ACID-CATALYZED PHOTOREACTION OF 6-CHLORO-1,3-DIMETHYLURACIL IN FROZEN BENZENE: FORMATION OF PHOTOCYCLOADDUCTS AND THEIR ISOMERIZATION THROUGH PHOTO-DIELS-ALDER REACTION[1]

Kazue Ohkura, Yukari Noguchi, and Koh-ichi Seki*
Faculty of Pharmaceutical Sciences, Health Sciences University of Hokkaido, Ishikari-Tobetsu, Hokkaido 061-02, Japan

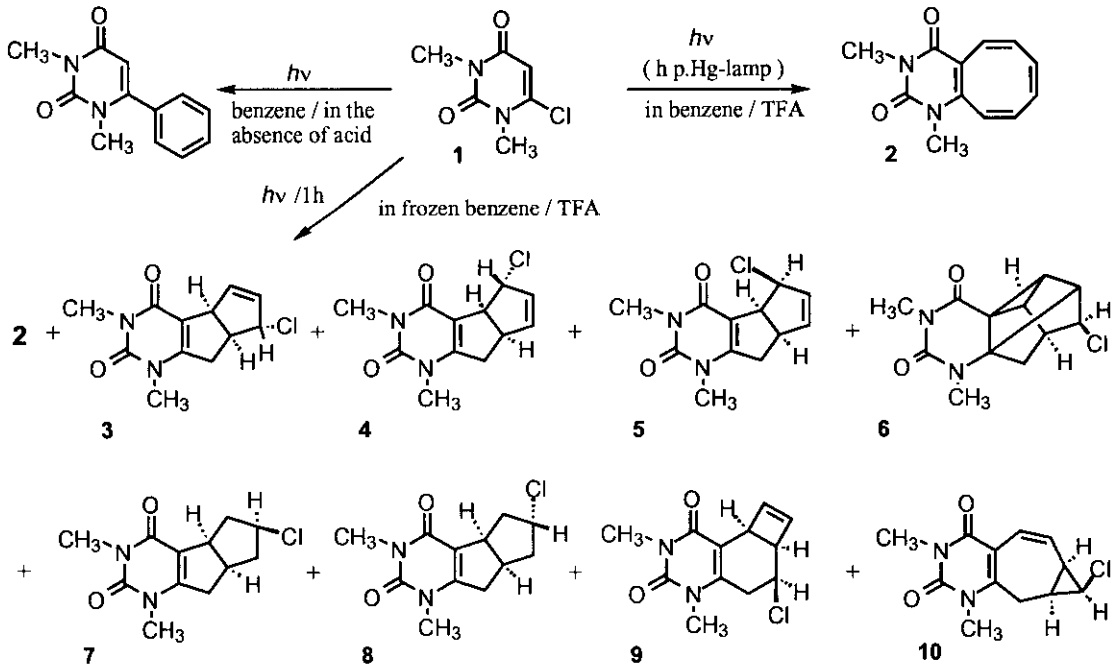
Abstract—Photolysis of 6-chloro-1,3-dimethyluracil (6-ClDMU) in frozen benzene in the presence of TFA gave novel photocycloadducts, pentalenopyrimidine derivatives and a diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane derivative as the major cycloadducts. Their formation is well explained by the mechanism involving the initial *ortho*-cycloaddition of 6-ClDMU to benzene, but not *meta*-cycloaddition.

In the course of our studies on the acid-catalyzed photoreaction of pyrimidine bases with substituted benzenes, we have reported that photolysis of 6-chloro-1,3-dimethyluracil (**1**) in benzene[2] and its monosubstituted derivatives[3] in the presence of trifluoroacetic acid (TFA) gave 1,3-dimethylcyclooctapyrimidine-2,4-dione (**2**) and the corresponding monosubstituted derivatives, presumably *via ortho*-cycloaddition. To explore the general feature of this photoreaction, we have extended our investigation to *p*- and *m*-xylenes, and found that, beside the cyclooctapyrimidines, novel diazapentacyclododecanes were produced probably *via* multi-photon reactions.[4] Meanwhile, it is well recognized that photoreactions in frozen solutions proceed in a different manner from those in liquid solutions, as demonstrated in the photodimerization of pyrimidine bases[5] or photocoupling of 5-bromouracil and 5-bromouridine to tryptophan.[6] These findings encouraged us to explore the further extension of the photocycloaddition of **1** to benzene. In the present paper, we describe our findings that photolysis of **1** in frozen benzene in the presence of TFA gave novel photocycloadducts, pentalenopyrimidine derivatives (**3**, **4**, **5**) and a diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane derivative (**6**) as the major cycloadducts, *via* [4πs + 2πa] type photo-Diels-Alder reaction of the initially formed tautomer of 1,3-dimethylcyclooctapyrimidine (**2**).

UV-irradiation of **1** in frozen benzene gave no detectable amounts of photoproducts. By contrast, addition of TFA[7] (1 h, 92 % consumption of **1**) gave rise to the formation[8] of 7-chloro-1,3-dimethyl-4b,7,7a,8-tetrahydro-(4bα,7α,7aα)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**3**) (2.8%), 5-chloro-1,3-dimethyl-4b,5,7a,8-tetrahydro-(4bα,5α,8α)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**4**) (4.1%), 5-chloro-1,3-dimethyl-4b,5,7a,8-tetrahydro-(4bα,5β,8α)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**5**) (4.1%), 5-chloro-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane-10,12-dione (**6**) (8.7%), and small amounts of 6-chloro-1,3-dimethyl-4b,5,6,7,7a,8-hexahydro-(4bα,6β,7aα)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**7**), 6-chloro-1,3-dimethyl-4b,5,6,7,7a,8-hexahydro-(4bα,6α,7aα)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**8**), 3-

chloro-5,7-dimethyl-2a,8b-dihydro-(2aα,3β,8bα)-buta[*f*]quinazoline-6,8-dione (**9**), and 1,3-dimethyl-(7α,8α,10β)-9H-7,8-chloromethanocycloheptapyrimidine-2,4-dione (**10**), beside the conventional cyclo-adduct, **2** (3.0%) (Scheme 1).[9]

The structures of **3**, **4**, and **5** were deduced essentially by means of ^{1}H-NMR spectroscopy and the NOE experiments (Figure 1). The structures of **6** and **3** were confirmed by the photolysis of a solution of a mixture of **3** and **4** in benzene for 10 min, whereby **3** was readily converted into **6** in high yield either in the presence or in the absence of TFA (63, and 86%, respectively), while no transformation was detected for the 5-isomer (**4**).



Scheme 1

The structure of **4** was confirmed by the transformation of **3** in benzene in the presence of TFA into **4** in high yield (90%) upon standing over night in the dark at room temperature. The structural assignment of **5** was made by the comparison of its ^{1}H-NMR spectra with those of **4**. The steric orientations of the Cl groups at C-5's were determined based on the observation of the coupling between 5-H's and 4b-H's (0.6 Hz for **4** and 7.8 Hz for **5**, respectively). The structures of **7** and **8** were deduced essentially by comparison of their ^{1}H-NMR spectra, which showed no peaks due to the absence of the vinyl protons, but the peaks due to six protons of the three methylene groups appeared. The 6-(β)chloro isomer (**7**) and the 6-(α)chloro isomer (**8**) showed long range couplings between 5-(β)H and 7-(β)H (0.5 Hz) and between 5-(α)H and 7-(α)H (1.5 Hz) caused by the intermediacy of the unshared pair of electrons of the chlorine atom at C-6,[10] respectively, supporting the assigned stereochemistry. The ^{1}H-NMR spectrum of **9** showed a pair of protons, which coupled with the respective adjacent bridgehead protons (2a-H and 8b-H). The ^{1}H-NMR spectrum of **10** exhibited the peaks due to bridgehead protons at appreciably high magnetic field (δ 0.66 and 1.00, both of which coupled with 10-H at δ 2.40), suggesting the presence of a three membered ring.

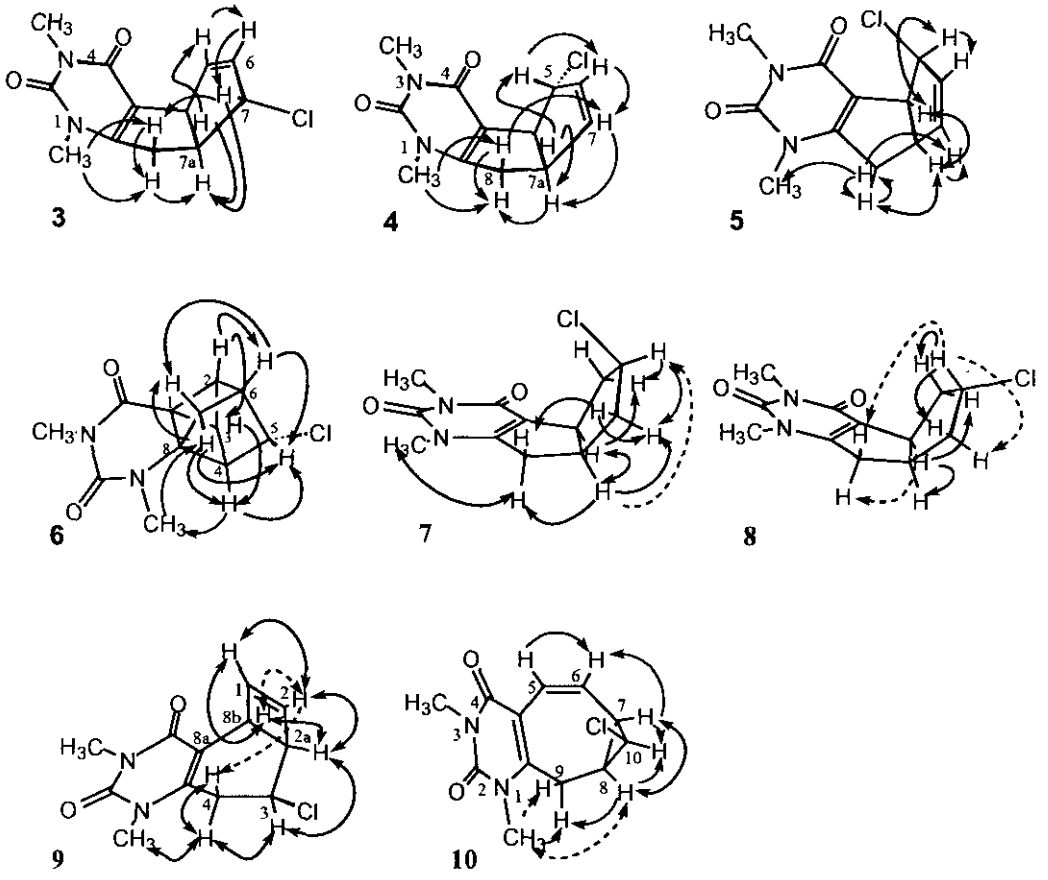


Figure 1. NOE correlations for the cycloadducts.

It was intriguing because in contrast to the reaction in liquid benzene whereby **2** was produced predominantly,[2,3] the present reaction proceeded quite differently to give rise to the remarkable formation of chlorinated pentalenopyrimidines (**3**, **4**, **5**) and the transannular derivative (**6**) through [2+2]-intramolecular photocycloaddition.

In order to obtain insight into the mechanism of this unique reaction, we then investigated the time course at -25 °C, and the yields of the resulting cycloadducts were determined by the ^{1}H-NMR spectra. The results are shown in Figure 2. Surprisingly the formation of **2**, which is recognized to be derived through the *ortho* cycloaddition,[4] occurred promptly at the initial stage of the reaction to reach the top in *ca.* 10 min and then decreased rapidly. With the decrease of **2**, formation of three pentaleno[1,2-*e*]pyrimidines (**3**, **4** and **5**) began to rise. The yield of **3** reached the maximum in *ca.* 20 min, then gradually reduced. The formation of **6** arose with the decrease of **3**, in consistent with the above mentioned result that **3** was photochemically converted smoothly into **6**. On the other hand, the yields of **4** and **5** kept increasing appreciably at the initial stage which reached a plateau after one hour of irradiation, and the slow formation of **7** and **8** arose (1

h; 0.4 and 0.2% : 3 h; 0.7 and 0.7%), suggesting that some parts of them (**4** and **5**) may be converted into the hexahydropentaleno derivatives (**7** and **8**).

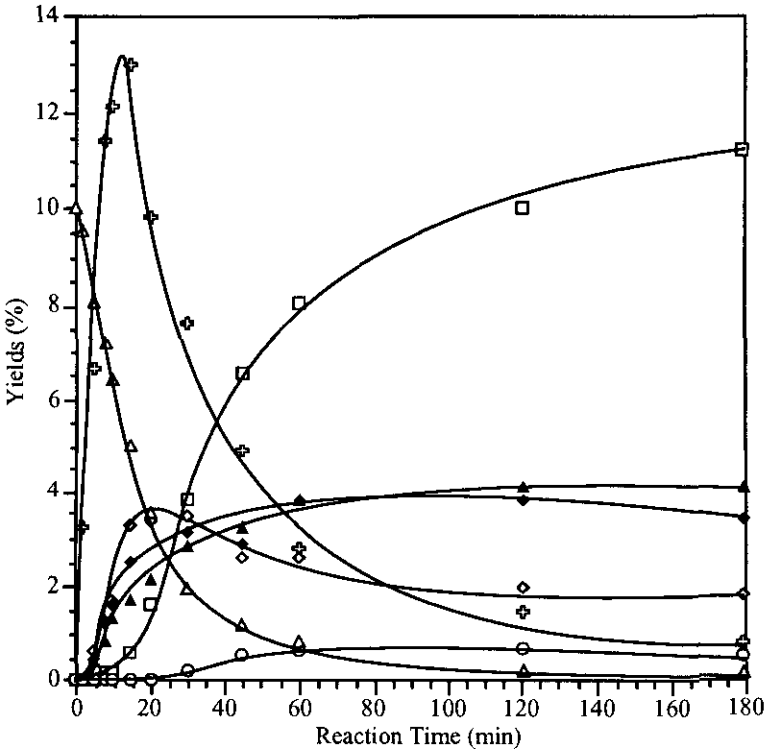
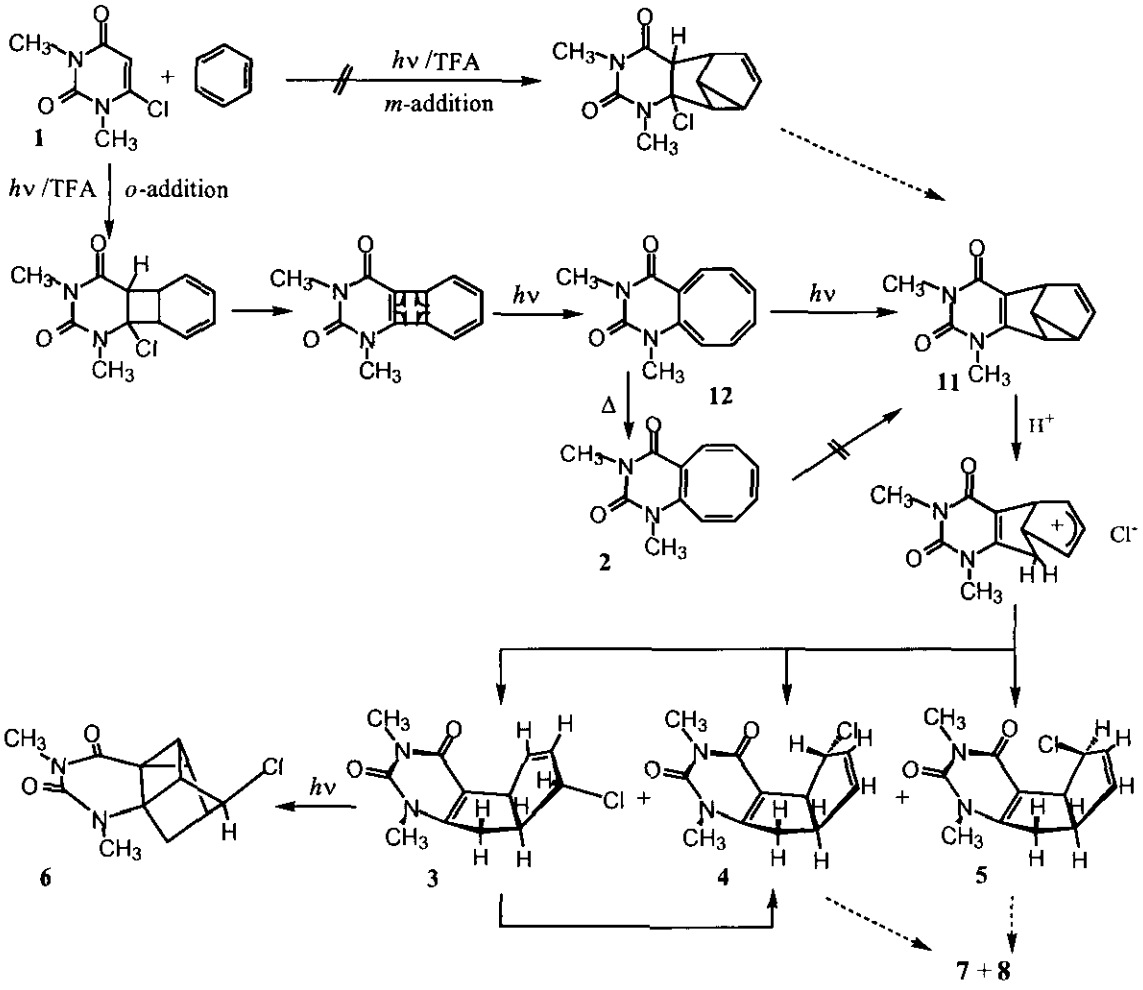


Figure 2. Time course of the photoreaction of **1** in frozene benzene:
1(x1/10), △; **2**, ✣; **3**, ◇; **4**, ▲; **5**, ◆; **6**, □; **9**, ○.

The preferential formation of the pentaleno[1,2-*e*]pyrimidines (**3**, **4** and **5**) may be explained plainly by invoking the semibullvalene derivative (**11**) as the precursor, the formation of the numerous analogies of which is well known as the results from *meta*-cycloaddition.[11]. Thus, it is noteworthy that present photoreaction may provide a new example for the formation of a semibullvalene skeleton *via* the *ortho*-cycloaddition, but not through the *meta*-cycloaddition.

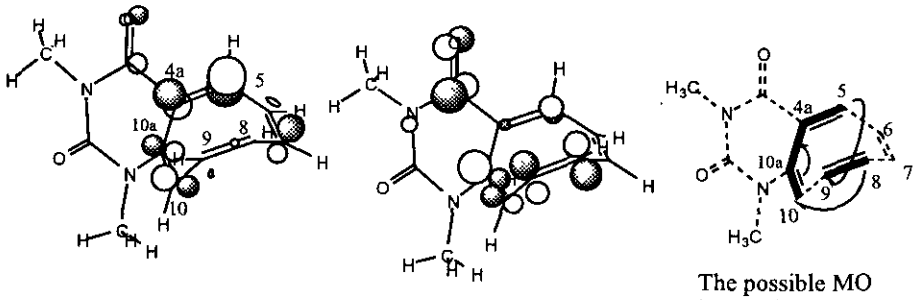
In order to confirm the transformation of **2** into the semibullvalene (**11**) and its hydrochlorinated derivatives (**3-6**), we have carried out the UV-irradiation of **2** in frozen benzene under the similar conditions employed for the present reaction either in the presence (2 molar equivs.) or in the absence of TFA for 10 min. However no formation of these compounds was observed. Hence the tautomer (**12**) of **2** was invoked as the precursor of **2**, which could be produced by the initial *ortho*-cycloaddition and the concomitant dehydrochlorination, followed by the symmetry allowed photochemical disrotatory cleavage[12] of the resulting cyclobutene moiety. The tautomer (**12**) would be converted rapidly into thermally stable **2**[13] upon being warmed up to room temperature during the work-up, which we isolated. At low temperature (-25°C), photoexcitation of **12** would lead to the key intermediate (**11**) before the tautomerization into **2**, which was

responsible for the formation of pentaleno derivatives (**3** - **6**). This idea may well explain our previous findings that the photoreaction of **1** in benzene at room temperature afforded **2** as the sole cycloadduct.[2] A similar result was obtained from UV-irradiation of **1** in the presence of TFA in frozen benzene but at 0°C, whereby **2** was produced predominantly, and no formation of pentaleno derivatives (**3** - **6**) was detected. Furthermore, when **1** was photolyzed in frozen benzene at -25 °C for 5 min (*ca.* 20 % **1** is consumed at this stage; see Figure 2) and warmed up to room temperature (during this procedure, intermediate (**12**) is presumed to tautomerize completely into inactive **2**), and again irradiated in frozen benzene at -25 °C for 5 min, the product ratio (*N*) of **2** (16.2%) / [**3** (1.1%) + **4** (0.6%) + **5** (0.6%)] (N = 7.0) was found to be appreciably higher than that obtained from the reaction continuously irradiated for 10 min at -25 °C (Figure 2, N = 2.6: yields of **2**, **3**, **4**, and **5** = 12.1, 1.7, 1.3, and 1.6%), and was close to that obtained from the analogous reaction (at -25 °C) for 5 min (N = 5.1: yields; **2**, **3**, **4**, and **5** = 6.6%, 0.6%, 0.3% and 0.4%), supporting the above consideration.



Scheme 2

The transformation of **12** into **11** may be regarded as a photo-Diels-Alder reaction,[12] which may require **12** to involve an unoccupied molecular orbital with a large extension over C-5, C-4a, C-10a, and C-10, and the other one, lying close in energy, with a large extension over C-8 and C-9. The intramolecular cycloaddition should occur through the bonding interaction between such two MO's *via* a symmetry allowed [π4s + π2a] or a [π4a + π2s] process.[12] Hence we have carried out the MO calculation for the intermediate (**12**).[14] As shown in Figure 2, the LUMO of **12** has a large extension over C-5, C-4a, C-10a, and C-10, and the next LUMO (NLUMO) extends largely over C-8, C-9, C-10, and C-10a, respectively. In view of the structure of the product and the presumed semibullvalene intermediate (**11**), the present transformation can be explained well by the mechanism involving a symmetry allowed [π4s + π2a] process through the interaction between the four carbons (C-5, C-4a, C-10a, and C-10) of the LUMO and the two carbons (C-8 and C-9) of the NLUMO. These results may furnish a sufficient basis for the above interpretation on the reaction mechanism.



LUMO (No42) of **12** (Eigen value, -0.50eV)

NLUMO (No 43) of **12** (Eigen value, 0.27eV)

The possible MO interaction

Figure 3. The molecular orbitals of **12**.

Addition of piperylene (0.26 mmol) to the present reaction (30 min) was essentially ineffective on the formation of **2** (5.5%), but suppressed the formation of **3**, **4**, **5**, and **6** (0.5, 0, 0, and 0%) significantly (cf., in the absence of piperylene; **2**, 7.6%; **3**+**4**+**5**+**6**, 13.2%), suggesting that **2** may be produced *via* the excited singlet states, while the excited triplet states may participate in the transformation of **12** into **11**. No quenching effect of piperylene was observed on the transformation of **3** into **6**, suggesting that the excited singlet states may participate in the process.

Although the reaction mechanism for the formation of **9** and **10** remains unelucidated, it is noteworthy that the present work provides a novel photochemical pathway through photo-Diels-Alder reaction into semibullvalene derivatives, which have been produced alternatively by the photoreaction involving di-π-methane rearrangement of benzobarrelenes[15] or cyclobutanaphthalenes,[16] or directly through *meta*-cycloaddition.[11]

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 with tetramethylsilane as an

internal standards. ^{13}C-NMR chemical shifts were recorded based on those of the signals of solvents. Mass spectra (MS) and high resolution mass spectra (HRMS) were determined on a Shimadzu GCMS 9100-MK and 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).

General procedure of the photoreaction-----A frozen solution of **1** (4.36 mg, 0.025 mmol) in benzene (5 mL) in the presence of TFA (5.70 mg, 0.05 mmol) was irradiated externally with the 500 W h.p. Hg lamp in a degassed Pyrex tube at -25 °C. The reaction mixture was concentrated *in vacuo*, and analyzed by means of ^{1}H-NMR spectroscopy in benzene-d_6 with terephthalaldehyde as an internal standard unless cited therein.

Isolation of the cycloadducts-----After the photoreaction for 1h according to the general procedure, the reaction mixtures in 22 Pyrex tubes were put together, washed with saturated aqueous $NaHCO_3$,[17] dried over anhydrous Na_2SO_4, 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 20-50 % ethyl acetate - hexane to give **1** (8.9 mg, 9.3%), **2** (5.8 mg, 4.9%), **9** (1.0 mg, 0.7%), **6** (10.4 mg, 7.5%), **10** (0.4 mg, 0.3%), **3** (3.2 mg, 2.3%), **8** (0.3 mg, 0.2%), **5** (6.3 mg, 4.5%), **7** (0.5 mg, 0.4%), and **4** (0.8 mg, 0.6%), successively.

7-Chloro-1,3-dimethyl-4b,7,7a,8-tetrahydro-(4bα,7α,7aα)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**3**): ^{1}H-NMR (benzene-d_6): δ 2.41(3H, s, 1-CH_3), 3.26 (3H, s, 3-CH_3), 4.10 (1H, m, *J* = 7.7, 2.4, 2.4, 2.0, and 1.8 Hz, 4b-H), 6.26 (1H, m, *J* = 5.2, 2.4, and 0.8 Hz, 5-H), 5.49 (1H, m, *J* = 5.2, 2.4, and 2.4 Hz, 6-H), 4.25 (1H, m, *J* = 2.4, 2.4, 2.0, and 0.8 Hz, 7-H), 2.79 (1H, m, *J* = 10.4, 7.7, 5.0, and 2.4 Hz, 7a-H), 1.41 (1H, m, *J* = 17.6, 5.0, and 1.8 Hz, 8-βH), 1.82 (1H, dd, *J* = 17.6 and 10.4 Hz, 8-αH). ^{13}C-NMR(benzene-d_6): δ 27.64 Hz, (3-CH_3), 31.59 Hz (1-CH_3), 36.32 Hz, (8), 48.83 (7a), 53.70 (4b), 69.95 (7), 111.39 (4a), 130.78 (6), 137.24 (5), 151.19 (8a), 152.38 (2), 159.99 (4). MS *m/z* (relative intensity) 254 (M^+, 17), 252 (M^+, 42), 217 (100). HRMS: Calcd for $C_{12}H_{13}N_2O_2{}^{37}Cl$: 254.0635. Found: 254.0644; Calcd for $C_{12}H_{13}N_2O_2{}^{35}Cl$: 252.0665. Found: 252.0651.

5-Chloro-1,3-dimethyl-4b,5,7a,8-tetrahydro-(4bα,5α,8α)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**4**): mp 157-159°C (recrystallized from ethyl acetate). ^{1}H-NMR ($CDCl_3$): δ 3.32 (3H, s, 1-CH_3), 3.33 (3H, s, 3-CH_3), 3.96 (1H, m, *J* = 6.8, 2.0, 2.0, and 0.6 Hz, 4b-H), 5.19 (1H, m, *J* = 2.0, 1.8, and 0.6 Hz, 5-H), 5.91 (1H, m, *J* = 5.6, 2.0, and 2.0 Hz, 6-H), 5.84 (1H, dd, *J* = 5.6 and 2.0 Hz, 7-H), 3.81 (1H, m, *J* = 9.2, 6.8, 2.0, 2.0, 2.0, and 1.8 Hz, 7a-H), 2.66 (1H, m, *J* = 17.6, 2.0, and 2.0 Hz, 8-βH), 3.11 (1H, m, *J* = 17.6, 9.2, and 2.0 Hz, 8-αH). ^{13}C-NMR ($CDCl_3$): δ 27.90 (3-CH_3), 32.69 (1-CH_3), 35.89 (8), 44.74 (7a), 55.99 (4b), 65.08 (5), 110.60 (4a), 132.47 (6), 137.09 (7), 152.75 (8a), 152.79 (2), 160.72 (4). MS *m/z* (relative intensity) 254 (M^+,15), 252 (M^+, 56), 217 (100). *Anal.* Calcd for $C_{12}H_{13}N_2O_2Cl$: C, 57.03; H, 5.19; N, 11.09. Found: C, 56.93; H, 5.31; N, 11.09.

5-Chloro-1,3-dimethyl-4b,5,7a,8-tetrahydro-(4bα,5β,8α)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**5**): ^{1}H-NMR ($CDCl_3$): δ 3.34 (3H, s, 1-CH_3), 3.37 (3H, s, 3-CH_3), 4.11 (1H, dt, *J* = 7.8 and 2.0 Hz, 4b-H), 5.25 (1H, dd, *J* = 7.8 and 2.0 Hz, 5-H), 5.94 (1H, dt, *J* = 5.9 and 2.0 Hz, 6-H), 6.00 (1H, dd, *J* = 5.9 and 2.9 Hz, 7-H), 3 66 (1H, m, *J* = 9.8, 7.8, 6.4, 2.9, and 2.0 Hz, 7a-H), 2.68 (1H, m, *J* = 17.6, 6.4, and 2.0 Hz, 8-βH), 3.04 (1H,

dd, J = 17.6 and 9.8 Hz, 8-αH). MS *m/z* (relative intensity) 254 (M^+, 14) 252 (M^+, 61), 217 (100). HRMS: Calcd for $C_{12}H_{13}N_2O_2{}^{35}Cl$: 252.0665. Found: 252.0654.

5-Chloro-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane-10,12-dione (**6**): mp 123-124°C (recrystallized from ether). ^{1}H-NMR ($CDCl_3$): δ 3.15 (1H, m, J = 5.2, 3.6, and 1.2 Hz, 2-H), 3.22 (1H, dd, J = 5.2 and 2.4 Hz, 3-H), 2.70 (1H, m, J = 2.4, 2.4, 2.4, and 1.2 Hz, 4-H), 3.82 (1H, dd, J = 2.4 and 0.8 Hz, 5-H), 2.86 (1H, m, J = 3.6, 4.4, and 0.8 Hz, 7a-H), 1.67 (1H, d, J = 10 Hz, 7-H^a), 1.63 (1H, dd, J = 10.0 and 2.4 Hz, 7-H^b), 2.89 (3H, s, 9-CH_3), 3.22 (3H, s, 11-CH_3).^{13}C-NMR ($CDCl_3$): δ 27.90 (11-CH_3), 31.12 (9-CH_3), 36.18 (2), 37.92 (3), 38.71 (1), 44.34 (7), 44.69 (6), 46.29 (4), 62.08 (8), 68.17 (5), 153.15 (10), 166.45 (12). HMBC spectrum; 2-H with C-4, C-5, C-6; 3-H with C-1, C-7, and C-8; 4-H with C-6; 5-H with C-2 and C-3; 6-H with C-4 and C-8; 7a-H with C-1, C-4, C-5, and C-6; 7b-H with C-1, C-2, C-5, C-6, and C-8; 9-CH_3 with C-1 and C-10; 11-CH_3 with C-10 and C-12. MS *m/z* (relative intensity) 254 (M^+, 27), 252 (M^+, 7.4), 217 (100). *Anal.* Calcd for $C_{12}H_{13}N_2O_2Cl$: C, 57.03; H, 5.19; N, 11.09. Found: C, 57.00; H, 5.25; N, 11.12.

6-Chloro-1,3-dimethyl-4b,5,6,7,7a,8-hexahydro-(4bα,6β,7aα)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**7**): ^{1}H-NMR ($CDCl_3$): δ 3.34 (3H, s, 1-CH_3), 3.34 (3H, s, 3-CH_3), 3.64 (1H, m, J = 8.8, 8.8, 4.9, and 2.4 Hz, 4b-H), 2.12 (1H, m, J = 14.2, 5.4, 4.9, and 0.5 Hz, 5-βH), 2.49 (1H, ddd J = 14.2, 8.8, and 5.4 Hz, 5-αH), 4.31 (1H, quintet, J = 5.4 Hz, 6-αH), 1.88 (1H, m, J = 13.7, 6.4, 5.4, and 0.5 Hz, 7-βH), 2.45 (1H, ddd, J = 13.7, 8.3, and 5.4 Hz, 7-αH), 2.98 (1H, m, J = 10.3, 8.8, 8.3, 6.4, and 2.9 Hz, 7a-H), 2.84 (1H, m, J = 17.6, 2.9, and 2.4 Hz, 8-βH), 3.16 (1H, dd, J = 17.6, and 10.3 Hz, 8-αH). MS *m/z* (relative intensity) 256 (M^+, 8), 254 (M^+, 24), 219 (58), 191 (11), 178 (100) 162 (22), 134 (11), 121 (34), 93 (29), 91 (14). HRMS: Calcd for $C_{12}H_{15}N_2O_2{}^{35}Cl$: 254.0824. Found: 254.0802; Calcd for $C_{12}H_{15}N_2O_2{}^{37}Cl$: 256.0794. Found: 256.0804.

6-Chloro-1,3-dimethyl-4b,5,6,7,7a,8-hexahydro-(4bα,6α,7aα)-pentaleno[1,2-*e*]pyrimidine-2,4-dione (**8**): ^{1}H-NMR ($CDCl_3$): δ 3.26 (3H, s, 1-CH_3), 3.33 (3H, s, 3-CH_3), 3.78 (1H, m, J = 8.3, 8.3, 5.4, and 2.0 Hz, 4b-H), 2.14 (1H, dt, J = 14.2, 5.4, and 5.4 Hz, 5-βH), 2.43 (1H, m J = 14.2, 8.3, 4.4, and 1.5 Hz, 5-αH), 4.37 (1H, m, J = 5.4, 4.9, 4.4, and 4.4 Hz, 6-βH), 1.80 (1H, ddd, J = 13.2, 7.3, and 4.9 Hz, 7-βH), 2.30 (1H, m, J = 13.2, 7.8, 4.4, and 1.5 Hz, 7-αH), 3.21 (1H, m, J = 8.8, 8.3, 7.8, 7.3, and 2.9 Hz, 7a-H), 2.58 (1H, ddd, J = 17.1, 2.9, and 2.0 Hz, 8-βH), 3.13 (1H, dd, J = 17.1 and 8.8 Hz, 8-αH). MS *m/z* (relative intensity) 256 (M^+,6), 255 (6), 254 (M^+, 19), 219 (61), 191 (15), 178 (100), 162 (21), 134 (13), 121 (31), 93 (25), 91 (13), 79 (10), 77 (16). HRMS: Calcd for $C_{12}H_{15}N_2O_2{}^{35}Cl$: 254.0824. Found: 254.0809; Calcd for $C_{12}H_{15}N_2O_2{}^{37}Cl$: 256.0794. Found: 256.0797.

3-Chloro-5,7-dimethyl-2a,8b-dihydro-(2aα,3β,8bα)-buta[*f*]quinazoline-6,8-dione (**9**): ^{1}H-NMR ($CDCl_3$): δ 6.07 (1H, dd, J = 2.8 and 0.8 Hz, 1-H), δ 6.23 (1H, dd, J = 2.8 and 0.8 Hz, 2-H), 3.62 (1H, m, J = 6.0, 4.0, 1.6, and 0.8 Hz, 2a-H), 4.02 (1H, ddd, J = 12.0, 6.0, and 4.4 Hz, 3-αH), 3.10 (1H, ddd, J = 16.0, 4.4, and 1.6 Hz, 4-αH), 2.81 (1H, ddd, J = 16.0, 12.0, and 0.8 Hz, 4-βH), 3.46 (3H, s, 5-CH_3), 3.36 (3H, s, 7-CH_3), 4.22 (1H, dt, J = 4.0, 0.8, and 0.8 Hz, 8b-H). ^{13}C-NMR ($CDCl_3$): δ 138.63 (1), 134.33 (2), 46.35 (2a), 55.80 (3), 31.77 (4), 145.47 (4a), 31.14 (5-CH_3), 151.89 (6), 28.24 (7-CH_3), 161.91 (8), 108.35 (8a), 39.67 (8b). HMBC spectrum; 2a-H with C-1, C-2, C-3, C-4, C-8b; 3-H with C-2 and C-2a; 4-αH with C-2a, C-3, and C-8a; 4-βH with C-2a, C-3, and C-8a; 8b-H with C-1 and C-2, C-2a, C-3, C-4a, C-8, and C-8a. MS *m/z* (relative intensity)254 (M^+, 3.3), 252 (M^+, 8.8), 217 (100). HRMS: Calcd for $C_{12}H_{13}N_2O_2{}^{35}Cl$: 252.0665. Found: 252.0680; Calcd for $C_{12}H_{13}N_2O_2{}^{37}Cl$: 254.0635. Found: 254.0668.

1,3-Dimethyl-(7α,8α,10β)-9*H*-7,8-chloromethanocycloheptapyrimidine-2,4-dione (**10**): ^{1}H-NMR (benzene-d_6): δ 2.66 (3H, s, 1-CH_3), 3.29 (3H, s, 3-CH_3), 6.78 (1H, dd, J = 11.2 and 2.0 Hz, 5-H), 5.84 (1H, dd, J = 11.2 and 2.4 Hz, 6-H), 1.00 (1H, m, J = 8.3, 8.3, 2.4, and 2.0 Hz, 7-H), 0.66 (1H, m, J = 11.2, 8.3, 6.8, and

5.9 Hz, 8-H), 2.33 (1H, dd, J = 14.7 and 11.2 Hz, 9-βH), 1.90 (1H, dd, J = 14.7 and 5.9 Hz, 9-αH), 2.40 (1H, dd, J = 8.3 and 6.8 Hz, 10-H). MS *m/z* (relative intensity) 254 (M^+,9), 252 (M^+, 22), 217 (100). HRMS: Calcd for $C_{12}H_{13}N_2O_2{}^{35}Cl$: 252.0665. Found: 252.0658.

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Received, 9th May, 1997