Nucleophilic Interception of the γ,δ-Acetylenic α,β-Olefinic Aldehyde Intermediate Formed from Furil Monotosylhydrazone

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The reaction of furil monotosylhydrazone (**1**) with nucleophiles under basic conditions led to the formation of 5-(2-furoylmethylene)-2-pyrrolidinones **3** when amines and hydrazine hydrate were used. Treatment with methylhydrazine led to production of 1-methyl-6-(2-furoylmethylene)-pyridazine (**4**) while treatment with phenylhydrazine and 4-nitrophenylhydrazine produced 1-(2-furoyl)-6-anilino-6-azafulvene (**5a**) and 1-(2-furoyl)-6-(4-nitroanilino)-6-azafulvene (**5b**), respectively. All products suggest interception of the γ,δ-acetylenic α,β-olefinic aldehyde intermediate **2** formed via the unstable 1,2-difuryldiazoethanone.

Although there have been some studies involving ring opening of furan adjacent to carbenic centers,[2-9] there have been no reports in which this type of intermediate is intercepted and used to form other cyclic systems. Diazoketones, which can lose N_2 to form ketocarbenes, are often prepared by treating monotosylhydrazones of diketones with base under mild conditions.[10,11] Here we report the results of our study involving reactions of nucleophiles with furil monotosylhydrazone (**1**) under conditions in which we generate products of the unstable 1,2-difuryldiazoethanone.

The nucleophiles studied are ammonia, primary aliphatic amines, anilines, hydrazine hydrate, methylhydrazine, phenylhydrazine, and (4-nitrophenyl)hydrazine. Although many of these nucleophiles are sufficiently basic to cause decomposition of **1**, all reactions were conducted in the presence of sodium carbonate.

In a typical reaction, **1** was first dissolved in the appropriate solvent. The nucleophile, followed by sodium carbonate, was then added and the mixture stirred at room temperature. Filtration, evaporation of the solvent, and column and/or preparative thin layer chromatography led to isolation of the main product.

The reactions of ammonia, primary aliphatic amines, and anilines in methylene chloride led to the same type of compound. The structural assigment was based on spectroscopic data. Thus, the presence of two carbonyl groups was determined by two absorptions in the IR spectra, one at approximately 1650 and the other at 1740 cm^{-1}, and by two absorptions in the ^{13}C NMR spectra, both at approximately 178 ppm. The proton NMR spectra show the presence of only one furan ring, a vinylic proton (5.83–6.71 ppm) and two neighboring methylene groups (2.51–2.82 and 2.99–3.64 ppm). These data, together with the mass spectra which show a molecular ion which in all cases corresponds to $C_{10}H_6O_3$ plus a molecule of nucleophile led us to N-substituted 5-(2-furoylmethylene)-2-pyrrolidinones (**3**) as the compounds formed. These products imply ring opening of the furan ring adjacent to the carbenic center generated from N_2 loss from the diazo ketone formed "in situ" to give 5-(2-furoyl)-2-penten-4-ynal (**2**) as an intermediate. Nucleophilic attack of the amine at the aldehydic center or at the γ acetylenic position, followed by ring closure and tautomerism, forms **3** (Scheme 1).

X-ray crystallographic analyses of **3b** and **3h** show that the stereochemistry in these cases is E. The ^1H NMR spectra for all of these compounds, with the exception of **3a**, show deshielding of the C-4 methylene group, most likely the result of an anisotropic effect with the carbonyl group that occurs for the *E* isomer. The absence of this effect in **3a** suggests that the correct configuration for this specific compound is *Z*. In fact, a NOE enhancement spectrum shows that irradiation of the vinylic hydrogen of **3a** at 6.10 ppm gives an enhancement of 3% for these C-4 hydrogens. Perhaps hydrogen bonding between the furoyl carbonyl group and NH stabilizes this structure with respect to the *E* configuration.

From the results shown in Table 1, it can be seen that this reaction is quite general and sensitive to steric effects. Thus, *tert*-butylamine forms **3g** in 31% yield while methylamine forms the analogous product **3b** in 90% yield. Anilines, which are much less nucleophilic than aliphatic amines, form **3** in reasonable yield if they do not have strong electron-withdrawing groups. A steric effect can be seen when one analyzes the yields of ortho isomers with respect to the para. Also, 2,6-dimethylaniline does not form this product.

Under the same conditions, hydrazine hydrate reacts with **1** to form the 1-aminopyrrolidin-2-one system (**3q**). X-ray analysis confirms *E* configuration.

Methylhydrazine does not lead to the same skeleton.

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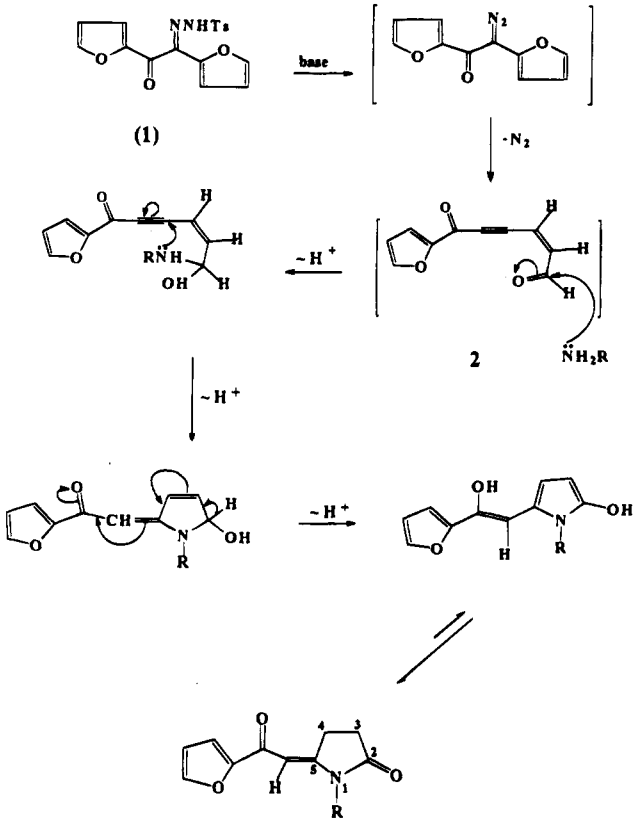
Scheme 1



Scheme 2

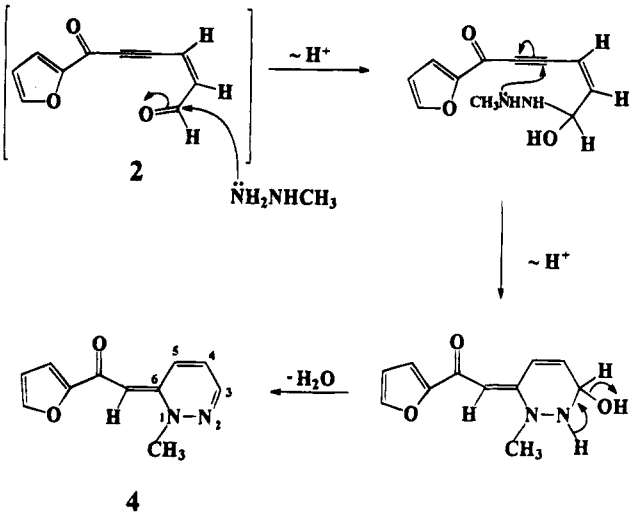


Table 1. 5-(2-Furoylmethylene)-2-pyrrolidinones 3

3	R	% yield
a	H	40
b	CH_3	90
c	CH_3CH_2	76
d	$CH_3CH_2CH_2$	41
e	$(CH_3)_2CH$	62
f	$CH_3CH_2CH_2CH_2$	44
g	$(CH_3)_3C$	31
h	$C_6H_5CH_2$	76
i	$HOCH_2CH_2$	41
j	C_6H_5	40
k	2-ClC_6H_4	20
l	4-ClC_6H_4	40
m	2-$CH_3C_6H_4$	18
n	4-$CH_3C_6H_4$	36
o	3-$CH_3OC_6CH_3$	40
p	4-$CH_3OC_6CH_3$	48
q	NH_2	44

The mass spectrum shows a molecular ion consistent with loss of water from the adduct formed with $C_{10}H_6O_3$ plus methylhydrazine. The IR spectrum shows only one carbonyl absorption at 1625 cm^{-1}. These data, together with NMR spectra were used to characterize the product as 1-methyl-6-(2-furoylmethylene)pyridazine (**4**). Interestingly, the vinylic proton (at 5.70 ppm) exchanges in D_2O. That this proton is indeed bonded to carbon was determined by ^{13}C NMR whereby the CH singlet at 84.3 ppm was transformed to a CD triplet after D_2O exchange. Perhaps exchange is favored because an aromatic pyridazinium cation is formed as an intermediate. The ^1H NMR spectrum shows long range coupling between the vinylic hydrogen and the C-4 hydrogen at 6.91 ppm (J = 1.1 Hz), which is consistent with the zig-zag orientation of the E isomer. Again, a NOE difference spectrum confirmed this configuration. Thus, irradiation of the vinylic proton gave enhancement of the methyl group (11%). The formation of this product implies nucleophilic interception of **2**. The nucleophilic attack of the less hindered nitrogen of methylhydrazine at the aldehydic center, followed by ring closure involving the other nitrogen leads to **4** after loss of H_2O (Scheme 2).

To our surprise, the reactions of phenylhydrazine and (4-nitrophenyl)hydrazine formed still another system. These products were formed in good yields in benzene but only in trace amounts in methylene chloride. Both products are red solids whose mass spectra show molecular ions that correspond to loss of water from the $C_{10}H_6O_3$ plus arylhydrazine adduct. However, this is the only similarity in the data when compared to **4**, the product formed with methylhydrazine. The IR shows a medium sized absorption at 1570 cm^{-1} and no absorption in the normal carbonyl region. However, ^{13}C NMR shows an absorption at 174.09 ppm, that is consistent with a carbonyl group, along with five other quaternary carbons. The ^1H NMR spectrum shows the presence of one furan ring and the phenyl or 4-nitrophenyl ring. A distinctive feature of this spectrum is the presence of an exchangeable hydrogen at 15.44 ppm. The COLOC spectrum[12] shows ^2J coupling between this downfield proton and the ipso carbon of the phenyl ring. Further analysis, that includes an INADEQUATE spectrum[12] of the product formed with phenylhydrazine, led us to identify these products as 1-(2-furoyl)-6-anilino-6-azafulvene (**5a**) and 1-(2-furoyl)-6-(4-nitroanilino)-6-azafulvene (**5b**), respectively. We suggest that in these compounds the resonance structure with charge separation contributes significantly. This would explain both the position of the NH proton at such a low field and the IR absorption of the carbonyl at 1570 cm^{-1}. A literature search showed two examples of compounds with carbonyl absorptions below 1600 cm^{-1}, one being N-pyridinium-2-formylcyclopentadienylid[13] and the other being 4-cyano-2-(dimethylamino)-6-phenyltropone.[14] The formation of these products can also be explained by nucleophilic interception of intermediate **2** (Scheme 3).

These results demonstrate that the intermediate **2** formed by carbenic ring opening of furil monotosylhydrazone (**1**) reacts with similar nucleophiles to afford

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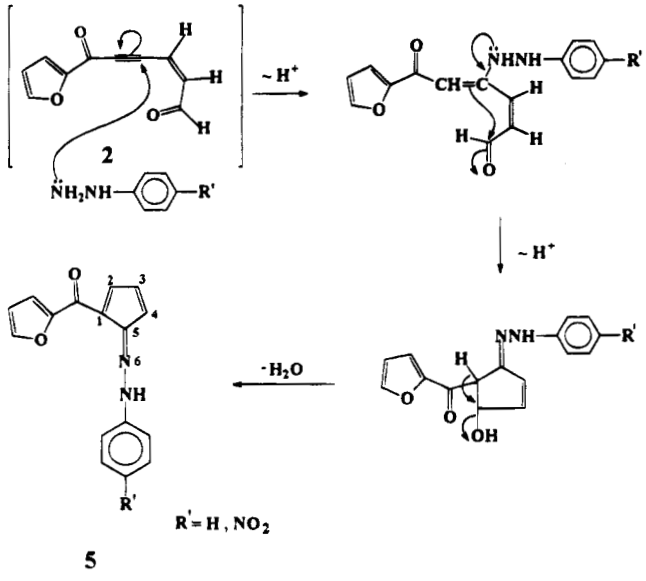
Scheme 3



5

different cyclization products. In the case of the reactions with hydrazines, the presence of diverse electrophilic centers in **2** in conjunction with subtle differences in the nucleophilic and steric natures of the hydrazine nitrogens precludes a comparison of the reaction pathways observed.

Experimental Section

Melting points are uncorrected. Proton and carbon chemical shifts were measured relative to internal tetramethylsilane. The electron impact mass spectra were obtained at 70 eV. X-ray crystallographic data of **3b**, **3h**, and **3q** were collected on an automated CAD-4 diffractometer, and the structures were solved by direct methods and refined by the least-squares method using the SHELX-76 programs.

Furil Monotosylhydrazone (1). A solution of tosylhydrazine (4.0 g, 20 mmol) in benzene 120 mL was added to a solution of furil (4.0 g, 20 mmol) in hot benzene (120 mL). After 96 h at 45 °C the solution was allowed to cool. The first precipitate that formed was furilbis(tosylhydrazone) (120 mg). After filtration and evaporation of the solvent the crude product was recrystallized from CH_2Cl_2/hexane and afforded **1** (56%) as yellow crystals, mp 137.0–137.5 °C; IR (KBr) 3435, 3180, 1645, 1390, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.42 (3 H, s), 6.58 (2 H, m), 7.29 (3 H, m), 7.59 (1 H, m), 7.66 (2 H, m), 7.84 (2 H, m), 10.40 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 175.72, 150.37, 147.83, 146.40, 144.80, 144.08, 135.05, 134.67, 129.87, 128.07, 123.83, 117.38, 112.67, 112.25, 21.63; MS *m/z* (relative intensity) 202 (6), 175 (34), 147 (19) 118 (33) 107 (52), 95 (71) 92 (77) 91 (100).

General Procedure for Reactions of 1 with Amines and Hydrazines. Compound **1** (200 mg, 0.56 mmol) in 50 mL of CH_2Cl_2 (for amines, hydrazine hydrate and methylhydrazine) or benzene (for phenylhydrazine and (4-nitrophenyl)-hydrazine) was added to the amine or hydrazine (1.12 mmol) and Na_2CO_3 (5.6 g). The mixture was left stirring at room temperature for a time that varied from several minutes to 48 h. The reaction mixture was then filtered and the sodium carbonate washed with solvent (3 × 50 mL) and three 50 mL portions of solvent/CH_3OH (1:20). After the resulting solution from the combined fractions were dried (Na_2SO_4), the solvent was evaporated, and the crude product was purified.

5-(2-Furoylmethylene)pyrrolidin-2-one (3a). Reaction time was 48 h. The product was purified by column chromatography, followed by preparative TLC (silica, $CHCl_3$/MeOH 1:20) to afford **3a** (40%) as colorless crystals, mp 185–185.5 °C: IR (KBr) 3265, 1740, 1640, 1580, 1470, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.55 (2H, m), 2.99 (2H, m), 6.10 (1H, t, J = 1.30 Hz), 6.54 (1H, dd, J = 1.77, 3.60 Hz), 7.18 (1H, dd, J = 0.85, 3.58 Hz), 7.58 (1H, dd, J = 0.86, J = 1.67 Hz), 10.95–10.98 (1H, br s, disappears with the addition of D_2O); ^{13}NMR ($CDCl_3$) δ 179.16, 178.54, 160.16, 153.53, 146.14, 116.12, 112.63, 95.26, 27.35, 26.73; MS *m/z* (relative intensity) 191 (39), 163 (15), 162 (22), 124 (23), 95 (100). Anal. Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33. Found: C,62.97; H, 4.85; N, 7.19.

1-Methyl-5-(2-furoylmethylene)pyrrolidin-2-one (3b). Reaction time was several minutes. The product was purified by successive recrystallizations with $CHCl_3$/hexane to afford **3b** as colorless crystals (90%), mp 194.5–195.0 °C: IR (KBr) 1725, 1645, 1575, 1465, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.62 (2H, m), 3.12 (3H, s), 3.42 (2H, m), 6.28 (1H, t, J = 1.77 Hz), 6.54 (1H, dd, J = 1.69, 3.52 Hz), 7.17 (1H, dd J = 0.87, 3.44 Hz), 7.56 (1H, dd, J = 1.66, 3.48 Hz); ^{13}C NMR ($CDCl_3$) δ 178.47, 177.24, 162.54, 154.54, 145.09, 114.99, 112.33, 95.73, 28.00 27.17, 25.87; MS *m/z* (relative intensity) 205 (M^+ 100), 177 ((35), 176 (91), 148 (33), 138 (30), 95 (82), 92(70). Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.52; H, 5.41; N, 6.61.

1-Ethyl-5-(2-furoylmethylene)pyrrolidin-2-one (3c). Reaction time was 30 min. The product was purified by column chromatography followed by preparative TLC (silica, hexane/$CHCl_3$ 1:10) to afford colorless crystals (76%), mp 134.5–135.0 °C: IR (KBr) 1725, 1650, 1585, 1475 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (3H, t), 2.59 (2H, m), 3.41 (2H, m), 3.70 (2H, q), 6.32 (1H, t, J = 1.77 Hz), 6.53 (1H, dd, J = 1.71, 3.55 Hz), 7.15 (1H, dd, J = 0.78, 3.53 Hz), 7.55 (1H, dd, J = 0.80, 1.70 Hz); ^{13}C NMR ($CDCl_3$) δ 178.85, 177.41,161.89, 154.87, 145.29, 115.10, 112.51, 95.50, 35.59, 28.03, 26.10, 11.88; MS *m/z* (relative intensity) 219 (M^+, 100), 204 (22), 202 (12), 192 (17), 191 (39), 176 (15), 162 (12), 148 (12), 124 (13), 96 (13), 95 (60). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.99; H, 6.06; N, 6.07.

1-Propyl-5-(2-furoylmethylene)pyrrolidin-2-one(3d). Reaction time was 1 h. The product was purified by column chromatography, followed by preparative TLC (silica, hexane/$CHCl_3$ 1:5) to afford **3d** as colorless crystals (41%), mp 81.5–82.0 °C: IR (KBr) 1735, 1650, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (3H, t) 1.68 (2H, m), 2.61 (2H, m), 3.42 (2H, m), 3.61 (2H, t), 6.31 (1H, t, J = 1.78 Hz), 6.53 (1H, dd, J = 1.71, 3.51 Hz), 7.15 (1H, dd, J = 0.78, 3.53 Hz), 7.55 (1H, dd, J = 0.81, 1.70 Hz); ^{13}C NMR ($CDCl_3$) δ 178.86, 177.71, 162.25, 154.89, 145.27, 115.07, 112.50, 95.69, 42.35, 27.97, 26.06, 19.98, 11.43; MS *m/z* (relative intensity) 233 (M^+, 100), 216 (13), 205 (20), 204 (78), 176 (24), 95(48). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 67.02; H, 6.82; N, 5.77.

1-Isopropyl-5-(2-furoylmethylene)pyrrolidin-2-one (3e). Reaction time was 4 h. The product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$/hexane 5:1) to afford **3e** as colorless crystals (62%), mp 117.5–118.0 °C: IR (KBr) 1745, 1645, 1590, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.49 (6H, d), 2.56 (2H, m), 3.39 (2H, m), 4.48 (1H, m), 6.46 (1H, t, J = 1.76 Hz), 6.53 (1H, dd, J = 1.56, 3.48 Hz), 7.14 (1H, dd, J = 0.76, 3.47 Hz), 7.55 (1H, dd, J = 0.80, 1.59 Hz); ^{13}C NMR ($CDCl_3$) δ 178.83, 177.83, 162.05, 155.02, 145.17, 114.93, 112.48, 96.15, 45.34, 28.31, 26.04, 18.82; MS *m/z* (relative intensity) 233 (M^+, 60), 218 (88), 204 (16), 190 (34), 176 (13), 163 (16), 162 (30), 124 (18), 122 (14), 110 (26), 95 (100). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 67.13; H,6.60; N, 5.83.

1-*n*-Butyl-5-(2-furoylmethylene)pyrrolidin-2-one (3f). Reaction time was 4 h. The product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$/hexane 1:1) to afford colorless crystals (44%), mp 85.5–86.0 °C: IR (KBr) 1754, 1645, 1580, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (3H, t,), 1.40 (2H, m), 1.62 (2H, m), 2.59 (2H, m), 3.41 (2H, m), 3.63 (2H, t), 6.30 (1H, t, J = 1.75 Hz), 6.53 (1H, dd, J = 1.69, 3.49 Hz), 7.13 (1H, dd, J = 0.80, 3.59 Hz), 7.54 (1H, J = 0.78, 1.77 Hz); ^{13}C NMR ($CDCl_3$) δ 178.88, 177.69, 162.23, 154.90, 145.29, 115.09, 112.51, 95.69, 40.60, 28.67, 27.99, 26.07, 20.26, 13.73; MS *m/z* (relative intensity) 247 (M^+, 37), 218 (11), 204 (39), 176 (15), 152 (19), 148 (16), 110 (16), 95 (100). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.83; H, 7.30; N, 5.45.

1-*tert*-Butyl-5-(2-furoylmethylene)pyrrolidin-2-one (3g). Reaction time was 48 h. The product was purified by column

chromatography followed by preparative TLC (silica, $CHCl_3$/MeOH 1:20) to afford colorless crystals (31%), mp 125.0–126.0 °C: IR (KBr) 1730, 1650, 1555, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71 (9H, s), 2.51 (2H, m), 3.32 (2H, m), 6.53 (1H, dd, J = 1.71, 3.50 Hz), 6.71 (1H, t, J = 1.79 Hz), 7.13 (1H, dd, J = 0.81, 3.52 Hz), 7.55 (1H, dd, J = 0.78, 1.70 Hz); ^{13}C NMR ($CDCl_3$) δ 178.63, 178.28, 163.17, 155.26, 145.18, 114.90, 112.49, 100.57, 58.58, 29.58, 29.17, 26.02; MS m/z (relative intensity) 247 (M^+, 63), 193 (61), 192 (98), 191 (19), 163 (68), 162 (40), 137 (20), 135 (17), 95(100). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.64; H, 6.85; N, 5.26.

1-Benzyl-5-(2-furoylmethylene)pyrrolidin-2-one (3h). Reaction time was 48 h. The product was purified by recrystallization with $CHCl_3$/hexane to afford colorless crystals (76%), mp 136.5–137.0 °C: IR (KBr) 1740, 1645, 1575, 1550, 1475 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.67 (2H, m,), 3.43 (2H, m), 4.82 (2H, s), 6.30 (1H, t, J = 1.79 Hz), 6.47 (1H, dd, J = 1.79, 3.62 Hz), 7.01 (1H, dd, J = 0.80, 3.65 Hz), 7.28 (5H, m), 7.50 (1H, dd, J = 0.79, 3.60 Hz); ^{13}C NMR ($CDCl_3$) δ 178.56, 177.69, 161.37, 154.64, 145.47, 135.15, 129.07, 128.10, 127.57, 115.18, 112.38, 96.96, 44.44, 27.94, 25.92; MS m/z (relative intensity) 281 (M^+, 20), 252 (19), 204 (14), 95 (18), 91 (100). Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.59; H, 5.37; N, 4.98. Found: C, 72.78; H, 5.15; N, 4.86.

1-(2-Hydroxyethyl)-5-(2-furoylmethylene)pyrrolidin-2-one (3i). Reaction time was 48 h. The product was recrystallized from $CHCl_3$/hexane to afford colorless crystals (41%), mp 155.0–155.5 °C: IR (KBr) 3400, 1745, 1620, 1545, 1470 cm^{-1}; ^1H- NMR ($CDCl_3$) δ 2.17 (1H, br s, disappears with the addition of D_2O), 2.62 (2H, m), 3.44 (2H, m), 3.87 (4H, m), 6.43 (1H, t, J = 1.81 Hz), 6.54 (1H , dd , J = 1.73, 3.56 Hz) , 7.17 (1H , dd, J = 0.78, 3.58 Hz), 7.55 (1H, dd, J = 0.85, 1.60 Hz); ^{13}C NMR ($CDCl_3$) δ 178.88, 178.68, 162.23, 154.74, 145.44, 115.39, 112.59, 96.11, 59.73, 43.47, 27.95, 26.22; MS m/z (relative intensity) 235 (M^+, 24), 206 (55), 204 (59), 191 (22), 95 (100), 81(38). Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 60.92; H, 5.29; N, 5.75.

1-Phenyl-5-(2-furoylmethylene)pyrrolidin-2-one (3j). Reaction time was 48 h. The product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$) to afford colorless crystals (40%), mp 213.0–214.0 °C: IR (KBr) 1740, 1640, 1575, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80 (2H, m), 3.60 (2H, m), 6.07 (1H, t, J = 1.84 Hz), 6.44 (1H, dd, J = 1.71, 3.54 Hz), 6.99 (1H, dd, J = 0.76, 3.65 Hz), 7.26 (2H, m), 7.45 (1H, dd, J = 0.81, 1.75 Hz), 7.54 (3H, m). ^{13}C NMR (KBr) δ 178.19, 177.19, 163.09, 154.55, 145.52, 134.37, 130.20, 129.48, 127.83, 115.40, 112.33, 97.57, 28.53, 26.30; MS m/z (relative intensity) 267 (M^+, 100), 239 (16), 238 (38), 212 (11), 210 (16), 172 (23), 144 (13), 95 (38), 78 (19). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.59; H, 4.43; N, 5.26.

1-(2-Chlorophenyl)-5-(2-furoylmethylene)pyrrolidin-2-one (3k). Reaction time was 48 h. The product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$) to afford colorless crystals (20%), mp 169.0–170.0 °C: IR (KBr) 1750, 1650, 1575, 1480 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.82 (2H, m), 3.64 (2H, m), 5.83 (1H, t, J = 1.87 Hz), 6.45 (1H, dd, J = 1.64, 3.48 Hz), 7.00 (1H, dd, J = 0.75, 3.65 Hz), 7.31 (1H, m) 7.44 (1H, dd, J = 1.65, 0.77 Hz), 7.47 (2H, m), 7.63 (1H, m); ^{13}C NMR ($CDCl_3$) δ 178.85, 176.53, 161.70, 154.46, 145.55, 132.85, 132.03, 131.25, 131.22, 130.26, 128.60, 115.53, 112.38, 97.56, 28.38, 26.42; MS m/z (relative intensity) 303 (M^+, 11), 301 (M^+, 41), 272 (18), 266 (100), 95 (98). Anal. Calcd for $C_{16}H_{12}NO_3Cl$: C, 63.69; H, 4.01; N, 4.64. Found: C, 63.14; H, 3.84; N, 4.45.

1-(4-Chlorophenyl)-5-(2-furoylmethylene)pyrrolidin-2-one (3l). Reaction time was 48 h. Product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$) to afford colorless crystals (40%), mp: 197.5–198.5 °C: IR (KBr) 1745, 1640, 1570, 1495, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) 2.80 (2H, m,), 3.59 (2H, m), 6.07 (1H, t, J = 1.67 Hz), 6.47 (1H, dd, J = 1.67, 3.50 Hz), 7.03 (1H, dd, J = 0.70, 3.52 Hz), 7.22 (2H, d, J = 8.62 Hz), 7.47 (1H, dd, J = 0.68, 1.65 Hz), 7.55 (2H, d, J = 8.79 Hz); ^{13}C NMR ($CDCl_3$) δ 178.84, 176.98, 162.52, 154.52, 145.60, 135.42, 132.42, 130.51, 129.24, 115.55, 112.44, 97.63, 28.47, 26.24; MS m/z (relative intensity) 303 (M^+, 35), 301 (M^+, 100), 274 (16), 273 (21), 272 (38), 246 (16), 230 (70), 206 (20), 95 (70). Anal. Calcd for $C_{16}H_{12}NO_3Cl$: C, 63.69; H, 4.01; N, 4.64. Found: C, 63.62; H, 4.08; N, 4.40.

1-(2-Methylphenyl)-5-(2-furoylmethylene)pyrrolidin-2-one (3m). Reaction time was 48 h. The product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$) to afford colorless crystals (18%), mp 175.5–176.5 °C: IR (KBr) 1750, 1650, 1570, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.16 (3H, s), 2.82 (2H, m), 3.63 (2H, m), 5.83 (1H, t, J = 1.89 Hz), 6.44 (1H, dd, J = 1.77, 3.56 Hz), 6.98 (1H, dd, J = 0.69, 3.71 Hz), 7.14 (1H, d, J = 7.00 Hz), 7.40 (3H, m), 7.44 (1H, dd, J = 0.69, 1.72 Hz); ^{13}C NMR ($CDCl_3$) δ 178.96, 176.95, 162.53, 154.51, 145.53, 136.09, 133.15, 131.87, 130.04, 128.31, 127.84, 115.40, 112.32, 97.40, 28.45, 26.40, 17.42; MS m/z (relative intensity) 281 (100), 252(25), 186 (32), 172 (30), 171 (64), 130 (18), 95 (81), 91 (31). Anal. Calcd for $C_{17}H_{14}NO_3$: C, 72.58; H, 5.38; N, 4.98 Found: C, 72.71; H, 5.50; N, 4.60.

1-(4-Methylphenyl)-5-(2-furoylmethylene)pyrrolidin-2-one (3n). Reaction time was 48 h. The product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$) to afford colorless crystals (36%), mp 224.5–225.5 °C: IR (KBR) 1740, 1650, 1575, 1515, 1465 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (3H, s),2.78 (2H, m), 3.58 (2H, m), 6.07 (1H, t, J = 1.85 Hz), 6.44 (1H, dd, J = 1.69, 3.48 Hz), 7.00 (1H, dd, J = 0.81, 3.42 Hz), 7.14 (2H, d, J = 8.26 Hz), 7.36 (2H, d, J = 8.06 Hz), 7.45 (1H, dd, J = 0.83, 1.64 Hz); ^{13}C NMR ($CDCl_3$) δ 178.97, 177.35, 163.29, 154.59, 145.48, 139.55, 131.63, 130.84, 127.49, 115.34, 112.30, 97.30, 28.50, 26.28, 21.35; MS m/z (relative intensity) 281 (100), 253 (17) 252 (35), 224 (14) 186 (26), 95 (41), 91 (16). Anal. Calcd for $C_{17}H_{15}NO_4$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.31; H, 5.35; N, 4.56.

1-(3-Methoxyphenyl)-5-(2-furoylmethylene)pyrrolidin-2-one (3o). Reaction time was 48 h. The product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$) to afford colorless crystals (40%), mp: 141.0–142.0 °C; IR (KBr) 1740, 1645, 1580, 1475 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80 (2H, m), 3.59 (2H, m), 3.85 (3H, s), 6.10 (1H, t, J = 1.92 Hz), 6.45 (1H, dd, J = 1.65, 3.48 Hz), 6.78 (1H, t, J = 2.20 Hz), 6.84 (1H, ddd, J = 0.94, 1.88, 7.81 Hz), 7.01(1H, dd, J = 0.75, 3.66), 7.04 (1H, ddd, J = 0.91, J = 2.54, 8.45 Hz), 7.46 (1H, dd, J = 0.81, 3.48 Hz), 7.47 (1H, t, J = 8.10 Hz); ^{13}C NMR ($CDCl_3$) δ 178.98, 177.10, 162.95, 161.03, 154.55, 145.54, 135.39, 130.92, 119.87, 115.42, 113.35, 112.34, 97.69, 55.61, 28.55, 26.27; MS m/z (relative intensity) 297 (100), 280 (30), 268 (25), 174 (13), 160 (13), 95(8). Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.65; H, 4.84; N, 4.73.

1-(4-Methoxyphenyl)-5-(2-furoylmethylene)pyrrolidin-2-one (3p). Reaction time was 48 h. The product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$) to afford colorless crystals (48%), mp 211.0–212.0 °C; IR (KBr) 1740, 1640, 1575, 1520, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.78 (2H, m) 3.58 (2H, m), 3.88 (3H, s), 6.06 (1H, t, J = 1.88 Hz), 6.45 (1H, dd, J = 1.86, 3.48 Hz), 7.00 (1H, dd, J = 0.74, 3.37 Hz), 7.06 (1H, d, J = 9.10 Hz), 7.17 (1H, d, J = 8.80 Hz), 7.45 (1H, dd, J = 0.74, 1.88 Hz); ^{13}C NMR ($CDCl_3$) δ 178.96, 177.48, 163.50, 160.20, 154.59, 145.48, 128.92, 126.74, 115.44, 115.33 112.32, 97.52, 55.65, 28.46, 26.22; MS m/z (relative intensity) 297 (100), 269 (18), 268 (30), 95 (54). Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.82; H, 4.86; N, 4.48.

1-Amino-5-(2-furoylmethylene)pyrrolidin-2-one (3q). Reaction time was 48 h. The product was purified by recrystallization with hot methanol to afford colorless crystals (44%), mp 193.0–194.0 °C: IR (KBr) 3330, 1715, 1640, 1575, 1550, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.63 (2H, m), 3.41 (2H, m), 4.26 (2H, s, disappers with the addition D_2O), 6.54 (1H, dd, J = 1.63, 3.54 Hz), 6.73 (1H, t, J = 1.89 Hz), 7.17 (1H, dd, J = 0.73, 3.66 Hz), 7.57 (1H, dd, J = 0.74, 1.60 Hz); ^{13}C NMR ($CDCl_3$) δ 178.81, 175.03, 159.13, 154.48, 145.38, 115.25, 112.21, 96.35, 26.40, 24.01; MS m/z (relative intensity) 206 (M^+, 14), 95 (100). Anal. Calcd for $C_{10}H_{10}N_2O_3$: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.11; H, 4.87; N, 13.60.

1-Methyl-6-(2-furoylmethylene)pyridazine (4). Reaction time was 48 h. The product was purified by column chromatography followed by preparative TLC (silica, $CHCl_3$/petroleum ether 3:4) to afford yellow crystals (48%), mp 114.5–115.0 °C: IR (KBr) 1620, 1585, 1565, 1520, 1480 cm^{-1}; ^1H NMR ($CDCL_3$) δ 9.41 (1H, dd, J = 1.86, 9.59 Hz), 7.66 (1H, dd, J = 1.91, 3.91 Hz), 7.46 (1H, dd, J = 0.72, 1.73 Hz), 7.05 (1H, dd, J = 0.68, 3.57 Hz), 6.91 (1H, ddd, J = 1.10, 3.94, J = 9.60 Hz), 6.48 (1H, dd, J = 1.71, 3.44 Hz), 5.70 (1H, d, J = 0.83 Hz, disappears with the addition of D_2O), 3.76 (3H, s); ^{13}C NMR ($CDCl_3$) δ 175.64, 155.98, 151.81, 143.53, 138.97, 131.08, 125.62, 112.38, 111.92, 84.30, 45.18; MS m/z (relative intensity) 202 (M^+, 100), 185 (25), 174 (19), 173 (60), 146 (14), 145 (17), 135 (36), 107 (35), 95 (34). Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.52; H, 5.41; N, 6.61.

1-(2-Furoyl)-6-anilino-6-azafulvene (5a). Reaction time was 48 h. The product was purified by column chromatography (silica, $CHCl_3$/petroleum ether 1:4) to afford red crystals (60%), mp 96.0–96.5 °C: IR (KBr) 3435, 1570, 1470, 1355 , 1207 cm^{-1}; ^1H NMR (CCl_4) δ 6.53 (1H, dd, J = 1.78, 3.50 Hz), 6.56 (1H, dd, J = 3.52, J = 4.50 Hz), 7.01 (1H, dd, J = 2.00, 4.59 Hz), 7.06 (1H, t, J = 7.34 Hz), 7.27 (1H, dd, J = 0.71, 3.45 Hz), 7.33 (2H, t, J = 7.92 Hz), 7.56 (2H, d, J = 7.80 Hz), 7.59 (1H, dd, J = 0.86, J = 1.78 Hz), 8.27 (1H, dd, J = 2.17, 3.08 Hz), 15.44 (1H, s, disappears with the addition of D_2O); ^{13}C NMR (CCl_4) δ 174.09, 154.20, 145.54, 144.71, 144.49, 142.30, 135.89, 128.96, 124.97, 124.45, 120.98, 118.06, 116.29, 111.63; MS m/z (relative intensity) 264 (M^+, 86), 119 (18), 103 (29), 95 (29), 77 (100). Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.43; H, 4.18; N, 10.49.

1-(2-Furoyl)-6-(4-nitroanilino)-6-azafulvene (5b). Reaction time was 48 h. The product was purified by column chromatography (silica, $CHCl_3$/petroleum ether 1:3) afforded red crystals (50%), mp 217.5–218.0 °C: IR (KBr) 3425, 1595, 1545, 1510, 1460 cm^{-1}; ^1H ($CDCl_3$) δ 6.64 (1H, dd, J = 1.75, 3.59 Hz), 6.75 (1H, dd, J = 3.27, 5.04 Hz), 7.05 (1H, dd, J = 2.04, 4.94 Hz), 7.38 (1H, dd, J = 0.80, 3.60 Hz), 7.59 (2H, d, J = 9.24 Hz), 7.71 (1H, dd, J = 0.90, 1.70 Hz), 8.28 (2H, d, J = 9.20 Hz), 8.37 (1H, dd, J = 2.09, 3.29 Hz), 15.13 (1H, s, disappears with the addition of D_2O); ^{13}C NMR ($CDCl_3$) δ 176.07, 153.43, 150.28, 148.06, 147.38, 146.92, 143.73, 136.57, 128.56, 125.97, 123.01, 119.91, 115.72, 112.60; MS m/z (relative intensity) 309 (M^+, 100), 172 (13), 131 (32), 119 (17), 103 (28), 102 (11), 95 (27). Anal. Calcd for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.58; N, 13.59. Found: C, 62.44; H, 3.63; N, 13.40.

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