HETEROCYCLES, Vol. 52, No. 2, 2000, Received, 21th May, 1999

PHOTOCYCLOADDITION OF 6-CHLORO-1,3-DIMETHYLURACIL TO OLEFINS

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Abstract-----Photoreaction of 6-chloro-1,3-dimethyluracil (6-ClDMU) with olefins having alkyl, alkoxy, and vinyl groups in acetone afforded the corresponding cyclobutapyrimidine derivatives with head-to-tail regiochemistry in appreciable yields, while the reaction with olefins bearing electron withdrawing groups gave no cycloadduct. Similar Photolysis of 6-ClDMU with phenylacetylene gave [2+2] cycloadduts, 3,5-diaza[4.2.0]oct-7-enes and diphenylquinazolines.

Since the photolysis of 6-chloro-1, 3-dimethyluracil (6-ClDMU; **1**) in benzene in the presence of TFA was found to give a cycloaddition product, 1,3-dimethylcyclooctapyrimidine-2,4-dione in a fair yield, [1] we have studied the photocycloaddition reaction of 6-ClDMU (**1**) with benzene and its derivatives systematically.[2]

During the course, we have found that the photoreaction proceeds through the initial *ortho*-cycloaddition followed by the elimination of hydrogen chloride and the subsequent isomerization into various cycloadducts depending on the reaction conditions and the substituents on the benzene ring.[2e, f]

Meanwhile, the photocycloaddition of **1** to olefins has been reported by Kaneko *et al.*[3] However the study was limited to only some simple alkylolefins, and no detail on the reactions has been given. In order to establish the utility and the scope of the photocycloaddition reaction of **1** for the construction of a new ring system including a pyrimidine ring, our attention was focused on the photoreaction of **1** with various olefins. In the present paper, we describe our findings that UV-irradiation of a solution of **1** and olefins in acetone afforded the corresponding cyclobutapyrimidines regioselectively in appreciable yields.

First, we have reinvestigated the photoreaction of **1** with 2,3-dimethyl-2-butene (**2a**), which had been reported to give the corresponding cyclobutapyrimidine (**3a**) quantitatively, without any detailed description about the reaction conditions or the analytical method.[3] A solution of **1** (0.075 mmol) and **2a** (7.5 mmol) in acetone (5 mL) in a degassed sealed tube (Pyrex) was irradiated for two hours with a 500 W high-pressure mercury lamp (>300 nm), and was found to give the desired cycloadduct (**3a**) in satisfactory yield (60% based on 47% of **1** consumed).

The structure of **3a** was identified by comparison of its melting point (152-153 ˚C, *lit.*[3] 151-153 ˚C) and

the ^{1}H-NMR spectroscopic data ($CDCl_3$) with those reported in the literature.[3]

We then carried out the photoreaction with other alkylolefins under the similar conditions. 3, 3-Dimethyl-1-butene(**2b**) (2 h) gave the head-to-tail (h-t) cycloadduct (**3b**) in 50% yield. The reaction with cyclohexene (**2c**) (1 h) gave the cycloadduct (**3c**) in 35% yield (based on **1** 49% consumed). Thus, the reactions with alkylolefins were shown to give the corresponding cyclobutapyrimidines in fair yields. The structure of **3b** was deduced by means of MS (M^+, m/z 222) and NMR spectroscopy. The ^{1}H-NMR spectrum (C_6D_6) showed C-8 methylene protons at δ 2.19 (J = 11.2 and 1.2 Hz) and δ 2.37 (J = 11.2 and 4.5 Hz), C-7 methine proton at δ 2.41 (J = 4.5 and 1.2 Hz), and a singlet peak due to *t*-butyl protons at δ 0.57. The ^{13}C-NMR spectrum showed two peaks due to C-1 and C-6 sp^2 carbons at δ 108.84 and δ 155.56 ppm, respectively, supporting the presence of cyclobutene ring in the molecule. Further, the cross peak between N^5-methyl protons and the *tert*-butyl protons was observed on the NOESY spectrum, confirming the structural assignment. The structure of **3c** was deduced from the spectral analogy with **3b**.

Hence, our attention was extended to the reaction with olefins having electron donating alkoxy groups (**2d-g**) and those bearing such electron withdrawing groups as -CN and -CO_2CH_3. In order to investigate an appropriate solvent for the reaction, we have first carried out the photoreaction (1 h) with ethyl vinyl ether (**2d**, 10 equiv. mol) in various solvents.

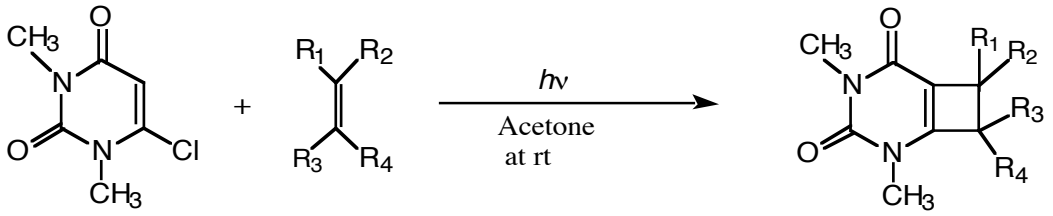
Table 1. Photoreaction of 6-Chloro-1, 3-dimethyluracil (**1**) with Ethyl Vinyl Ether (**2d**) in Various Solvents.

Solvent	Acetone	MeCN	AcOEt	Benzene	CH_2Cl_2	EtOH	MeOH
1 consumed(%)	41	5	4	4	4	5	3
3d(%)	42	9	10	0	0	0	0

As shown in Table 1, no reaction proceeded in benzene, dichloromethane (CH_2Cl_2), ethanol (EtOH) or methanol (MeOH). In ethyl acetate (AcOEt), or acetonitrile (MeCN), the desired cycloadduct (**3d**) was obtained with head-to-tail (h-t) regiochemistry, albeit in low yields. The best result (42% yield) was obtained when the reaction was performed in acetone. As the amount of **2d** increased from 10 to 100 equiv. mol, the yields of **3d** increased from 42% (based on **1**, 41% consumed) to 57% (based on **1**, 39% consumed) (Scheme 1). Hence, the following reactions were performed essentially with 100 equiv. molar olefins in acetone, unless cited therein.

The photoreaction with *tert*-butyl vinyl ether (**2e**) and 2-methoxypropene (**2f**) gave the corresponding [2+2] cycloadducts (**3e**, **3f**) with h-t regiochemistry[4] in 30% and 79% yields, respectively (Scheme 1). Similarly, cyclic vinyl ether, 2, 3-dihydropyran (**2g**), afforded **3g** in 30% yield (based on **1**, 27% consumed). By contrast, the photoreaction with electron deficient olefins, methyl acrylate and acrylonitrile, gave no cycloadduct.

The structures of the cycloadducts (**3d**, **3e**, **3f**, and **3g**) were deduced from the spectral (^{1}H-NMR) analogy with **3b**. The nuclear Overhauser enhancement (NOE) experiments confirmed their structural assignments (Figure 1).



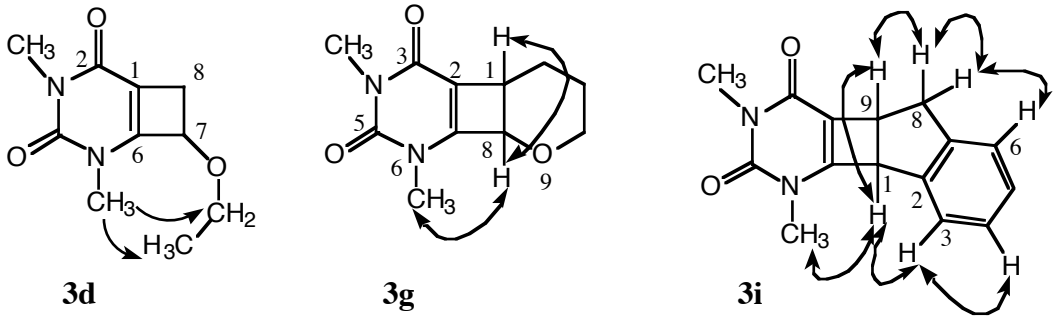
1 (6-ClDMU)

2a; R_1=R_2=R_3=R_4=CH_3[a]
2b; R_1=R_2=R_3=H, R_4=$C(CH_3)_3$[a]
2c; R_1=R_3=H, R_2, R_4=$CH_2CH_2CH_2CH_2$[b]
2d; R_1=R_2=R_3=H, R_4=OCH_2CH_3[b]
2e; R_1=R_2=R_3=H, R_4=$OC(CH_3)_3$[b]
2f; R_1=R_2=H, R_3=CH_3, R_4=OCH_3[b]
2h; R_1=R_2=R_3=H, R_4=*trans*-CH=$CHCH_3$[c]

3a; 60% (consumed **1**, 47%)[d]
3b; 50% (consumed **1**, 28%)[d]
3c; 35% (consumed **1**, 49%)[d]
3d; 57% (consumed **1**, 39%)[d]
3e; 30% (consumed **1**, 28%)[d]
3f; 79% (consumed **1**, 32%)[d]
3h; 32% (consumed **1**, 23%)[d,e]

a, Irradiated for 2 h. *b*, Irradiated for 1 h. *c*, Irradiated for 24 h. *d*, Yields aregiven based on **1** consumed. *e*. *trans* + *cis*-isomer (3:1)

Scheme 1



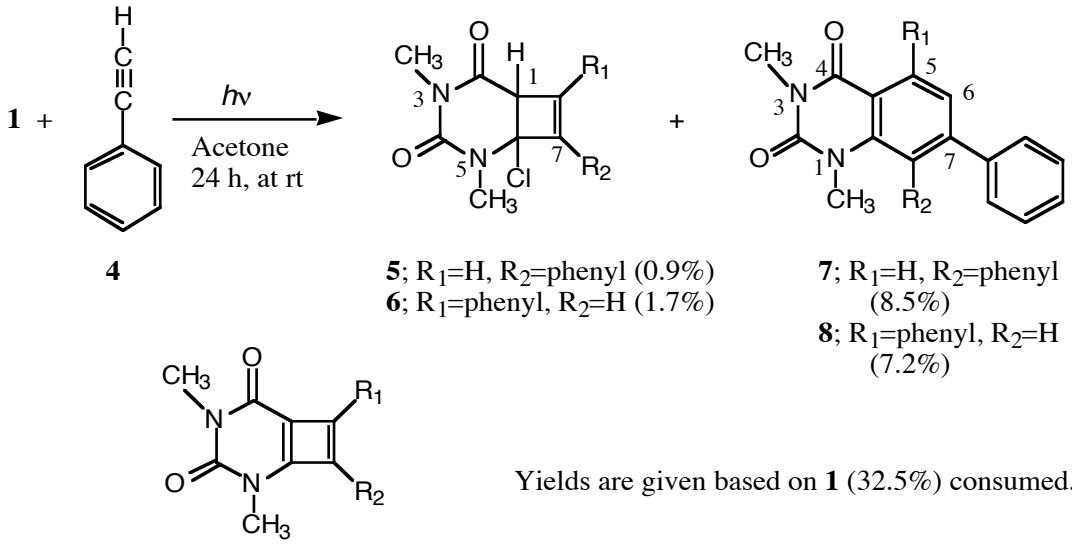
3d **3g** **3i**

Figure 1. NOE Correlation for **3d**, **3g**, and **3i**

We then extended the present method to the reaction with conjugated olefins, *trans*-piperylene (**2h**) and indene (**2i**). It is well recognized that some conjugated olefins such as piperylene (**2h**) serve as an efficient triplet quencher,[5] and hence these olefins were presumed to retard the photoreaction significantly. In fact, the reaction with **2h** proceeded inefficiently to consume only 23% of **1** even upon prolonged irradiation (24 h). Nonetheless, the desired [2+2] cycloadduct (**3h-*t***) and its *cis*-isomer (**3h-*c***) were obtained with h-t regiochemistry in 24% and 8% yields, respectively. The adduct (**3h-*c***) may result from the *trans*-isomer (**3h-*t***) through its photoisomerization.[6] Similarly the photoreaction with indene (**2i**) proceeded slowly (10 h, 11% of **1** consumed), but gave the h-t cycloadduct **3i** (Figure 1) in 10% yield.

The above findings that the conjugated olefins afforded the corresponding cycloadduct, though restrained the reaction significantly, encouraged us to investigate the photoreaction with phenylacetylene (**4**),

which was expected to provide a simple synthesis of cyclobutadiene derivatives. UV-irradiation of a solution of **1** (0.075 mmol) and **4** (3.75 mmol) in acetone (5 mL) in a degassed Pyrex test tube for 24 h resulted in the formation of a complicated mixture of the products. After submission to HPLC, cycloadducts (**5** and **6**), having a cyclobutane ring with the hydrogen and chlorine atoms at C-5 and C-6 of the pyrimidine ring intact, and the quinazoline derivatives (**7** and **8**) were isolated (Scheme 2).[7]

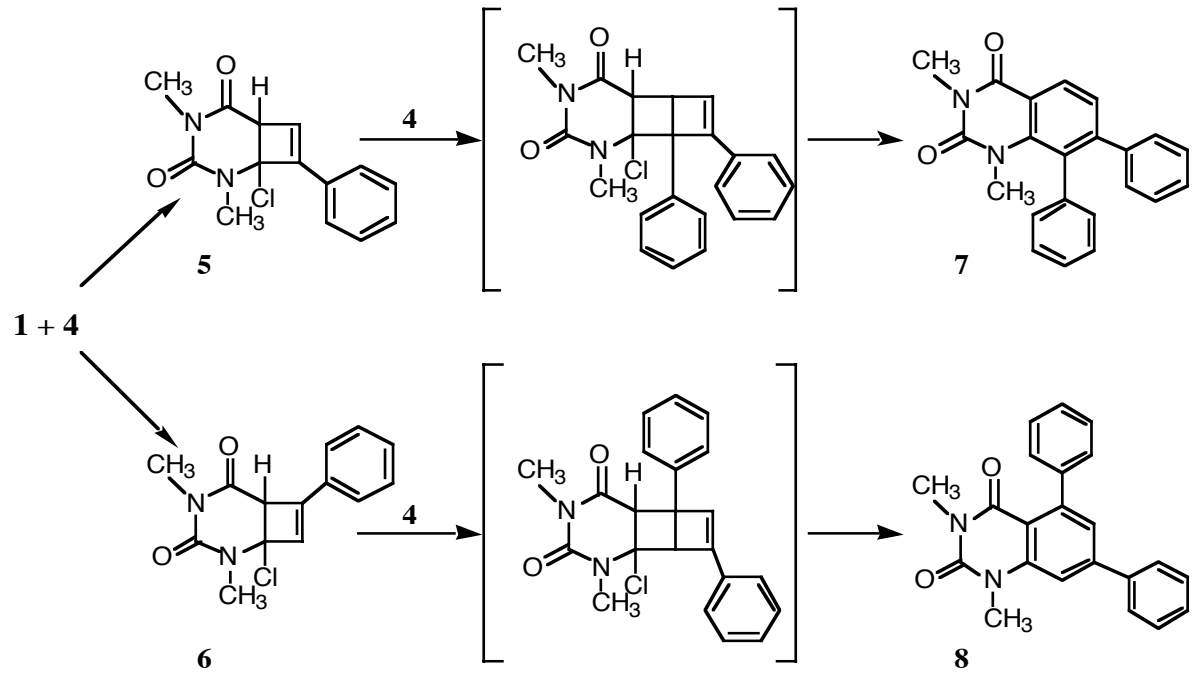


Scheme 2

The structures of **5** and **6** were determined by the followings: The MS spectra showed M^+ *m/z* 276 (**5**; 33%, **6**; 4.5%) and *m/z* 278 (**5**; 11.5%, **6**; 1.6%) in the ratio of 3 : 1, respectively. The ^{1}H-NMR spectrum of **5** showed two doublet peaks due to H-1 and H-8 with a coupling constant of J = 4 Hz, while that of **6** revealed two singlet peaks ascribed to H-1 and H-7. The NOE experiments confirmed the structural assignments. The ^{1}H-NMR spectra of the quinazolines (**7** and **8**), exhibited no peaks due to aliphatic protons except for two singlet peaks due the *N*-methyl protons, but twelve peaks due to aromatic protons. The ^{13}C-NMR spectra and the NOE experiments supported their structures.

The formation of **7** and **8** can be explained by the further [2+2] addition of **4** to the initially produced cycloadducts (**5** and **6**), followed by the aromatization by eliminating hydrogen chloride (HCl) (Scheme 3). Thus, the formation of cyclobutadiene derivatives (**9**) failed to be detected. These findings may imply that the formation of **9** through the elimination of HCl from **5** and **6** is energetically unfavorable, or the cyclobutadienes (**9**) thus formed might be too labile to subsist at room temperature.[8]

Although the reaction mechanism remains unelucidated, from a mechanistic point of view it may be interesting to note that the present cycloaddition reaction takes place with olefins bearing electron donating groups, but not with those having electron withdrawing groups, implying that participation of the formation of polar intermediates could not be excluded from the present reaction.[9] In addition, the present reaction proceeds most preferentially in a triplet sensitizer, acetone, suggesting that the triplet excited states may be involved.



Scheme 3

EXPERIMENTAL

All melting points are uncorrected. NMR spectra were measured with a JEOL JNM-EX400 (400 MHz) spectrometer, and ^{1}H-NMR chemical shifts are given on the δ (ppm) scale based on those of the signals of solvents; $CDCl_3$ (δ 7.26), C_6D_6 (δ 7.15), CD_3CN (δ 1.93), and following abbreviations are used; s = singlet, d = doublet, dd = double doublet, ddd = double double doublet, br dd = broad double doublet, t = triplet, dt = double triplet, q = quartet, dq = double quartet, ddq = double double quartet, m = multiplet. ^{13}C-NMR chemical shifts were recorded based on those of the signals of solvents; $CDCl_3$ (δ 77.0) C_6D_6 (d 128.0) CD_3CN (δ 118.2). MS spectra and high-resolution MS (HRMS) spectra were determined on a JEOL JMS-DX303 spectrometer with ionization potential at 70 eV. Short-column chromatography was performed on Kieselgel Si-60 (Merck). HPLC was conducted on a Shim-pac PREP-Sil (H) (25 cm x 20 mm *i.d.*) (silica gel), using a Shimadzu LC-6A apparatus with monitoring at 254 nm. UV-irradiation was carried out externally with a 500 W high-pressure mercury (h.p.Hg) lamp (Eiko-sha) in a degassed Pyrex tube (> 300 nm) on a merry-go-round apparatus at room temperature.

General procedure of the photoreaction ----- A solution of **1** (13.08 mg, 0.075 mmol) and an olefin (100 equiv. molar; 7.5 mmol) in acetone (5 mL) in a degassed Pyrex test tube was irradiated externally for 1 h unless cited therein. The reaction mixture was concentrated *in vacuo*, and analyzed by means of ^{1}H-NMR spectroscopy with terephthalnitrile as an internal standard.

Typical procedure for the isolation of the cycloadduct ----- After the photoreaction according to the general procedure, the reaction mixtures in several Pyrex tubes were put together, and evaporated *in vacuo*. The residual oil was passed through a short column of silica gel with ethyl acetate. The eluate was submitted to HPLC with following solvent systems; ethyl acetate-hexane for **3b-i**, and ethyl acetate-dichloromethane for **3a**.

3,5,7,7,8,8-Hexamethyl-3,5-diazabicyclo[4.2.0]oct-1(6)-ene-2,4-dione (3a) ----- Color-

less plates, mp 152-153 ˚C (recrystallized from hexane). ^{1}H-NMR ($CDCl_3$) δ: 1.30 (6H, s), 1.32 (6H, s), 3.21 (3H, s), 3.24 (3H, s). MS *m/z* (%): 222 (M^+, 52), 207 (100), 164 (29), 150 (41), 122 (58), 82 (23), 42 (44). HRMS: Calcd for $C_{12}H_{18}N_2O_2$: 222.1368. Found: 222.1364. *Anal.* Calcd for $C_{12}H_{18}N_2O_2$: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.82; H, 8.18; N, 12.55.

7-(*tert*-Butyl)-3,5-dimethyl-3,5-diazabicyclo[4.2.0]oct-1(6)-ene-2,4-dione (3b) ----- Color-less oil. ^{1}H-NMR (C_6D_6) δ: 0.57 (9H, s, $C(C\underline{H}_3)_3$-7), 2.19 (1H, dd, *J* = 1.2, 11.2 Hz, H-8), 2.37 (1H, dd, *J* = 4.5, 11.2 Hz, H-8), 2.41 (1H, dd, *J* = 4.5, 1.2 Hz, H-7), 2.70 (3H, s, N^5-CH_3), 3.35 (3H, s, N^3-CH_3). ^{13}C-NMR (C_6D_6) δ: 26.83 (C-8), 27.51 ($C(\underline{C}H_3)_3$-7), 28.01 (N^3-CH_3), 31.58 ($\underline{C}(CH_3)_3$-7), 32.71 (N^5-CH_3), 55.73 (C-7), 108.84 (C-1), 153.88 (C-4), 158.64 (C-2). MS *m/z* (%) : 222 (M^+, 49), 207 (100), 193 (11), 179 (7), 165 (9), 150 (72), 122 (19), 96 (31). HRMS: Calcd for $C_{12}H_{18}N_2O_2$: 222.1368. Found: 222.1367.

4,6-Dimethyl-4,6-diazatricyclo[6.4.0.0^{2,7}]dodec-2(7)-ene-3,5-dione (3c) ----- Colorless plates; mp 74-75 ˚C (recrystallized from hexane). ^{1}H-NMR (C_6D_6) δ: 1.00-1.10 (1H, m, H-9), 1.00-1.12 (2H, m, H-10), 1.14-1.28 (2H, m, H-11), 1.29-1.41 (1H, m, H-9), 1.47-1.58 (1H, m, H-12), 1.64-1.76 (1H, m, H-12), 2.47 (1H, ddd, *J* = 5.0, 5.2, 5.2 Hz, H-8), 2.54 (3H, s, N^6-CH_3), 2.89 (1H, ddd, *J* = 5.0, 4.8, 4.8 Hz, H-1), 3.36 (3H, s, N^4-CH_3). ^{13}C-NMR (C_6D_6) δ: 17.77 (C-11), 18.28 (C-10), 22.06 (C-9), 23.19 (C-12), 27.85 (N^4-CH_3), 30.29 (N^6-CH_3), 37.07 (C-1), 41.13 (C-8), 111.40(C-2), 153.59 (C-5), 158.71 (C-3): MS *m/z* (%): 220 (M^+, 64), 205 (23), 191 (100), 178 (20), 148 (17), 134 (46), 107 (18), 82 (26). HRMS: Calcd for $C_{12}H_{16}N_2O_2$: 220.1212. Found: 220.1213. *Anal.* Calcd for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.60; H, 7.32; N, 12.68.

7-Ethoxy-3,5-dimethyl-3,5-diazabicyclo[4.2.0]oct-1(6)-ene-2,4-dione (3d) ----- Colorless oil (13.5 mg, 26.3%). ^{1}H-NMR (C_6D_6) δ: 0.91 (3H, t, *J* = 7.0 Hz, OCH_2CH_3-7), 2.40 (1H, dd, *J* = 1.1, 11.0 Hz, H-8), 2.56 (1H, dd, *J* = 3.5, 11.0 Hz, H-8), 2.70 (3H, s, N^5-CH_3), 2.93 (2H, m, OCH_2CH_3-7), 3.30 (3H, s, N^3-CH_3), 4.05 (1H, dd, *J* = 1.1, 3.5 Hz, H-7). ^{13}C-NMR (C_6D_6) δ: 15.21 ($OCH_2\underline{C}H_3$-7), 27.98 (N^3-CH_3), 30.63 (N^5-CH_3), 63.60 ($O\underline{C}H_2CH_3$-7), 75.07 (C-7), 107.82 (C-1), 152.88 (C-6), 153.17 (C-4), 159.46 (C-2). MS *m/z* (%): 210 (M^+, 57), 181 (40), 124 (100), 96 (63), 70 (26), 42 (42). HRMS: Calcd for $C_{10}H_{14}N_2O_3$: 210.1004. Found: 210.0994.

7-(*tert*-Butoxy)-3,5-dimethyl-3,5-diazabicyclo[4.2.0]oct-1(6)-ene-2,4-dione (3e) ----- Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.29 (9H, s, $OC(CH_3)_3$-7), 2.70 (1H, dd, *J* = 1.0, 11.1 Hz, H-8), 3.13 (1H, dd, *J* = 3.4, 11.1 Hz, H-8), 3.28 (3H, s, N^5-CH_3), 3.31 (3H, s, N^3-CH_3), 5.06 (1H, dd, *J* = 1.0, 3.4 Hz, H-7). ^{13}C-NMR ($CDCl_3$) δ: 27.94 ($OC(CH_3)_3$-7), 28.21 (N^3-CH_3), 30.87 (N^5-CH_3), 38.63 (C-8), 69.36 (C-7), 75.73 ($\underline{O}C(CH_3)_3$-7), 108.22 (C-1), 153.58 (C-4), 153.85 (C-6), 159.94 (C- 2). MS

*80*for $C_{12}H_{18}N_2O_3$: 238.1317. Found: 238.1319.

3,5,7-Trimethyl-7-methoxy-3,5-diazabicyclo[4.2.0]oct-1(6)-ene-2,4-dione (3f) ----- Colorless crystals; mp 91-92 ˚C (recrystallized from hexane). ^{1}H-NMR (C_6D_6) δ: 1.12 (3H, s, CH_3-7), 2.28 (1H,d,*J* = 11.3 Hz, H-8), 2.71 (3H, s, N^5-CH_3), 2.72 (3H, s, OCH_3-7), 2.75 (1H, d, *J* = 11.3Hz, H-8), 3.32 (3H, s, N^3-CH_3). ^{13}C-NMR (C_6D_6) δ: 22.50 (CH_3-7), 27.98 (N^3-CH_3), 30.32 (N^5- CH_3), 36.74 (C-8), 51.96 (OCH_3-7), 83.29 (C-7), 106.89 (C-1), 153.28 (C-4), 155.64 (C-6), 159.44 (C-2). MS *m/z* (%): 210 (M^+, 39), 195 (49), 138 (100), 110 (33), 84 (44), 68 (28), 42 (58). HRMS: Calcd for $C_{10}H_{14}N_2O_3$: 210.1004.Found:210.0988.*Anal.*Calcd for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.33. Found: C, 57.34; H, 6.75; N, 13.18.

4,6-Dimethyl-9-oxa-4,6-diazatricyclo[6.4.0.0^{2,7}]dodec-2(7)-ene-3,5-dione (3g) ----- Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.60-1.70 (2H, m, H-11), 1.98-2.14 (2H, m, H-12), 3.32 (3H, s, N^6-CH_3), 3.33 (3H, s, N^4-CH_3), 3.44-3.49 (1H, m, H-1), 3.72-3.87 (2H, m, H-10), 5.01 (1H, d, *J* = 4.2 Hz, H-8). NOE δ: (irradiation at H-8) 3.44-3.49 (H-1), 3.32 (N^6-CH_3). ^{13}C-NMR ($CDCl_3$) δ: 19.35 (C-11), 22.31 (C-12), 28.23 (N^4-CH_3), 31.57 (N^6-CH_3), 38.75 (C-1), 63.07 (C-10), 72.56 (C-8), 113.03 (C-2), 153.48 (C-5), 155.13 (C-7), 159.73 (C-3). MS *m/z* (%): 222 (M^+, 87), 193 (100), 166 (56), 136 (25), 108 (37), 81 (72), 43 (31). HRMS: Calcd for $C_{11}H_{14}N_2O_3$: 222.1044. Found: 222.1002.

3,5-Dimethyl-7-*trans*-prop-1-enyl-3,5-diazabicyclo[4.2.0]oct-1(6)-ene-2,4-dione (3h-*t*) ----- Colorless oil. ^{1}H-NMR (C_6D_6) δ: 1.38 (3H, dd, *J* = 1.5, 6.4 Hz, CH=CHC$\underline{H}_3$-7), 2.18 (1H, dd, *J* = 1.5, 11.2 Hz, H-8), 2.56 (3H, s, N^5-CH_3), 2.65 (1H, dd, *J* = 4.4, 11.2 Hz, H-8), 2.97 (1H, br dd, *J* = 1.0, 1.5, 4.4, 8.3 Hz, H-7), 3.37 (3H, s, N^3-CH_3), 4.93 (1H, ddq, *J* = 15.1, 8.3, 1.5 Hz, C$\underline{H}$=CHCH_3-7), 5.12 (1H, ddq, *J* = 1.0, 15.1, 6.4 Hz, CH=C$\underline{H}$$CH_3$-7). MS *m/z* (%): 206 ($M^+$, 17), 205 (30), 191 (100), 134 (58), 120 (31), 106 (47). HRMS: Calcd for $C_{11}H_{14}N_2O_2$: 206.1055. Found: 206.1024.

3,5-Dimethyl-7-*cis*-prop-1-enyl-3,5-diazabicyclo[4.2.0]oct-1(6)-ene-2,4-dione (3h-*c*) ----- Colorless oil. ^{1}H-NMR (C_6D_6) δ: 1.24 (3H, dd, *J* = 1.7, 7.0 Hz, CH=CHC$\underline{H}_3$-7), 2.18 (1H, dd, *J* = 2.0, 11.2 Hz, H-8), 2.45 (3H, s, N^5-CH_3), 2.68 (1H, dd, *J* = 4.2, 11.2 Hz, H-8), 3.32 (1H, br dd, *J* = 1.1, 2.0, 4.2, 8.6 Hz, H-7), 3.38 (3H, s, N^3-CH_3), 4.92 (1H, ddq, *J* = 10.7, 8.6, 1.7 Hz, C$\underline{H}$=CHCH_3-7), 5.26 (1H, ddq, *J* = 1.1, 10.7, 7.0 Hz, CH=C$\underline{H}$$CH_3$-7).

12,14-Dimethyl-12,14-diazatetracyclo[7.6.0.0^{2,7}0.^{10,15}]pentadeca-2(3),4,6,10(15)-tetraene-11,13-dione(3i) ----- Colorless crystals; mp 175-176 ℃ (recrystallized from methanol). ^{1}H-NMR (C_6D_6) δ: 2.58 (3H, s, N^{14}-CH_3), 2.70 (1H, dd, *J* = 9.2, 17.2 Hz, H-8), 3.00 (1H, dd, *J* = 2.2, 17.2 Hz, H-8), 3.23 (3H, s, N^{12}-CH_3), 3.41 (1H, ddd, *J* = 2.2, 3.7, 9.2 Hz, H-9), 3.83 (1H, d, *J* = 3.7 Hz, H-1), 6.78 (1H, br d, *J* = 7.1 Hz, H-3), 6.90 (1H, br d, *J* = 7.1 Hz, H-6), 6.94-7.04 (2H, m, H-4), 6.94-7.04 (2H, m, H-5). NOE δ: (irradiation at N^{14}-CH_3) 6.78 (H-3), 3.83 (H-1), (irradiation at H-3) 6.94-7.04 (H-4), 2.58 (N^{14}-CH_3), 3.83 (H-1), (irradiation at H-8) 3.00 (H-8), 3.41 (H-9), (irradiation at H-8) 2.70 (H-8), 6.90 (H-6). ^{13}C-NMR (C_6D_6) δ : 27.79 (N^{12}-CH_3), 30.08 (N^{14}-CH_3), 32.62 (C-8), 41.26 (C-9), 54.93 (C-1), 110.30 (C-10), 124.98 (C-3), 126.70 (C-4), 127.33 (C-6), 128.40 (C-5), 138.07 (C-7), 145.46 (C-2), 152.92 (C-13), 157.79 (C-15), 158.53 (C-11). MS *m/z* (%): 254 (M^+, 100), 197 (35), 169 (59), 142 (35), 128 (71), 115 (87), 89 (18), 63 (28). HRMS: Calcd for $C_{15}H_{14}N_2O_2$: 254.1055. Found: 254.1061. *Anal.* Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.78; H, 5.71; N, 10.97.

Photoreaction of 1 with phenylacetylene (4) ----- Eight tubes of a solution of **1** (13.08 mg, 0.075 mmol) and an olefin (50 equiv. mol; 3.75 mmol, 0.412 mL) in acetone (5 mL) were irradiated externally for 1 h. The reaction mixtures were put together and evaporated *in vacuo*. The residual oil was passed through a short column of silica gel (20 g) with ethyl acetate. The eluate was submitted to HPLC with 3% ethyl acetate in dichloromethane, and separated into a fraction (F1) consisting of **5** and **6**, and a fraction (F2) of **7** and **8**, together with recovered **1** (67.5%). F1 was submitted to HPLC with 5% ethyl acetate in dichloromethane to give **5** (0.6 mg, 0.9%) and **6** (1.0 mg, 1.7%), and submission of the F2 onto HPLC with 1% ethyl acetate in dichloromethane afforded **7** (6.2 mg, 8.5%) and **8** (5.8 mg, 7.2%).[7]

6-Chloro-3,5-dimethyl-7-phenyl-3,5-diazabicyclo[4.2.0]oct-7-ene-2,4-dione (5): Color-less oil.^{1}H-NMR (C_6D_6) δ: 2.30 or 3.29 (3H, s, N^3-CH_3), 2.30 or 3.29 (3H, s, N^5-CH_3), 3.76 (1H, d, *J* = 4.0, H-1), 4.92 (1H, d, *J* = 4.0, H-8), 6.71-6.68 (2H, m, C_6H_5-7), 7.10-7.06 (3H, m, C_6H_5-7). MS *m/z* (%): 278 (M^+, 2), 276 (M^+, 5),

241 (80), 184 (67), 156 (100), 116 (49), 89 (22), 43 (44). HRMS : Calcd for $C_{14}H_{13}N_2O_2Cl$: 276.0666. Found: 276.0677.

6-Chloro-3,5-dimethyl-8-phenyl-3,5-diazabicyclo[4.2.0]oct-7-ene-2,4-dione (6): Color-less oil. ^{1}H-NMR (C_6D_6) δ: 2.66 or 3.30 (3H, s, N^3-CH_3), 2.66 or 3.30 (3H, s, N^5-CH_3), 5.65 or 5.91 (1H, s, H-1), 5.65 or 5.91 (1H, s, H-7), 6.67-6.97 (2H, m, C_6H_5-8), 6.88-7.00 (3H, m, C_6H_5-8). MS *m/z* (%): 278 (M^+, 11), 276 (M^+, 33), 241 (64), 184 (70), 156 (61), 115 (28), 82 (68), 43 (100). HRMS: Calcd for $C_{14}H_{13}N_2O_2Cl$: 276.0666. Found: 276.0689.

1,3-Dimethyl-7,8-diphenylquinazoline-2,4-dione (7): Colorless crystals, mp 223-224 ℃ (recrystallized from methanol). ^{1}H-NMR ($CDCl_3$) δ: 2.85 (3H, s, N^1-CH_3), 3.51 (3H, s, N^3-CH_3), 7.00-7.04 (3H, m, C_6H_5-8), 6.93-6.89 (2H, m, C_6H_5-7), 7.10-7.24 (3H, m, C_6H_5-7), 7.10-7.24 (3H, m, C_6H_5-8), 7.28 (1H, d, J = 8.1 Hz, H-6), 8.28 (1H, d, J = 8.1 Hz, H-5). NOE: irradiation at N^1-CH_3, enhancement observed for C_6H_5-8; irradiation at H-5, enhancement observed for H-6. MS *m/z* (%): 342 (M^+, 100), 284 (14), 256 (35), 241 (14), 180 (8), 128 (14), 91 (66). HRMS: Calcd for $C_{22}H_{18}N_2O_2$: 342.1368. Found: 342.1347.

1,3-Dimethyl-5,7-diphenylquinazoline-2,4-dione (8): Colorless crystals, mp 269-270 ℃ (recrystallized from methanol). ^{1}H-NMR ($CDCl_3$) δ: 3.53 (3H, s, N^3-CH_3), 3.66 (3H, s, N^1-CH_3), 7.22 (1H, s, H-8), 7.30-7.10 (5H, m, C_6H_5-5), 7.30-7.10 (5H, m, C_6H_5-7), 8.29 (1H, s, H-6). NOE: irradiation at N^1-CH_3, enhancement observed for H-8; irradiation at H-6, enhancement observed for C_6H_5-5 and C_6H_5-7. MS m/z (%): 342 (M^+, 100), 285 (9), 256 (29), 229 (15), 215 (15), 143 (6), 114 (9) HRMS: Calcd for $C_{22}H_{18}N_2O_2$: 342.1368. Found: 342.1394.

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