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# THE PHOTOCHEMICAL REACTION OF HETEROCYCLIC KETENE AMINALS WITH METHYL ACRYLATE

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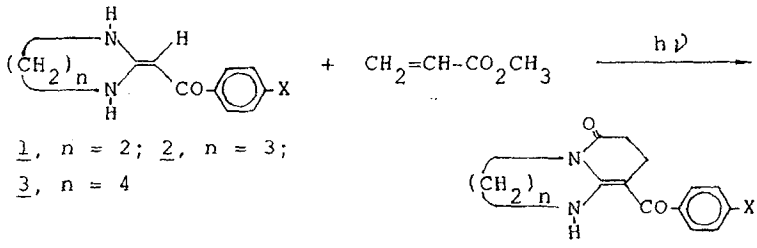
Abstract: Heterocyclic ketene aminals 1 - 3 and methyl acrylate were irrdiated in methanol to give the fused heterocyclic compounds 4 - 6. The characteristics and mechanism of this photochemical reaction were discussed.

Heterocyclic ketene aminals can react with wide variety of organic compounds to afford different kinds of heterocyclic or fused heterocyclic compounds,[1-11] therefore, they may be used as versatile synthetic intermediates in heterocyclic synthesis. However, the photochemical reaction of heterocyclic ketene aminals has not been reported yet. Here, we wish to report some results of photochemical reaction of heterocyclic ketene aminals with methyl acrylate.

Hetrocyclic ketene aminals 1 - 3 and methyl acrylate were irradiated in methanol to afford the fused heterocyclic compounds 4 - 6.



1, n = 2; 2, n = 3;
3, n = 4

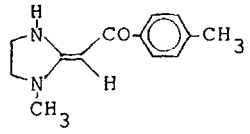
4, n = 2; 5, n = 3;
6, n = 4

| 1 - 7 | a | b | c | d |
|---|---|---|---|---|
| X | H | $CH_3$ | $OCH_3$ | Cl |

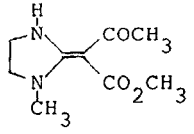
The reaction time and yield of product are listed in the following Table

| starting material | reaction time, h | product | yield, % |
|---|---|---|---|
| 1a | 5 | no reaction | |
| 1b | 5 | no reaction | |
| 1c | 5 | 4c | 90 |
| 1d | 5 | no reaction | |
| 2a | 3 | 5a | 79 |
| 2b | 5 | 5b | 86 |
| 2c | 5 | 5c | 91 |
| 2d | 4 | 5d | 82 |
| 3a | 5 | 6a | 80 |

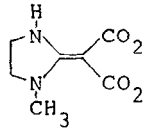
Other ketene aminals with five-membered imidazolidine ring (1e - g) and fused imidazolidine ring (7) show also no reaction with methyl acrylate in the same reaction conditions. In addition, 2c shows no reaction with vinyl acetate, acrylonitrile or crotyl chloride too.



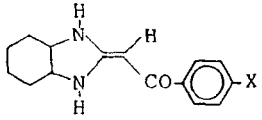
1e



1f



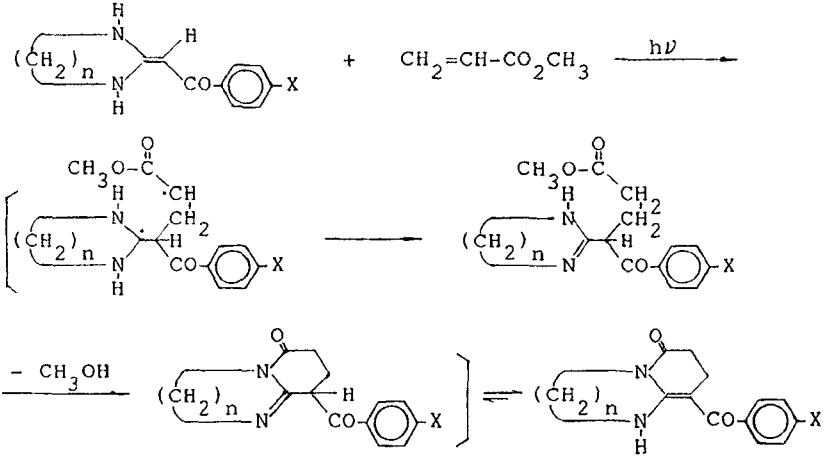
1g



7a - c

The thermal reaction of heterocyclic ketene aminals with methyl acrylate has been reported under reflux in dioxane for long period to give the same fused heterocyclic products.[4,7] However, the photochemical reaction of heterocyclic ketene aminals with methyl acrylate possesses the following characteristics: Firstly, the photochemical reaction with methyl acrylate is sensitive to the structure of heterocyclic ketene aminals, the reaction is favorable for ketene aminals with six-membered tetrahydropyrimidine or seven-membered hexahydrodiazepine rings and unsuitable for that with five-membered imidazolidine ring except 1c, however, this is not the feature in thermal reaction. Secondly, the photochemical reaction of heterocyclic ketene aminals with methyl acrylate is clear-cut, the reaction gives high yield of product, otherwise it shows no reaction, therefore, the product is easy to purify and always shows a higher melting point. And thirdly, the photochemical reaction proceeds at milder conditions, such as at ambient temperature and for a shorter reaction time.

The mechanism of the photochemical reaction is proposed as follows, and the reaction mechanism details are under investigation.



## EXPERIMENTAL

Melting points were uncorrected. Microanalyses were carried out by the Analytical Laboratory of the Institute. Mass spectra were recorded on a AEI MS-50 equipment. IR spectra were measured on a Perkin-Elmer 983 spectrometer using KBr tablets. $^{1}H$- and $^{13}C$-NMR spectra were recorded on a Varian 200 machine in $CDCl_3$.

General Procedure for Preparation of 4 - 6:

A mixture of 2 mmol of 1 - 3, excess of methyl acrylate (4.0 g) and 30 ml of anhydrous methanol was irradiated by 450 W medium-pressure mercury lamp under nitrogen atmosphere. The reaction was monitored by TLC, and the reaction time was indicated in the Table. After removal of solvent

and excess of methyl acrylate, the crude product was recrystallized from ethyl acetate.

8-(4-Methoxybenzoyl)-2,3,6,7-tetrahydroimidazo[1,2-a]-pyridin-5(1H)-one (4c):

Yield: 90%; m.p. 201-202°C. MS: m/z = 272 ($M^+$, 35), 271 (80), 244 (32), 229 (13), 215 (5), 163 (10), 135 (100). IR: $\nu$ = 3296 (NH), 1679 (lactam C=O), 1627 (C=O), 1599, 1521 $cm^{-1}$. $^1$H-NMR: $\delta$ = 9.46 (s, 1H), 7.42 (d, 2H), 6.87 (d, 2H), 3.94 (t, 2H), 3.80 (t, 2H), 3.81 (s, 3H), 2.74 (t, 2H), 2.50 ppm (t, 2H). $^{13}$C-NMR: $\delta$ = 190.1, 169.3, 160.5, 156.8, 133.5, 128.9, 113.1, 85.2, 55.2, 42.6, 41.7, 32.5, 22.5 ppm. Anal. calcd. for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29. Found C, 66.74; H, 5.73; N, 10.40.

9-Benzoyl-1,2,3,4,7,8-hexahydropyrido[1,2-a]pyrimidin-6-one (5a):

Yield: 79%; m.p. 172-173°C. MS: m/z = 256 ($M^+$, 96), 255 (100), 241 (15), 227 (36), 213 (7), 199 (7), 179 (9), 151 (95). IR: $\nu$ = 3200 (NH), 1688 (lactam C=O), 1611 (C=O), 1533 $cm^{-1}$. $^1$H-NMR: $\delta$ = 12.77 (s, 1H), 7.21 (s, 5H), 3.70 (t, 2H), 3.32 (quin, 2H), 2.40 (s, 4H), 1.90 ppm (quin, 2H). $^{13}$C-NMR: $\delta$ = 188.8, 170.5, 156.5, 141.9, 128.6, 127.9, 126.9, 87.2, 39.0, 38.5, 32.7, 21.6, 20.6 ppm. Anal. calcd. for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found C, 70.81; H, 6.11; N, 11.04.

9-(4-Methylbenzoyl)-1,2,3,4,7,8-hexahydropyrido[1,2-a]-pyrimidin-6-one (5b):

Yield: 86%; m.p. 155-156°C. MS: m/z = 270 ($M^+$, 69), 269 (100), 255 (11), 241 (50), 227 (7), 213 (4), 179 (5),

151 (72). IR: $\nu$ = 3210 (NH), 1690 (lactam C=O), 1609 (C=O), 1568, 1535 $cm^{-1}$. $^1$H-NMR: $\delta$ = 12.70 (s, 1H), 7.27 (d, 2H), 7.16 (d, 2H), 3.83 (t, 2H), 3.46 (t, 2H), 2.53 (t, 2H), 2.51 (t, 2H), 2.36 (s, 3H), 2.02 ppm (quin, 2H). $^{13}$C-NMR: $\delta$ = 189.1, 170.5, 155.9, 139.0, 138.1, 128.6, 126.9, 87.4, 39.1, 38.6, 32.8, 21.8, 21.4, 20.8 ppm. Anal. calcd. for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.73. Found C, 70.14; H, 6.49; N, 10.40.

9-(4-Methoxybenzoyl)-1,2,3,4,7,8-hexahydropyrido[1,2-a]-pyrimidin-6-one (5c):

Yield: 91%; m.p. 183-184°C. MS; m/z = 286 ($M^+$, 63), 285 (80), 271 (7), 257 (50), 243 (10), 229 (7), 177 (9), 151 (82), 135 (100). IR: $\nu$ = 3210 (NH), 1686 (lactam C=O), 1600 (C=O), 1532 $cm^{-1}$. $^1$H-NMR: $\delta$ = 12.75 (s, 1H), 7.35 (d, 2H), 6.86 (d, 2H), 3.81 (t, 2H), 3.79 (s, 3H), 3.44 (quin, 2H), 2.59 (t, 2H), 2.48 (t, 2H), 2.01 ppm (quin, 2H). $^{13}$C-NMR: $\delta$ = 188.4, 170.5, 160.0, 156.4, 134.4, 128.6, 113.0, 87.3, 55.2, 39.0, 38.5, 32.7, 21.9, 20.6 ppm. Anal. calcd. for $C_{16}H_{18}N_2O_3$: C, 67.11; H, 6.34; N, 9.79. Found C, 67.08; H, 6.35; N, 9.76.

9-(4-Chlorobenzoyl)-1,2,3,4,7,8-hexahydropyrido[1,2-a]-pyrimidin-6-one (5d):

Yield: 82%; m.p. 174-175°C. MS: m/z = 292 (20), 291 (31), 290 ($M^+$, 59), 289 (72), 275 (13), 261 (30), 247 (6), 179 (8), 151 (100). IR: $\nu$ = 3200 (NH), 1692 (lactam C=O), 1600 (C=O), 1569, 1533 $cm^{-1}$. $^1$H-NMR: $\delta$ = 12.76 (s, 1H), 7.31 (s, 4H), 3.82 (t, 2H), 3.44 (quin, 2H), 2.50 (s, 4H), 2.02 ppm (quin, 2H). $^{13}$C-NMR: $\delta$ = 187.3, 170.4, 156.8,

140.3, 134.5, 128.3, 128.2, 87.2, 39.0, 38.6, 32.7, 21.6, 20.6 ppm. Anal. calcd. for $C_{15}H_{15}ClN_2O_2$: C, 61.96; H, 5.20; N, 9.64. Found C, 61.66; H, 5.00; N, 9.53.

10-Benzoyl-2,3,4,5,8,9-hexahydropyrido[1,2-a]-1,3-diazepin-7(1H)-one (6a);

Yield: 80%; m.p. 191-192°C. MS: m/z = 270 ($M^+$, 93), 269 (88), 255 (20), 241 (14), 213 (8), 193 (9), 165 (100). IR: $\nu$ = 3205 (NH), 1689 (lactam C=O), 1609 (C=O), 1534 $cm^{-1}$. $^1$H-NMR: $\delta$ = 11.70 (s, 1H), 7.38 (s, 5H), 3.90 (t, 2H), 3.41 (quin, 2H), 2.46 (s, 4H), 1.81 ppm (t, 4H). $^{13}$C-NMR: $\delta$ = 191.3, 171.3, 161.9, 142.0, 129.1, 128.0, 126.7, 92.9, 45.2, 44.8, 34.1, 26.4, 26.1, 22.2 ppm. Anal. calcd. for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.37. Found C, 71.62; H, 6.80; N, 10.45.

5a[4], 5b,d[7] and 6a[7] have been synthesized from the same starting materials and methyl acrylate under reflux in dioxane. 5c has been synthesized from reaction of 2c with ethyl $\beta$-bromopropionate.[7]

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