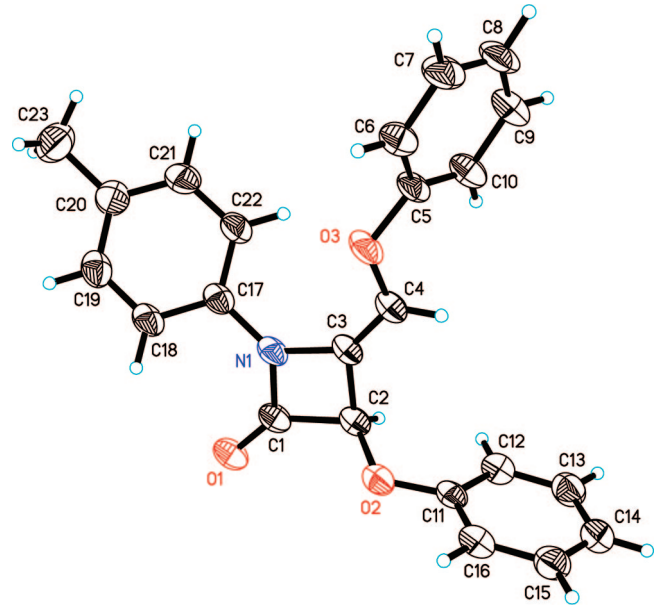
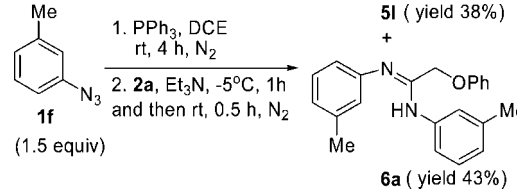


FIGURE 1. X-ray structure of compound **5b**.

SCHEME 2. Cascade Reaction Using Excess Azide 1f



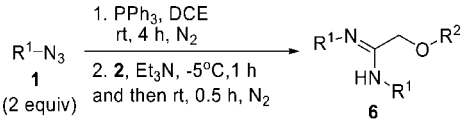
variety of aryl azides **1** and aryloxyacetyl chlorides **2** were investigated. As shown in Table 1, the electron-rich phenylazides (Table 1, entries 1−20) gave better yield than the electron-deficient phenyl azides (Table 1, entry 21). We also examined the strong electron-withdrawing group substituted phenyl azides such as 4-nitrophenyl azide, but did not isolate the desired product due to the poor reactivity of the phosphazene intermediate derived from 4-nitrophenyl azide. According to the mechanism of aza-Wittig reaction,[13] the electron-deficient phosphazenes are less reactive than the electron-rich phosphazenes.

It is noteworthy that only *Z*-isomers were obtained in all cases. The *Z* configuration of the C=C bond was established by the X-ray diffraction analysis of compounds **5b** (Figure 1) and **5m** (see the Supporting Information).

During screening of the reaction conditions, we surprisingly found that excess of azide **1f** resulted in a mixture of 4-alkylidene-β-lactam **5l** and amidine **6a** (Scheme 2). When 2 equiv of **1f** was used, the reaction only gave **6a** in 72% isolated yield. We examined the scope of amidine formation reaction with regard to the aryl azide (2 equiv) and the aryloxyacetyl chloride components. As shown in Table 2, both the electron-rich and the electron-deficient aryl azides gave good yields (70−85%).

Using two different azides to perform this reaction, we obtained the amidines bearing two different substituted groups at *N* and *N′* atoms. For example, when 1 equiv of azide **1m** was used as starting material at the first step and then 1 equiv of azide **1a** or **1i** was introduced at the second step of the reaction sequence, we obtained a mixture of amidine **7** and its tautomer **8** (Scheme 3).

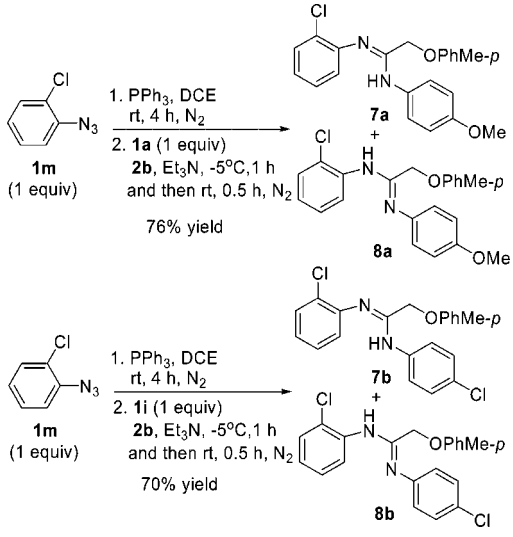
TABLE 2. Synthesis of Amidines 6 from Azides 1 and Acyl Chlorides 2[a]



entry	R^1	R^2	product	yield[b] (%)
1	**1f**	**2a**	**6a**	72
2	**1d**	**2d**	**6b**	80
3	**1d**	**2b**	**6c**	79
4	**1d**	**2c**	**6d**	75
5	**1f**	**2b**	**6e**	73
6	**1d**	**2a**	**6f**	70
7	**1f**	**2c**	**6g**	75
8	**1f**	**2d**	**6h**	81
9	4-ClC_6H_4 (**1i**)	**2a**	**6i**	77
10	3-ClC_6H_4 (**1k**)	**2c**	**6j**	85
11	3-BrC_6H_4 (**1j**)	**2c**	**6k**	72
12	4-BrC_6H_4 (**1l**)	**2c**	**6l**	82
13	2-ClC_6H_4 (**1m**)	**2c**	**6m**	81

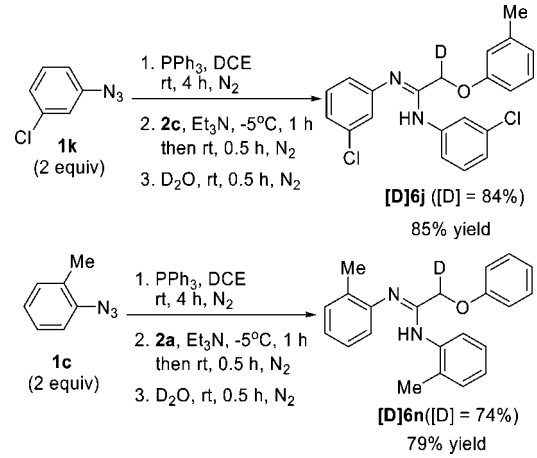
[a] Reaction conditions: (1) **1** (2.0 mmol), PPh_3 (1.0 mmol), DCE (8 mL), rt, 4 h, N_2; (2) Et_3N (1.0 mmol), **2** (1.0 mmol), −5 °C, 1 h, then rt, 0.5 h, N. [b] Isolated yields.

SCHEME 3. Synthesis of Amidines 7 and 8 from Two Kind of Azides[19a]

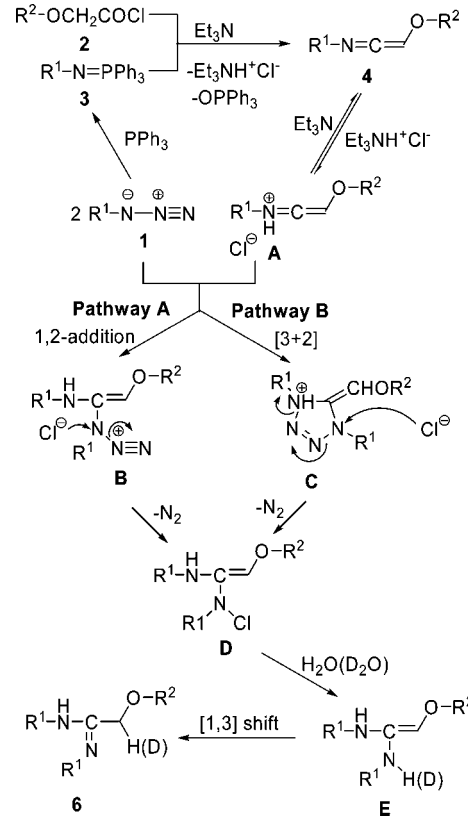


Amidines are important constituents of many biological active compounds[14] and highly useful in coordination chemistry and materials science.[15] In addition, amidines have long been regarded as useful intermediates in the synthesis of heterocyclic compounds.[16] Consequently, a number of synthetic methods have been developed for the preparation of amidines.[17] Most of these methods rely on the nucleophilic addition of amines or ammonia equivalents to nitriles under forcing conditions or to suitably activated carboxylate equivalents. As a complement to these methods, our one-pot tandem reaction provides a rapid procedure for the synthesis of *N*,*N*′-diarylamidines.

SCHEME 4. Synthesis of the Deuterated Amidines [D]6



SCHEME 5. Possible Mechanism for the Formation of Amidines 6



Having achieved an efficient process for the formation of *N*,*N*′-diarylamidines, we performed deuterium-labeling experiments to gain mechanistic insight into the reaction. When treating the mixture with D_2O or CD_3OD after the reaction completed, we obtained the deuterated amidines **[D]6j** and **[D]6n** (Scheme 4).

On the basis of the above results, the possible reaction mechanism is outlined as in Scheme 5. First, ketenimine **4** is formed cleanly by an aza-Wittig reaction of triphenylphosphazene **3** with ketene generated from phenoxyacetyl chloride.[13] Intermediate **4** is then protonated to form **A**. In the next cascade

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process, two possibilities remain. One is the intermolecular 1,2-addition of azide **1** to **A** to form intermediate **B**, followed by the nucleophilic attack of Cl^- and extrusion of molecular nitrogen (Scheme 4, pathway A). Another is the intermolecular [3 + 2] cycloaddition of azide **1** to **A** to form tetrazolium intermediate **C** and subsequent retro-[3 + 2] reaction with a concomitant attack of nucleophile Cl^- (Scheme 5, pathway B). The use of azido group as a nucleophile in the 1,2-addition reactions and as a 1,3-dipole in the [3 + 2] cycloaddition reactions have been reported previously.[17a,18,19] Thus, the possibility of neither pathway A nor pathway B can be excluded. The resulting chlorinating species **D** is scavenged with water during workup process to give **E**, which easily transforms into more stable amidine **6** by a [1,3] shift.

In conclusion, we have developed a ketenimine-participating tandem reaction, which furnished a simple and efficient one-pot synthesis of 4-alkyliden-β-lactams and *N*,*N*′-diarylamidines from azides and aryloxyacetyl chlorides. The chemical outcome of the reaction can be controlled selectively by an appropriate choice of the stoichiometric ratio of different substrates and reagents. The products will find their applications in pharmaceutical discovery, especially in the development of new antimicrobial agents against multidrug-resistant pathogens. Further investigations in the mechanism of the cascade process are currently underway.

Experimental Section

General Procedure for the Synthesis of 4-Alkyliden-β-lactams 5. The solution of aryl azide **1** (1.25 mmol) and triphenylphosphine (1.25 mmol) in DCE (8 mL) was stirred under nitrogen atmosphere at 50 °C for 3−4 h. After the mixture was cooled to −5 °C, Et_3N (2.5 mmol) was added. Then the solution of phenoxyacetyl chloride **2** (2.5 mmol) in DCE (5 mL) was added dropwise at −5 °C over 1 h. The reaction mixture was stirred at room temperature for 0.5 h. After removal of triethylamine hydrochloride by filtration, the filtrate was evaporated in vacuum. The crude product was purified by silica gel column chromatography using hexane−EtOAc (20:1) as eluant to afford pure β-lactam **5**.

Compound **5a**: colorless solid; mp 77–78 °C; IR (KBr) 1794, 1712, 1598, 1517, 1492, 1250, 1230, 1103 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 9.0 Hz, 2 H), 7.36–7.30 (m, 4 H), 7.16 (d, J = 8.0 Hz, 2 H), 7.08–7.05 (m, 2 H), 7.00 (d, J = 8.0 Hz, 2 H), 6.86 (d, J = 8.0 Hz, 2 H), 6.38 (s, 1 H), 5.77 (s, 1 H), 3.78 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 158.1, 157.4, 157.0, 130.0, 128.0, 124.1, 123.4, 123.3, 123.0, 119.8, 116.3, 116.0, 114.1, 81.9, 55.7; MS (ESI) *m*/*z* 374 (M + H); HRMS (ESI) *m*/*z* calcd for ($C_{23}H_{19}NO_4$ + Na) 396.1206, found 396.1209.

General Procedure for the Synthesis of *N*,*N*′-Diarylamidines 6. The solution of azide **1** (2.0 mmol) and triphenylphosphine (1.0 mmol) in DCE (8 mL) was stirred under nitrogen atmosphere at room temperature for 4 h. After the solution was cooled to −5 °C, Et_3N (1.0 mmol) was added. Then the solution of phenyloxyacetyl chloride **2** (1.0 mmol) in DCE (5 mL) was added dropwise at −5 °C over 1 h. The reaction mixture was stirred at room temperature for 0.5 h. The mixture was filtered to remove triethylamine hydrochloride, and the filtrate was evaporated in vacuum. The product was purified through a silica gel column using hexane−EtOAc (16:1).

Compound **6a**: colorless solid; mp 94–95 °C; IR (KBr) 3418, 1652, 1589, 1548, 1496, 1240 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2 H), 7.29–7.26 (m, 3 H), 7.20–7.17 (m, 2 H), 7.01–6.98 (m, 1 H), 6.89–6.84 (m, 4 H), 6.71–6.67 (m, 2 H), 4.64 (s, 2 H), 2.33 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 150.4, 149.2, 139.6, 139.2, 138.9, 130.0, 129.2, 128.9, 123.9, 123.6, 122.5, 122.0, 120.2, 118.2, 116.8, 115.2, 64.8, 21.8, 21.7; MS *m*/*z* 331 (M + H); HRMS *m*/*z* calcd for ($C_{22}H_{22}N_2O$ + H) 331.1805, found 331.1803.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 20672093) and the Natural Science Foundation of Zhejiang Province (R404109).

Supporting Information Available: Experimental procedures. Spectra data for other products. Copies of ^1H and ^{13}C NMR spectra for all products. X-ray structure details for compounds **5b** and **5m** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO702733H

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