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Reaction of *C*-alkylated heterocyclic ketene aminals with diethyl azodicarboxylate: synthesis of polyfunctionalized quaternary carbon derivatives and their thermal fragmentation

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Abstract—Five-membered ring *C*-alkylated heterocyclic ketene aminals react with diethyl azodicarboxylate to give the quaternary carbon-containing adducts in moderate to excellent yields while the six-membered analogs afford imidazo[1,5-*a*]pyrimidin-6-one derivatives. The formation of the addition products and their fragmentation reaction pathways are discussed.

1. Introduction

As a unique enamine analog, heterocyclic ketene aminals **1** (Fig. 1) have been shown to exhibit intriguing multi-nucleophilic reactivity.[1] For example, alkylation[2] and acylation reactions[3] of aroyl-substituted heterocyclic ketene aminals **1** (EWG=COAr) could occur either on the α-carbon and/or on the secondary amino nitrogen, the selectivity depending on the reaction conditions employed. On treatment with tetra-*O*-acetyl-α-D-glucopyranosyl and -galactopyranosyl bromide in the presence of a Lewis acid or a base, the carbonyl of the heterocyclic ketene aminals **1** was regiospecifically glycosidated.[4] One of the most noticeable features of heterocyclic ketene aminals is their bisnucleophilicity via the α-carbon and the secondary amino nitrogen toward bis-electrophilic reagents and this has been successfully and frequently applied in the preparation of a wide range of fused heterocyclic compounds that are hardly accessible by other synthetic methods.[5]

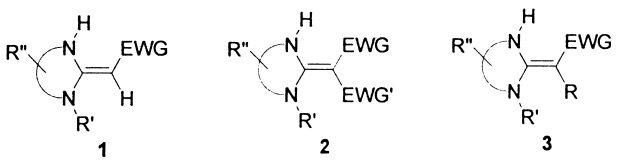

Figure 1. Structures of heterocyclic ketene aminals.

Though the chemistry of heterocyclic ketene aminals **1** and **2** has been extensively studied, surprisingly, the reaction of the *C*-alkylated analogs has remained largely unexplored. This is most probably due to the speculation that tetra-substituted species **3** are very stable and are as inert as **2**. On the other hand, the study of these heterocyclic ketene aminals was probably further harnessed by the observation of the cleavage of alkyl when treated with other electrophilic reagents.[6] Nevertheless, we envisaged that the nucleophilic reaction of **3** at the α-carbon would generate a polyfunctionalized quaternary carbon center. By using a chiral auxiliary or a chiral catalyst, it would also be feasible to develop a method to synthesize optically active quaternary carbon compounds. As a prelude to investigating the asymmetric synthesis of quaternary carbon compounds utilizing heterocyclic ketene aminals protocol, we undertook the current study.

2. Results and discussion

Our previous study demonstrated that diethyl azodicarboxylate (DEAD) **8** is an active agent and can react with heterocyclic ketene aminals **1** to form hydrazine derivatives.[7] To begin our study, we first chose DEAD as probe to examine the reactivity of *C*-alkylated heterocyclic ketene aminals. It was also hoped that the reaction would lead to the formation of hydrazo- and then amino-containing quaternary carbon products.

Keywords: *C*-alkylated heterocyclic ketene aminals; diethyl azodicarboxylate; thermal fragmentation.

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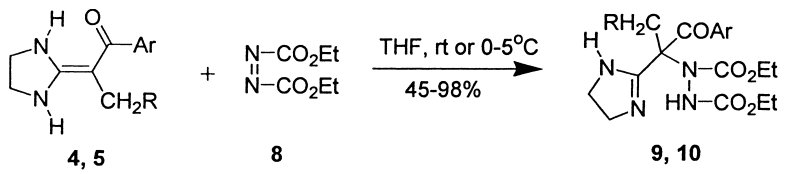


4, 9: R = phenyl; **5, 10**: R = CH=CH_2.
a: Ar = C_6H_5; **b**: Ar = 4-$CH_3C_6H_4$; **c**: Ar = 4-$CH_3OC_6H_4$; **d**: Ar = 4-ClC_6H_4.

Scheme 1.

Table 1. Reaction of heterocyclic ketene aminals **4** and **5** with DEAD **8**

Entry	Reactant	Ar	R	Reaction conditions	Yield of **9** and **10** (%)[a]
1	**4a**	C_6H_5	Ph	rt, 2 h	83
2	**4b**	4-$CH_3C_6H_4$	Ph	rt, 0.3 h	45
3	**4c**	4-$CH_3OC_6H_4$	Ph	rt, 2.5 h	98
4	**4d**	4-ClC_6H_4	Ph	rt, 0.5 h	65
5	**5a**	C_6H_5	CH=CH_2	0–5°C, 9 h	72
6	**5b**	4-$CH_3C_6H_4$	CH=CH_2	0–5°C, 2 h	89
7	**5c**	4-$CH_3OC_6H_4$	CH=CH_2	0–5°C, 1 h	76
8	**5d**	4-ClC_6H_4	CH=CH_2	0–5°C, 2 h	64

[a] Isolated yield.

The *C*-alkylated heterocyclic ketene aminals **4**–**7**, which were readily obtained from the allylation and benzylation of tri-substituted heterocyclic ketene aminals **1**, reacted rapidly and efficiently with DEAD to afford the desired addition products in moderate to excellent yields. For the benzyl-substituted reactant **4**, the reaction proceeded smoothly at room temperature while for the allyl-substituted analogs **5**, the reaction took place effectively at 0–5°C (Scheme 1, Table 1). The structure of the adducts was established on the basis of spectroscopic data and elemental analyses. Both mass spectrum and microanalysis showed the constitution of product being the adduct between **4** or **5** and **8** in a 1:1 ratio. ^{1}H NMR indicated the existence of an imidazoline moiety. Though the IR gave a characteristic carbonyl absorption band at ~1738 cm^{-1} corresponding to the aroyl carbonyl, ^{13}C NMR spectra showed an ambiguous and debatable ketonic carbon peak at ~160 ppm. The structure of **9a** was unambiguously determined by X-ray crystallography (Fig. 2).[8] It should be noted that the addition products **9** and **10** appeared to be not very stable, and they are sensitive to silica gel and acid. On exposure to air at slightly higher temperature, they underwent decomposition in a period of time.

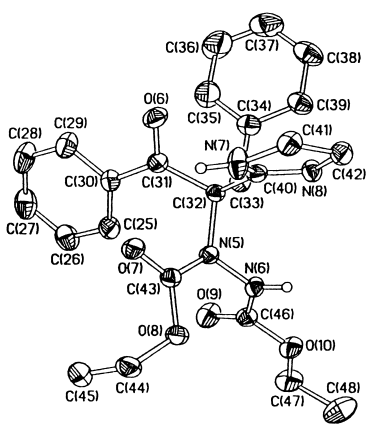
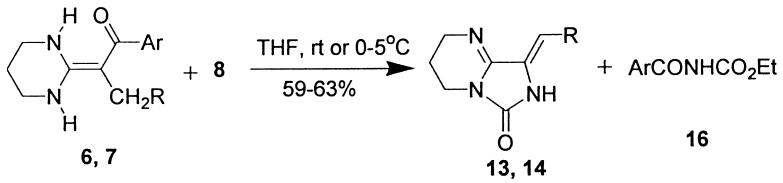


Figure 2. X-Ray crystal structure of compound **9a**.

In contrast to the five-membered analogs, the six-membered heterocyclic ketene aminals **6** or **7** reacted with **8** under similar conditions to give no desired quaternary carbon product. Instead, imidazo[1,5-*a*]pyrimidin-6-one derivatives **13** or **14** were obtained in moderate yield. In addition, ethyl *N*-aroyl carbamate **16** was also isolated (Scheme 2). When the reaction temperature is lowered below −5°C, the addition product was observed by thin layer chromatography. But they were found to decompose rapidly at room temperature resulting in the formation of **13** or **14** and **16**. The structure of fused heterocycles **13** or **14** was confirmed by the spectroscopic data and elemental analyses. The configuration of the double bond in **13** and **14** was determined by NOE experiments.

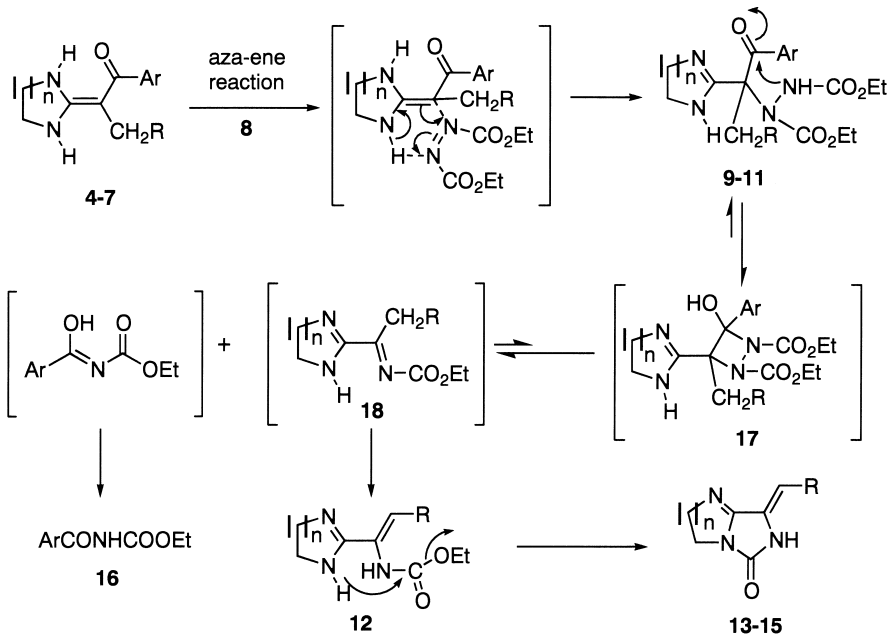
In order to shed further light on the reaction pathway, thermal decomposition of adduct **9** was examined. When **9a** was refluxed in ethanol, it was decomposed to give **16a** as the sole isolable product. A mixture of compounds **12a** and **16a** was obtained from the heating of **9a** in tetrahydrofuran (Scheme 3). Compound **12a** is the precursor of fused heterocyclic compound **15a** and it was indeed transformed into **15a** in a prolonged reaction period. Moreover, the addition product **11c** once precipitated from the reaction between **7c** and DEAD, albeit in lower purity, and its structure was evidenced by the spectroscopic data.

To account for the results aforementioned, the mechanism of the reaction between *C*-alkylated heterocyclic ketene aminals with DEAD was proposed in Scheme 3. As heterocyclic ketene aminals are a unique aza−ene component,[9] **4**–**7** reacted with DEAD in most likely a conceited aza−ene addition mechanism to produce quaternary carbon adducts **9**–**11**. Upon heating, intermediate **9**–**11** underwent a thermal fragmentation probably via intermediate **17** followed by a decomposition to give product **16** and



6, 13: R = phenyl; **7, 14**: R = $CH{=}CH_2$.
a: Ar = C_6H_5; **b**: Ar = 4-$CH_3C_6H_4$; **c**: Ar = 4-$CH_3OC_6H_4$; **d**: Ar = 4-ClC_6H_4.

Scheme 2.



Scheme 3.

intermediate **18**. Isomerization and consecutive intramolecular cyclocondensation of **18** led to the formation of product **13**–**15**.

It is important to address that the introduction of an alkyl group such as allyl and benzyl at the α-carbon led to the enhancement of the nucleophilicity of the heterocyclic ketene aminals, which is in sharp contrast to the outcome of introducing an electron-withdrawing group. The six-membered heterocyclic ketene aminals **6**–**7** appeared more reactive than their five-membered analogs, which is consistent with the reactivity of the parent tri-substituted heterocyclic ketene aminals.[10] The hydrazo-containing quaternary carbon compounds obtained are not very stable and they are ready to fragmentate to yield fused imidazolinone compounds and ethyl aroyl carbamate **16**. The driving force of fragmentation is probably the steric hindrance of the bulky substituents around the quaternary carbon and the stabilization energy gained from the conjugation effect of the fused heterocycles formed. Because of steric bulkiness, the six-membered adducts **11** more readily undergo fragmentation reactions than their five-membered analogs.

3. Conclusion

The introduction of an alkyl group such as allyl and benzyl at the α-carbon led to enhancement of the nucleophilicity of heterocyclic ketene aminals. The five-membered *C*-alkylated heterocyclic ketene aminals reacted with diethyl azodicarboxylate to give the hydrazo-containing quaternary carbon adducts while the six-membered analogs afforded the imidazo[1,5-*a*]pyrimidine derivatives. The formation of the imidazo[1,5-*a*]pyrimidine derivatives has been shown to result from the fragmentation reaction. This investigation has provided important guidance for our future study on the asymmetric synthesis of quaternary carbon compounds utilizing heterocyclic ketene aminal protocols.

4. Experimental

4.1. General

Melting points are uncorrected. IR spectra were obtained on a Perkin–Elmer 782 instrument as KBr discs. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or d_6-DMSO solution with TMS as internal standard on a Bruker DMX-300 spectrometer. Chemical shifts are reported in ppm and coupling constants are in Hz. Mass spectra were measured on AEI MS-50 and KYKY-ZHP-5FAB spectrometers. Elemental analyses were carried out at the Analytical Laboratory of the Institute. All solvents and chemicals were commercially available and, unless otherwise indicated, were used as received.

4.2. General procedure for the reaction of heterocyclic ketene aminals (4, 5) with diethyl azodicarboxylate (DEAD)

To a solution of **4** or **5** (2 mmol) in tetrahydrofuran (15 mL) was added dropwise DEAD **8** (2 mmol) in tetrahydrofuran (5 mL) solution. The mixture was stirred (for **4**, at room temperature; for **5**, at ice-bath) for several hours. After removal of the solvent under vacuum, the residue was recrystallized in diethyl ether to give colorless crystals **9** or **10**.

4.2.1. Diethyl *N*-[(1-benzyl-1-imidazolinyl-2-phenyl)-2-oxoethyl]-hydrazine-*N*,*N*′-dicarboxylate (9a). Colorless crystals; yield: 83%; mp 75–77°C. ^{1}H NMR (d_6-DMSO): 8.40 (1H, s, N*H*), 7.88–7.21 (10H, m, Ar*H*), 6.89 (1H, s, N*H*), 4.21–4.09 (4H, m, 2×OCH_2CH$_3$), 3.97 (2H, s, CH_2), 3.83 (2H, t, J=9.9 Hz, NCH_2), 3.59–3.53 (2H, m, NCH_2), 1.26 (3H, t, J=7.2 Hz, OCH$_2$CH_3), 1.14 (3H, t, J=7.2 Hz, OCH$_2$CH_3); ^{13}C NMR (d_6-DMSO): 165.7, 163.9, 154.1, 151.5, 134.8, 133.2, 132.4, 128.9, 128.3, 128.2, 127.9, 127.8, 125.9, 60.9, 60.0, 50.0, 49.6, 14.4, 14.1; IR (KBr, cm^{-1}): 3416 (N–H), 3175 (N–H), 1739, 1711, 1682; MS (FAB): 453 (M+1)$^+$. Anal. calcd for $C_{24}H_{28}N_4O_5$: C, 63.70; H, 6.24; N, 12.38; found: C, 63.79; H, 6.44; N, 12.17.

4.2.2. Diethyl *N*-[(1-benzyl-1-imidazolinyl-2-*p*-methylphenyl)-2-oxoethyl]-hydrazine-*N*,*N*′-dicarboxylate (9b). Colorless crystals; yield: 45%; mp 90–92°C; ^{1}H NMR (d_6-DMSO): 10.82 (1H, s, N*H*), 7.78–7.20 (9H, m, Ar*H*), 6.75 (1H, s, N*H*), 4.19–4.08 (4H, m, 2×OCH_2CH$_3$), 3.95 (2H, s, CH_2), 3.82 (2H, t, J=9.9 Hz, NCH_2), 3.34–3.30 (2H, m, NCH_2), 2.34 (3H, s, CH_3), 1.24 (3H, t, J=7.2 Hz, OCH$_2$CH_3), 1.14 (3H, t, J=7.2 Hz, OCH$_2$CH_3); ^{13}C NMR (d_6-DMSO): 165.8, 164.3, 154.4, 151.9, 143.1, 135.1, 130.7, 129.3, 129.2, 128.9, 128.6, 128.3, 126.3, 61.2, 60.3, 50.2, 50.0, 21.3, 14.7, 14.5; IR (KBr, cm^{-1}): 3406 (N–H), 3171 (N–H), 1738, 1704, 1679, 1603; MS (FAB): 467 (M+1)$^+$. Anal. calcd. for $C_{25}H_{30}N_4O_5$: C, 64.36; H, 6.48; N, 12.01; found: C, 64.18; H, 6.46; N, 11.79.

4.2.3. Diethyl *N*-[(1-benzyl-1-imidazolinyl-2-*p*-methoxyphenyl)-2-oxoethyl]-hydrazine-*N*,*N*′-dicarboxylate (9c). Colorless crystals; yield: 98%; mp 79–81°C; ^{1}H NMR (d_6-DMSO): 10.78 (1H, s, N*H*), 7.90–6.90 (9H, m, Ar*H*), 6.76 (1H, s, N*H*), 4.20–4.10 (4H, m, 2×OCH_2CH$_3$), 3.97 (2H, s, CH_2), 3.91–3.83 (7H, m, 2×NCH_2+OCH_3), 1.26 (3H, t, J=6.9 Hz, OCH$_2$CH_3), 1.17 (3H, t, J=6.9 Hz, OCH$_2$CH_3); ^{13}C NMR (d_6-DMSO): 164.8, 164.0, 162.6, 154.1, 151.6, 134.8, 130.4, 128.9, 128.0, 127.9, 125.9, 125.2, 113.5, 60.8, 60.0, 55.4, 50.0, 49.8, 14.4, 14.1; IR (KBr, cm^{-1}): 3401 (N–H), 3178 (N–H), 1737, 1717, 1673, 1599; MS (FAB): 483 (M+1)$^+$. Anal. calcd for $C_{25}H_{30}N_4O_6$: C, 62.23; H, 6.27; N, 11.61; found: C, 61.80; H, 6.57; N, 11.37.

4.2.4. Diethyl *N*-[(1-benzyl-1-imidazolinyl-2-*p*-chlorophenyl)-2-oxoethyl]-hydrazine-*N*,*N*′-dicarboxylate (9d). Colorless crystals; yield: 65%; mp 76–78°C; ^{1}H NMR (d_6-DMSO): 8.49 (1H, s, N*H*), 7.90–7.28 (9H, m, Ar*H*), 6.90 (1H, s, N*H*), 4.18 (2H, q, J=6.9 Hz, OCH_2CH$_3$), 3.93 (2H, q, OCH_2CH$_3$), 3.39–3.35 (6H, m, 2×NCH_2+CH_2), 1.26 (3H, t, J=6.9 Hz, OCH$_2$CH_3), 1.09 (3H, t, J=7.2 Hz, OCH$_2$CH_3); ^{13}C NMR (d_6-DMSO): 164.8, 163.9, 154.1, 151.5, 137.3, 134.7, 132.1, 130.1, 129.0, 128.3, 128.2, 128.0, 125.9, 61.0, 60.0, 49.6, 49.5, 14.4, 14.1; IR (KBr, cm^{-1}): 3415 (N–H), 3169 (N–H), 1738, 1714, 1686, 1588; MS (FAB): 487 (M+1)$^+$. Anal. calcd for $C_{24}H_{27}ClN_4O_5$: C, 59.19; H, 5.59; N, 11.51; found: C, 59.09; H, 5.76; N, 11.38.

4.2.5. Diethyl *N*-[(1-allyl-1-imidazolinyl-2-phenyl)-2-oxo-ethyl]-hydrazine-*N*,*N*′-dicarboxylate (10a). Colorless crystals; yield: 72%; mp 78–80°C; ^{1}H NMR (d_6-DMSO): 8.60 (1H, s, N*H*), 8.33 (1H, s, N*H*), 7.87–7.45 (5H, m, Ar*H*), 6.52–6.45 (1H, m, =C*H*), 5.43–5.24 (2H, m, =CH_2), 4.17 (2H, q, J=7.2 Hz, OCH_2CH$_3$), 3.99 (2H, q, J=7.2 Hz, OCH_2CH$_3$), 3.49–3.36 (6H, m, CH_2+2×NCH_2), 1.25 (3H, t, J=7.2 Hz, OCH$_2$CH_3), 1.15 (3H, t, J=7.2 Hz, OCH$_2$CH_3); ^{13}C NMR (d_6-DMSO): 166.3, 163.7, 154.7, 152.1, 133.8, 133.0, 132.6, 128.8, 128.7, 126.8, 121.2, 61.5, 60.7, 50.1, 49.9, 14.9, 14.6; IR (KBr, cm^{-1}): 3379 (N–H), 3184 (N–H), 1742, 1701, 1681, 1611; MS (FAB): 403 (M+1)$^+$. Anal. calcd for $C_{20}H_{26}N_4O_5$: C, 59.69; H, 6.51; N, 13.92; found: C, 59.77; H, 6.43; N, 13.81.

4.2.6. Diethyl *N*-[(1-allyl-1-imidazolinyl-2-*p*-methylphenyl)-2-oxoethyl]-hydrazine-*N*,*N*′-dicarboxylate (10b). Colorless crystals; yield: 89%; mp 92–94°C. ^{1}H NMR (d_6-DMSO): 8.66 (1H, s, N*H*), 8.39 (1H, s, N*H*), 7.79 (2H, d, J=7.8 Hz, Ar*H*), 7.29 (2H, d, J=7.8 Hz, Ar*H*), 6.54–6.47 (1H, m, =C*H*), 5.45–5.28 (2H, m, =CH_2), 4.17 (2H, q, J=7.2 Hz, OCH_2CH$_3$), 4.01 (2H, q, J=7.2 Hz, OCH_2CH$_3$), 3.62–3.38 (6H, m, CH_2+2×NCH_2), 2.37 (3H, s, CH_3), 1.26 (3H, t, J=7.2 Hz, OCH$_2$CH_3), 1.17 (3H, t, J=7.2 Hz, OCH$_2$CH_3); ^{13}C NMR (d_6-DMSO): 165.8, 163.5, 154.6, 152.0, 143.1, 132.5, 130.8, 129.2, 128.7, 126.7, 121.0, 61.3, 60.7, 50.0, 48.8, 21.3, 14.8, 14.5; IR (KBr, cm^{-1}): 3384 (N–H), 3102 (N–H), 1740, 1702, 1684, 1606; MS (FAB): 417 (M+1)$^+$. Anal. calcd for $C_{21}H_{28}N_4O_5$: C, 60.56; H, 6.78; N, 13.45; found: C, 60.51; H, 6.86; N, 13.45.

4.2.7. Diethyl *N*-[(1-allyl-1-imidazolinyl-2-*p*-methoxyphenyl)-2-oxoethyl]-hydrazine-*N*,*N*′-dicarboxylate (10c). Colorless crystals; yield: 76%; mp 97–99°C; ^{1}H NMR (d_6-DMSO): 8.61 (1H, s, N*H*), 8.32 (1H, s, N*H*), 7.86 (2H, d, J=8.7 Hz, Ar*H*), 6.99 (2H, d, J=8.7 Hz, Ar*H*), 6.50–6.44 (1H, m, =CH), 5.41–5.24 (2H, m, =CH_2), 4.14 (2H, q, J=7.2 Hz, OCH_2CH$_3$), 3.98 (2H, q, J=7.2 Hz, OCH_2CH$_3$), 3.80 (3H, s, OCH_3), 3.46–3.35 (6H, m, CH_2+2×NCH_2), 1.23 (3H, t, J=7.2 Hz, OCH$_2$CH_3), 1.14 (3H, t, J=7.2 Hz, OCH$_2$CH_3); ^{13}C NMR (d_6-DMSO): 165.3, 163.6, 163.1, 154.7, 152.2, 132.5, 130.9, 126.9, 125.7, 121.2, 114.1, 61.3, 60.8, 55.9, 49.7, 49.5, 14.9, 14.7; IR (KBr, cm^{-1}): 3345 (N–H), 3150 (N–H), 1715, 1679, 1655, 1578; MS (FAB): 433 (M+1)$^+$. Anal. calcd for $C_{21}H_{28}N_4O_6$: C, 58.32; H, 6.53; N, 12.96; found: C, 58.31; H, 6.62; N, 13.07.

4.2.8. Diethyl *N*-[(1-allyl-1-imidazolinyl-2-*p*-chloro-phenyl)-2-oxoethyl]-hydrazine-*N*,*N*′-dicarboxylate (10d). Colorless crystals; yield: 64%; mp 92–94°C; ^{1}H NMR (d_6-DMSO): 8.65 (1H, s, N*H*), 8.33 (1H, br., N*H*), 7.83 (2H, d, J=8.4 Hz, Ar*H*), 7.51 (2H, d, J=8.4 Hz, Ar*H*), 6.48–6.41 (1H, m, =C*H*), 5.38–5.22 (2H, m, =CH_2), 4.12 (2H, q, J=7.2 Hz, OCH_2CH$_3$), 3.98 (2H, q, J=7.2 Hz, OCH_2CH$_3$), 3.40–3.30 (6H, m, CH_2+2×NCH_2), 1.21 (3H, t, J=6.9 Hz,

OCH_2CH_3), 1.12 (3H, t, J=6.9 Hz, OCH_2CH_3); ^{13}C NMR (d_6-DMSO): 165.4, 163.7, 154.7, 152.1, 137.8, 132.6, 130.7, 128.9, 128.8, 126.9, 121.3, 61.5, 60.7, 49.9, 49.7, 14.9, 14.6; IR (KBr, cm^{-1}): 3382 (N–H), 3184 (N–H), 1739, 1699, 1686, 1609; MS (FAB): 437 $(M+1)^+$. Anal. calcd for $C_{20}H_{25}ClN_4O_5$: C, 54.98; H, 5.77; N, 12.82; found: C, 55.20; H, 5.86; N, 12.65.

4.3. Reaction of heterocyclic ketene aminals (6a) with DEAD (8)

To a solution of **6a** (2 mmol) in tetrahydrofuran (15 mL) was added dropwise DEAD **8** (2 mmol) in tetrahydrofuran (5 mL). The mixture was stirred at room temperature for 2 h. After removal of solvent under vacuum, the residue was chromatographed on a silica gel column (ether acetate/petroleum ether as an eluant) to give products **13** and **16a**.

4.3.1. 8-Benzylidene-3,4,7,8-tetrahydro-2*H*-imidazo[1,5-*a*]pyrimidin-6-one (13). Colorless crystals; yield: 63%; mp 177–179°C; ^1H NMR ($CDCl_3$): 7.66 (1H, s, N*H*), 7.42–7.30 (5H, m, Ar*H*), 6.54 (1H, s, =C*H*), 3.66 (4H, t, J=5.7 Hz, 2×NCH_2), 1.91 (2H, q, J=5.7 Hz, CH_2); ^{13}C NMR ($CDCl_3$): 154.9, 148.4, 134.2, 128.7, 128.3, 128.0, 127.3, 104.0, 44.7, 37.2, 19.4; IR (KBr, cm^{-1}): 3448 (NH), 1740, 1738, 1649; MS (EI): 227 (M^+, 21%), 226 (M−1, 100), 198 (28). Anal. calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.76; N, 18.49; found: C, 68.56; H, 5.75; N, 18.52.

4.3.2. Ethyl *N*-benzoyl carbamate (16a). White solid; yield: 70%; mp 90–92°C; ^1H NMR (d_6-DMSO): 10.97 (1H, s, N*H*), 7.89–7.47 (5H, m, Ar*H*), 4.18 (2H, q, J=7.2 Hz, OCH_2CH_3), 1.26 (3H, t, J=7.5 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): 165.6, 151.7, 133.3, 129.1, 129.1, 128.1, 62.6, 14.6. IR (KBr, cm^{-1}): 3260, 1758, 1740; MS (EI): 193 (M^+, 8%), 149 (10), 105 (100). Anal. calcd for: $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74; N, 7.25; found: C, 62.09; H, 5.77; N, 7.19.

4.4. Reaction of heterocyclic ketene aminals (7c) with DEAD (8)

To a solution of heterocyclic ketene aminals **7c** (2 mmol) in tetrahydrofuran (15 mL) was added dropwise diethyl azodicarboxylate **8** (2 mmol) at room temperature. After 0.5 h, white solid participated from the mixture, collected the solid by filtration and dried to give the crude adduct **11c**.

4.4.1. Diethyl *N*-[(1-allyl-1-tetrahydropyrimidinyl-2-*p*-methoxyphenyl)-2-oxoethyl]-hydrazine-*N*,*N*′-dicarboxylate (11c). White solid. ^1H NMR (d_6-DMSO): 9.54 (1H, s, N*H*), 8.55 (1H, s, N*H*), 7.89 (2H, d, J=8.4 Hz, Ar*H*), 7.00 (2H, d, J=8.4 Hz, Ar*H*), 5.57–5.49 (1H, m, =C*H*), 5.19–5.12 (2H, m, =CH_2), 4.30–4.21 (2H, m, OCH_2CH_3), 3.93–3.85 (5H, m, OCH_2CH_3+OCH_3), 3.45–3.35 (6H, m, CH_2+2×NCH_2), 1.91–1.84 (2H, m, CH_2), 1.28 (3H, t, J=6.6 Hz, OCH_2CH_3), 0.87 (3H, t, J=6.6 Hz, OCH_2CH_3); IR (KBr, cm^{-1}): 3350 (N–H), 3128 (N–H), 1742, 1694, 1645, 1598; MS (FAB): 447 $(M+1)^+$.

A solution of **11c** (1 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature for another 4 h and the process was monitored by thin layer chromatography. After the substrate disappeared, the solvent was removed by reduced pressure. The residue was chromatographed on a silica gel column to give the decomposed product **14**.

4.4.2. 8-Allylidene-3,4,7,8-tetrahydro-2*H*-imidazo[1,5-*a*]pyrimidin-6-one (14). Colorless crystals; yield: 59%; mp 119–121°C; ^1H NMR ($CDCl_3$): 9.55 (1H, s, N*H*), 6.58–6.45 (1H, m, =C*H*), 6.15 (1H, d, J=11.7 Hz, =C*H*), 5.37 (1H, d, J=16.5 Hz, =C*H*), 5.24 (1H, d, J=10.2 Hz, =C*H*), 3.65–3.56 (4H, m, 2×NCH_2), 1.89–1.81 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$): 155.3, 148.3, 129.5, 129.0, 120.0, 105.3, 44.5, 37.2, 19.3; IR (KBr, cm^{-1}): 3195 (NH), 1744, 1728, 1649, 1429; MS (EI): 177 (M^+, 28%), 176 (M−1, 100), 148 (50). Anal. calcd for $C_9H_{11}N_3O$: C, 61.00; H, 6.26; N: 23.71; found: C, 60.82; H, 6.38; N, 23.80.

4.5. Thermal fragmentation of adducts (9a)

A solution of adducts **9a** (1 mmol) in tetrahydrofuran (15 mL) was refluxed for about 5 h (monitored by TLC). Removal of the solvent and chromatographed by silica gel column (ethyl acetate/petroleum ether as eluant) to afford the product **12a** and **16a**. **12a** and **16a** can also be obtained by refluxing the mixture of heterocyclic ketene aminal **4a** and DEAD **8** in tetrahydrofuran in a one-pot reaction.

4.5.1. Ethyl *N*-(1-imidazolinyl-2-phenyl-vinyl)carbamate (12a). Colorless crystals; yield: 65%; mp 134–136°C; ^1H NMR ($CDCl_3$): 7.73 (1H, s, N*H*), 7.46–7.23 (5H, m, Ar*H*), 6.99 (1H, s, NH), 6.75 (1H, s, =C*H*), 4.08 (2H, q, J=6.9 Hz, OCH_2CH_3), 3.68 (4H, s, 2×NCH_2), 1.17 (3H, m, OCH_2CH_3); ^{13}C NMR ($CDCl_3$): 164.3, 154.1, 134.7, 129.0, 128.4, 128.3, 124.9, 124.8, 61.7, 50.4, 14.4; IR (KBr, cm^{-1}): 3308 (NH), 1781, 1586, 1535; MS (EI): 259 (M^+, 3%), 258 (M−1, 16), 212 (100). Anal. calcd for $C_{14}H_{17}N_3O_2$: C, 64.84; H, 6.61; N, 16.21; found: C, 64.47; H, 6.58; N, 16.08.

Prolonging the reaction time lead to the formation of imidazo[1,5-*a*]imidazolinone **15a**.

4.5.2. 7-Benzylidene-2,3,6,7-tetrahydroimidazo[1,5-*a*]imidazol-5-one (15a). White solid; yield: 66%; mp 197–199°C; ^1H NMR (d_6-DMSO): 10.08 (1H, s, N*H*), 7.54–7.23 (5H, m, Ar*H*), 6.31 (1H, s, =C*H*), 4.26 (2H, t, J=8.7 Hz, NCH_2), 3.64 (2H, t, J=8.7 Hz, NCH_2); ^{13}C NMR (d_6-DMSO): 160.7, 152.6, 133.9, 128.9, 127.8, 125.1, 125.0, 105.1, 61.6, 41.5; IR (KBr, cm^{-1}): 3227 (NH), 1748, 1645, 1407; MS (EI): 213 (M^+, 31%), 212 (M−1, 100), 117 (59). Anal. calcd for $C_{12}H_{11}N_3O$: C, 67.59; H, 5.20; N, 19.71; found: C, 67.16; H, 5.09; N, 19.68.

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