Regiospecific Allylation of Benzoyl-Substituted Heterocyclic Ketene Aminals and Their Zinc Chloride-Promoted 3-Aza-Cope Rearrangement

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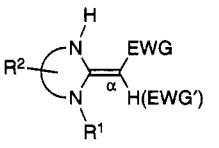
The regiospecific allylation of benzoyl-substituted heterocyclic ketene aminals **2** is reported. Compound **2** reacted with allyl bromide in refluxing acetonitrile to give, exclusively, *C*-allylated products **5** in moderate to good yields, while only *N*-allylated compounds **7** were obtained in dimethylformamide with the use of sodium hydride. Under neutral conditions, reaction between **2** and allyl bromide proceeded *via* a six-membered transition state involving the secondary enamine segment (HNC=C) and carbon–bromine bond (C–Br). Without the secondary amino group, *C*-allylation was inhibited, which was illustrated by the fact that 1,3-dimethyl-2-(aroylmethylene)-imidazolidines did not react with allyl bromide. No 3-aza-Cope rearrangement of *N*-allylated heterocyclic ketene aminals **7** was observed at temperatures up to 140 °C. Only with the use of zinc chloride did the rearrangement take place at 140 °C to give allyl-shifted products **5**. *N*-Benzylated heterocyclic ketene aminal analogues did not undergo the rearrangement under the same conditions, indicating that the 3-aza-Cope rearrangement proceeds through a charge-accelerated concerted mechanism.

Introduction

The chemistry of enamines has been extensively developed since the pioneering work conducted by Stork and colleagues,[1] and it is an important aspect of organic chemistry.[2] In contrast, heterocyclic ketene aminals or cyclic 1,1-enediamines **1** have been studied little until recently. Nevertheless, heterocyclic ketene aminals, being enamines, show some intriguing structure characteristics and have demonstrated potential for the synthesis of heterocycles.[3] Owing to the conjugation effect of the electron-donating amino groups and electron-withdrawing substituents, the double bond is highly polarized, with a concomitant increase of electron density on the α-carbon, leading to greater nucleophilicity at the carbon than the nitrogen. Thus, under neutral conditions, the carbon center always attacks the electropositive site of electrophiles,[4] even 1,3-dipoles such as azides[5] and nitrile oxides.[6] Since secondary amino groups in the molecule may also participate in the reaction, cyclic 1,1-enediamines **1** (Figure 1) can serve as bis-nucleophilic reagents to give a wide variety of fused heterocyclic compounds by nucleophilic addition[7] or substitution[8] and consecutive cyclocondensation reactions.[3,7,8] Further interest in heterocyclic ketene aminals has been generated by their biological activities.[9]

One of the notable features of heterocyclic ketene aminals **1** is the greater nucleophilic reactivity of the



1

EWG, EWG' = NO_2, CN, COR', CO_2R'...

Figure 1.

α-carbon atom, and considerable effort has been put forth to investigate enaminic reactions during the past decade.[3-8] Our recent study[10] of the spectral and structural properties of these secondary 1,1-enediamines, however, has revealed that there is an extensive conjugation system in the molecule involving nitrogen atoms and double bond and electron-withdrawing substituents. In such ambident conjugative compounds, the α-carbon atom, secondary amino groups, and even carbonyl oxygen atom of benzoyl-substituted heterocyclic ketene aminals would act as nucleophilic centers to react with electrophiles, under different conditions. The regiospecific behaviors of these compounds should be of interest in both physical and synthetic organic chemistry.

The alkylation of enamines with alkyl halides is well-documented and constitutes an important reaction for carbon–carbon bond formation.[2] However, reactions of

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1,1-enediamines with alkyl halides have been reported in only a few cases.[11-13] Simple 1,1-enediamines such as 1,1-bis(dimethylamino)ethene[11] and 1,3-dimethyl-2-methyleneimidazoline[12] underwent ready alkylation with alkyl halides to give amidinium salts and, after hydrolysis under basic conditions, the substituted amides. *C*-Alkylation of heterocyclic ketene aminals has been reported[8] to proceed smoothly in refluxing acetonitrile with benzyl chloride and ethyl bromoacetate, and in the latter case, γ-lactam-fused diazaheterocycles are obtained by consecutive intramolecular cyclocondensation. *N*-Alkylation was observed in basic medium,[9a,14,15] and the same reaction between heterocyclic ketene aminals and ethyl bromoacetate afford 3-pyrrolidinone-fused heterocyclic compounds in the presence of a strong base.[16]

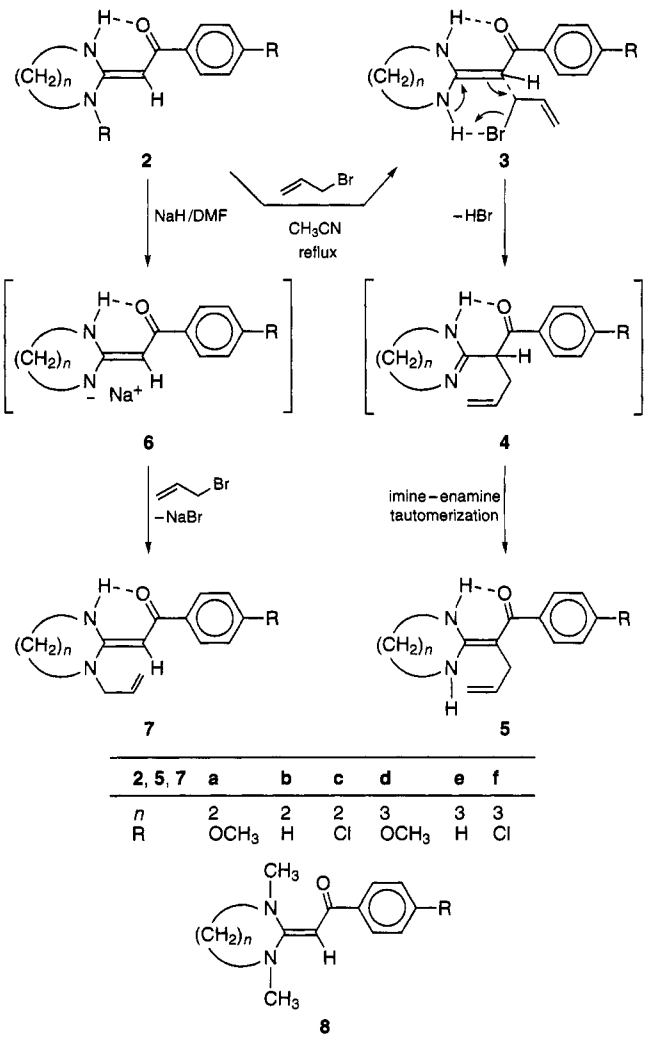
Our research interests have focused on the reactions of heterocyclic ketene aminals and their applications in heterocyclic synthesis. In order to gain a better understanding of the reactivity, and particularly the selective reactivity toward alkyl halides, the allylation of benzoyl-substituted heterocyclic ketene aminals was investigated. The allylated products would be important intermediates for the synthesis of heterocyclic derivatives. Interest in the [3,3]-sigmatropic rearrangement of allylenamines[17] led us to study the transformation of *N*-allylated compounds into *C*-allylated compounds by a charge-accelerated 3-aza-Cope rearrangement.

Results and Discussion

Regiospecific Allylation of Benzoyl-Substituted Heterocyclic Ketene Aminals. The reaction of benzoyl-substituted heterocyclic ketene aminals **2**[18] with allyl bromide in refluxing acetonitrile produced, exclusively, the *C*-allylated compounds **5** in moderate to good yields. In the presence of sodium hydride, **2** reacted with allyl bromide in dimethylformamide to afford *N*-allylated products **7** in satisfactory yields, and neither *C*-allylation nor *O*-allylation was observed (Scheme 1).

The structures of compounds were established on the basis of spectroscopic data and elemental analyses. In the case of **5**, disappearance of the ethylenic proton and the observation of allylic methylene protons at ca. 3.00 ppm in the ^{1}H-NMR spectra indicated *C*-allylation rather than *N*- or *O*-allylation. The two secondary amino groups and the carbonyl moiety, indicated by the IR and ^{1}H- and ^{13}C-NMR spectra, were also consistent with the 1,1-enediamine structure. Interestingly, the two secondary amino groups in **5** were easily differentiated in the ^{1}H-NMR spectra. Because of the strong intramolecular hydrogen bond, the proton signal corresponding to the secondary amino group *cis* to the aroyl substituent is shifted downfield (10.19–12.59 ppm) while the other amino proton resonates at normal frequency (4.82–5.02 ppm). Compounds **7** exhibited ethylenic proton signals at 5.19–5.30 ppm in the ^{1}H-NMR spectra and a carbonyl signal at 181.5–185.5 ppm in the ^{13}C-NMR spectra,

Scheme 1



indicating that the allylation occurred on the secondary amino group, precluding *C*- or *O*-allylation. The *E*-configuration of the enamine double bond of compounds **7** was assigned due to the strong intramolecular hydrogen bond between the secondary amino group and the carbonyl moiety, which was evidenced by the downfield shift of the amino proton in ^{1}H-NMR spectra. All of the possible amidine–ketone and amidine–enol tautomers of compounds **5** and **7** were also excluded by the spectral data.

As we know, alkylation of enamines with alkyl halides proceeds *via* a dipolar intermediate.[2] If this was also the case for 1,1-enediamine species, heterocyclic ketene animals **2** would undergo alkylation irrespective of the substituents on the nitrogen atoms. In order to understand the mechanism, the reaction between the *N,N'*-dimethylated analogues of **2**, 1,3-dimethyl-2-(aroylmethylene)imidazolidines **8**,[10] and allyl bromide was designed. No reaction occurred but the starting materials were recovered. This implied that the secondary amino group is essential to the alkylation of **2** under neutral conditions. A similar result for the reaction between **2** and ethyl propiolate has been reported.[19] To explain the results, a reaction pathway is postulated that entails a key six-membered transition intermediate **3** (Scheme 1). Without a secondary amino moiety, as in compounds **8**,

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Table 1. Zinc Chloride-Promoted 3-Aza-Cope Rearrangement of 7

7	a	b	c	d	e	f
time (h)	24	24	36	8	7	8
yield of 5[a] (%)	70	70	49	81	85	62

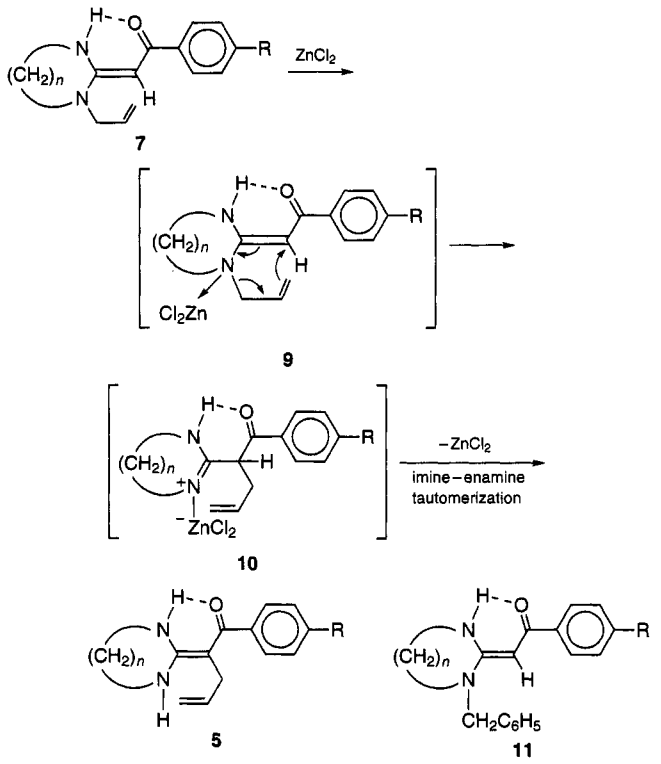
[a] Isolated yield.

allylation does not occur. However, the regiospecificity of *N*-allylation under basic conditions is quite different. Exclusive formation of *N*-allylated compounds suggests that the nitrogen anion species of heterocyclic ketene aminals **6** is the most stable resonance structure and that only it is readily available to react with allyl bromide under these conditions (Scheme 1).

3-Aza-Cope rearrangement. The [3,3]-sigmatropic shift of *N*-allylenamines, named the 3-aza-Cope rearrangement, provides a useful entry into γ,δ-unsaturated carbonyl compounds and δ,ϵ-unsaturated amines.[17] Thermally-induced [3,3]-sigmatropic rearrangement has been reported to occur at 250 °C.[20] The limitations of elevated temperatures were overcome by several methods for accelerating this rearrangement. By forming a cationic quaternary nitrogen center or a complex of enamine to Lewis acids, the rearrangement proceeded easily at lower or even at ambient temperatures.[21,22] The rearrangement has also been accelerated by converting the *N*-allylenamines into the *N*-allylketene *N,O*-acetals[23] or the *N*-allylamide enolates.[24] The 3-aza-Cope rearrangement of ketene aminals had been studied little but appeared interesting.[25,26] The effect on the rearrangement of *N*-allylketene animals of substituent modification had been investigated.[25,26] With *N*-allyl-substituted heterocyclic ketene aminals **7** in hand, we proceeded to investigate their [3,3]-sigmatropic rearrangement. This rearrangement might also provide an alterative route to the *C*-allylated heterocyclic ketene aminals, which would be of special interest when an asymmetric allyl halide species is used. Asymmetric synthesis might also be achieved by the rearrangement, if the substrates were appropriately functionalized by a chiral element.

Refluxing *N*-allylated heterocyclic ketene aminals **7** in dioxane, toluene, and xylene did not affect the shift of the allyl group, indicating that the rate of the 3-aza-Cope rearrangement could not be enhanced by modifying the *N*-allylenamine with an amino and an aroyl substituent at C-2 and C-1, respectively. The rearrangement, however, was promoted by 2 equiv of zinc chloride and resulted in satisfactory yields. The use of 1 or 1.5 equiv of zinc chloride resulted in incomplete conversion of **7** to **5**, while excess Lewis acid (3 equiv, for instance) decreased the yields, mostly due to the formation of oligomers. The results of the Lewis acid-promoted 3-aza-Cope rearrangement of **7** under optimal conditions are listed in Table 1.

Scheme 2



From the data in Table 1, it is apparent that **7d-f**, with sex-membered heterocyclic rings, more readily undergo [3,3]-sigmatropic rearrangement. However, *N*-benzylated heterocyclic ketene aminals **11**[15] were found to not undergo [3,3]-sigmatropic rearrangement. Therefore, the reaction of the Lewis acid-promoted 3-aza-Cope rearrangement of the *N*-allylated heterocyclic ketene aminals is proposed to proceed by a charge-accelerated concerted mechanism (Scheme 2).

Summary

Regiospecific allylation of benzoyl-substituted heterocyclic ketene aminals has been demonstrated. Under neutral conditions, heterocyclic ketene aminals **2** exclusively underwent *C*-allylation with allyl bromide, while only *N*-allylated products were obtained from the same reactants with the aid of sodium hydride in dimethylformamide. Unlike in the case of the enamines, the *C*-allylation of heterocyclic ketene aminals proceeded mostly *via* a six-membered transition state involving the secondary enamine segment (HNC=C) and the C–Br bond of allyl bromide. The 3-aza-Cope rearrangement of *N*-allylated heterocyclic ketene aminals was promoted by zinc chloride at 140 °C. The rearrangement probably occurs by a charge-accelerated concerted mechanism.

Experimental Section

Melting points are not corrected. NMR spectra were obtained on a Varian Unity 200 spectrometer with $CDCl_3$ as solvent. Chemical shifts are reported in ppm downfield from Me_4Si. IR spectra were recorded with a Perkin-Elmer 782 spectrometer. UV spectra were determined with a Hitachi 340 spectrometer in methanol solution. Mass spectra were recorded on a AEI MS-50 instrument. Elemental analyses were performed at the analytical laboratory of the Institute.

General Procedure for the Synthesis of 2-[(1-Allyl-1-aroyl)methylene]-imidazolidines and 2-[(1-Allyl-1-aroyl)-methylene]hexahydropyrimidines 5. A mixture of het-

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erocyclic ketene aminals **2** (3 mmol) and allyl bromide (3.3 mmol) was refluxed in acetonitrile (35 mL) for 2 days. After removal of solvent, the residue was treated with saturated sodium carbonate solution (10 mL), and then the mixture was extracted with chloroform (2 × 25 mL). The extract was dried over anhydrous sodium sulfate. After removal of chloroform, the crystalline products **5** were obtained by recrystallization from ethyl acetate/methanol in moderate to good yields.

2-[1-Allyl-1-(4-methoxybenzoyl)methylene]imidazolidine (5a): 69% yield; mp 179.5–180.5 °C; IR (KBr) 3420, 3180 (NH), 1590 (C=O), 1570, 1518 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 262 (4.02), 316 nm (3.87); ^1H NMR ($CDCl_3$) δ 10.20 (s, 1H), 7.38 (d, 2H), 6.86 (d, 2H), 5.83–6.02 (m, 1H), 5.19, 5.11 (dd, 1H each), 4.82 (s, 1H), 3.81 (s, 3H), 3.79, 3.58 (A_2B_2, 2H each), 3.00 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 189.1, 166.3, 159.6, 135.5, 128.4, 112.8, 139.0, 114.6, 84.8, 55.2, 43.8, 42.8, 32.9; MS (EI, direct probe) *m/z* (rel intensity) 258 (6, M^+), 257 (8), 230 (10), 135 (62), 123 (100). Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.85. Found: C, 69.86; H, 7.07; N, 10.91.

2-(1-Allyl-1-benzoylmethylene)imidazolidine (5b): 82% yield; mp 184–185 °C; IR (KBr) 3423, 3225 (NH), 1591 (C=O), 1570, 1525 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 240 (3.87), 312 nm (3.80); ^1H NMR ($CDCl_3$) δ 10.22 (s, 1H), 7.29–7.42 (m, 5 H), 5.80–5.99 (m, 1H), 5.17, 5.11 (dd, 1H each), 4.88 (s, 1H), 3.79, 3.58 (A_2B_2, 2H each), 2.93 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 189.6, 166.2, 143.0, 128.2, 127.7, 126.5, 138.9, 114.3, 84.8, 43.8, 42.7, 32.7; MS *m/z* 228 (7, M^+), 227 (9), 199 (9), 123 (100), 105 (44). Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.65; H, 7.07; N, 12.27. Found: C, 73.61; H, 7.09; N, 12.34.

2-[1-Allyl-1-(4-chlorobenzoyl)methylene]imidazolidine (5c): 82% yield; mp 186–188 °C; IR (KBr) 3419, 3180 (NH), 1585 (C=O), 1562, 1523 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 247 (4.06), 314 nm (3.62); ^1H NMR ($CDCl_3$) δ 10.19 (s, 1H), 7.26–7.37 (m, 4H), 5.79–5.98 (m, 1H), 5.18, 5.10 (dd, 1H each), 4.82 (s, 1H), 3.79, 3.60 (A_2B_2, 2H each), 2.92 (d, 2); ^{13}C NMR ($CDCl_3$) δ 187.9, 166.3, 141.4, 133.9, 128.1, 127.9, 138.6, 114.8, 84.8, 43.8, 42.7, 32.5; MS *m/z* 262 (7, M^+), 261 (7), 233 (8), 139 (27), 123 (100). Anal. Calcd for $C_{14}H_{15}ClN_2O$: C, 64.00; H, 5.75; N, 10.66. Found: C, 63.30; H, 5.67; N, 10.72.

2-[1-Allyl-1-(4-methoxybenzoyl)methylene]hexahydropyrimidine (5d): 44% yield; mp 172.5–173.5 °C; IR (KBr) 3420, 3289 (NH), 1599 (C=O), 1570, 1505 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 233 (3.54), 299 nm (4.04); ^1H NMR ($CDCl_3$) δ 12.59 (s, 1H), 7.34 (d, 2H), 6.84 (d, 2H), 5.81–6.01 (m, 1H), 5.20, 5.12 (dd, 1H each), 4.97 (s, 1H), 3.80 (s, 3H), 3.27–3.49 (m, 4H), 2.92 (d, 2H), 1.94 (quin, 2H); ^{13}C NMR ($CDCl_3$) δ 186.0, 160.1, 159.1, 136.5, 128.1, 112.7, 139.2, 115.1, 85.7, 55.2, 39.1, 37.9, 32.5, 20.3; MS *m/z* 272 (6, M^+), 271 (6), 244 (9), 137 (100), 135 (39), 123 (22). Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.48; H, 7.30; N, 10.08.

2-(1-Allyl-1-benzoylmethylene)hexahydropyrimidine (5e): 54% yield; mp 190.5–193.5 °C; IR (KBr) 3418, 3283 (NH), 1600 (C=O), 1562, 1513 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 237 (3.73), 310 nm (3.86); ^1H NMR ($CDCl_3$) δ 12.52 (s, 1H), 7.24–7.39 (m, 5H), 5.78–5.97 (m, 1H), 5.20, 5.12 (dd, 1H each), 5.00 (s, 1H), 3.30–3.52 (m, 4H), 2.90 (d, 2H), 1.98 (quin, 2H); ^{13}C NMR ($CDCl_3$) δ 185.7, 159.3, 143.2, 127.1, 126.9, 125.8, 138.5, 114.3, 85.3, 38.3, 37.3, 31.6, 19.6; MS *m/z* 242 (7, M^+), 241 (8), 137 (100), 123 (21), 105 (32). Anal. Calcd for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.56. Found: C, 74.40; H, 7.43; N, 11.45.

2-[1-Allyl-1-(4-chlorobenzoyl)methylene]hexahydropyrimidine (5f): 60% yield; mp 190–192 °C; IR (KBr) 3420, 3275 (NH), 1600 (C=O), 1580, 1515 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 249 (3.98), 310 nm (3.67); ^1H NMR ($CDCl_3$) δ 12.53 (s, 1H), 7.28–7.40 (m, 4H), 5.77–5.96 (m, 1H), 5.20, 5.12 (dd, 1H each), 5.02 (s, 1H), 3.31–3.52 (m, 4H), 2.90 (d, 2H), 1.97 (quin, 2H); ^{13}C NMR ($CDCl_3$) δ 184.6, 159.9, 142.2, 133.2, 127.9, 127.8, 138.7, 115.1, 86.0, 39.0, 37.9, 32.0, 20.2; MS *m/z* 278 (3), 276 (11, M^+), 275 (10), 139 (22), 137 (100), 123 (25). Anal. Calcd for $C_{15}H_{17}ClN_2O$: C, 65.09; H, 6.19; N, 10.12. Found: C, 65.01; H, 6.00; N, 10.01.

General Procedure of the Synthesis of 1-Allyl-2-(aroylmethylene)imidazolidines and 1-Allyl-2-(aroylmethylene)hexahydropyrimidines 7. To a suspension of sodium hydride (5.5 mmol, 80% in mineral oil, washed with petroleum ether (30–60 °C) before use) in dry dimethylformamide (DMF) (30 mL), heterocyclic ketene animals **2** (5 mmol) was added portionwise with stirring. After evolution of hydrogen gas ceased, a solution of allyl bromide (5 mmol) in dry DMF (10 mL) was dropped into the mixture cooled in an ice bath. The mixture was stirred at ambient temperature overnight. The reaction was quenched by addition of 5 mL of water. After removal of solvent under vacuum, 15 mL of water added, and the mixture was extracted with chloroform (2 × 30 mL). The extract was dried over anhydrous sodium sulfate, and after removal of chloroform, the residue was chromatographed on a silica gel column with an eluent of ethyl acetate/methanol (5:1, v/v) to give products **7**.

1-Allyl-2-[(4-methoxybenzoyl)methylene]imidazolidine (7a): 41% yield; mp 110–111 °C; IR (KBr) 3291 (NH), 1576 (C=O), 1527 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 252 (3.98), 322 nm (4.26); ^1H NMR ($CDCl_3$) δ 9.61 (s, 1H), 7.80 (d, 2H), 6.91 (d, 2H), 5.72–5.91 (m, 1H), 5.31, 5.23 (dd, 1H each), 5.27 (s, 1H), 3.85 (d, 2H), 3.83 (s, 3H), 3.69, 3.46 (A_2B_2, 2H each); ^{13}C NMR ($CDCl_3$) δ 184.9, 164.2, 160.0, 134.2, 128.3, 113.2, 131.8, 118.2, 72.3, 55.3, 48.1, 47.6, 42.1; MS *m/z* 258 (21, M^+), 257 (43), 230 (15), 135 (50), 123 (100), 109 (38). Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.85. Found: C, 69.45; H, 7.10; N, 10.84.

1-Allyl-2-(benzoylmethylene)imidazolidine (7b): 45% yield; mp 90–92 °C; IR (KBr) 3290 (NH), 1585 (C=O), 1566, 1530 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 236 (3.96), 319 nm (4.15); ^1H NMR ($CDCl_3$) δ 9.66 (s, 1H), 7.35–7.87 (m, 5H), 5.71–5.90 (m, 1H), 5.29, 5.22 (dd, 1H each), 5.30 (s, 1H), 3.83 (d, 2H), 3.69, 3.48 (A_2B_2, 2H each); ^{13}C NMR ($CDCl_3$) δ 185.5, 164.3, 141.6, 129.7, 128.0, 126.7, 131.7, 118.3, 73.0, 48.1, 47.6, 42.1; MS *m/z* 228 (18, M^+), 227 (36), 200 (14), 123 (100), 109 (32), 105 (35). Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.65; H, 7.07; N, 12.27. Found: C, 73.60; H, 7.20; N, 12.18.

1-Allyl-2-[(4-chlorobenzoyl)methylene]imidazolidine (7c): 58% yield; mp 129–131 °C; IR (KBr) 3280 (NH), 1583 (C=O), 1559, 1528 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 244 (4.20), 327 nm (4.31); ^1H NMR ($CDCl_3$) δ 9.62 (s, 1H), 7.77 (d, 2H), 7.33 (d, 2H), 5.70–5.91 (m, 1H), 5.30, 5.24 (dd, 1H each), 5.25 (s, 1H), 3.84 (d, 2H), 3.71, 3.50 (A_2B_2, 2H each H); ^{13}C NMR ($CDCl_3$) δ 184.1, 164.4, 139.9, 135.7, 128.2, 128.1, 131.6, 118.4, 72.8, 48.1, 47.7, 42.1; MS *m/z* 264 (3), 262 (12, M^+), 261 (28), 234 (15), 139 (26), 123 (100), 109 (55). Anal. Calcd for $C_{14}H_{15}ClN_2O$: C, 64.00; H, 5.75; N, 10.66. Found: C, 63.71; H, 5.87; N, 10.60.

1-Allyl-2-[(4-methoxybenzoyl)methylene]hexahydropyrimidine (7d): 42% yield; oil; IR (KBr) 3220 (NH), 1580 (C=O), 1557, 1544 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.78 (s, 1H), 7.74 (d, 2H), 6.86 (d, 2H), 5.73–5.92 (m, 1H), 5.20, 5.16 (dd, 1H each), 5.26 (s, 1H), 3.87 (d, 2H), 3.83 (s, 3H), 3.37, 3.28 (t, 2H each), 1.99 (quin, 2H); ^{13}C NMR ($CDCl_3$) δ 182.4, 160.6, 159.8, 135.1, 127.9, 113.1, 131.8, 117.1, 75.0, 55.3, 53.0, 46.0, 37.7, 21.3; MS *m/z* 272 (13, M^+), 271 (49), 137 (66), 135 (54), 123 (100); exact mass 272.1487, $C_{16}H_{20}N_2O_2$ requires 272.1524.

1-Allyl-2-(benzoylmethylene)hexahydropyrimidine (7e): 77% yield; oil; IR (KBr) 3215 (NH), 1580 (C=O), 1559, 1548 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.80 (s, 1H), 7.33–7.80 (m, 5H), 5.71–5.90 (m, 1H), 5.25, 5.16 (dd, 1H each), 5.19 (s, 1H), 3.86 (d, 2H), 3.37, 3.27 (t, 2H each), 1.97 (quin, 2H); ^{13}C NMR ($CDCl_3$) δ 182.9, 159.9, 142.5, 129.1, 127.9, 126.4, 131.7, 117.1, 75.8, 53.0, 46.0, 37.3, 21.2; MS *m/z* 242 (14, M^+), 241 (47), 137 (56), 123 (100), 105 (41); exact mass 242.1425, $C_{15}H_{18}N_2O$ requires 242.1417.

1-Allyl-2-[(4-chlorobenzoyl)methylene]hexahydropyrimidine (7f): 70% yield; mp 86–88 °C; IR (KBr) 3175 (NH), 1581 (C=O), 1569, 1550 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 242 (4.11), 326 nm (4.27); ^1H NMR ($CDCl_3$) δ 11.78 (s, 1H), 7.70 (d, 2H), 7.29 (d, 2H), 5.71–5.92 (m, 1H), 5.24, 5.15 (dd, 1H each), 5.30 (s, 1H), 3.80 (d, 2H), 3.42, 3.30 (t, 2H each); 2.01 (quin, 2H); ^{13}C NMR ($CDCl_3$) δ 181.5, 160.0, 140.9, 135.0, 128.1, 127.9, 131.6, 117.3, 75.7, 53.1, 46.1, 37.8, 21.2; MS *m/z* 278 (2), 276 (8, M^+), 275 (23), 139 (24), 123 (100). Anal. Calcd for $C_{15}H_{17}ClN_2O$: C, 65.09; H, 6.19; N, 10.12. Found: C, 64.13; H, 5.92; N, 9.79.

General Procedure for the Charge-Accelerated 3-Aza-Cope Rearrangement of *N*-Allylated Heterocyclic Ketene Aminals 7. A mixture of *N*-allylated heterocyclic ketene

aminals **7** (1 mmol) and anhydrous zinc chloride (2 mmol) in dry xylene (20 mL) was refluxed for a period of time (see Table 1) with stirring. After cooling, chloroform (30 mL) was added, and the organic layer was washed with water (2 × 15 mL) and dried over anhydrous sodium sulfate. *C*-Allylated products **5** were obtained after removal of solvent and recrystallization from ethyl acetate/methanol.

Attempt To Rearrange Heterocyclic Ketene Aminals 11. A mixture of 278 mg (1 mmol) of 1-benzyl-2-(benzoylmethylene)imidazolidine (**11**, n = 2, R = H) and 272 mg (2 mmol) of anhydrous zinc chloride in 20 mL of dry xylene was refluxed for 50 h. After workup of the reaction mixture, the raw material was almost wholly recovered.

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