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INTRAMOLECULAR [2+2] PHOTOCYCLOADDITION OF $\underline{N}^1$-(ω -ALKENYL)-PYRIMIDINES: FORMATION OF DIAZATRICYCLODIONES

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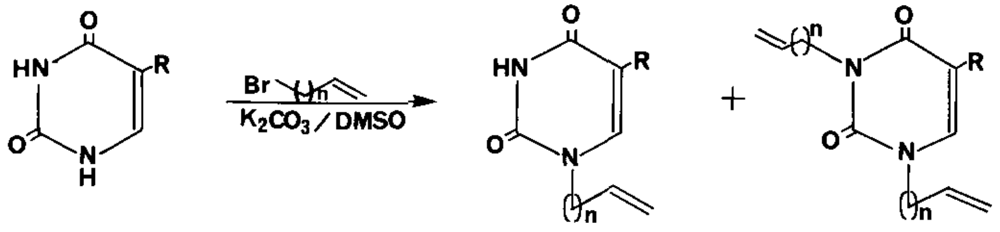
Abstract - Irradiation of N^1-(ω -alkenyl)pyrimidines in a CH_3CN solution gave parallel cycloadducts, diazatricyclodiones, as the sole photoproduct.

Intramolecular [2+2] photocycloadditions of cyclic α,β-enone tethered to an alkene have been shown to be one of the useful synthetic methods for the construction of carbocyclic and heterocyclic systems.[1] Subsequent cleavage of the cyclobutane ring of photoproducts by various chemical means results an annelative two-carbon ring or carbon-hetero ring expansion of the original enones.[2] We now report the preliminary results with the intramolecular photocycloaddition of N^1-(ω -alkenyl) pyrimidines which leads to regiospecific nitrogen containing ring systems. Diazatricyclodione, (7) or (8), was produced from N^1-(ω -alkenyl)uracil(3) or N^1-(ω -alkenyl)thymine(4) with a remarkable efficiency at room temperature in CH_3CN solution. Treatment of uracil(1) or thymine(2) with ω -alkenyl bromides under basic conditions in the presence of a catalytic amount of KI, (3) or (4) was formed as a crystalline product in 30-40% yield along with oily N^1,N^3-dialkenyl-pyrimidines, (5) or (6), in 50% yield. The structural assignments of (3) and (4) were consistent with ir, uv, ^{1}H nmr and mass spectral data(Scheme Ⅰ).[3]



1. R = H

2. R = CH_3

3a. R = H n = 2

b. R = H n = 3

c. R = H n = 4

4a. R = CH_3 n = 2

b. R = CH_3 n = 3

c. R = CH_3 n = 4

5a. R = H n = 2

b. R = H n = 3

c. R = H n = 4

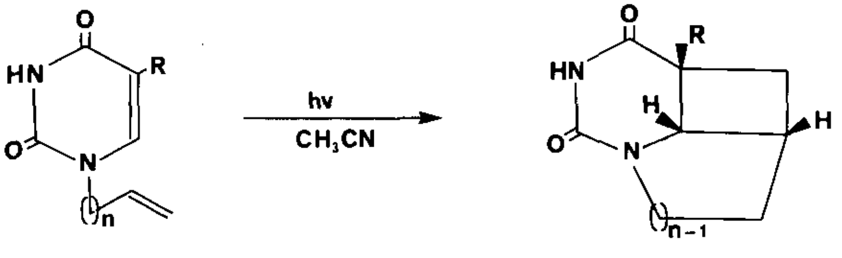
6a. R = CH_3 n = 2

b. R = CH_3 n = 3

c. R = CH_3 n = 4

Scheme I

Irradiation of a 10^{-3}M solution of (3a) or (4a) in CH_3CN under a nitrogen atmosphere through quartz tube, using germicidal lamp, for 3 h resulted in the complete disappearance of (3a) or (4a).



3 or 4

7a. R = H n = 2

b. R = H n = 3

c. R = H n = 4

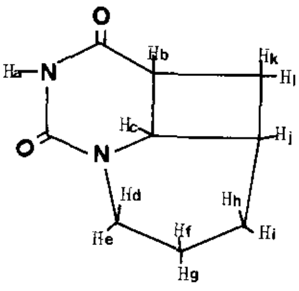
8a. R = CH_3 n = 2

b. R = CH_3 n = 3

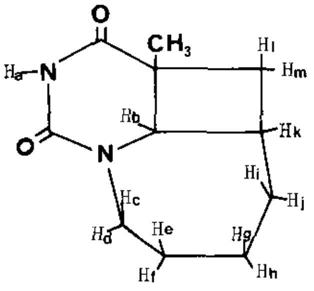
c. R = CH_3 n = 4

Scheme II

Under the same conditions, only 50% of (3c) or (4c) was converted to the product even after 6 h irradiation while 70-75% of (3b) or (4b) was consumed within 4 h irradiation. The nature of relationship between the length of the ω-alkenyl group and the rate of photocycloaddition remains to be established. Irradiation of (3) or (4) in CH_3CN-acetone(9:1) solution also provided identical photoproducts. In both cases examination of nmr spectrum of the reaction mixture after evaporation of solvent indicated the formation of *single photoproduct, (7) or (8). Assignment of the* ^1H nmr spectra of (7) and (8) was facilitated by examination of the COSY spectra. The chemical shift values for individual proton signals were obtained from the COSY cross-peak pattern.[4] The results of ^1H nmr of (7b) and (8c) are summerized in Table I. The distinguishing feature of cross or parallel in (7b) is the signal of the proton(Hb and Hc) in cyclobutane ring which appeared in δ 3.13and 3.94-3.96. If this product was a cross adduct, by the coupling pattern of COSY spectra, the chemical shift of Hb and Hc should be exchanged. Since the signal of proton next to nitrogen *should appear more downfield* when compared to that of proton next to carbonyl, (7b) should not be a cross product but a parallel one. The ^1H nmr spectra of (8c) provides more obvious information on its structure. Since the signal of Hb in cyclobutane ring which appeared in δ 3.72 splitted to doublet, this compound is a parallel product. We assume that Hb does not have a long range coupling because of the flexibility of a long methylene chain.



(7b)



(8c)

Table 1. ^{1}H nmr data for (7b) and (8c)[a]

H no.	δ (7b)	δ (8c)
a	8.51 (1H, s)	7.42 (1H, s)
b	3.13 (1H, ddd)	3.72 (1H, d)
CH_3	–	1.56 (3H, s)
c	3.94-3.96 (1H, m)	4.36-4.41 (1H, m)
d	4.41-4.44 (1H, m)	2.48-2.54 (1H, m)
e	2.48-2.54 (1H, m)	1.69-1.76 (1H/2H, m)
f	1.58-1.72 (1H/4H, m)	1.69-1.76 (1H/2H, m)
g	1.58-1.72 (1H/4H, m)	1.82-1.92 (1H/2H, m)
h	1.58-1.72 (1H/4H, m)	1.14-1.22 (1H, m)
i	1.58-1.72 (1H/4H, m)	1.34-1.42 (1H, m)
j	2.65-2.72 (1H, m)	1.82-1.92 (1H/2H, m)
k	2.40-2.45 (1H/2H, m)	2.57-2.64 (1H, m)
l	2.40-2.45 (1H/2H, m)	2.21-2.26 (1H, m)
m	–	2.03-2.08 (1H, m)

[a] Chemical shifts in ppm from TMS

Unambiguous assignments of the structures of the photoproducts, (7) and (8), were not possible from the ^{1}H nmr data alone due to the interference of long range coupling which commonly occurs in small bicyclic ring compounds.[5] The structure of (7a) was determined by a standard X-ray analysis.[6] The molecular structure is shown in Figure 1.

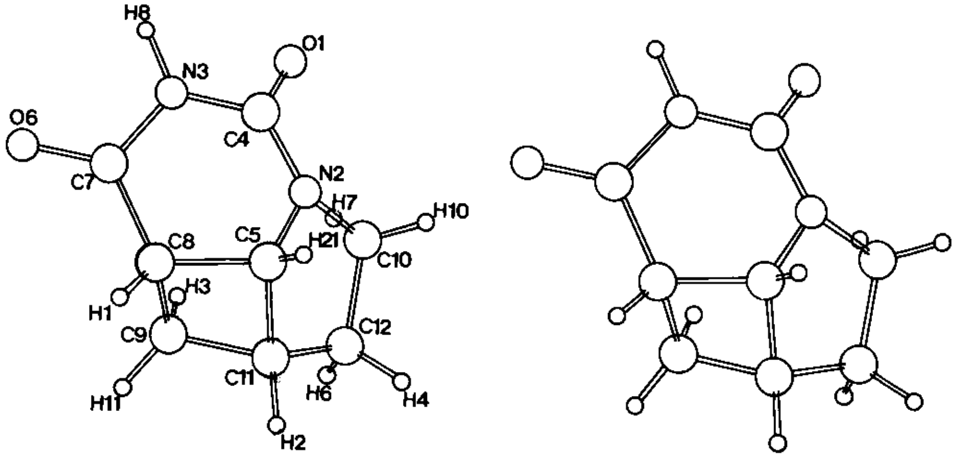


Figure 1. Pluto drawing of the X-ray structure of 1,3-diazatricyclo[5.2.1.0^{5,10}]decane-2,4-dione.

As it can be seen in the X-ray structure of (**7a**), in this system, regardless of the chain length of the alkenyl group, the photoproducts were always the parallel adducts, diazatricyclodiones. We obtained MM2 optimized structure of (**7a**) with the same, nearly planar tricycloring as the crystallographic structure.[7]

ACKNOWLEDGEMENT

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3. Melting points are uncorrected. Routine ^{1}H and 2D-^{1}H nmr spectra were recorded on a Bruker AW 80(80 MHz), Bruker AM 300(300 MHz) or JEOL JNM-GSX(500 MHz) spectrometer, and ^{13}C nmr spectra were recorded on a Bruker AM 300(75.4 MHz) spectrometer. The DEPT technique was used to distinguish methyl, methylene, methine, and quarternary carbon in ^{13}C nmr spectra. Apparent coupling constants are given in hertz. Ir spectra were recorded on a BIO-RAD FTS 40 spectrophotometer, and uv spectra on a Varian Superscan 3 instrument. Low- and high-resolution mass spectra were determined on a Hewllet-Packard 5988A GC/MS system in electron ionization mode at 70eV. **3a**. mp 99-100°C ; ir($CHCl_3$) 3023, 1699, 1670 cm^{-1} ; ^{1}H nmr(80 MHz, $CDCl_3$) δ 2.52 (2H, q, *J*=13.3 Hz), 3.83 (2H, t, *J*=7.0 Hz), 5.04-5.19 (2H, m), 5.71 (1H, d, *J*=9.4 Hz), 5.87-6.02 (1H, m), 7.22 (1H, d, *J*=7.3 Hz), 9.84 (1H, s) ; ms, m/z, 166(M^+). **4a**. mp 137-138°C ; ir($CHCl_3$) 3023, 1686, 1654 cm^{-1} ; ^{1}H nmr(80 MHz, $CDCl_3$) δ 1.93 (3H, s), 2.38 (2H, q, *J*=14.0 Hz), 3.81 (2H, t, *J*=7.0 Hz), 5.02-5.19 (2H, m), 5.58-6.03 (1H, m), 7.04 (1H, s), 8.76 (1H, s) ; ms, m/z, 180(M^+). **3b**. mp 86°C ; ir($CHCl_3$) 3017, 1699, 1668 cm^{-1} ; ^{1}H nmr(80 MHz, $CDCl_3$) δ 1.69-1.88 (2H, m), 2.04-2.29 (2H, m), 3.83 (2H, t, *J*=6.6 Hz), 4.92-5.21 (2H, m), 5.73 (1H, d, *J*=9.3 Hz), 5.90-6.07 (1H, m), 7.17 (1H, d, *J*=7.5 Hz), 9.93 (1H, s) ; ms, m/z, 180(M^+). **4b**. mp 102°C ; ir($CHCl_3$) 3030, 1689, 1656 cm^{-1} ; ^{1}H nmr(80 MHz, $CDCl_3$) δ 1.72-1.83 (2H, m), 1.88 (3H, s), 2.03-2.26 (2H, m), 3.69 (2H, t, *J*=7.5 Hz), 4.88-5.17 (2H, m), 5.60-5.98 (1H, m), 6.91 (1H, s), 8.83 (1H, s) ; ms, m/z, 194(M^+). **3c**. mp 79-80°C ; ir($CHCl_3$) 3047, 1679 cm^{-1} ; ^{1}H nmr(80 MHz, $CDCl_3$) δ 1.19-1.87 (4H, m), 2.14 (2H, q, *J*=13.1 Hz), 3.66 (2H, t, *J*=6.8 Hz), 4.93-5.19 (2H, m), 5.72 (1H, d, *J*=7.7 Hz), 5.87-6.07 (1H, m), 7.16 (1H, d, *J*=5.2 Hz), 9.80 (1H, s) ; ms, m/z, 194(M^+). **4c**. mp 128°C ; ir($CHCl_3$) 3036, 1694, 1679 cm^{-1} ; ^{1}H nmr(80 MHz, $CDCl_3$) δ 1.41-1.79 (4H, m), 1.92 (3H, s), 2.13-2.22 (2H, m), 3.68 (2H, t, *J*=6.8 Hz), 4.94-5.07 (2H, m), 5.62-5.93 (1H, m), 6.88 (1H, s), 8.31 (1H, s) ; ms, m/z, 208(M^+).

4. **7a**. (1,3-Diazatricyclo[5.2.1.$0^{5,10}$]decane-2,4-dione) mp 135-136°C ; ir($CHCl_3$) 3212, 1701 cm^{-1} ; ^{1}H nmr(300 MHz, $CDCl_3$) δ 1.75-1.86 (1H, m), 2.03-2.14(2H, m), 2.80-2.91 (1H, m), 2.98-3.08 (1H, m), 3.15 (1H, ddd, *J*=9.2, 9.2, 5.2 Hz) 3.27 (1H, dtd, *J*=11.6, 6.5, 4.1 Hz), 4.05 (1H, ddd, *J*=5.2, 5.2, 3.2 Hz), 4.35 (1H, ddd, *J*=12.3, 9.2, 3.1 Hz), 8.90 (1H, s) ; ms, m/z, 166(M^+). **8a**. (5-Methyl-1,3-diazatricyclo[5.2.1.$0^{5,10}$]decane-2,4-dione) mp 143-144°C ; ir($CHCl_3$) 3212,

2938, 1706 cm^{-1} ; ^{1}H nmr(500 MHz, CDCl$_3$) δ 1.51 (3H, s), 1.73-1.84 (1H, m), 2.02-2.09 (1H, m), 2.15-2.18 (1H, m), 2.35 (1H, ddd, *J*=11.8, 8.1, 3.5 Hz) 3.07-3.14 (1H, m), 3.26 (1H, dtd, *J*=11.5, 6.1, 4.1 Hz), 3.70-3.72 (1H, m), 4.37 (1H, ddd, *J*=12.2, 9.2, 2.9 Hz), 8.70 (1H, s) ; ms, m/z, 180(M$^+$). **7b**. (1,3-Diazatricyclo[5.3.1.0^{5,11}]undecane-2,4-dione) mp 154-155 °C ; ir(CHCl$_3$) 3208, 2937, 1717, 1689 cm^{-1} ; ^{1}H nmr(500 MHz, CDCl$_3$) δ 1.58-1.72 (4H, m), 2.40-2.45 (2H, m), 2.48-2.54 (1H, m), 2.65-2.72 (1H, m), 3.13 (1H, ddd, *J*=9.1, 9.0, 5.6 Hz), 3.94-3.96(1H, m), 4.41-4.44 (1H, m), 8.51 (1H, s) ; ms, m/z, 180(M$^+$). **8b**. (5-Methyl-1,3-diazatricyclo[5.3.1.0^{5,11}]undecane-2,4-dione) mp 183-184 °C ; ir (CHCl$_3$) 3195, 3062, 1711, 1673 cm^{-1} ; ^{1}H nmr(300 MHz, CDCl$_3$) δ 1.52 (3H, s), 1.58-1.83 (4H, m), 1.97 (1H, ddd, *J*=11.3, 7.6, 4.0 Hz), 2.35-2.62 (2H, m), 2.81-2.90 (1H, m), 3.63 (1H, t, *J*=4.6 Hz), 4.31-4.43 (1H, m), 7.38 (1H, s) ; ms, m/z, 194(M$^+$). **7c**. (1,10-Diazatricyclo[6.3.1.0^{6,12}]dodecane-9,11-dione) mp 173-174 °C ; ir(CHCl$_3$) 3067, 2950, 1684 cm^{-1} ; ^{1}H nmr(300 MHz, CDCl$_3$) δ 1.13-1.28 (1H, m), 1.39-1.51 (1H, m), 1.67-1.79 (2H, m), 1.80-1.96 (3H, m), 2.48-2.58 (1H, m), 2.60-2.79 (2H, m), 3.37-3.46 (1H, m), 4.13 (1H, t, *J*=8.0 Hz), 4.37-4.45 (1H, m), 7.40 (1H, s) ; ms, m/z, 194(M$^+$). **8c**. (8-Methyl-1,10-diazatricyclo[6.3.1.0^{6,12}]dodecane-9,11-dione) mp 120 °C ; ir(CHCl$_3$) 3047, 1672 cm^{-1} ; ^{1}H nmr(500 MHz, CDCl$_3$) δ 1.14-1.22 (1H, m), 1.34-1.42 (1H, m), 1.56 (3H, s), 1.69-1.76 (2H, m), 1.82-1.92 (2H, m), 2.03-2.08 (1H, m), 2.21-2.26 (1H, m), 2.48-2.54 (1H, m), 2.57-2.64 (1H, m), 3.72 (1H, d, *J*=6.7 Hz), 4.36-4.41 (1H, m), 7.42 (1H, s) ; ms, m/z, 208(M$^+$).

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6. Data for crystallographic were measured on an Enraf-Nonius CAD 4 diffractometer. The principle crystallographic parameters of compound (**7a**) are as follows ; F.W = 180.21 ; White plate ; Crystal dimension=0.80 X 0.80 X 0.20 mm; Space group $P2_1/n$(No. 14) ; a=6.585(7)Å, b=9.089(4)Å, c=12.937(10)Å, β=95.72(5)° V=770.35Å^3 ; Z=4 ; Dcalcd=1.5540 g/cm^3 ; Radiation=Mo Kα, λ=0.70930Å ; μ=1.0 cm^{-1} ; F(000)=192 ; Temperature=19±1 °C ; Final R=0.041 ; Number of unique reflections=718 with Fo0 $>$ 3σ(Fo0).
7. Molecular mechanics calculations were carried out by use of the program Chem-X, Mac II workstation available from Chemical Design Ltd, Oxford, England.

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