Acid-Catalyzed Photoreaction of 6-Chloro-1,3-Dimethyluracil and Mesitylene: Formation of Photocycloadducts and Their Characterization[1)]

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In contrast to the previously reported short time required (1 h) for photolysis of 6-chloro-1,3-dimethyluracil (6-ClDMU) and mesitylene, in the presence of TFA, resulting in two major products: 1,3,6,8,10-pentamethylcyclooctapyrimidine derivative (1d), and diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane (2c), prolonged irradiation (18 h) of this same mixture yields novel pentalenopyrimidine derivatives, including diazapentacyclo-[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane (3c).

Key words acid-catalyzed photoreaction; 6-chloro-1,3-dimethyluracil; mesitylene; photocycloaddition; cyclobutaquinazoline; pentalenopyrimidine

In the course of our continuing studies on the acid-catalyzed photoreaction of pyrimidine bases with aryl compounds, we reported that photolysis of 6-chloro-1,3-dimethyluracil (6-ClDMU) in benzene and monosubstituted benzene derivatives, in the presence of trifluoroacetic acid (TFA), yields 1,3-dimethylcyclooctapyrimidine-2,4-dione[2)] and its derivatives,[3)] presumably *via ortho*-cycloaddition. As an extension of this study, we further investigated the photoreaction with *p*- and *m*-xylenes.[4)] We have found that two types of highly strained pentacyclic cage compounds, each of which involve a pyrimidine ring fused to either a tetracyclo[3.3.0.0^{2,4}.0^{3,6}]octane system (**2a**, **b**), or a tetracyclo-[3.3.0.0^{2,4}.0^{3,7}]octane system (**3a**, **b**), are produced (Chart 1).

Interestingly both pentacyclic compounds bear an *exo*-methylene group on their skeleton, suggesting that the methyl groups introduced onto the benzene ring are responsible for the formation of these unique skeletons.[5)] Hence, our attention was focused on the photoreaction involving mesitylene.

In a previous paper, we reported that 1 h photolysis of 6-ClDMU in mesitylene, in the presence of TFA, produces a diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane derivative (**2c**), together with two cyclooctapyrimidines (**1c**, **d**), as well as 9-methylenecyclooctapyrimidine (**4**), and cyclobutaquinazoline (**5a**) (Chart 2).[6)] In addition, we clearly demonstrated the reaction pathway leading to the formation of compound **2c** (Chart 3).[6)] In contrast, the alternative pentacyclododecane derivative consisting of a [6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane system (**3c**) failed to form.

In the present paper, we describe our new findings that prolonged UV-irradiation (18 h) of 6-ClDMU and mesitylene, in the presence of TFA, yields the desired pentacyclododecane (**3c**) in addition to various cycloadducts, including the alternative pentacyclododecane (**2c**).

UV-irradiation of 6-ClDMU in mesitylene, in the presence of TFA, for 18 h resulted in a complex mixture of the 1 : 1

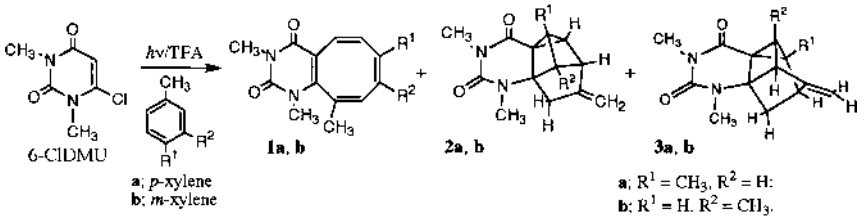

Chart 1

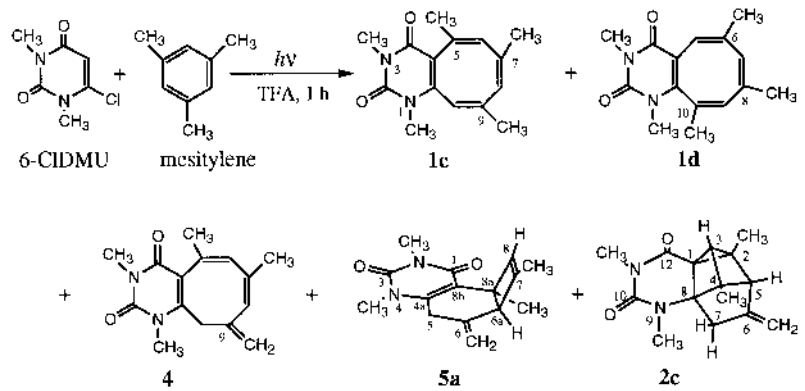

Chart 2

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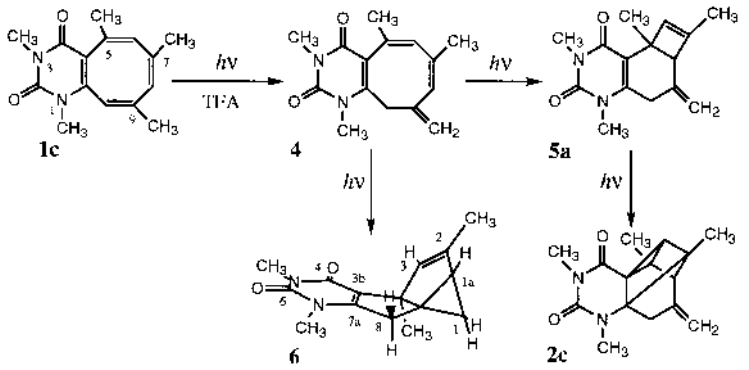

Chart 3

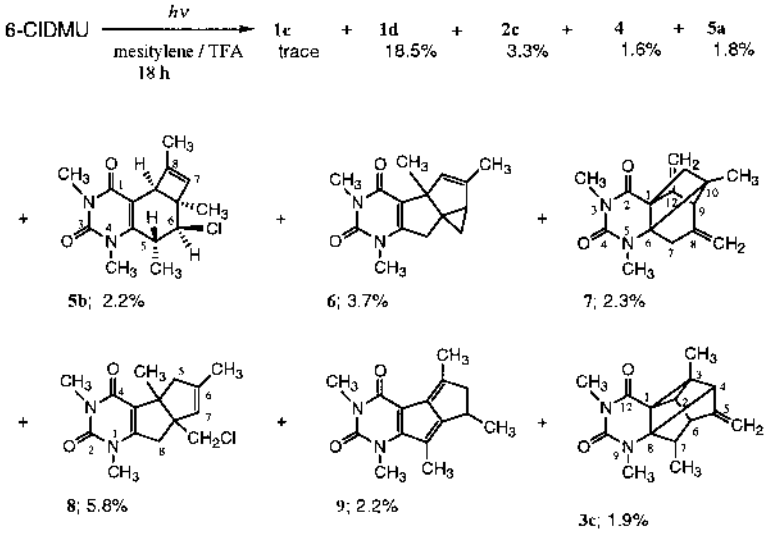

Chart 4

cycloadducts of 6-ClDMU and mesitylene. Separation by HPLC afforded the desired cycloadduct (**3c**), and the pentacyclododecane (**2c**), 9-methylcyclooctapyrimidine (**1c**), 10-methyl isomer (**1d**), 9-methylenecyclooctapyrimidine (**4**), cyclobutaquinazolines (**5a**, **b**), tetracyclododecane (**7**), together with three pentalenopyrimidine derivatives, cyclopropa[3a,4]-pentaleno[2,1-*d*]pyrimidine (**6**), chloromethylpentalenopyrimidine (**8**), and 6,7-dihydropentalenopyrimidine (**9**) (Chart 4).

The structure of **2c**[6] was determined by comparing its ^{1}H-NMR spectra with those of **2a**[4] and **2b**,[4] as shown in Table 1. The nuclear Overhauser effect (NOE) experiment supported the structure assigned to **2c** (Fig. 1). The structure of **3c** was determined by comparing its ^{1}H-NMR spectra with those of **3a**[4] and **3b**,[4] as summarized in Table 2. The NOE experiment supported the structure assigned to **3c** (Fig. 1).

The ^{1}H-NMR (C_6D_6) spectrum of **5a**[6] showed signals due to C6-*exo*-methylene protons at δ 4.67 and 4.82. Signals ascribable to C5 geminal protons appeared as doublets (J=20.0 Hz) at δ 2.45 and 2.53 ppm. Signals due to a C6a-methyne proton and a C8 vinyl proton were observed at δ 2.64 (1H, br s, H-2a), and 6.44 (br s) ppm, respectively. The NOE experiments supported the structure assigned to **5a** (Fig. 2).

Hydrochlorinated cyclobutaquinazoline (**5b**) was formulated as $C_{15}H_{19}N_2O_2Cl$ on the basis of HRMS. The ^{1}H-NMR (C_6D_6) spectrum showed three singlet signals due to N2–CH_3, N4–CH_3, and C6a–CH_3 at δ 3.24, 2.84, and 1.11 ppm, respectively. A doublet peak due to C5–CH_3 appeared at δ 0.50 ppm with coupling with H-5 (δ 2.76 ppm, J=7.3 Hz). A signal due to C8–CH_3 appeared at δ 2.05 ppm with long range couplings with H-8a and H-7. A broad singlet peak ascribable to H-8a appeared at δ 3.36 ppm and a peak ascribed to H-7 was at δ 5.91 ppm. Relative stereochemistry between H-6/H-5 and C6–Cl/C6a–CH_3 was determined to be *trans* on the basis of the significant NOE enhancements (*ca.* 5%) from H-6 to C5–C$\underline{H}_3$ and C6a–C$\underline{H}_3$ (Fig. 2).

Cyclopropapentalenopyrimidine (**6**) was formulated as $C_{15}H_{18}N_2O_2$ on the basis of HRMS. The ^{1}H-NMR spectrum ($CDCl_3$) showed signals ascribed to C1 methylene protons, Ha-1 and Hb-1, at δ 1.05 (Ha) (dd, J=5.0, 7.9 Hz) and 0.58 (Hb) (dd, J=3.6, 5.0 Hz) ppm. A signal due to the methyne proton at C1a appears at δ 1.48 ppm, which couples with C1 methylene protons (J=3.6, 7.9 Hz). A signal due to a C3 vinyl proton is seen at δ 5.41 (br s) ppm, which shows a long range coupling with C2–CH_3 (J=1.5 Hz). Two doublet signals assigned to C8 methylene protons, Ha-8 and Hb-8, were observed at δ 3.27 (d, J=17.2 Hz) and 2.60 (d, J=17.2 Hz) ppm, respectively. NOEs observed from N4–CH_3 to Ha-8,

Table 1. ^{13}C- and ^{1}H-NMR Data for **2c**,[a] **2a**,[b] and **2b**[c]

Position	**2c**		**2a**		**2b**	
	^{13}C-NMR	^{1}H-NMR (J=Hz)	^{13}C-NMR	^{1}H-NMR (J=Hz)	^{13}C-NMR	^{1}H-NMR (J=Hz)
1	30.35		46.53		41.89	
2	37.95		34.61	2.82 (dd, 5.1, 2.6)	27.23	2.81 (dd, 3.4, 2.4)
C2–CH_3	11.21	1.62 (3H, s)				
3	42.96	2.64 (s)	32.54		38.66	3.38 (d, 3.4)
C3–CH_3	40.78		10.50	1.45 (3H, s)		
4	55.58		50.64	2.78 (dd, 5.1, 4.4)	59.05	
C4–CH_3	13.87	0.56 (3H, s)		3.65 (dd, 4.4, 2.6)	13.85	1.18 (3H, s)
5	62.38	2.46 (br s)	51.17		58.54	3.28 (d, 2.4)
6	146.12		147.31		148.03	
C6–CHa	107.41	4.62 (br s)	106.96	4.73 (t, 2.5)	107.58	4.76 (t, 2.3)
C6–CHb	107.41	4.75 (br s)	106.96	4.90 (t, 2.5)	107.58	4.92 (t, 2.3)
7 (Ha)	34.34	1.89 (dt, 17.0, 2.5)	35.07	2.42 (dt, 16.9, 2.5)	34.61	2.53 (dt, 17.1, 2.3)
7 (Hb)	34.34	2.00 (dt, 17.0, 2.5)	35.07	2.52 (dt, 16.9, 2.5)	34.61	2.66 (dt, 17.1, 2.3)
8	68.85		66.91		69.19	
N9–CH_3	31.16	2.59 (3H, s)	30.26	2.98 (3H, s)	31.74	2.96 (3H, s)
10	155.40	2.52 (s)	155.34		155.88	
N11–CH_3	27.64	3.33 (3H, s)	27.79	2.98 (3H, s)	27.50	3.08 (3H, s)
12	167.14		166.88		167.16	

a) C_6D_6. *b*) $CDCl_3$. *c*) CD_3OD.

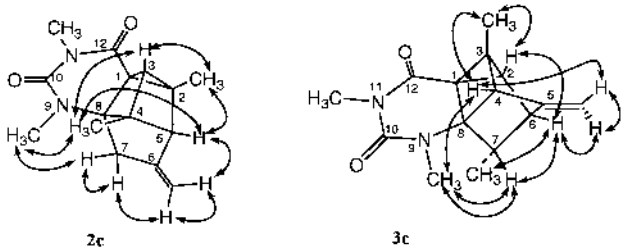

Fig. 1. NOE Correlations for **2c** and **3c**

from Ha-8 to Ha-1, from H-1a to Ha-1, from H-1a to C2–CH_3, from C2–CH_3 to H-3, from H-3 to C3a–CH_3, from C3a–CH_3 to Hb-1, and from Hb-1 to Ha-1 elucidated the structure assigned to **6** (Fig. 3). The HMBC spectrum confirmed the structural assignment (Table 3).

Compound **7** was formulated as $C_{15}H_{18}N_2O_2$ on the basis of HRMS. The ^{1}H-NMR spectrum ($CDCl_3$) showed three singlet peaks due to N3–CH_3, N5–CH_3, and C10–CH_3 at δ 3.19, 3.01, and 1.22 ppm, respectively. Four peaks, due to the C8 and C12-*exo*-methylene protons, were observed at δ 4.69 (1H, br s, C8=Hb), 4.99 (1H, t, J=2.4 Hz, C8=Ha), 5.00 (1H, s, C12=Hb), 5.64 (1H, d, C12=Ha, J=1.3 Hz). Signals ascribable to C7 and C11 geminal protons appeared at δ 2.41 (1H, br d, J=17.0 Hz, Ha-7), 2.32 (1H, dt, J=2.4, 17.0 Hz, Hb-7), 2.50 (doublet, J=7.3 Hz, H-11a), and 1.97 (d, J=7.3 Hz, H-11b), respectively. A signal due to the methyne proton at C9 was observed at δ 3.03 (1H, br s, H-9). Photolysis of **2c** in the presence of TFA resulted in cleavage of the C2–C3 bond to give **7** (Chart 5), supporting the structure assigned to **7**.

The structure of the second dominant cycloadduct (**8**) was determined *via* single-crystal X-ray diffraction (Fig. 4) (Tables 4 and 5). The ^{1}H-NMR spectrum (acetone-d_6) of **8** showed peaks due to four methyl groups (C2–CH_3, C5–CH_3, N12–CH_3, N9–CH_3) at δ 1.36, 1.66, 3.18, and 3.31, in addition to a peak at δ 5.28 representing one vinyl proton, and three pairs of signals which can be attributed to C3, C6, and C7 methylene protons. These findings support the structure assigned to **8**.

The structure of **9** was deduced on the basis of MS and ^{1}H-NMR ($CDCl_3$) spectroscopy. NOEs were observed for H-7, C7–CH_3, and N1–CH_3 upon irradiation at C8–CH_3. The ^{1}H-NMR ($CDCl_3$) spectrum showed a doublet peak due to C7–CH_3 (δ 1.27, J=7.1 Hz), and a signal at δ 3.15 due to H-7 coupled with C7–CH_3 and H-6, with coupling constants of J=7.1 and 5.5 Hz. There were also peaks due to geminal C6 protons at δ 2.55 (br d, J=19.5 Hz) and δ 3.28 (br dd, J=19.5, 5.5 Hz).

Thus, the present photoreaction furnished various novel cycloadducts which can be classified into two groups: the cyclobutaquinazolines (**2c**, **5a**, **b**), or the pentalenopyrimidines (**3c**, **8**, **9**). The reaction mechanism governing the formation of **7** is clearly demonstrated in this paper (Chart 5), however,

Table 2. ^{13}C- and ^{1}H-NMR Data for **3c**,[a] **3a**,[b] and **3b**[c]

Position	**3c**		**3a**		**3b**	
	^{13}C-NMR	^{1}H-NMR (J=Hz)	^{13}C-NMR	^{1}H-NMR (J=Hz)	^{13}C-NMR	^{1}H-NMR (J=Hz)
1	46.54		48.42		48.54	
2	39.58	2.45 (br dd, 3.4, 1.0)	40.02		44.35	2.78 (dd, 3.4, 1.0)
C2–CH_3			12.32	1.64 (3H, s)		
3	40.78		41.39	2.85 (d, 2.9)	31.53	
C3–CH_3	12.37	1.11 (3H, s)			13.10	1.39 (3H, s)
4	50.48	2.09 (br s)	46.31	2.77 (dd, 2.9, 2.4)	51.23	2.58 (br s)
5	157.39		157.56		159.96	
C5=CHa	97.32	4.35 (s)	97.96	4.63 (s)	99.54	4.64 (s)
C5=CHb		4.25 (s)		4.51 (s)		4.53 (s)
6	46.60	2.06 (dd, 3.4, 2.4)	46.20	2.68 (t, 2.4)	43.16	2.91 (br dd, 3.4, 2.4)
7-Ha	51.48	1.54 (br q, 6.3)	45.80	1.71 (dt, 9.8, 2.4)	47.86	1.65 (dd, 9.3, 2.4)
7-Hb				1.55 (d, 9.8)		1.58 (d, 9.3)
C7–CH_3	8.24	0.52				
8	64.66		63.98		64.03	
N9–CH_3	30.31	2.52 (s)	27.59	2.84 (3H, s)	28.84	2.87 (3H, s)
10	154.15		153.59		155.96	
N11–CH_3	27.76	3.35 (3H, s)	30.38	3.20 (3H, s)	31.95	3.22 (3H, s)
12	166.40		167.69		169.75	

a) C_6D_6. *b*) $CDCl_3$. *c*) CD_3OD.

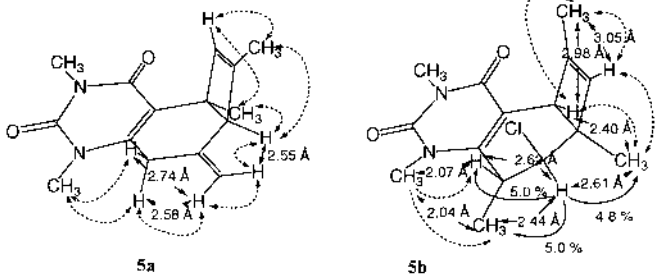

Fig. 2. Atomic Distances[7] and NOE Correlations Assigned from the NOESY Spectrum for **5a** and **5b**

The difference NOEs by the irradiation of H-6 of **5b** are shown as solid lines.

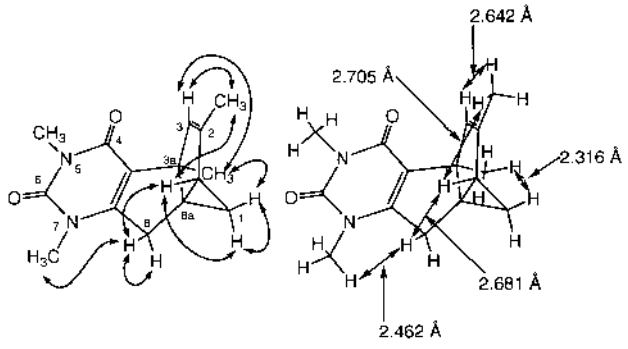

Fig. 3. NOE Correlations and Atomic Distances for **6**[7]

Table 3. NMR and HMBC Data for **6**

Position	^{13}C-NMR	^{1}H-NMR (multi, J in Hz)	HMBC (C#)[a]
1	15.79	Ha 1.05 (dd, J=5.0, 7.9 Hz)	1a, 2, 3a, 3a–CH_3, 8, 8a
		Hb 0.58 (dd, J=3.6, 5.0 Hz)	1a, 2, 3a, 8a
1a	35.03	1.48 (dd, J=3.6, 7.9 Hz)	3, 8, 3a–CH_3
2	143.66		
C2–CH_3	16.14	1.73 (d, J=1.5 Hz)	1a, 2, 3, 3b
3	129.72	5.41 (br s)	1a, 2, 3a, 8a
3a	58.76		
C3a–CH_3	20.90	1.24 (s)	3, 3a, 3b
3b	119.08		
4	160.27		
N5–CH_3	32.61	3.34 (s)	4, 6
6	152.71		
N7–CH_3	27.73	3.33 (d, 6.3)	6, 7a
7a	159.93		
8	36.54	Ha 3.27 (d, J=17.2 Hz)	1, 1a, 2, 3, 7a, 8, 8a
		Hb 2.60 (d, J=17.2 Hz)	1a, 2, 3a, 7a, 8a
8a	33.75		

a) Carbon number.

the reaction mechanism governing the formation of **5b** remains unclear.

Among the pentalenopyrimidine derivatives (**3c**, **8**, **9**), the second most dominant (**8**) might result from attack on the cyclopropane moiety of **6** by hydrogen chloride generated dur-

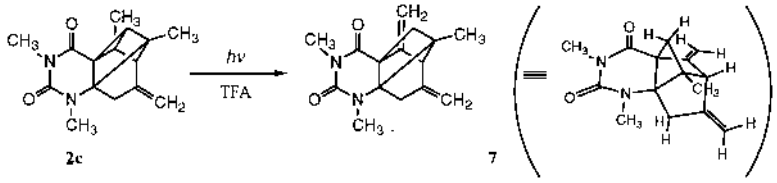

Chart 5

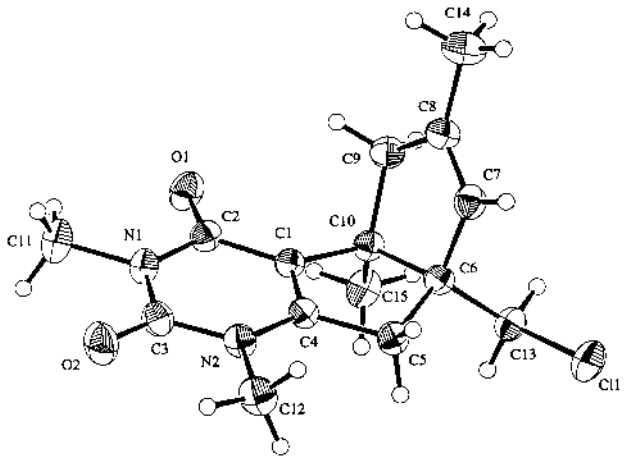

Fig. 4. ORTEP Drawing of the Structure of **8**

Table 4. Bond Lengths (Å) and Standard Deviations in Parenthesis

Atom	Atom	Distance	Atom	Atom	Distance
Cl (1)	C (13)	1.810 (2)	O (1)	C (2)	1.227 (2)
O (2)	C (3)	1.212 (3)	N (1)	C (2)	1.405 (3)
N (1)	C (3)	1.388 (3)	N (1)	C (11)	1.470 (3)
N (2)	C (3)	1.380 (3)	N (2)	C (4)	1.375 (3)
N (2)	C (12)	1.464 (3)	C (1)	C (2)	1.438 (3)
C (1)	C (4)	1.347 (3)	C (1)	C (10)	1.508 (3)
C (4)	C (5)	1.483 (3)	C (5)	C (6)	1.548 (3)
C (6)	C (7)	1.504 (3)	C (6)	C (10)	1.588 (3)
C (6)	C (13)	1.521 (3)	C (7)	C (8)	1.324 (3)
C (8)	C (9)	1.488 (3)	C (8)	C (14)	1.498 (3)
C (9)	C (10)	1.539 (3)	C (10)	C (15)	1.534 (3)

Table 5. Bond Angles (°) and Standard Deviations in Parenthesis

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C (2)	N (1)	C (3)	125.6 (2)	C (2)	N (1)	C (11)	118.5 (2)
C (3)	N (1)	C (11)	115.9 (2)	C (3)	N (2)	C (4)	120.5 (2)
C (3)	N (2)	C (12)	118.5 (2)	C (4)	N (2)	C (12)	121.0 (2)
C (2)	C (1)	C (4)	120.5 (2)	C (2)	C (1)	C (10)	126.8 (2)
C (4)	C (1)	C (10)	112.6 (2)	O (1)	C (2)	N (1)	120.2 (2)
O (1)	C (2)	C (1)	125.7 (2)	N (1)	C (2)	C (1)	114.0 (2)
O (2)	C (3)	N (1)	121.8 (2)	O (2)	C (3)	N (2)	121.6 (2)
N (1)	C (3)	N (2)	116.5 (2)	N (2)	C (4)	C (1)	122.8 (2)
N (2)	C (4)	C (5)	123.9 (2)	C (1)	C (4)	C (5)	113.3 (2)
C (4)	C (5)	C (6)	102.8 (1)	C (5)	C (6)	C (7)	112.4 (2)
C (5)	C (6)	C (10)	106.5 (1)	C (5)	C (6)	C (13)	111.1 (2)
C (7)	C (6)	C (10)	101.7 (1)	C (7)	C (6)	C (13)	111.5 (2)
C (10)	C (6)	C (13)	113.3 (2)	C (6)	C (7)	C (8)	113.7 (2)
C (7)	C (8)	C (9)	111.7 (2)	C (7)	C (8)	C (14)	126.5 (2)
C (9)	C (8)	C (14)	121.8 (2)	C (8)	C (9)	C (10)	104.8 (2)
C (1)	C (10)	C (6)	101.0 (1)	C (1)	C (10)	C (9)	112.0 (2)
C (1)	C (10)	C (15)	109.6 (2)	C (6)	C (10)	C (9)	104.8 (1)
C (6)	C (10)	C (15)	115.5 (2)	C (9)	C (10)	C (15)	113.3 (2)
Cl (1)	C (13)	C (6)	111.0 (1)				

ing the photoreaction. This supposition is consistent with our previous finding[6] that **6** is the major product in a sequence of photorearrangements initiated from **1c** (see Chart 3).

Two other pentalenopyrimidines (**3c**, **9**) were produced in the present reaction. The production of these compounds coincides with our previous finding that certain pentalenopyrimidines are preferentially produced by short time photolysis of 6-ClDMU in benzene at low temperature (−25 °C).[8] However, it should be noted that compounds **3c** and **9** were synthesized under contrasting conditions, namely a prolonged irradiation period at an elevated temperature (20—30 °C). These facts suggest that a different type of reaction mechanism may be involved in the formation of **3c** and **9**.

At present, further work on the reaction mechanisms underlying the products formed from this photoreaction is being done.

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 signals produced by solvents; $CDCl_3$ (δ 7.26), C_6D_6 (δ 7.15), acetone-d_6 (δ 2.04), CD_3OD (δ 3.30). The following abbreviations are used: s=singlet, br s=broad singlet, d=doublet, dd=double doublet, ddd=double 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 the chemical shifts of signals governing the solvents; $CDCl_3$ (δ 77.0), C_6D_6 (δ 128.0), acetone-d_6 (δ 30.3), methanol-d_4 (δ 49.8). MS and high-resolution MS (HRMS)

were performed on a JEOL JMS-DX303 spectrometer with an ionization potential of 70 eV. Short-column chromatography was performed on Kieselgel Si-60 (Merck). Reverse-phase liquid chromatography (RP-HPLC) was carried out on a Shim-pac PREP-ODS (25 cm×20 mm i.d.) (Shimadzu) with aqueous methanol, using a Shimadzu LC-6A apparatus with monitoring at 254 nm. Silica gel LC (Si-HPLC) was conducted on a Shim-pac PREP-Sil (H) (25 cm×20 mm i.d.) (silica gel), using the same apparatus. UV-irradiation was carried out externally using 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.

Photolysis of 6-ClDMU and Mesitylene in the Presence of TFA A solution of 6-ClDMU (122.2 mg, 0.7 mmol) and TFA (2 eq mol: 108 μl) in mesitylene (35 ml) was put portion-wise (5 ml each) into seven degassed Pyrex tubes, and irradiated externally for 18 h. The reaction mixture was evaporated *in vacuo*. The residual oil was passed through a short column of silica gel (5 g) first with hexane and then with ethyl acetate. The ethyl acetate-eluate was submitted to RP-LC with 35% and 60% methanol–H_2O. From the 35%-aqueous methanol solution, 6-ClDMU (61.9 mg, 50.7%) was recovered. After Si-HPLC with ethyl acetate–hexane (1 : 3), 60% methanol–H_2O eluate afforded **3c** (1.7 mg, 1.0%), **1b** (16.5 mg, 9.1%), and **6** (4.0 mg, 2.2%), **2c** (2.95 mg, 1.6%), **7** (2.1 mg, 1.1%), **4** (1.4 mg, 0.8%), **5a** (1.6 mg, 0.9%), **9** (2.0 mg, 1.1%), **8** (5.9 mg, 2.9%), and **5b** (1.8 mg, 0.9%).

1,3,5,7,9-Pentamethylcyclooctapyrimidine-2,4-dione (**1c**): Colorless crystals, mp 113—114 °C (recrystallized from 2-propanol). ^{1}H-NMR (C_6D_6) δ: 1.47 (3H, s, C9–CH_3), 1.59 (3H, s, C7–CH_3), 2.19 (3H, s, C5–CH_3), 2.79 (3H, s, N1–CH_3), 3.24 (3H, s, N3–CH_3), 5.19 (1H, br s, H-10), 5.33 (1H, br s, H-8), 5.67 (1H, br s, H-6). ^{13}C-NMR (C_6D_6) δ: 22.90 (C5–CH_3), 23.12 (C7–CH_3), 23.46 (C9–CH_3), 27.81 (N1–CH_3), 31.69 (N3–CH_3), 113.15 (4a), 119.75 (10), 126.68 (8), 130.55 (6), 136.45 (5), 140.68 (7), 145.47 (9), 147.33 (10a), 151.75 (2), 160.78 (4). HMBC: H-10 with C9, C9–CH_3, C8, C4a; C9–CH_3 with C10, C9, C8; H-8 with C10, C7–CH_3, C6; C7–CH_3 with C8, C7, C6; H-6 with C8, C5–CH_3, C4a; C5–CH_3 with C6, C5, C4a; N3–CH_3 with C4, C2; N1–CH_3 with C10a, C2. NOE: H-10 with N1–CH_3, C9–CH_3, C9–CH_3 with H-10, H-8; H-8 with C7–CH_3, C9–CH_3, C7–CH_3 with H-8, H-6, H-6 with C7–CH_3, C5–CH_3, C7–CH_3 with C-6; N1–CH_3 with H-10. Ms *m/z* (%): 258 (M^+, 100), 243 (61), 218 (7), 200 (9), 186 (49), 158 (44), 143 (8), 128 (11), 115 (16), 91 (19). HRMS: Calcd for $C_{15}H_{18}N_2O_2$: 258.1368. Found: 258.1369.

1,3,6,8,10-Pentamethylcyclooctapyrimidine-2,4-dione (**1d**): Colorless crystals, mp 123—125 °C (recrystallized from 2-propanol). ^{1}H-NMR (acetone-d_6) δ: 1.77 (3H, dd, J=0.72, 1.47 Hz, C6–CH_3), 1.80 (3H, dd, J=0.75, 1.47 Hz, C8–CH_3), 1.93 (3H, d, J=1.47 Hz, C10–CH_3), 3.20 (3H, s, N3–CH_3), 3.27 (3H, s, N1–CH_3), 5.63 (1H, br s, H-7), 5.92 (1H, q, J=1.47 Hz, H-5), 6.05 (1H, br s, H-9). ^{13}C-NMR (acetone-d_6) δ: 21.37 (C10–CH_3), 22.42 (C8–CH_3), 23.62 (C6–CH_3), 27.74 (N3–CH_3), 33.44 (N1–CH_3), 110.96 (4a), 122.51 (5), 129.90 (7), 133.22 (10), 135.18 (9), 138.70 (8), 140.85 (6), 151.51 (10a), 152.88 (2), 162.25 (1). HMBC: C10–CH_3 with C10a, C10, C9; H-9 with C10a, C10–CH_3, C7; C8–CH_3 with C9, C8, C7; H-7 with C9, C8–CH_3, C5; C6–CH_3 with C5, C6, C7; H-5 with C10a, C6–CH_3, C7; N3–CH_3 with C2, C4; N1–CH_3 with C10a, C2. NOE: C10–CH_3 with N1–CH_3, H-9; H-9 with C10–CH_3, C8–CH_3; C8–CH_3 with H-9, H-7; H-7 with C8–CH_3, C6–CH_3; C6–CH_3 with H-5; H-5 with C6–CH_3; N1–CH_3 with C10–CH_3. MS *m/z* (%): 258 (M^+, 100), 243 (49), 218 (10), 201 (10), 186 (53), 172 (19), 158 (48), 143 (10), 115 (21), 91 (19). HRMS: Calcd for $C_{15}H_{18}N_2O_2$: 258.1368. Found: 258.1357.

2,4,9,11-Tetramethyl-6-methylene-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]-dodecane-10,12-dione (**2c**): Colorless crystals, mp 109—111 °C (recrystallized from ether). ^{1}H- and ^{13}C-NMR, see Table 1. HMBC: C2–CH_3 with C1, C2, C3, C5; H-3 with C1, C4, C4–CH_3, C5, C6, C7, C12; C4–CH_3 with C3, C4, C5, C8; H-5 with C1, C2, C2–CH_3, C3, C4, C4–CH_3; *exo*-methylene protons (C6=CHa, C6=CHb) with C5, C7; Ha-7 with C1, C4, C6, C6=CH_2, C8; Hb-7 with C1, C4, C5, C6, C6=CH_2, C8; N9–CH_3 with C8, C10; N11–CH_3 with C10, C12. NOE: C2–CH_3 with H-3, H-5; H-3 with C2–CH_3, C4–CH_3; C4–CH_3, with H-3, H-5, N9–CH_3; H-5 with C2–CH_3, C4–CH_3, C6=CHb; C6=CHa with H-5, C6=CHb; C6=CHb with H-5, C6=CHa; Ha,b-7; Ha-7 with C6=CHb, Hb-7, N9–CH_3, Hb-7 with C6=CHb, Ha-7, N9–CH_3, N9–CH_3 with C4–CH_3, Ha,b-7. MS *m/z* (%): 258 (M^+, 11), 243 (39), 218 (16), 186 (14), 172 (14), 158 (31), 133 (24), 91 (23). HRMS: Calcd for $C_{15}H_{18}N_2O_2$ *m/z*: 258.1368. Found: 258.1346.

3,7,9,11-Tetramethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane-10,12-dione (**3c**): ^{1}H- and ^{13}C-NMR, see Table 2. HMBC spectrum: H-2 with C1, C6, C8, C7–CH_3; C3–CH_3 with C1, C2, C3, C4; H-4 with C1, C6; C7–CH_3 with C6, C7, C8; H-7 with C2, C3, C8; *exo*-methylene protons (C5=CHa, b) with C4, C5, C6; N9–CH_3 with C8, C10; N11–CH_3 with C10, C12. NOE: H-2 with H-6, C3–CH_3, C7–CH_3; C3–CH_3 with H-2, H-4; H-4 with C3–CH_3, C5=CHb, C5–CHa, N9–CH_3; C5–CHa with H-6, C5=CHb; C5=CHb with H-4, C5=CHa; N9–CH_3 with H-4, H-7. MS *m/z* (%) 258 (M^+, 75), 243 (100), 186 (35), 172 (13), 158 (54). HRMS: Calcd for $C_{15}H_{18}N_2O_2$ *m/z*: 258.1368. Found *m/z*: 258.1367.

9,10-Dihydro-1,2,5,7-tetramethyl-9-methylenecyclooctapyrimidine-2,4-dione (**4**): mp 142—144 °C (re-crystallized from 2-propanol). ^{1}H-NMR ($CDCl_3$) δ: 1.79 (3H, s, C7–CH_3), 2.09 (3H, s, C5–CH_3), 3.27 (1H, d, J=13.6 Hz, H10-a), 3.34 (3H, s, N3–CH_3), 3.54 (3H, s, N1–CH_3), 4.05 (1H, d, J=13.6 Hz, Hb-10), 5.00 (1H, s, C9=CHa), 5.10 (1H, s, C9=CHb), 5.82 (1H, s, H-6), 6.00 (1H, s, H-8). ^{13}C-NMR ($CDCl_3$) δ: 22.95 (C5–CH_3), 26.70 (C7–CH_3), 28.14 (N3–CH_3), 30.32 (N1–CH_3), 36.88 (10), 112.99 (4a), 117.52 (C9=CH_2), 128.10 (8), 130.81 (6), 132.53 (5), 135.91 (7), 141.77 (9), 149.56 (10a), 152.09 (2), 161.07 (4). HMBC; Ha-9 with C10a, C9, C9=CH_2, C4a; Hb-9 with C10a, C9, C9=CH_2, C8, C4a; *exo*-methylene protons (C9=CHa, C9=CHb) with C10, C8; H-8 with C10, C9, C9=CH_2, C7–CH_3, C6; C7–CH_3 with C9, C9=CH_2, C8, C7, C6; C5–CH_3 with C6, C5, C4a; N3–CH_3 with C4, C2; N1–CH_3 with C10a, C2. NOE: N1–CH_3 with Hb-10, C9=CHb; C5–CH_3 with H-6; H-6 with C7–CH_3, C5–CH_3; C7–CH_3 with H-8, H-6; H-8 with C7–CH_3, C9=CHa; C9=CHa with C9=CHb, H-8; C9=CHb with Hb-10, N1–CH_3, C9=CHa; Ha-10 with Hb-10; Hb-10 with N1–CH_3, C9–CH_3, Ha-10. Ms *m/z* (%); 258 (M^+, 65), 243 (50), 186 (23), 172 (23), 158 (47), 118 (29). HRMS; Calcd for $C_{15}H_{18}N_2O_2$: 258.1368. Found: 258.1368.

5,6,6a,8a-Tetrahydro-2,4,7,8a-tetramethyl-6-methylenecyclobuta[*f*]quinazoline-1,3-dione (**5a**): Colorless oil. ^{1}H-NMR (C_6D_6) δ: 1.56 (3H, t-like, C7–CH_3), 1.76 (3H, s, C8a–CH_3), 2.45 (1H, d, J=20.0 Hz, Hb-5), 2.53 (1H, d, J=20.0 Hz, Ha5), 2.59 (3H, s, N4–CH_3), 2.64 (1H, br s, H-6a), 3.30 (3H, s, N2–CH_3), 4.67 (1H, br s, C6=Hb), 4.82 (1H, br s, C6=Ha), 6.44 (1H, br s, H-8). Ms *m/z* (%); 258 (M^+, 92), 243 (90), 218 (48), 186 (45), 172 (50), 158 (79), 91 (100).

6-Chloro-5,6,6a,8a-tetrahydro-2,4,5,6a,8-pentamethylcyclobuta[*f*]quinazoline-1,3-dione (**5b**): Colorless oil. ^{1}H-NMR (C_6D_6) δ: 0.50 (3H, d, J=7.3 Hz, C5–CH_3), 1.11 (3H, s, C6a–CH_3), 2.05 (3H, t-like, J=1.3 Hz, C8–CH_3), 2.76 (1H, dq, J=2.9, 7.1 Hz, H-5), 2.84 (3H, s, N4–CH_3), 3.24 (3H, s, N2–CH_3), 3.36 (1H, br s, H-8a), 3.77 (1H, d, J=2.9 Hz, H-6), and 5.91 (d-like, J=1.3 Hz, H-7). ^{13}C-NMR (C_6D_6) δ: 13.96 (C5–CH_3), 17.07 (C8–CH_3), 21.06 (C6a–CH_3), 27.78 (N2–CH_3), 30.19 (N4–CH_3), 40.04 (5), 44.66 (6a), 50.67 (8a), 67.84 (6), 107.45 (8b), 137.66 (7), 148.58 (8), 150.52 (4a), 151.76 (3), 162.09 (1). MS *m/z* (%); 296 (M^+, 4), 294 (M^+, 12), 259 (71), 219 (51), 202 (14), 162 (100), 134 (19). HRMS: Calcd for $C_{15}H_{19}N_2O_2Cl$ *m/z*: 294.1135. Found *m/z*: 294.1136.

1a,2,3,3a,8,8a-Hexahydro-2,3a,5,7-tetramethyl-1*H*-cyclopropa[3a,4]-pentaleno[2,1-*d*]pyrimidine-4,6-dione (**6**): Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 0.58 (1H, dd, J=3.6, 5.0 Hz, Hb-1), 1.05 (1H, dd, J=5.0, 7.9 Hz, Ha-1), 1.24 (3H, s, C3a–CH_3), 1.48 (1H, dd, J=3.6, 7.9 Hz, H-1a), 1.73 (3H, d, J=1.5 Hz, C2–CH_3), 2.60 (1H, d, J=17.2 Hz, Hb-8), 3.27 (1H, d, J=17.2 Hz, Ha-8), 3.33 (1H, s, N5–CH_3), 3.34 (3H, s, N7–CH_3), 5.41 (1H, br s, H-3). ^{13}C-NMR ($CDCl_3$) δ: 15.79 (1), 16.14 (C2–CH_3), 20.90 (C3a–CH_3), 27.73 (N7–CH_3), 32.61 (N5–CH_3), 33.75 (8a), 35.03 (1a), 36.54 (8), 58.76 (3a), 119.08 (3b), 129.72 (3), 143.66 (2), 152.71 (6), 159.93 (7a), 160.27 (4). HMBC: Ha-8 with C8a, C7a, C3b, C3, C1a, C1; Hb-8 with C8a, C7a, C3b, C3a, C1a; N7–CH_3 with C7a, C6; N5–CH_3 with C6, C4; H-3 with C8a, C3a, C2, C1a; C3a–CH_3 with C8a, C3b, C3a, C3; C2–CH_3 with C3, C2, C1a; Ha-1 with C8a, C8, C3a, C2, C1a, C3a–CH_3; Hb-1 with C8a, C3a, C2, C1a. MS *m/z* (%); 258 (M^+, 75), 243 (100), 186 (35), 172 (13), 158 (54). HRMS: Calcd for $C_{15}H_{18}N_2O_2$ *m/z*: 258.1368. Found *m/z*: 258.1367.

3,5,10-Trimethyl-8,12-dimethylene-3,5-diazatetracyclo[7.2.1.0^{1,6}.0^{6,10}]-dodecane-2,4-dione (**7**): Colorless crystals, mp 124—125 °C (recrystallized from ether). ^{1}H-NMR ($CDCl_3$) δ: 1.22 (3H, s, C10–CH_3), 1.97 1H, d, J=7.3 Hz, Hb-11), 2.32 (1H, dt, J=2.4, 17.0 Hz, Hb-7), 2.41 (1H, br d, J=17.0 Hz, Ha-7), 2.50 (1H, d, J=7.3 Hz, Ha-11), 3.01 (3H, s, N5–CH_3), 3.03 (1H, br s, H-9), 3.19 (3H, s, N3–CH_3), 4.69 (1H, br s, C8=CHb), 4.99 (1H, t, J=2.4 Hz, C8=CHa), 5.00 (1H, s, C12=CHb), 5.64 (1H, d, C12=CHa, J=1.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 14.36 (C10–CH_3), 27.40 (N3–CH_3), 30.88 (7), 31.61 (N5–CH_3), 43.91 (11), 53.83 (1), 53.92 (10), 60.58 (9), 72.34 (6), 104.79 (C8=CH_2), 105.71 (C12=CH_2), 146.19 (12), 148.58 (8), 154.03 (4), 166.73 (2). HMBC: C10–CH_3 with C6, C9, C10, C11; Hb-11 with C1, C6, C7, C9, C10, C12; Hb-7 with C1, C6, C8, C9, C10, C8=CH_2; Ha-7 with C1, C6, C8, C10, C8=CH_2; Ha-11a with C1, C2, C6, C9, C10, C12, C10–CH_3, N5–CH_3 with C4, C6; H-9 with C7, C10, C12, C8=CH_2, C12=CH_2; N5–CH_3 with C2, C4; C4–CH_3 with C3, C4, C5, C8; H-5 with C1, C2, C2–CH_3, C3, C4, C4–CH_3; C8=CHb with C7, C8, C9; C8=CHa with C7, C8, C9, C10; C12=CHb with C1, C8, C9, C11, C12; C12=CHa with C1,

C8, C9, C12. NOE: C10–CH_3 with H-9, Ha-11, N5–CH_3; Hb-11 with H-9, Ha-11); Hb-7 with Ha-7, C8=CHb, N5–CH_3; Ha-7 with Hb-7, C8=CHb, N5–CH_3; Ha-11 with C10–CH_3, Hb-11; N5–CH_3 with C10–CH_3, Ha,b-7; H-9 with C10–CH_3, C12=CHb; C8=CHb with Ha,b-7, C8=CHa; C8=CHa with C8=CHb; C12=CHb with H-9, C12=CHa; C12=CHa with C12=CHb. MS *m/z* (%); 258 (M^+, 26), 243 (100), 218 (9), 200 (9), 186 (36), 172 (14), 158 (28). HRMS: Calcd for $C_{15}H_{18}N_2O_2$ *m/z*: 258.1368. Found *m/z*: 258.1363.

7a-Chloromethyl-4b,5,7a,8-tetrahydro-1,3,4b,6-tetramethylpentaleno[2,1-*d*]pyrimidine-2,4-dione (**8**): Colorless crystals, mp 97—98 °C (recrystallized from hexane). ^{1}H-NMR (acetone-d_6) δ: 1.36 (3H, s, C4b–CH_3), 1.66 (3H, d-like, J=1.0 Hz, C6–CH_3), 2.33 [1H, d, J=15.8 Hz, Hb-5], 2.86 [1H, d, J=15.8 Hz, Ha-5], 2.92 [1H, d, J=17.6 Hz, Hb-8], 3.04 [1H, d, J=17.6 Hz, Ha-8], 3.18 (3H, s, N3–CH_3), 3.31 (3H, s, N1–CH_3), 3.70 (1H, d, J=10.7 Hz, C7a–CHb), 3.81 (1H, d, J=10.7 Hz, C7a–CHa), and 5.28 (1H, br s, H-7). ^{13}C-NMR (C_6D_6) δ: 16.73 (C6–CH_3), 19.90 (C4b–CH_3), 27.59 (N3–CH_3), 32.54 (N1–CH_3), 41.09 (8), 48.00 (5), 51.19 (C7a–CH_2), 56.51 (4a or 7a), 61.14 (4a or 7a), 116.59 (4a), 129.63 (7), 142.43 (6), 152.63 (8a), 153.20 (2), 160.67 (4). HMBC: C4b–CH_3 with C4a, C4b, C5, C7a; Ha-5 with C4a, C4b, C6, C7, C7a; Hb-5 with C4a, C6, C7; C6–CH_3 with C5, C6, C7; C7a–CHa with C4b, C7, C7a, C8; C7a–CHb with C4b, C7, C7a, C8; Ha-8 with C4a, C4b, C7, C7a, C7a–CH_2, C8a; Hb-8 with C4a, C4b, C7, C7a, C7a–CH_2, C8a; N1–CH_3 with C8a, C2; N3–CH_3 with C2, C4. MS *m/z* (%); 296 (M^+, 10), 294 (M^+, 29), 259 (100), 245 (31), 202 (14), 188 (21). HRMS: Calcd for $C_{15}H_{19}N_2O_2Cl$ *m/z*: 294.1135. Found *m/z*: 294.1128.

X-Ray Crystallography of **8**: The diffraction experiment was carried out using a colorless transparent prism with the dimensions 0.50×0.20×0.15 mm. A diffractometer RAXIS-IV (RIGAKU) imaging plate area detector was used with graphite-monochromated Mo$K\alpha$ radiation (λ=0.71070 Å) to obtain the following crystal data: $C_{15}H_{19}N_2O_2Cl$ M_r=294.78., a=13.062 (1) Å, b=14.123 (2) Å, c=8.321 (1) Å, β=90.053 (8)°, V=1535.2 Å^3, monoclinic, $P2_1/n$, Z=4, D_x=1.275 g/cm^3, F(000)=624.00, μ (Mo$K\alpha$)=2.52 cm^{-1}. 2918 unique reflections ($2\theta \leq 55°$) were measured, of which 2064 with $|F_O| \geq 4\sigma(F_O)$ were considered as shown in Fig. 2. No absorption corrections were applied. The structure was solved by a direct method using SIR92[9] and expanded with Fourier techniques.[10] Neutral atom scattering factors were taken from the International Tables for X-ray crystallography.[11] The final R factor was 0.045.

1,3,5,7,8-Pentamethyl-6,7-dihydropentaleno[2,1-*d*]pyrimidine-2,4-dione (**9**): Yellow crystals, mp 171—173 °C (recrystallized from ether). ^{1}H-NMR ($CDCl_3$) δ: 1.27 (3H, d, J=7.1 Hz, C7–CH_3), 2.29 (3H, br s, C7–CH_3), 2.55 (1H, br d, J=19.5 Hz, H-6), 2.60 (3H, br s, C5–CH_3), 3.15 (1H, br dq, J=5.5, 7.1 Hz, H-7), 3.28 (1H, br dd, J=19.5, 5.5 Hz, H-6), 3.41 (3H, s, N3–CH_3), and 3.71 (3H, s, N1–CH_3). NOE: Ha-6 with Hb-6, H-7; Hb-6 with Ha-6, C7–CH_3; H-7 with Ha-6, C7–CH_3, C8–CH_3; C7–CH_3 with Hb-6, H-7, C8–CH_3; C8–CH_3 with H-7, C7–CH_3, N1–CH_3; N1–CH_3 with C8–CH_3. MS *m/z* (%): 258 (M^+, 100), 243 (35), 186 (47), 173 (15), 158(26). HRMS: Calcd for $C_{15}H_{18}N_2O_2$ *m/z*: 258.1368. Found *m/z*: 258.1355.

Photolysis of 2c in the Absence of TFA A solution of **2c** (5.1 mg, 0.02 mmol) in benzene-d_6 was irradiated for 30 min in a degassed NMR-sample tube, yielding **5a** (3.8%), together with unused **2c** (96.2%). These yields were determined *via* ^{1}H-NMR spectroscopy.

Photolysis of 2c in the Presence of TFA Photolysis of a solution containing **2c** (3.0 mg, 0.012 mmol) and TFA in benzene-d_6 for 2 h in a degassed NMR-sample tube yielded **6** (4.4%), together with unused **2c** (88.5%) (NMR yields).

References and Notes

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