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Aza-Baylis−Hillman Reactions of *N*-Tosylated Aldimines with Activated Allenes and Alkynes in the Presence of Various Lewis Base Promoters

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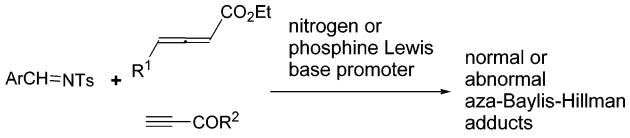
Received August 21, 2005



Ar = various aromatic groups or aliphatic group, R^1 = H, Me, R^2 = Me, OEt

The attempted aza-Baylis−Hillman reactions of *N*-tosylated aldimines with ethyl 2,3-butadienoate, ethyl penta-2,3-dienoate, penta-3,4-dien-2-one, methyl propiolate, and but-3-yn-2-one have been systematically investigated in the presence of various nitrogen or phosphine Lewis base promoters. We found that a series of nitrogen-containing heterocyclic compounds, as "abnormal" aza-Baylis−Hillman reaction products, can be formed in the presence of an appropriate Lewis base promoter. The Lewis base and solvent effects in these reactions have been discussed along with the corresponding plausible mechanism.

Introduction

Investigation of the Baylis−Hillman reaction has made great progress,[1] including development of a catalytic, asymmetric version,[2] since Baylis and Hillman first reported the reaction of acetaldehyde with ethyl acrylate and acrylonitrile in the presence of catalytic amounts of a strong Lewis base such as 1,4-diazabicyclo[2,2,2]octane (DABCO) in 1972.[3] During our ongoing investigations on the aza-Baylis−Hillman reaction of *N*-tosylated aldimines with a variety of α,*β*-unsaturated ketones or esters, we found that either normal or abnormal aza-Baylis−Hillman adducts could be formed depending on the employed Lewis base promoter under otherwise identical conditions.[4] For example, we previously reported in a short communication that aza-Baylis−Hillman reactions of *N*-tosylated aldimines with ethyl 2,3-butadienoate or penta-3,4-diene-2-one catalyzed by BABCO and *p*-(*N*,*N*-dimethyl)aminopyridine (DMAP) Lewis base promoters gave the corresponding normal aza-Baylis−Hillman adducts, azetidine and dihydropyridine derivatives in moderate to good yields.[4e] Therefore, to comprehensively understand aza-Baylis−Hillman reaction behavior between *N*-arylmethylidene-4-methylbenzenesulfonamides (ArCH=NTs, *N*-tosylated aldimines) and activated allenes and alkynes,[5] we intensely studied the aza-Baylis−Hillman reaction behavior of *N*-tosylated aldimines with

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(3) (a) Morita, K.; Suzuki, Z.; Hirose, H. *Bull. Chem. Soc. Jpn*. **1968**, *41*, 2815−2819. (b) Baylis, A. B.; Hillman, M. E. D. German Patent 2155113, 1972.

10.1021/jo051763d CCC: $30.25
Published on Web 10/20/2005

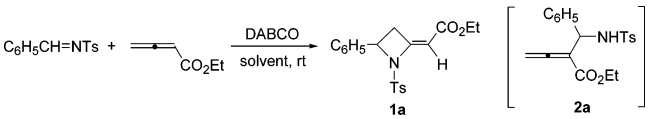
various activated allenes and alkynes, and found many unusual results. Herein, we wish to report the full details of the abnormal aza-Baylis−Hillman reaction behavior of *N*-tosylated aldimines with activated allenes and alkynes, including ethyl 2,3-butadienoate, ethyl penta-2,3-dienoate, penta-3,4-dien-2-one, methyl propiolate, and but-3-yn-2-one, in the presence of various Lewis base promoters. In this full paper, we have significantly extended the scope and the limitations of these aza-Baylis−Hillman reactions, and have comprehensively investigated the Lewis base and solvent effects in these reactions as well. Some unprecedented reaction patterns with the formation of a variety of nitrogen-containing heterocyclic compounds are disclosed in this paper.

Results and Discussion

Aza-Baylis−Hillman Reactions of *N*-Tosylated Aldimines with Ethyl 2,3-Butadienoate. First of all, we examined the reactions of *N*-tosylated aldimines (0.25 mmol) with ethyl 2,3-butadienoate (0.3 mmol) in the presence of a variety of nitrogen-containing Lewis base promoters in various solvents.[6,7] We found that DABCO (10 mol %) is an effective Lewis base promoter in this reaction, giving azetidine derivatives **1**, abnormal aza-Baylis−Hillman adducts, with *E* configuration under mild conditions. In addition, we ound that the employed solvent played a very important role in this reaction. The results when using *N*-benzylidene-4-methylbenzenesulfonamide as the substrate are summarized in Table 1. With *N*,*N*-dimethylformamide (DMF), CH_3CN, or CH_2Cl_2 (DCM) as a solvent, the corresponding azetidine product **1a** was produced in relatively lower yields with *E* configuration (Table 1, entries 2, 3, and 5). Using tetrahydrofuran (THF), Et_2O, C_6H_6, or acetone as a solvent, these reactions proceeded smoothly to produce **1a** in higher yields (Table 1, entries 1, 4, 6, and 7). However, when using benzene as a solvent in the presence of molecular sieve 4A (MS 4A; 100 mg),[8] **1a** can be obtained exclusively in 82% yield with *E* configuration (Table 1, entry 6). Therefore, benzene is the best solvent in this reaction. Interestingly, when using benzene as a solvent in the absence of MS 4A, **1a** was formed in 57% yield with *E* configuration along with the formation ofnormal aza-Baylis−Hillman adduct 5-phenyl-5-(toluene-4-sulfonylamino) penta-2,3-dienoic acid ethyl ester **2a** in 41% yield (Table 2, entry 6). The structure of **2a** was determined by spectroscopic data, microanalyses, and X-ray diffraction. The ORTEP drawing of **2a** is shown in the Supporting Information.[9] Although the exact role of the MS 4A additive is not yet clear in this reaction, we believe that traces of ambient water in the reaction system can assist proton transfer in the Baylis−Hillman reaction, which has recently been recognized as a rate-determining step. This observation will be discussed in a mechanistic survey.

We next carefully examined reactions of other *N*-tosylated aldimines (0.25 mmol) with ethyl 2,3-butadienoate (0.3 mmol) catalyzed by DABCO (10 mol %) in the absence of MS 4A in benzene, and found that the corresponding 4-aryl-1-(toluene-4-sulfonyl)azetidin-2-ylidene]acetic acid ethyl esters **1** were produced in moderate to good yields with *E* configuration in most

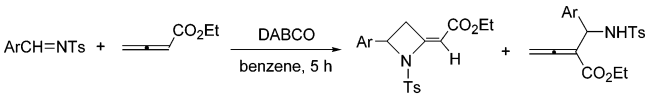
TABLE 1. Solvent Effects in the Aza-Baylis−Hillman Reaction of *N*-Tosylated Aldimine with Ethyl 2,3-Butadienoate Catalyzed by DABCO in the Absence of MS 4A



entry	solvent	yield[a] of **1a** (%)
1	THF	56
2	DMF	27
3	MeCN	25
4	Et_2O	42
5	CH_2Cl_2	28
6	C_6H_6	57[b] (82)[c]
7	$Me_2C{=}O$	54

[a] Isolated yield. [b] In the absence of MS 4A, **2a** was formed in 41% yield. [c] In the presence of MS 4A.

TABLE 2. Aza-Baylis−Hillman Reaction of Various *N*-Tosylated Aldimines with Ethyl 2,3-Butadienoate Catalyzed by DABCO in Benzene in the Absence of MS 4A



		yield[a] (%)	
entry	Ar	**1**	**2**
1	C_6H_5	**1a**, 57	**2a**, 41
2	*p*-MeC_6H_4	**1b**, 64	**2b**, 11
3	*p*-$MeOC_6H_4$	**1c**, 45	**2c**, 14
4	*p*-FC_6H_4	**1d**, 58	**2d**, 13
5	*m*-FC_6H_4	**1e**, 49	**2e**, 13
6	*p*-ClC_6H_4	**1f**, 61	**2f**, 10
7	*p*-BrC_6H_4	**1g**, 69	**2g**, 8

[a] Isolated yields.

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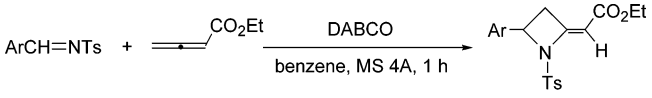
(5) Using triphenylphosphine or tributylphosphine as a Lewis base in the reaction of allenoates with *N*-tosylated aldimines generates a [3+2] cycloaddition to give five-membered pyrrolidine derivatives. (a) Xu, Z.; Lu, X. *Tetrahedron Lett*. **1997**, *38*, 3461−3464. (b) Xu, Z.; Lu, X. *J. Org. Chem.* **1998**, *63*, 5031−5041. (c) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535−544. (d) Du, Y.; Lu, X.; Yu, Y. *J. Org. Chem.* **2002**, *67*, 8901−8905. (e) Zhang, C.; Lu, X. *J. Org. Chem.* **1995**, *60*, 2906−2908. (f) Methot, J. L.; Roush, W. R. *Adv. Synth. Catal.* **2004**, *346*, 1035−1050.

(6) Reaction of 2-methyl-2,3-butadienoate with *N*-tosylated aldimines catalyzed by tributylphosphine gave six-membered tetrahydropyridines in high yields: (a) Zhu, X.-F.; Lah, J.; Kwon, O. *J. Am. Chem. Soc*. **2003**, *125*, 4716−4717. (b) Zhu, X.-F.; Henry, C. E.; Wang, J.; Dudding, T.; Kwon, O. *Org. Lett.* **2005**, *7*, 1387−1390. (c) Zhu, X.-F.; Henry, C. E.; Wang, J.; Dudding, T.; Kwon, O. *Org. Lett.* **2005**, *7*, 2977−2980. (d) Shi, Y.-L.; Shi, M. *Org. Lett.* **2005**, *7*, 3057−3060.

(7) Baylis−Hillman reaction of aldehydes with ethyl 2,3-butadienoate and penta-3,4-dien-2-one in the presence of DABCO gave the corresponding normal Baylis−Hillman adduct. See: Tsuboi, S.; Kuroda, H.; Takatsuka, S.; Fukawa, T.; Sakai, T.; Utaka, M. *J. Org. Chem*. **1993**, *58*, 5952−5957.

(8) MS 4A was used to eliminate ambient water or moisture in order to improve the isolated yields because the employed *N*-tosylated aldimines can decompose to the corresponding aldehydes and N-tosylated amines by ambient water or moisture during a prolonged reaction time (Table 1, entries 1 and 2). However, MS 4A may also have some other effects on this reaction. This will be discussed in a mechanistic survey.

TABLE 3. Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimines with Ethyl 2,3-Butadienoate Catalyzed by DABCO in Benzene in the Presence of MS 4A



1

entry	Ar	yield[a] of **1** (%)
1	C_6H_5	**1a**, 82
2	*p*-MeC_6H_4	**1b**, 92
3	*p*-EtC_6H_4	**1c**, 90
4	*p*-$MeOC_6H_4$[b]	**1d**, 75
5	*p*-FC_6H_4	**1e**, 93
6	*m*-FC_6H_4	**1f**, 76
7	*p*-ClC_6H_4	**1g**, 92
8	*p*-BrC_6H_4	**1h**, 99
9	*o*,*m*-$Cl_2C_6H_3$	**1i**, 99
10	*p*-$CF_3C_6H_4$	**1j**, 85
11	*m*-$NO_2C_6H_4$	**1k**, 87
12	1-naphthyl	**1l**, 99
13	3-pyridyl	**1m**, 42

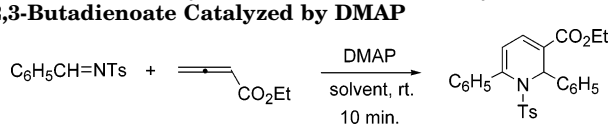
[a] Isolated yield. [b] The reaction was carried out at room temperature for 3 h.

cases along with 5-aryl-5-(toluene-4-sulfonylamino) penta-2,3-dienoic acid ethyl esters **2**. The results are summarized in Table 2.

Moreover, we also carried out the aza-Baylis–Hillman reactions of other *N*-tosylated aldimines (0.25 mmol) with ethyl 2,3-butadienoate (0.3 mmol) in the presence of DABCO (10 mol %) and MS 4A (100 mg) in benzene. The corresponding 4-aryl-1-(toluene-4-sulfonyl)azetidin-2-ylidene]acetic acid ethyl esters **1** were produced exclusively in good to high yields within 1 h with *E* configuration in most cases (Table 3, entries 1–13). In some cases, the reactions proceeded smoothly to furnish products **1** quantitatively (Table 3, entries 8, 9, and 12). Only for *N*-(*p*-methoxybenzylidene)-4-methylbenzenesulfonamide is a prolonged reaction time (3 h) required (Table 3, entry 4).

Other nitrogen Lewis bases such as 1,8-diazabicyclo-[5,4,0]-7-undecene (DBU) and triethylamine (Et_3N) showed no catalytic activities for this reaction. However, using *p*-(*N*,*N*-dimethylamino)pyridine (DMAP) as a Lewis base promoter in the aza-Baylis–Hillman reaction of *N*-benzylidene-4-methylbenzenesulfonamide with ethyl 2,3-butadienoate, we found that the reaction proceeded quickly to produce 2,6-diphenyl-1-(toluene-4-sulfonyl)-1,2-dihydropyridine-3-carboxylic acid ester **3a** in moderate yield within 10 min. The solvent effects have also been examined using DMAP as a Lewis base promoter. The results are summarized in Table 4. In dichloromethane, the adduct **3a** was produced in 60% yield, which is the solvent of choice (Table 4, entry 3).

TABLE 4. Solvent Effect in the Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimines with Ethyl 2,3-Butadienoate Catalyzed by DMAP



3a

entry	solvent	yield[a] of **3a** (%)
1	THF	40
2	C_6H_6	40
3	CH_2Cl_2	60
4	DMF	20
5	MeCN	38
6	Et_2O	23

[a] Isolated yield.

TABLE 5. Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimines with Ethyl 2,3-Butadienoate Catalyzed by DMAP

3

entry	Ar	yield[a] of **3** (%)
1	C_6H_5	**3a**, 60
2	*p*-MeC_6H_4	**3b**, 44
3	*p*-$MeOC_6H_4$	**3c**, 30
4	*p*-FC_6H_4	**3d**, 36
5	*m*-FC_6H_4	**3e**, 41
6	*p*-ClC_6H_4	**3f**, 49
7	*p*-BrC_6H_4	**3g**, 34
8	*p*-$CF_3C_6H_4$	**3h**, 45
9	*m*-$NO_2C_6H_4$	**3i**, 31

[a] Isolated yield.

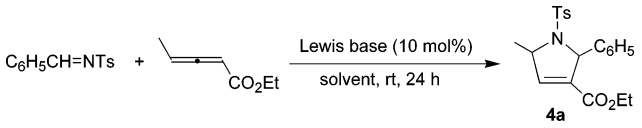
For the reactions of other *N*-tosylated aldimines (0.25 mmol) with ethyl 2,3-butadienoate (0.3 mmol) in the presence of DMAP (10 mol %) under these optimized conditions, the products **3** were obtained in moderate yields in most cases (Table 5, entries 1–9). Their structures were determined by spectroscopic data, microanalyses, and X-ray diffraction. The ORTEP drawing of **3a** is shown in the Supporting Information.[9]

Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimines with Ethyl Penta-2,3-dienoate. Because Kwon and co-workers recently reported that the reactions of 2-methyl-2,3-butadienoate with *N*-tosylated aldimines catalyzed by tributylphosphine (PBu_3) gave six-membered tetrahydropyridines in high yields,[6] we decided to examine the aza-Baylis–Hillman reaction of *N*-tosylated aldimines with ethyl penta-2,3-dienoate in the presence of a variety of Lewis base promoters in order to understand this type of reaction comprehensively.

For the aza-Baylis–Hillman reactions of *N*-tosylated aldimines with ethyl penta-2,3-dienoate, we first system-

(9) The crystal data of **2a** have been deposited in CCDC as entry 266291. Empirical formula: $C_{20}H_{21}NO_4S$. Formula weight: 371.44. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.492 × 0.403 × 0.357 mm. Crystal system: monoclinic. Lattice type: primitive. Lattice parameters: a = 11.0446(10) Å, b = 12.4582(12) Å, c = 14.1435(13) Å, α = 90°, β = 91.214(2)°, γ = 90°, V = 1945.6(3) Å^3. Space group: $P2(1)/n$. Z = 4, D_{calc} = 1.268 g/cm^3, F_{000} = 784. Diffractometer: Rigaku AFC7R. Residuals: R, R_w = 0.0442, 0.1055. The crystal data of **3a** have been deposited in CCDC as entry 211894. Empirical formula: $C_{27}H_{25}NO_4S$. Formula weight: 459.54. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.468 × 0.375 × 0.245 mm. Crystal system: triclinic. Lattice type: primitive. Lattice parameters: a = 7.6675(8) Å, b = 13.8140(15) Å, c = 22.914(3) Å, α = 92.491(2)°, β = 93.885(2)°, γ = 98.992(2)°, V = 2388.1(4) Å^3. Space group: P-1. Z = 4, D_{calc} = 1.278 g/cm^3, F_{000} = 968. Diffractometer: Rigaku AFC7R. Residuals: R, R_w = 0.0605, 0.1271. The crystal data of **4j** have been deposited in CCDC as entry 235749. Empirical formula: $C_{21}H_{22}N_2O_6S$. Formula weight: 430.47. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.368 × 0.327 × 0.163 mm. Crystal system: monoclinic. Lattice type: primitive. Lattice parameters: a = 20.5357(16) Å, b = 11.4427(9) Å, c = 20.5964(15) Å, α = 90°, β = 117.564(2)°, γ = 90°, V = 4290.5(6) Å^3. Space group: $P2(1)/n$. Z = 8, D_{calc} = 1.333 g/cm^3, F_{000} = 1808. Diffractometer: Rigaku AFC7R. Residuals: R, R_w = 0.0632, 0.1559.

TABLE 6. Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimine with Ethyl Penta-2,3-dienoate in the Presence of Various Lewis Base Promoters and Solvents



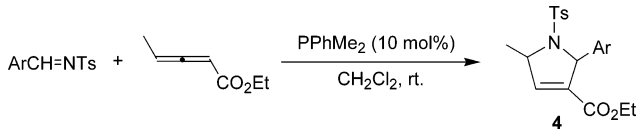
entry	Lewis base	solvent	yield[a] of **4a** (%) (syn:anti)
1	DABCO	CH_3CN	trace
2	DABCO	DMF	trace
3	DABCO	THF	trace
4	DABCO	CH_2Cl_2	trace
5	DMAP	THF	trace
6	PPh_3	THF	trace
7	PPh_2Me	THF	24 (10:1)
8	$PPhMe_2$	THF	79 (13:1)
9	$PPhMe_2$	CH_2Cl_2	95 (13:1)
10	$PPhMe_2$	CH_3CN	31 (>30:1)
11	$PPhMe_2$	DMF	22 (20:1)
12	$PPhMe_2$	DMSO	disordered
13	PBu_3	THF	15 (8:1)
14	PBu_3	CH_2Cl_2	trace
15	PBu_3	DMF	trace
16	PBu_3	DMF[b]	disordered
17	PBu_3	DMSO[b]	disordered
18	PMe_3	THF	12 (14:1)

[a] Isolated yields. [b] The reaction was carried out at 100 °C.

atically examined the Lewis base and solvent effects in this reaction. We found that the Lewis base and solvent played very important roles in this reaction. The results are summarized in Table 6. Using DABCO, DMAP, or PPh_3 as a Lewis base promoter, no reaction occurred (Table 6, entries 1–6). Using PPh_2Me as a Lewis base promoter, this reaction was sluggish, and gave the corresponding [3+2] cycloaddition product **4a** in 24% yield after 24 h in THF as mixtures of syn and anti isomers, in which the major isomer was obtained in the syn configuration (Table 6, entry 7). However, we were pleased to find that using a more-nucleophilic phosphine Lewis base promoter $PPhMe_2$ in THF, the reaction proceeded smoothly to give the product **4a** in 79% yield after 24 h (Table 6, entry 8). The solvent effects were then carefully examined using $PPhMe_2$ as a Lewis base promoter (Table 6, entries 8–12). The best result was obtained in dichloromethane, in which **4a** was obtained in 95% yield after 24 h as a diastereomeric syn:anti ratio of 13:1 (Table 6, entry 9). Using PBu_3 as a phosphine Lewis base promoter, **4a** was formed in 15% yield in THF and in trace amounts in DMF and dichloromethane (Table 6, entries 13–15). In addition, this reaction became disordered in DMF or DMSO upon heating at 100 °C with PBu_3 as a phosphine Lewis base promoter (Table 6, entries 16 and 17). Using PMe_3 (1.0 M in THF) as a phosphine Lewis base promoter, **4a** was obtained in 12% yield under identical conditions (Table 6, entry 17). Therefore, it seems to us that the best reaction conditions are to carry out this reaction in dichloromethane with $PPhMe_2$ as a Lewis base promoter at room temperature.

Under these optimized reaction conditions, we next examined the aza-Baylis–Hillman reaction of other *N*-tosylated aldimines with ethyl penta-2,3-dienoate. The results are summarized in Table 7. For *N*-tosylated aldimines having an electron-withdrawing group on the aromatic ring, the corresponding [3+2] cyclized

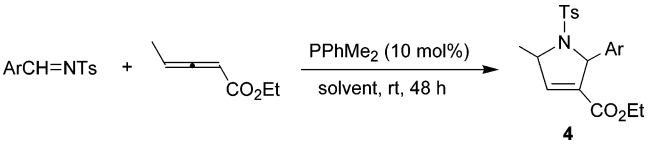
TABLE 7. Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimines with Ethyl Penta-2,3-dienoate in the Presence of $PPhMe_2$ in CH_2Cl_2



entry	Ar	time[b] (h)	yield[a] of **4** (%) (syn:anti)
1	C_6H_5	24	**4a**, 95 (13:1)
2	*p*-MeC_6H_4	24	**4b**, 28 (18:1)
3	*p*-EtC_6H_4	48	**4c**, 47 (13:1)
4	*p*-$MeOC_6H_4$	48	**4d**, 31 (15:1)
5	*p*-$Me_2NC_6H_4$	48	**4e**, 28 (>30:1)
6	*p*-FC_6H_4	3	**4f**, 77 (8:1)
7	*p*-ClC_6H_4	6	**4g**, 72 (16:1)
8	*p*-BrC_6H_4	3	**4h**, 77 (10:1)
9	*m*-$NO_2C_6H_4$	1.5	**4i**, 78 (25:1)
10	*p*-$NO_2C_6H_4$	3	**4j**, 84 (16:1)
11	3-pyridyl	6	**4k**, 38 (24:1)
12	*o,m*-$Cl_2C_6H_3$	6	**4l**, 44 (12:1)

[a] Isolated yields. [b] Reaction time to consume all of the starting materials.

TABLE 8. Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimines Having an Electron-Donating Methyl Group on the Phenyl Ring with Ethyl Penta-2,3-dienoate in the Presence of $PPhMe_2$



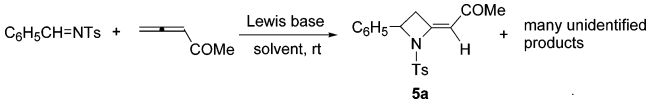
entry	Ar	solvent	yield[a] of **4** (%)
1	*p*-MeC_6H_4	CH_3CN	**4b**, 20
2	*p*-MeC_6H_4	DMF	**4b**, 25
3	*p*-MeC_6H_4	THF	**4b**, 69
4	*p*-EtC_6H_4	THF	**4c**, 76
5	*p*-$MeOC_6H_4$	THF	**4d**, 71
6	*p*-$Me_2NC_6H_4$	THF	**4e**, 57

[a] Isolated yields.

product **4** was obtained in moderate to good yield within a short reaction time as mixtures of syn and anti isomers, in which the major products were obtained in the syn configuration (Table 7, entries 6–12). For *N*-tosylated aldimines having an electron-donating group on the aromatic ring, the products were still produced in lower yields as mixtures of syn and anti isomers under identical conditions (Table 7, entries 2–5). Therefore, we reexamined the solvent effects in this reaction, using the *N*-tosylated aldimine having an electron-donating methyl group on the aromatic ring as a substrate. The results are summarized in Table 8. In THF, the yield of the corresponding cyclized product **4b** can be improved to 69% at room temperature (Table 8, entries 1–3). Under these revised optimized conditions, the corresponding aza-Baylis–Hillman adducts **4b–e**, having an electron-donating group on the aromatic ring, were obtained in 57–76% yields in THF after 48 h (Table 8, entries 3–6).

Their structures were determined by NMR spectroscopic data, microanalyses, and X-ray crystal structure diffraction. The ORTEP drawing of the major product **4j**

TABLE 9. Solvent and Lewis Base Effects in the Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimine with Penta-3,4-dien-2-one Catalyzed by Nitrogen-Containing Lewis Base Promoters



5a

entry	Lewis base	solvent	yield[a] of **5a** (%)
1	DABCO	THF	25
2	DABCO	MeCN	15
3	DABCO	DMF	15
4	DABCO	C_6H_6	16
5	DABCO	CH_2Cl_2	43
6	DABCO	Et_2O	33
7	DABCO	EtOAc	25
8	DMAP	CH_2Cl_2	trace
9	DBU	CH_2Cl_2	trace
10	Et_3N	CH_2Cl_2	trace

[a] Isolated yield.

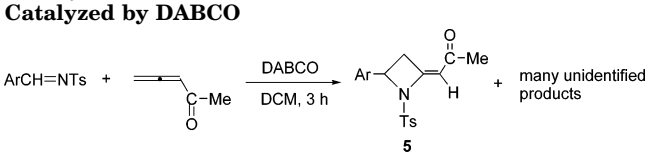
with syn configuration is shown in the Supporting Information.[9]

Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimines with Penta-3,4-dien-2-one. Using penta-3,4-dien-2-one as a substrate, we found that the same reaction can also take place to give the corresponding azetidine derivatives under the similar conditions. The nitrogen-containing Lewis base promoters and solvents for this reaction were systematically examined in order to seek out these optimized reaction conditions. The results are summarized in Table 9. We found that only DABCO can catalyze this reaction to give the corresponding abnormal aza-Baylis–Hillman adduct **5a** in low to moderate yields with *E* configuration along with many unidentified products (Table 9, entries 1–7).[10] With other nitrogen Lewis base promoters, such as DMAP, DBU, or Et_3N, only trace amounts of the corresponding product **5a** can be formed (Table 9, entries 8–10). Using DABCO as the Lewis base promoter, we obtained the best result in 43% yield in CH_2Cl_2 at room temperature (Table 9, entry 5).

Subsequently, the aza-Baylis–Hillman reaction of other *N*-tosylated aldimines with penta-3,4-dien-2-one was carried out under these optimized conditions, and the corresponding 1-[4-aryl-1-(toluene-4-sulfonyl)azetidin-2-ylidene]propan-2-ones **5** were obtained as the major products in moderate yields with *E* configuration, along with many unidentified products. The results are listed in Table 10 (entries 1–10). Their structures were determined by NMR spectroscopic data, microanalyses, and X-ray diffraction. The ORTEP drawing of **5d** is shown in the Supporting Information.[11]

Mechanistic Survey. The mechanism of these unprecedented abnormal aza-Baylis–Hillman reactions has not been unequivocally established, but a plausible explanation is proposed in Schemes 1–3 on the basis of previous investigations.[1,5–7] The nitrogen-containing Lewis base promoters DABCO and DMAP act as nucleophilic triggers, and produce the intermediate **A-1**, which exists as a resonance-stabilized zwitterionic intermediate **A-1** (enolate) or **B-1** (allylic carbanion). In the case of DABCO,

TABLE 10. Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimines with Penta-3,4-dien-2-one Catalyzed by DABCO



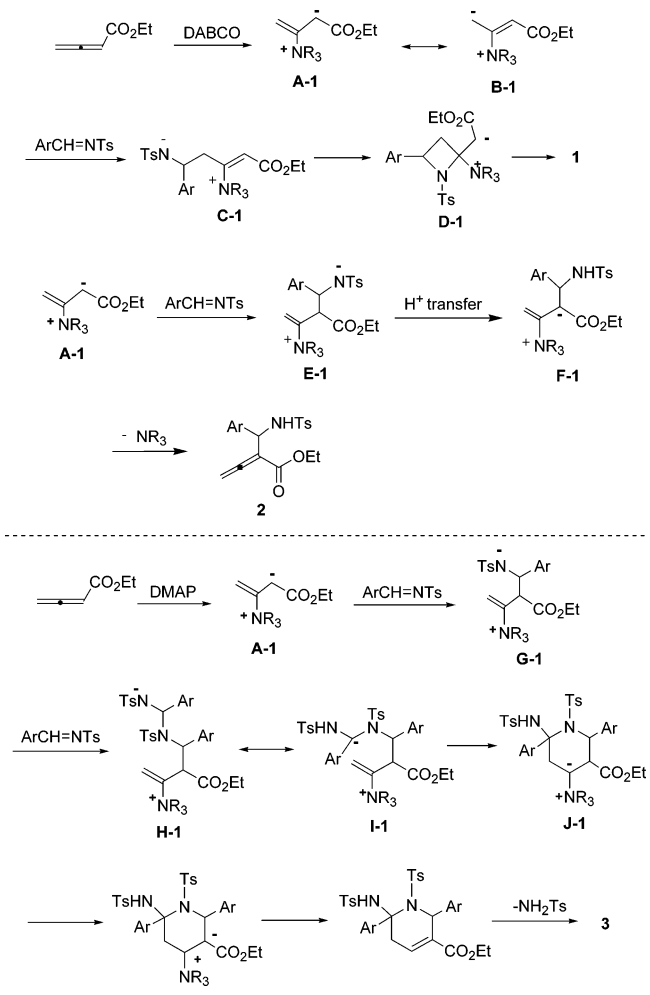
5

entry	Ar	yield[a] of **5** (%)
1	C_6H_5	**5a**, 43
2	*p*-MeC_6H_4	**5b**, 38
3	*p*-$MeOC_6H_4$	**5c**, 35
4	*p*-FC_6H_4	**5d**, 34
5	*m*-FC_6H_4	**5e**, 32
6	*p*-ClC_6H_4	**5f**, 39
7	*p*-BrC_6H_4	**5g**, 40
8	*m*-$NO_2C_6H_4$	**5h**, 32
9	*o,m*-$Cl_2C_6H_3$	**5i**, 31
10	1-naphthyl	**5j**, 55

[a] Isolated yield.

SCHEME 1. Plausible Mechanism for This Abnormal Aza-Baylis–Hillman Reaction

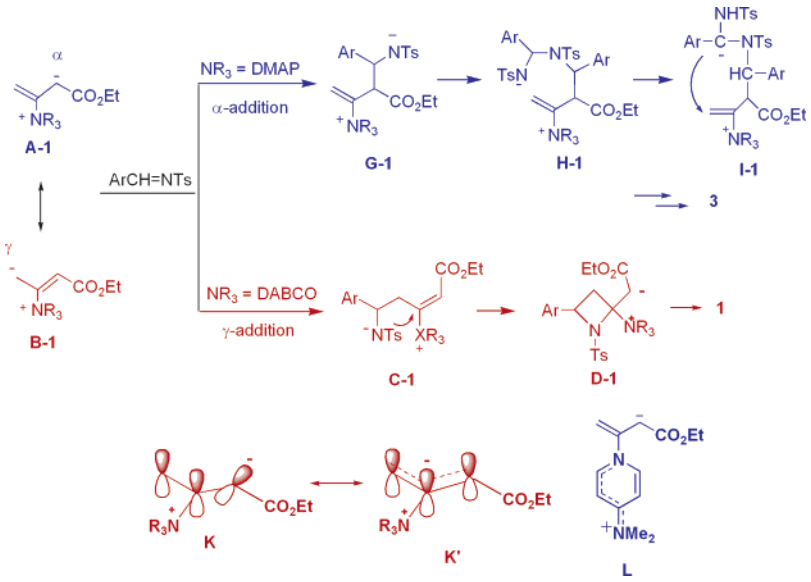
Scheme 1. A plausible mechanism for this abnormal aza-Baylis-Hillman reaction.



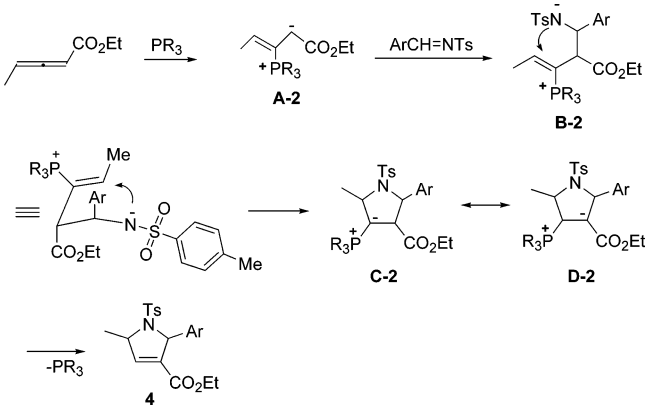
(10) On TLC plates, many spots were recognized, and the major spot is the product **5a**.

(11) The crystal data of **5d** have been deposited in CCDC as entry 211895. Empirical formula: $C_{19}H_{18}NO_3FS$. Formula weight: 359.40. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.478 × 0.237 × 0.226 mm. Crystal system: monoclinic. Lattice type: primitive. Lattice parameters: $a = 6.3576(9)$ Å, $b = 8.9534(13)$ Å, $c = 31.589(5)$ Å, $\alpha = 90°$, $\beta = 91.829(3)°$, $\gamma = 90°$, $V = 1797.2(4)$ Å^3. Space group: $P2(1)/n$. $Z = 4$, $D_{calc} = 1.328$ g/cm^3, $F_{000} = 752$. Diffractometer: Rigaku AFC7R. Residuals: R, $R_w = 0.0568$, 0.1278.

SCHEME 2. Explanation of the Different Reactivities with DABCO and DMAP



SCHEME 3. Plausible Mechanism for This Abnormal Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimine with Ethyl Penta-2,3-dienoate in the Presence of $PPhMe_2$



the allylic carbanion **B-1** adds to the *N*-tosylated aldimine to give intermediate **C-1**, which undergoes an intramolecular nucleophilic attack (Michael addition type) to give another zwitterionic intermediate **D-1**. The trans elimination (*E*2 type) of NR_3 from **D-1** affords product **1**, and regenerates DABCO. When the zwitterionic intermediate **A-1** directly reacts with *N*-tosylated aldimine to give the zwitterionic intermediate **E-1**, the corresponding normal aza-Baylis–Hillman reaction intermediate **F-1** is formed after proton transfer, which undergoes the elimination of NR_3 to afford the corresponding product **2**. Recently, on the basis of kinetic isotope effect studies, it has been proven that the proton-transfer process of intermediate **E-1** to **F-1** in the Baylis–Hillman reaction is a rate-determining step.[12] Therefore, the presence of trace amounts of ambient water in the reaction system can accelerate this process for producing the aza-Baylis–Hillman product because of the existence of a proton source. However, in the presence of MS 4A, the ambient moisture is removed. In addition, it is conceivable that MS 4A can coordinatively absorb the proton source by the Brønsted acid site to disturb the proton-transfer process in the Baylis–Hillman reaction,[13] although we do not have concrete evidence at present. Therefore, in the presence of MS 4A, the corresponding abnormal aza-Baylis–Hillman products **1** are produced exclusively.

However, in the case of DMAP,[14] the enolate **A-1** adds to the *N*-tosylated aldimine to afford intermediate **G-1**, which adds to another *N*-tosylated aldimine to give intermediate **H-1**. The proton transfer produces the corresponding intermediate **I-1**, and the subsequent intramolecular Michael addition gives intermediate **J-1**. Proton shift and NHTs elimination furnish product **3** and regenerate DMAP to accomplish the catalytic cycle.[15]

The different reactivity by DABCO and DMAP is outlined in Scheme 2. The π orbitals of the two carbon–carbon double bonds in allenes are perpendicular to each other. In the initially formed intermediate **A-1**, the orbital of the unshared electron pair is also perpendicular to the π orbital of the α,β-carbon–carbon double bond (orbital structure **K**). After a 90° rotation around the α,β-carbon–carbon bond, the delocalized structure **K′** is generated. When DMAP was used as a Lewis base promoter, the initially generated corresponding zwitterionic intermediate **A-1** is stabilized by the pyridyl aromatic system as the intermediate **L** shown in Scheme 2. Therefore, it can have enough time to react with *N*-tosylated aldimine via

(12) (a) Price, K. E.; Broadwater, S. J.; Jung, H. M.; McQuade, D. T. *Org. Lett.* **2005**, *7*, 147–150. (b) Aggarwal, V. K.; Fulford, S. Y.; Lloyd-Jones, G. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 1706–1708. (c) Price, K. E.; Broadwater, S. J.; Walker, B. J.; McQuade, D. T. *J. Org. Chem.* **2005**, *70*, 3980–3987.

(13) (a) Anderson, M. W.; Klinowski, J.; Barrie, P. J. *J. Phys. Chem.* **1991**, *95*, 235–239. (b) Weglarski, J.; Datka, J.; He, H.; Klinowski, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 5161–5164. (c) Chen, T.-H.; Wouters, B. H.; Grobet, P. J. *J. Phys. Chem. B* **1999**, *103*, 6179–6184.

(14) We believe that the nitrogen Lewis bases DABCO and DMAP should have different catalytic abilities in the Baylis–Hillman reaction as Lewis base promoters because they have different nucleophilicities and basicities. At present, we cannot give a clear-cut explanation of this interesting Lewis base effect, although a mechanistic explanation has been given in Scheme 2.

(15) Reaction of methylallene with *N*-tosylated aldimines gives alkylideneazetidines in 3% yield at 130 °C. See: Baumann, H.; Duthaler, R. O. *Helv. Chim. Acta* **1988**, *71*, 1025–1034. The reaction of ketenes with aldimines gives azetidinones and 2:1 adducts. See: Mukerjee, A. K.; Srivastava, R. C. *Synthesis* **1973**, 327–346.

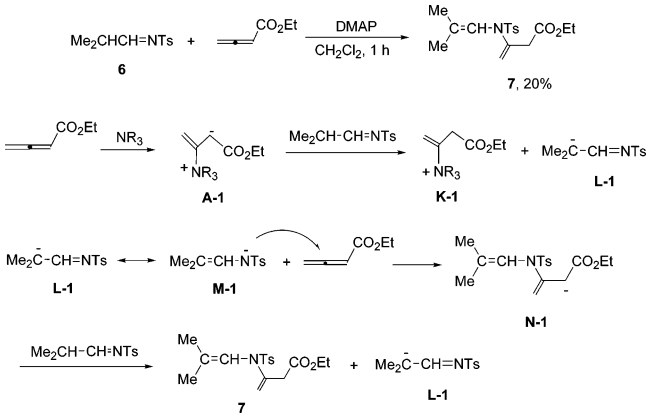
the α-addition pathway to afford the intermediate **G-1** and so on, and as a consequence, a kinetically controlled product **3** was formed. When DABCO was used as a Lewis base promoter, the initially generated corresponding zwitterionic intermediate **A-1** is immediately transformed to the delocalized structure **K′**, which should be the corresponding stabilized structure. The zwitterionic intermediate **B-1** is subsequently generated via **K′**, which more easily reacts with *N*-tosylated aldimine via the γ-addition pathway to afford intermediate **C-1** and so on, and as a consequence, a thermodynamically controlled product was formed (Scheme 2).

On the other hand, the reaction mechanism using tertiary phosphine as a Lewis base in the reaction of allenoates with *N*-tosylated aldimines to generate the corresponding [3+2] cycloaddition products, a series of five-membered pyrrolidine derivatives, has been well discussed.[5] On the basis of these reports, a plausible reaction mechanism is outlined in Scheme 3. The phosphine Lewis base promoter $PPhMe_2$ acts as a nucleophilic trigger to produce the corresponding zwitterionic enolate **A-2**, which reacts with *N*-tosylated aldimine to afford intermediate **B-2**. This species may then undergo an intramolecular cycloaddition to deliver the phosphonium ylide **C-2**. The facile 1,2-proton transfer and elimination of the tertiary phosphine yield the [3+2] cycloaddition product **4** via intermediate **D-2**, and regenerate the catalyst. This mechanism, as proposed by others,[16] benefits from the ability of phosphorus to stabilize the ylide-like structure **C-2**. In contrast, the amine-catalyzed (DABCO or DMAP) pathway does not benefit from similar stabilization. Therefore, the similar reactions produce different products in the presence of phosphine and nitrogen-containing Lewis base promoters. Moreover, in the cyclization reaction from intermediate **B-2** to **C-2**, the nitrogen anion (TsN^-) attacks the double bond from the backside of a methyl group, because of the steric hindrance between the tosyl and methyl groups, to give the corresponding product **4** mainly in syn configuration.

Moreover, many aliphatic *N*-tosylated aldimines are, in general, labile. We synthesized a relatively stable aliphatic *N*-tosylated aldimine **6** according to the literature,[17] and used it in this reaction catalyzed by DMAP. However, we found that the corresponding 3-[(2-methylpropenyl)(toluene-4-sulfonyl)amino] but-3-enoic acid ethyl ester **7** was produced in this reaction in 20% yield. A plausible reaction is shown in Scheme 4.) The allylic H of **6** is abstracted by intermediate **A-1** to give the corresponding intermediates **K-1** and **L-1**. The intermediate **L-1** can produce another more stable anion, **M-1**. The reaction between intermediate **M-1** and ethyl 2,3-butadienoate furnishes intermediate **N-1**, which subsequently produces the corresponding product **7** from the reaction with **6**, and regenerates the species **L-1**. Therefore, using aliphatic *N*-tosylated aldimines as substrates, this aza-Baylis−Hillman reaction proceeds in a different reaction route.

Aza-Baylis−Hillman Reactions of *N*-Tosylated Aldimines with Methyl Propiolate. We next examined the aza-Baylis−Hillman reaction of *N*-tosylated aldimines with methyl propiolate in the presence of various Lewis base promoters and in various solvents. The results are summarized in Table 11. When PPh_3 was used as the Lewis base promoter in MeCN or in other solvents, no reaction occurred (Table 11, entry 1). By using of DABCO as a nitrogen Lewis base promoter in benzene under reflux, we produced product **10** as the sole product in 10% yield (Table 11, entry 2). In DMF, THF, or dichloromethane, two other products **8** and **9** were produced at the same time in totally moderate yields, without the formation of **10** (Table 11, entries 3−5). Their structures were determined by NMR spectroscopic data, microanalyses, and X-ray diffraction. The ORTEP drawings of **8**, **9**, and **10** are shown in the Supporting Information.[18] Because the yields of products **8**, **9**, and **10** are only moderate, we did not further examine this type of aza-Baylis−Hillman reaction with other *N*-tosylated imines. Plausible mechanistic explanations for these unprecedented abnormal aza-Baylis−Hillman reactions are proposed in Schemes 5, 6, and 8.

SCHEME 4. Aza-Baylis−Hillman Reaction of Aliphatic *N*-Tosylated Aldimine 6 with Ethyl 2,3-butadienoate in the Presence of DMAP



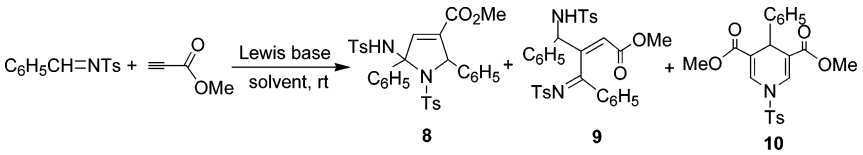
For the formation of **8**, the nitrogen Lewis base promoter DABCO acts as a nucleophilic trigger to produce the enolate intermediate **A-3**, which adds to the *N*-tosylated aldimine to give intermediate **B-3**. The intermediate **B-3** adds to another molecule of *N*-tosylated aldimine to give intermediate **C-3**. The proton transfer

(16) Evans, C. A.; Miller, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 12394−12395.

(17) Chemla, F.; Hebbe, V.; Normant, J. F. *Synthesis* **2000**, 75−77.

(18) The crystal data of **8** have been deposited in CCDC as entry 216649. Empirical formula: $C_{35}H_{36}N_2O_7S_2$. Formula weight: 660.78. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.439 × 0.262 × 0.206 mm. Crystal system: monoclinic. Lattice type: primitive. Lattice parameters: a = 11.5923(8) Å, b = 17.0433(12) Å, c = 17.9971(13) Å, α = 90°, β = 108.321(2)°, γ = 90°, V = 3375.5(4) Å^3. Space group: $P2(1)/n$. Z = 4, D_{calc} = 1.300 g/cm^3, F_{000} = 1392. Diffractometer: Rigaku AFC7R, Residuals: R, R_w = 0.0469, 0.0806. The crystal data of **9** have been deposited in CCDC as entry 216648. Empirical formula: $C_{32}H_{30}N_2O_6S_2$. Formula weight: 602.70. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.450 × 0.339 × 0.226 mm. Crystal system: monoclinic. Lattice type: primitive. Lattice parameters: a = 15.3098(13) Å, b = 15.6606(10) Å, c = 12.3382(10) Å, α = 90°, β = 91.245(2)°, γ = 90°, V = 2957.5(4) Å^3. Space group: $P2(1)/n$. Z = 4, D_{calc} = 1.354 g/cm^3, F_{000} = 1264. Diffractometer: Rigaku AFC7R. Residuals: R, R_w = 0.0581, 0.1411. The crystal data of **10** have been deposited in CCDC with number 216650. Empirical formula: $C_{22}H_{21}NO_6S$. Formula weight: 427.46. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.478 × 0.365 × 0.310 mm. Crystal system: orthorhombic. Lattice type: primitive. Lattice parameters: a = 10.1562(8) Å, b = 10.4485(8) Å, c = 19.7286(15) Å, α = 90°, β = 90°, γ = 90°, V = 2093.5(3) Å^3. Space group: $P2(1)2(1)2(1)$. Z = 4, D_{calc} = 1.356 g/cm^3, F_{000} = 896. Diffractometer: Rigaku AFC7R. Residuals: R, R_w = 0.0383, 0.0632.

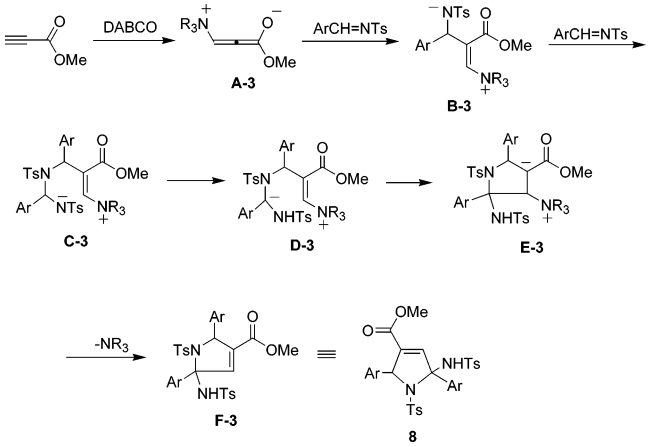
TABLE 11. Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimines with Methyl Propiolate in the Presence of Various Lewis Bases



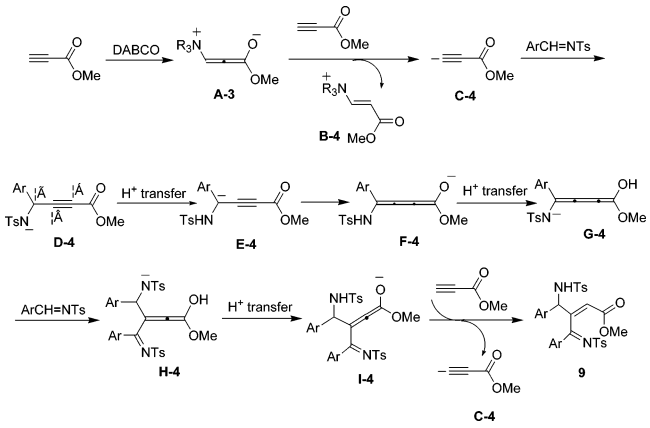
entry	Lewis base	solvent	time (h)	yield[a] (%) 8	9	10
1	PPh_3	CH_3CN	12	0	0	0
2	DABCO	C_6H_6[b]	48	0	0	<10
3	DABCO	DMF	10	21	20	0
4	DABCO	THF	10	23	37	0
5	DABCO	CH_2Cl_2	10	29	34	0

[a] Isolated yields. [b] The reaction was carried out in benzene under reflux.

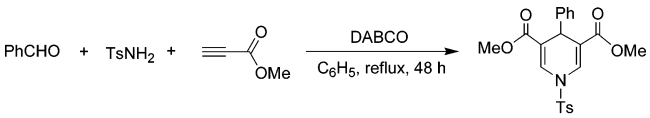
SCHEME 5. Plausible Mechanism for the Formation of 8 in the Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimines with Methyl Propiolate



SCHEME 6. Plausible Mechanism for the Formation of 9 in the Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimines with Methyl Propiolate



SCHEME 7. Reaction of Benzaldehyde and $TsNH_2$ with Methyl Propiolate in the Presence of DABCO in Benzene under Reflux



10, yield: 19%

produces intermediate **D-3**, and the subsequent intramolecular Michael addition gives intermediate **E-3**. The elimination of DABCO from intermediate **E-3** affords the corresponding product **8** (Scheme 5).

For the formation of **9**, the enolate intermediate **A-3** serves as a base, and captures one proton from methyl propiolate to form anionic intermediate **C-4** (along with formation of intermediate **B-4**), which adds to the *N*-tosylated aldimine to give the corresponding intermediate **D-4**. Two consecutive proton-transfer processes from intermediate **D-4** to **E-4** and from **F-4** to **G-4** shuffle the proton on the γ-carbon to the oxygen atom of the carbonyl group in intermediate **D-4** (also in intermediate **G-4**). Thus, the formed enamine **G-4** adds to another molecule of *N*-tosylated aldimine to give intermediate **H-4**. The proton transfer furnishes intermediate **I-4**, which receives one proton from methyl propiolate, affording the corresponding product **9** and regenerating the anionic intermediate **C-4** (Scheme 6).

On the basis of the structure of compound **10**, we believed that product **10** was formed by the reaction of benzaldehyde, derived from the decomposition of *N*-tosylated aldimine by ambient water, $TsNH_2$, and methyl propiolate in the presence of DABCO. To confirm this speculation, we carried out the control experiment shown in Scheme 7 under identical conditions. As a result, compound **10** was indeed obtained in 19% yield (Scheme 7). It should also be noted that no reaction occurred in the absence of DABCO. Therefore, a proposed mechanism was shown in Scheme 8 on the basis of this control experiment. The enolate intermediate **A-3** also serves as a strong base, and captures one proton from $TsNH_2$ to form the anion of $TsNH^-$ and the corresponding intermediate **B-5**. Then, $TsNH^-$ adds to intermediate **B-5** to give intermediate **C-5** (enolate), which adds to benzaldehyde to form intermediate **D-5** via the aldol reaction pathway. Proton transfer produces intermediate **E-5**, and H_2O elimination furnishes intermediate **F-5** upon heating. The subsequent intermolecular Michael addition of **F-5** to methyl propiolate as well as the subsequent intramolecular Michael addition gives the corresponding intermediate **H-5**. Elimination of DABCO affords the corresponding product **10**.

Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimines with But-3-yn-2-one. For the aza-Baylis–

SCHEME 8. Plausible Mechanism for the Formation of 10 in the Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimines with Methyl Propiolate

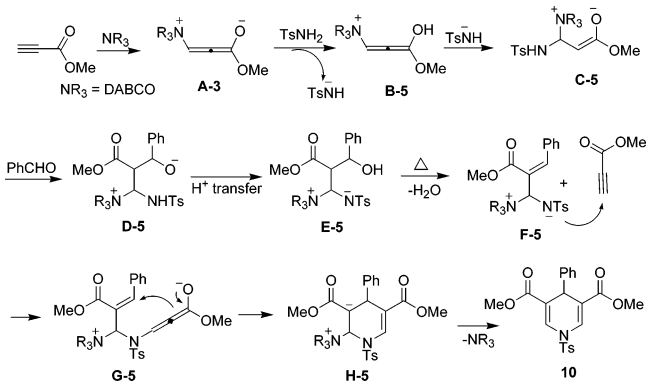
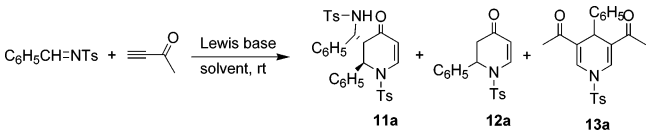


TABLE 12. Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimines with But-3-yn-2-one in the Presence of Various Lewis Bases



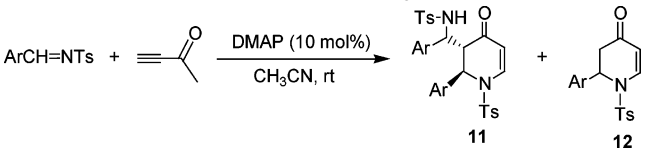
				yield[a] (%)		
entry	Lewis base	solvent	time (h)	**11a** (anti)	**12a**	**13a**
1	PPh_3	CH_3CN	24	0	0	0
2	DABCO	CH_3CN	24	21	0	0
3	DABCO	DMF	24	28	0	0
4	DABCO	THF	24	trace	0	0
5	DABCO	CH_2Cl_2	24	trace	0	0
6	DABCO	CH_3CN[b]	24	30	0	0
7	DABCO	C_6H_6[c]	48	0	0	12
8	DMAP	CH_3CN	24	13	30	0

[a] Isolated yield. [b] The reaction was carried out at 0 °C. [c] The reaction was carried out under reflux.

Hillman reaction of *N*-tosylated aldimines with but-3-yn-2-one, the Lewis base promoter and solvent effects were similarly carefully examined. The results are summarized in Table 12. When PPh_3 (10 mol %) was used as a Lewis base promoter in CH_3CN or in other solvents, no reaction occurred (Table 12, entry 1). When a nitrogen-containing Lewis base promoter such as DABCO or DMAP was used in this reaction, the reaction proceeded smoothly to give some abnormal aza-Baylis–Hillman reaction products under mild conditions. Once again, the solvent played a significant role in this reaction. For example, in benzene under reflux, product **13a** was obtained in 12% yield, which is similar to that of methyl propiolate (Table 12, entry 7). On the other hand, when the reaction was carried out in CH_3CN or DMF in the presence of DABCO, product **11a** was produced in 21 or 28% yields, respectively (Table 12, entries 2 and 3). The yield of **11a** could be improved to 30% at 0 °C in CH_3CN (Table 12, entry 6). In THF or DCM, no reaction occurred (Table 12, entries 4 and 5). We were pleased to find that in the presence of DMAP in CH_3CN, another abnormal aza-Baylis–Hillman product **12a** was produced in 30% yield along with the product **11a** in 13% yield (Table 12, entry 8).

We next carried out the aza-Baylis–Hillman reaction of other *N*-tosylated aldimines with but-3-yn-2-one in the presence of DMAP in CH_3CN at room temperature. The results are summarized in Table 13. The corresponding products **12** were formed in moderate yields in most cases along with the formation of the minor products **11** in some cases (Table 13, entries 1–7). The adduct **11** was formed exclusively in the anti configuration, which was determined by ^1H NMR and DEPT spectroscopy (see Supporting Information).

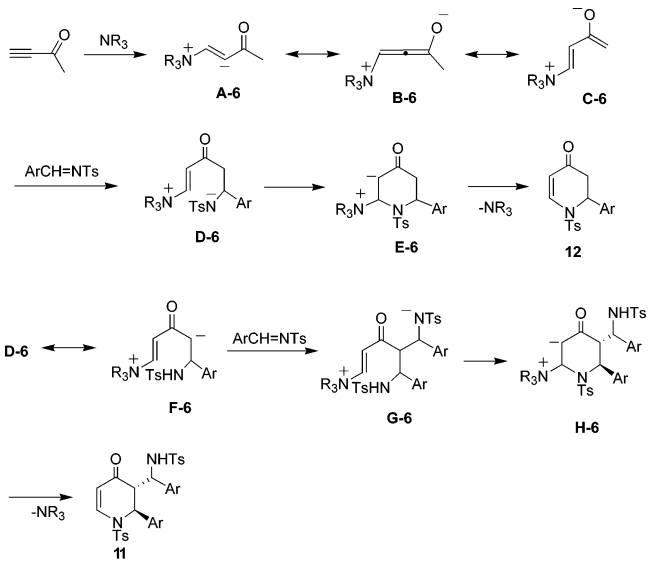
TABLE 13. Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimines with But-3-yn-2-one in the Presence of DMAP (10 mol %) in CH_3CN



			yield[a] (%)	
entry	Ar	time (h)	**11** (anti)	12
1	C_6H_5	24	**11a**, 13	**12a**, 30
2	*p*-MeC_6H_4	48	trace	**12b**, 45
3	*p*-EtC_6H_4	48	**11c**, 15	**12c**, 38
4	*p*-$MeOC_6H_4$	72	trace	**12d**, 32
5	*p*-FC_6H_4	24	trace	**12e**, 31
6	*p*-ClC_6H_4	24	**11f**, 10	**12f**, 35
7	*p*-BrC_6H_4	24	trace	**12g**, 43

[a] Isolated yield.

SCHEME 9. Plausible Mechanism for the Aza-Baylis–Hillman Reaction of *N*-Tosylated Aldimines with But-3-yn-2-one



presence of DMAP in CH_3CN at room temperature. The results are summarized in Table 13. The corresponding products **12** were formed in moderate yields in most cases along with the formation of the minor products **11** in some cases (Table 13, entries 1–7). The adduct **11** was formed exclusively in the anti configuration, which was determined by ^1H NMR and DEPT spectroscopy (see Supporting Information).

A plausible mechanistic explanation for the above unprecedented abnormal aza-Baylis–Hillman reaction of *N*-tosylated imines with but-3-yn-2-one is proposed in Scheme 9. But-3-yn-2-one reacts with DMAP to generate intermediate **A-6**. The main difference between the reaction of aldimine with but-3-yn-2-one and methyl propiolate is that intermediate **A-6** can resonate to the corresponding enolate intermediate **C-6** through intermediate **B-6**. Then, the enolate intermediate **C-6** adds to *N*-tosylated aldimine to give intermediate **D-6**. The subsequent intramoleculer Michael addition gives intermediate **E-6**. The elimination of DMAP from intermediate **E-6** affords product **12**. Intramolecular proton trans-

fer of intermediate **D-6** can also take place to afford intermediate **F-6**, which adds to another *N*-tosylated aldimine to give intermediate **G-6**. The intramolecular proton transfer and subsequent intramolecular Michael addition produces intermediate **H-6** in the anti configuration, presumably because of the steric hindrance between the aryl group and the branched CHAr(NHTs) group. Elimination of DMAP furnishes the corresponding product **11**.

Conclusion

In this paper, we disclose several unprecedented abnormal aza-Baylis−Hillman reactions of *N*-tosylated aldimines with ethyl 2,3-butadienoate, ethyl penta-2,3-dienoate, penta-3,4-dien-2-one, methyl propiolate, and but-3-yn-2-one by means of different nitrogen or phosphine Lewis bases under mild conditions. Most of these aza-Baylis−Hillman reactions reached completion at 20 °C within 10 min to 3 h or after 24 and 48 h, giving the unexpected abnormal aza-Baylis−Hillman adducts **1**−**13** in moderate to excellent yields. The importance of this finding was exemplified by their expedient formal [2+2], [3+2], and [4+2] annulation reactions with *N*-tosylated aldimines to give the azetidine, pyrrolidine, and dihydropyridine derivatives, respectively, under mild conditions by nitrogen- and phosphine-containing Lewis base promoters. The mechanistic details have been described on the basis of control experiments and previous investigation. Efforts are underway to elucidate the mechanistic details, scopes and limitation, and Lewis base effects of this abnormal aza-Baylis−Hillman reaction.

Experimental Section

General Remarks. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI, MALDI, and ESI methods, and HRMS was measured by the EI method. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored on TLC plates. Flash column chromatography was carried out using silica gel or Al_2O_3 at increased pressure.

Typical Aza-Baylis−Hillman Reaction Procedure for *N*-Tosylated Aldimines with Ethyl 2,3-Butadienoate Catalyzed by DABCO at Room Temperature. To a Schlenk tube with *N*-(*p*-methylbenzenesulfonyl)benzaldimine (65 mg, 0.25 mmol), DABCO (6 mg, 0.05 mmol), and MS 4A (100 mg) in benzene (0.5 mL) was added ethyl 2,3-butadienoate (34 mg, 0.30 mmol), and the reaction mixture was stirred for 1 h at room temperature (20 °C). The reaction mixture was washed with water (3 × 10 mL) and extracted with dichloromethane (2 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: EtOAc/petroleum 1:6 to 1:4) to give adduct **1a** (75 mg, yield 82%) as a white solid.

[4-Phenyl-1-(toluene-4-sulfonyl)-azetidin-2-ylidene] acetic acid ethyl ester 1a: a white solid; mp. 100−103 °C; IR (CH_2Cl_2) ν 1703 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.27 (3H, t, J = 7.2 Hz, CH_3), 2.43 (3H, s, CH_3), 3.10 (1H, ddd, J = 16.8, 4.2, 2.4 Hz, CH_2), 3.49 (1H, ddd, J = 16.8, 6.9, 1.8 Hz, CH_2), 4.13 (2H, q, J = 7.2 Hz, CH_2), 5.19 (1H, dd, J = 6.9, 4.2 Hz, CH), 5.84−5.85 (1H, m, ═CH), 7.26 (2H, d, J = 8.4 Hz, ArH), 7.34 (5H, s, ArH), 7.56 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.3, 21.6, 37.4, 59.7, 66.0, 94.7, 126.7, 127.3, 128.6, 128.8, 129.8, 134.1, 137.2, 144.8, 158.2, 167.2; MS (EI) *m/z* 371 (M^+, 2.44), 232 (M^+ − 139, 64.22), 216 (M^+ − 155, 44.63), 155 (M^+ − 216, 51.98), 91 (M^+ − 280, 100). Anal. Calcd for $C_{20}H_{21}NO_4S$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.66; H, 5.71; N, 3.56.

Acknowledgment. We thank the State Key Project of Basic Research (Project 973, G2000048007), Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China (20472096, 203900502, and 20272069) for financial support.

Supporting Information Available: ^{1}H and ^{13}C NMR spectroscopic data and analytical data for aza-Baylis−Hillman reaction products **1**−**13**; X-ray crystal data of **2a**, **3a**, **5d**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO051763D