ACID-CATALYZED PHOTOREACTION OF 6-CHLORO-1,3-DIMETHYLURACIL TO *p*- AND *m*-XYLENE: FORMATION OF NOVEL PHOTOCYCLOADDUCTS, 6-METHYLENE-9,11,X-TRIMETHYL-9,11-DIAZAPENTACYCLO[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]DODECANE-10,12-DIONES AND 5-METHYLENE-9,11,X-TRIMETHYL-9,11-DIAZAPENTACYCLO-[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]DODECANE-10,12-DIONES[1]

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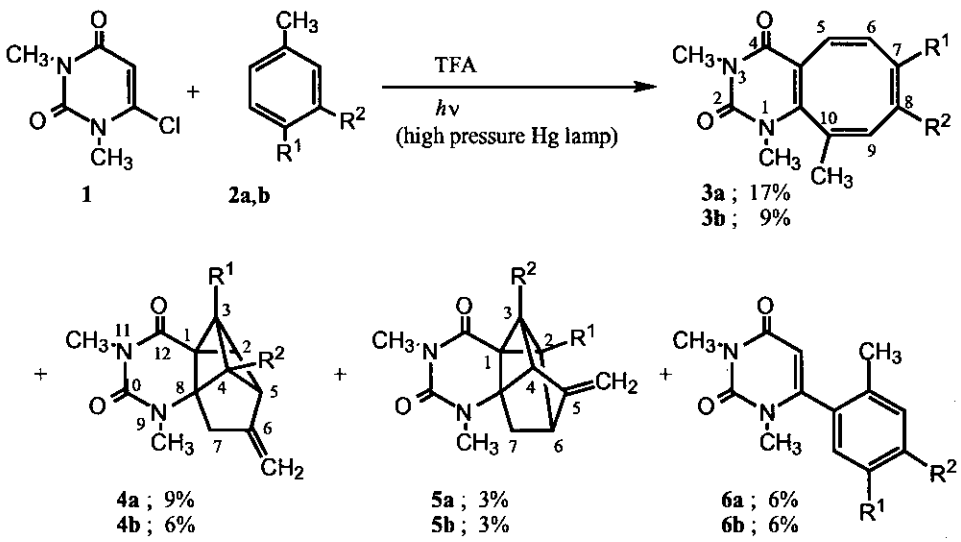
Abstract——Uv irradiation of 6-chloro-1,3-dimethyluracil in *p*- and *m*-xylenes in the presence of trifluoroacetic acid gave novel photocycloadducts, 6-methylene-9,11,x-trimethyl-9,11-diazapentacyclo-[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones and 5-methylene-9,11,x-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane-10,12-diones, together with tetramethylcyclooctapyrimidine-2,4-diones as the sole regioisomer. The modes of the cycloaddition were discussed.

In the course of our studies on the acid-catalyzed photoreaction of pyrimidine bases with substituted benzenes, we have reported that 1,3-dimethylcyclooctapyrimidine-2,4-diones were produced by the photolysis of 6-chloro-1,3-dimethyluracil (**1**) in benzene[2] and its monosubstituted derivatives[3] in the presence of trifluoroacetic acid (TFA), presumably *via ortho*-cycloaddition. In order to explore the general feature of this photocycloaddition reaction, we have extended our work to disubstituted benzenes. In the present paper, we describe our findings that photoreaction of **1** in *p*- and *m*-xylenes (**2a**, **b**) afforded cyclooctapyrimidine derivatives (**3a**, **b**) and two novel pentacyclic compounds consisting of 3, 4, 4, and 5-membered rings (**4a**, **b**) and 3, 4, 5, and 5-membered rings (**5a**, **b**) probably *via* multi-photon reactions. On the basis of the substitution sites of the methyl groups, compounds **3(a,b)** and **4(a,b)** are presumed to be derived *via ortho*-addition, while the compounds **5(a,b)** may be the products through *meta*-addition.

Uv irradiation of **1** in *p*-xylene (**2a**) in the presence of trifluoroacetic acid (TFA) was shown to give numerous products by hplc. Chromatography of the reaction mixture afforded three types of cycloadducts as the single regioisomers; *i. e.*, 1,3,7,10-tetramethylcyclooctapyrimidine-2,4-dione (**3a**) and two novel

pentacyclic compounds, 6-methylene-3,9,11-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-dione (**4a**) and 5-methylene-2,9,11-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane-10,12-dione (**5a**), together with 6-substituted products, 1,3-dimethyl-6-(*p*-xylyl)uracil (**6a**) and 1,3-dimethyl-6-(*p*-methylbenzyl)uracil (**7**). Similarly the photoreaction with *m*-xylene (**2b**) afforded 1,3,8,10-tetramethylcyclooctapyrimidine-2,4-dione (**3b**) and two pentacyclic compounds, 6-methylene-4,9,11-trimethyl-9,11-diazapentacyclo-[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-dione (**4b**) and 5-methylene-3,9,11-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane-10,12-dione (**5b**).



a; $R^1 = CH_3$, R^2 = H: **b**; R^1 = H, $R^2 = CH_3$. Yields are given based on **1** consumed.

Scheme 1

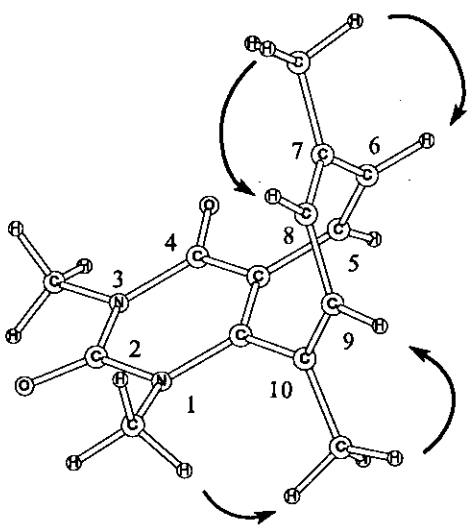


Figure 1. NOE correlation for **3a**: The optimized structue was obtained by the PM3 method.

The structural assignment of 1,3,7,10-tetramethyl-cyclooctapyrimidine-2,4-dione (**3a**), colorless crystals, was made essentially on the basis of ms and ^{1}H-nmr spectrum. The ms of **3a** showed the molecular ion peak (M^+) at *m/z* 244 (100%). The ^{1}H-nmr spectrum exhibited four signals at δ 1.70, 1.93, 3.22, and 3.27 ppm due to the N- and C-methyl groups and peaks ascribable to four vinyl protons between δ 5.83-6.18 ppm. In a differential nuclear Overhauser effect (differential NOE) experiment on **3a**, irradiation of the N^1-methyl signal at δ 3.27 caused selective enhancement of the C^{10}-methyl signal at δ 1.93. The NOEs for N^1-methyl and H-9 at δ 6.04 were observed on irradiation at C^{10}-methyl signal. Strong NOE for H-8 at δ 5.83 and weak NOE for H-6

at δ 5.93 were observed on irradiation at C^7-methyl signal (Figure 1). Similarly the structural assignment of **3b** was made on the basis of ^{1}H-nmr including NOE measurements. ^{1}H-^{1}H Coupling constants of **3a, b** including C-methyl groups were determined by triple resonance methods. The coupling constants of vinyl protons of **3(a,b)**, $J_{5\text{-}6}$, $J_{7\text{-}8}$, $J_{9\text{-}10}$ = *ca.* 11~12 Hz and $J_{6\text{-}7}$, $J_{8\text{-}9}$ = *ca.* 3~4 Hz revealed the configurations to be all *cis*[4] (see experimental section).

Table 1. ^{13}C-Nmr and ^{1}H-nmr data for **4a**[a)] and **4b**[b)]

Position	**4a**		**4b**	
	^{13}C-Nmr	^{1}H-Nmr	^{13}C-Nmr	^{1}H-Nmr
1	46.53		41.89	
2	34.61	2.82 (dd, 5.1, 2.6)	27.23	2.81 (dd, 3.4, 2.4)
3	32.54		38.66	3.38 (d, 3.4)
C^3-CH_3	10.50	1.45 (3H, s)		
4	50.64	2.78 (dd, 5.1, 4.4)	59.05	
C^4-CH_3			13.85	1.18 (3H, s)
5	51.17	3.65 (dd, 4.4, 2.6)	58.54	3.28 (d, 2.4)
6	147.31		148.03	
C^6=CH^a	106.96	4.73 (t, 2.5)	107.58	4.76 (t, 2.3)
C^6=CH^b		4.90 (t, 2.5)		4.92 (t, 2.3)
7 (H^a)	35.07	2.52 (dt, 16.9, 2.5)	34.61	2.66 (dt, 17.1, 2.3)
7 (H^b)		2.42 (dt, 16.9, 2.5)		2.53 (dt, 17.1, 2.3)
8	66.91		69.19	
N^9-CH_3	30.26	2.98 (3H, s)	31.74	2.96 (3H, s)
10	155.34		155.88	
N^{11}-CH_3	27.79	3.20 (3H, s)	27.50	3.08 (3H, s)
12	166.88		167.16	

a) $CDCl_3$. *b)* Acetone-d_6.

Compound(**4a**), colorless crystals, was formulated as $C_{14}H_{16}N_2O_2$ from the high resolution mass spectrum (HRms). The ^{1}H and ^{13}C-nmr spectra including ^{13}C-^{1}H correlation spectroscopy (^{13}C-^{1}H COSY) showed signals due to three methyl groups, two methylene groups, three methine groups, and six quaternary carbon atoms. The spin-spin decoupling experiments revealed the correlation between C^6- and C^7-methylene, and among 2-H, 4-H, and 5-H (Table 1).

Heteronuclear multiple-bond connectivity (HMBC) (Table 2) and NOE (Figure 2) experiments also provided the information to enable us to construct pentacyclic compound consisting of 3, 4, 4, and 5-membered rings. The cross peak observed between C-3 and H-7 in the HMBC spectrum was compatible with C-H long range "W" coupling.[5] Finally the structure of **4a** was determined by X-ray crystallographic analysis (Figure 3).

The structure of **4b** was determined by comparison with the nmr data for **4a** including ^{13}C-^{1}H COSY (Table 1), HMBC (Table 2): In the HMBC spectrum, the cross peaks due to C-H four bonded coupling in 'W' geometry[5] were observed between C-6 and H-3, and C-7 and H-3. NOEs observed for C^4-methyl and H-7 on irradiation at N^9-methyl, and for N^9-methyl, H-3, and H-5, on irradiation at C^4-methyl supported the structural assignment (Figure 4).

Table 2. ^{13}C-^{1}H Long range correlations in the HMBC spectrum of **4a** and **4b**

Carbon	H in **4a**	H in **4b**
1	C^3-CH_3	H-3, H-5, H^a-7, H^b-7
2	C^3-CH_3, H-4	H-5
3	C^3-CH_3, H-4, H-5, H^a-7, H^b-7	C^4-CH_3
4	H-2, C^3-CH_3, H^a-7, H^b-7	H-2, H-3, C^4-CH_3, H-5, H^b-7
C^4-CH_3		H-5
5	C^6=CH_2	H-3, C^4-CH_3, C^6=CH_2
6	C^6=CH_2, H^a-7, H^b-7	H-3, H^a-7, H^b-7
C^6-CH_2	H^a-7, H^b-7	H-5, H^b-7
7	H-5, C^6=CH_2	H-3, H-5, C^6=CH_2
8	H-5, H^a-7, H^b-7	C^4-CH_3, H-5, H^b-7, N^9-CH_3
10	N^9-CH_3, N^{11}-CH_3	
12		H-3, N^{11}-CH_3

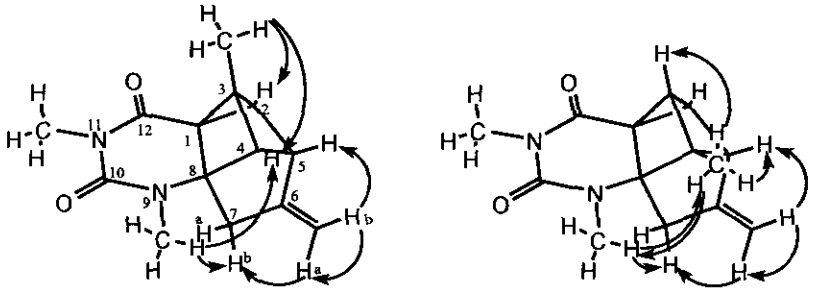


Figure 2. NOE Correlation for **4a** (left) and **4b** (right)

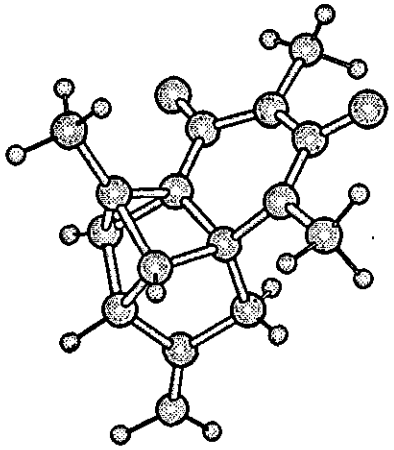


Figure 3. X-Ray crystallography of **4a**.

The structural assignment of **5a** was made essentially on the basis of the ^{1}H-nmr spectroscopy. ^{1}H-Nmr spectrum exhibited signals due to two methylene groups at δ 1.55 and δ 1.71, and at δ 4.51 and δ 4.63 (Table 3). The double resonance methods revealed the correlation between H-6 and H^b-7, and among H-3, H-4, and H-6. NOE experiments confirmed the sites of methyl and methylene substituents (Figure 4) and the structure was supported by the HMBC spectrum (Table 4). Finally the structure of **5a**, consisting of the enantiomeric isomers (molecule A and B) , was determined by X-Ray crystallographic analysis (Figure 5).

The structure of **5b** was deduced from the spectral analogy with **5a** (Table 3 and Figure 4).

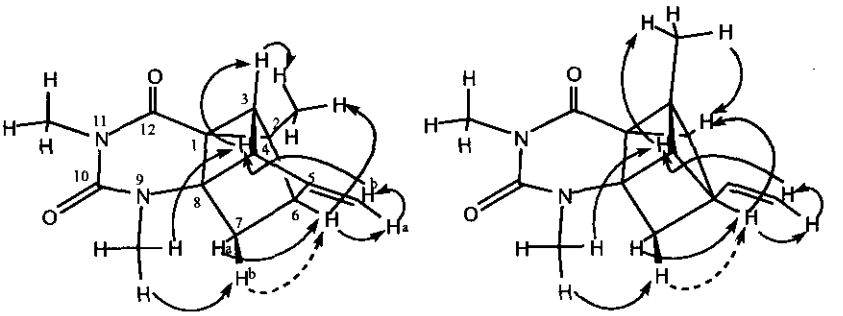


Figure 4. NOE Correlation for **5a** (left) and **5b** (right)

Table 3. ^{13}C-Nmr and ^{1}H-nmr data for **5a**[a] and **5b**[b]

	5a		**5b**	
Position	^{13}C-Nmr	^{1}H-Nmr	^{13}C-Nmr	^{1}H-Nmr
1	48.42		48.54	
2	40.02		44.35	2.78 (dd, 3.4, 1.0)
C^2-CH_3	12.32	1.64 (3H, s)		
3	41.39	2.85 (d, 2.9)	31.53	
C^3-CH_3			13.10	1.39 (3H, s)
4	46.31	2.77 (dd, 2.9, 2.4)	51.23	2.58 (br. s)
5	157.56		159.96	
C^5=CH^a	97.96	4.63 (s)	99.54	4.64 (s)
C^5=CH^b		4.51 (s)		4.53 (s)
6	46.20	2.68 (t, 2.4)	43.16	2.91 (br. dd, 3.4, 2.4)
7 (H^a)	45.80	1.71 (dd, 9.8, 2.4)	47.86	1.65 (dd, 9.3, 2.4)
7 (H^b)		1.55 (d, 9.8)		1.58 (d, 9.3)
8	63.98		64.03	
N^9-CH_3	27.59	2.84 (3H, s)	28.84	2.87 (3H, s)
10	153.59		155.96	
N^{11}-CH_3	30.38	3.20 (3H, s)	31.95	3.22 (3H, s)
12	167.69		169.75	

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

Table 4. ^{13}C-^{1}H Long range correlations in the HMBC spectrum of **5a** and **5b**

Carbon	H in **5a**	H in **5b**
1	C^2-CH_3, H^b-7	C^3-CH_3
2	C^2-CH_3, H^b-7	C^3-CH_3, H^a-7, H^b-7
4	C^2-CH_3, C^5=CH_2, H-6	H-2, H-6, C^5=CH_2, H^a-7
5	H^a-7	H^a-7
6	H-4, H^a-7	H-2, C^3-CH_3, H-4, C^5=CH_2, H^b-7
8	H-5, H^a-7, H^b-7	H-2, H^a-7, H^b-7, N^9-CH_3
12		N^{11}-CH_3

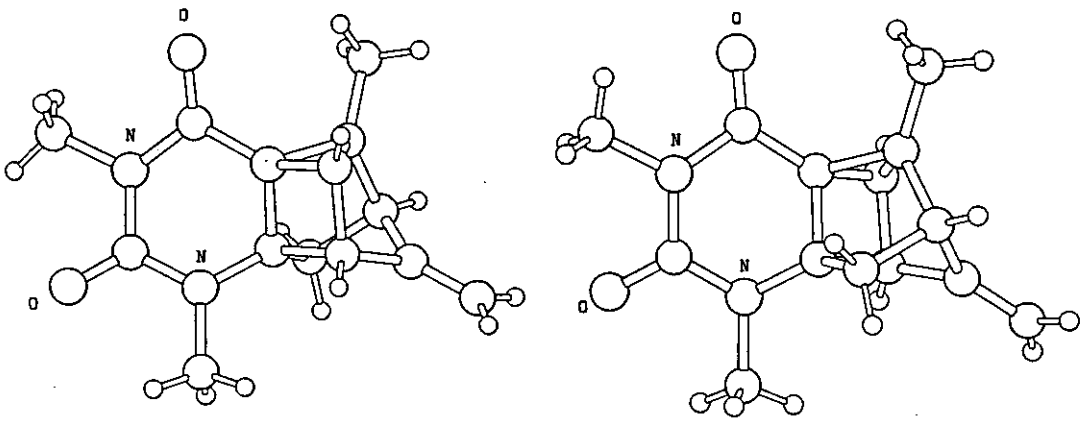
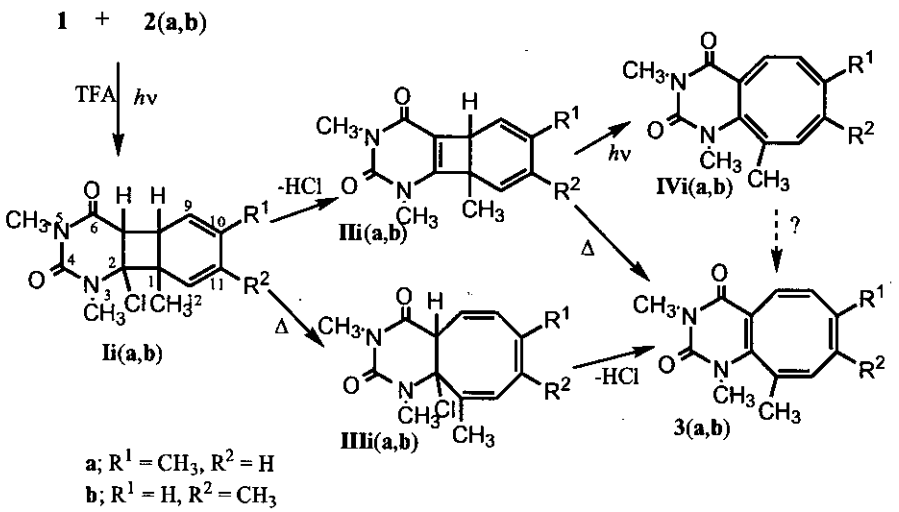


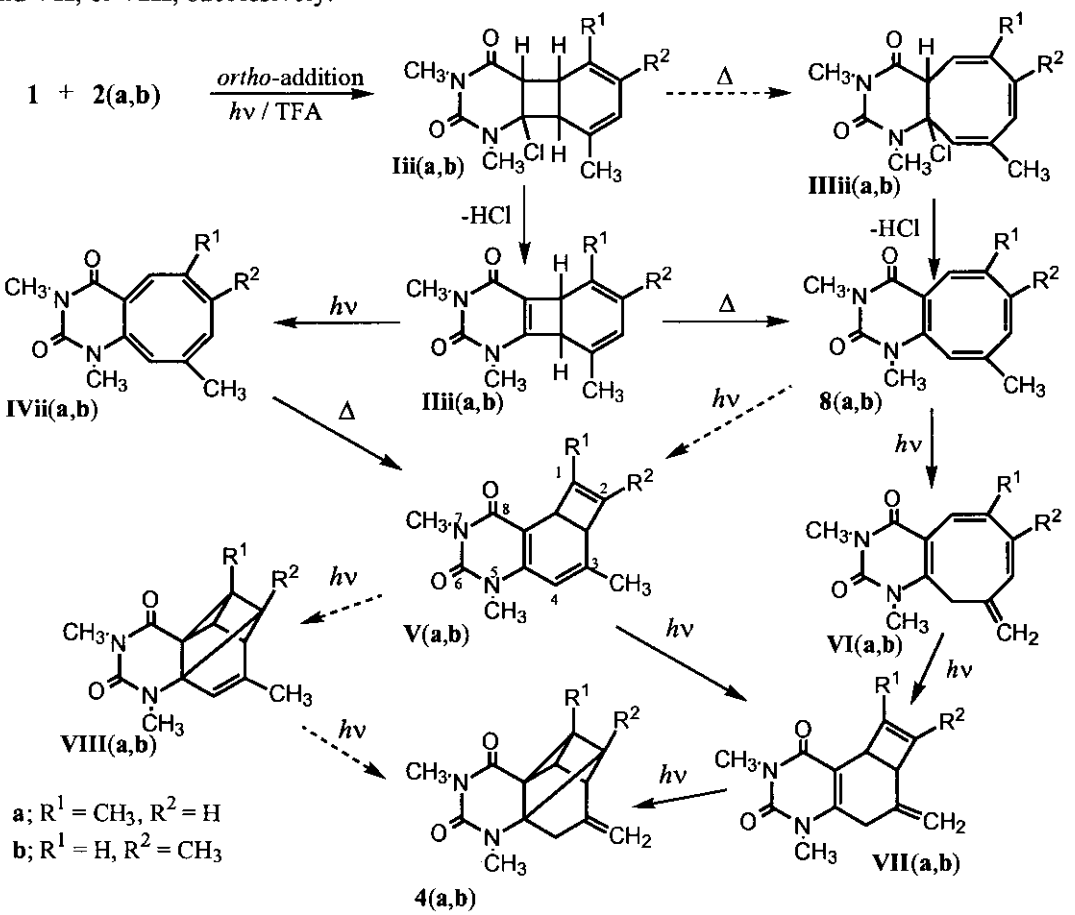
Figure 5. X-Ray crystallography of **5a**; molecule A (left) and B (right).

Interestingly each of theses cycloaddition products was given as the sole regioisomer due to the methyl groups. However these cycloadducts consist of multi-step reactions involving the elimination of hydrogen chloride, causing the elucidation of the reaction pathway significantly difficult. The formation of cyclooctapyrimidine (**3**) can be explained in terms of the initial formation of the *ortho*-adduct, 1,x-dimethyl derivative of 2-chloro-3,5-dimethyl-3,5-diazatricyclo[6.4.0.0^{2,7}]dodeca-9,11-diene-4,6-dione (**IIa**; x = 10 and **b**; x = 11),[3] wherein C-6 of the pyrimidine ring bonds to the methyl substituted aromatic carbon. The thermal disrotatory scission[6] of the cyclohexadiene moiety and the concomitant dehydrochlorination would lead to the formation of **3**. We have no evidence to exclude the possible pathway involving the intermediacy of **IVi** which could be derived photochemically from **IIi** *via* the disrotatory cleavage[6] of the cyclobutene moiety (Scheme 2).



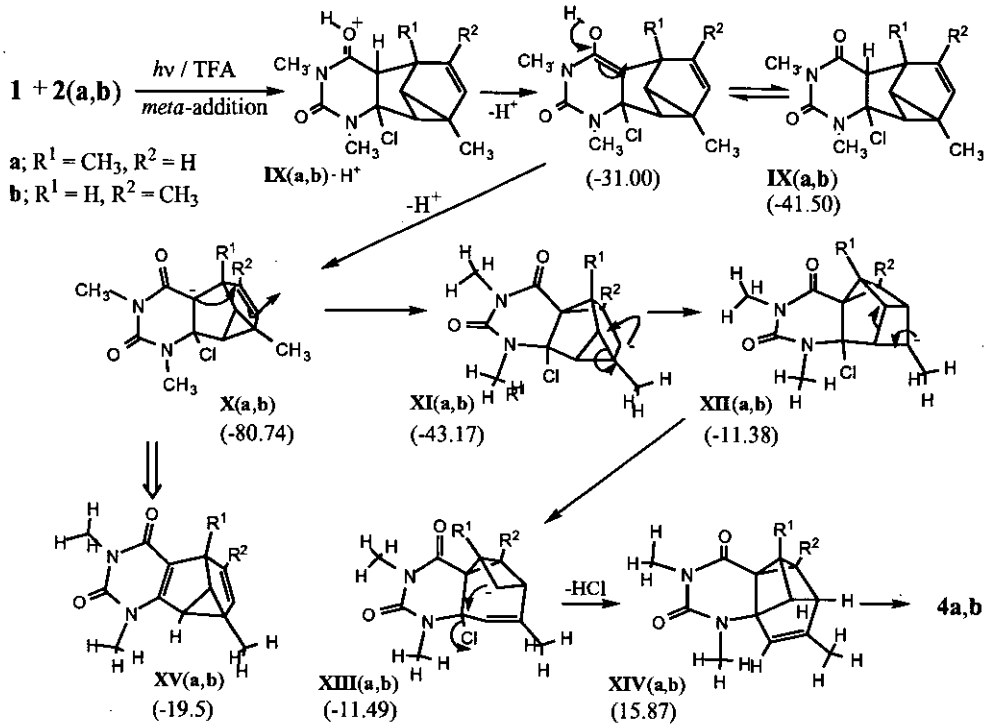
Scheme 2

The formation of the pentacyclic compound (**4**) can be explained by the mechanism involving *ortho*-cycloaddition, wherein the C-6 of pyrimidine moiety bonds to xylene (**2**) at *ortho* as to construct a 3,5-diazatricyclo[6.4.0.0^{2,7}]dodecane ring with a methyl substituent at C-12 (**Iii**) (Scheme 3). The thermal disrotatory opening of the cyclohexadiene ring of **Iii** or the dehydrochlorinated derivative (**IIii**) would lead to the formation the 9-methylcyclooctapyrimidine derivative (**8**), resulting in the ultimate product (**4**) through **VI** and **VII**, or 3-methylene-5,7,x-trimethyl-2a,8b-dihydrocyclobuta[*f*]quinazoline-6,8-dione derivative **V(a,b**; x = 1, 2) and **VII**. However the latter photo-rearrangement of **8** into **V** seems less likely, since uv-irradiation of 1,3-dimethylcyclooctapyrimidine, obtained from the reaction with benzene gave no transformed product. Alternatively given that the disrotatory cleavage of the cyclobutene ring of **IIii** is effected photochemically, the resulting **IVii** would lead to the formation of **4** through the intermediacy of **V** and **VII**, or **VIII**, successively.



Scheme 3

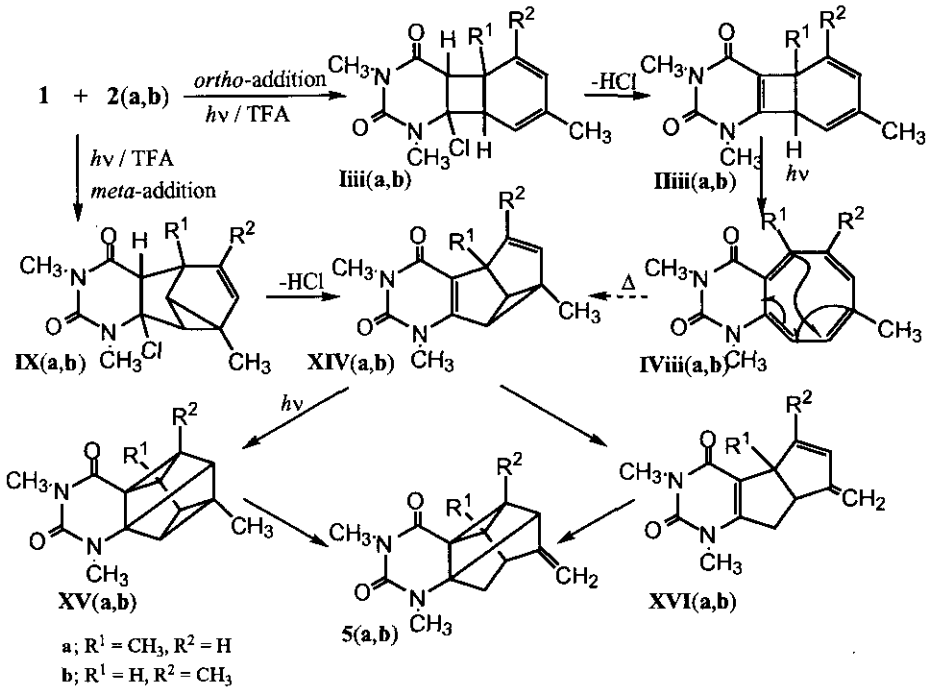
In the preceding paper,[1] we proposed a mechanism involving *meta*-cycloaddition, which should have been depicted as a successive rearrangement of the anionic species initiated by the deprotonation from the *meta*-cycloadducts **IX** (Scheme 4). Although we have no experimental evidences to support or exclude the mechanism, MO calculation[7] showed that the rearrangement of the intermediate of **X** into **XIII** and **XIV** may be accompanied by a great loss in energy, suggesting that the formation of **4** could not be explained by the step-wise mechanism.



Scheme 4: The heats of formation (kcal) shown in the parentheses were calculated for the intermediates from *p*-xylene (**2a**) by fixing the bond lengths between C-5 of the pyrimidine ring and the carbon bearing R^2 = 1.54 Å.

For the explanation of the formation of diazapentacyclododecane (**5**), both mechanisms involving *ortho*- and *meta*-cycloaddition might be available (Scheme 5). If the reaction proceeds by way of the *ortho*-adduct with a methyl group at C-11 (**Iiii**), the process entails the intermediacy of **IViii**. Its thermal [$\pi 4a+\pi 2a$] rearrangement might lead to the formation of the key intermediate **XV**. However the transformation through the mechanism which is presumed to require elevated temperature seems unlikely under the present reaction condition.[8] Alternatively *meta*-cycloaddition is invoked. The initially formed *meta*-cycloadduct (**IX**) would be transformed into the ultimate product (**5**) through the intermediacy of **XV** and **XVI** or **XVII**.[9]

The photoreaction of **1** in *p*-xylene (**2a**) under similar conditions but in the absence of TFA recovered a large amount of unreacted **1** (92%) and gave barely detectable **6** (1.4%) and **3a** (<0.1% on hplc), and no formation of the pentacyclic adducts (**4a** or **5a**) was observed. The uv spectrum of **1** (λ_{max} 262 nm) (0.08 mmol • dm^{-3}) shifted *ca.* 6 nm to the red in cyclohexane by the addition of TFA (9 equiv. molar). This new spectrum was insensible to the added **2a**, whereas the fluorescence of this solution was quenched efficiently with **2a**. Taking into consideration that the present reaction was performed in a non-polar solvent in the presence of a strong acid, it might be supposed that the present reaction may involve the initial excitation of protonated **1** in the singlet states, followed by an electron-transfer or the exciplex formation between **1** and **2**.



Scheme 5

Thus the reaction pathway remains obscure, however it may be noteworthy that the present acid-catalyzed photoreaction afforded two novel pentacyclododecanes including a pyrimidine ring, whose structures were determined by X-Ray crystallographic analyses.

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 are recorded based on those of the signals of solvents [acetone-d_6 (δC29.8), methanol-d_4 (δC49.8)]. 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. Uv and fluorescent spectra were taken on a Shimadzu UV-240 and a Shimadzu RF-540, respectively. Short-column chromatography was performed on Kieselgel Si-60 (Merck). Reverse-phase column chromatography (RP-LC) was conducted on LiChroprep RP-18 size B (Merck) with a FMI pump (Fluid Metering, Inc.). Reverse-phase high-performance liquid chromatography (RP-hplc) was performed either on a Wakosil II-5C18-100 column eluting with aqueous methanol (30-70 %) (25 cm x 4.6 mm *i.d.*, for analytical-scale) or on a Shim-pac PREP-ODS (25 cm x 20 *i.d.*, for preparative-scale) (Shimadzu), using a Shimadzu LC-6A apparatus with monitoring at *254* nm. Similarly, silica gel hplc (Si-hplc) was conducted on a Shim-pac PREP-Sil (25 cm x 20 mm *i.d.*), using the same apparatus. Uv-irradiation was carried out externally with a 500 W high-pressure mercury (Hg) lamp (Eiko-sha) in a doughnut type Pyrex vessel (500 ml), under an argon atmosphere at room temperature (> 300 nm).

Photoreaction of 6-chloro-1,3-dimethyluracil (1) in *p*-Xylene (2a)-----A solution of **1** (349 mg, 2 mmol) and TFA (308 μl, 4 mmol) in **2a** (400 ml) was irradiated with the 500 W high-pressure Hg lamp in a doughnut type Pyrex vessel for 20 h. The reaction mixture was concentrated *in vacuo*, and the residual oil was passed through a short column of silica gel with hexane, ether and ethyl acetate successively. The ethereal eluate was submitted to RP-LC with 38 % aqueous methanol to give **1** (108 mg, 31%), 6-methylene-3,9,11-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones (**4a**) (30 mg, 6.1%), 6-(*p*-xylyl)uracil (**6**) (21 mg, 4.3%) and the mixture of the photoproducts. The mixture was further submitted to Si-hplc (5 % ethyl acetate-hexane) to afford 5-methylene-2,9,11-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane-10,12-dione (**5a**) (9.6 mg, 2.0%), 1,3,7,10-tetramethylcyclooctapyrimidine-2,4-dione (**3a**) (56 mg, 11.5%), and 1,3-dimethyl-6-(4-methylbenzyl)-uracil (**7**) (9.2 mg, 1.9%). 6-(*p*-Xylyl)uracil (**6**) was identified with authentic sample on the bases of comparison of the ^{1}H-nmr and ms spectra.

1,3,7,10-tetramethylcyclooctapyrimidine-2,4-dione (**3a**): Colorless crystals, mp 104-105°C (recrystallized from 2-propanol). ^{1}H-Nmr (acetone-d_6,)δ : 1.70 (3H, m, C^7-CH$_3$), 1.93 (3H, t, J = 1.5 Hz, C^{10}-CH$_3$), 3.22 (3H, s, N^3-CH$_3$), 3.27 (3H, s, N^1-CH$_3$), 5.83 (1H, dd, J = 3.4, 1.0 Hz, H-8), 5.93 (1H, d, J = 11.2 Hz, H-6), 6.04 (1H, d, J = 3.4 Hz, H-9), 6.18 (1H, dd, J = 11.2, 1.0 Hz, H-5). Ms *m/z* (%): 244 (M$^+$, 100), 229 (30). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.80; H, 6.51; N, 11.45.

6-methylene-3,9,11-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones (**4a**): Colorless crystals, mp 106-107 °C, (recrystallized from ether). Ms *m/z* (%): 244 (M$^+$, 28), 243 (100), 229 (63), 204 (94), 187 (18), 172 (20), 158 (37), 147 (80), 144 (33). HR-ms: Anal. Calcd for $C_{14}H_{16}N_2O_2$: 244.1211. Found: 244.1212. 5-methylene-2,9,11-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]-dodecane-10,12-diones (**5a**): Colorless crystals, mp 97.5-98.5 °C, recrystallized from hexane. Ms *m/z* (%): 244 (M$^+$, 9), 243 (14), 229 (100), 173 (9), 172 (64), 144 (25). HRms: Anal. Calcd for $C_{14}H_{16}N_2O_2$: 244.1211. Found: 244.1188.

1,3-dimethyl-6-(4-methylbenzyl)uracil (**7**): Pale yellow crystals, mp 108-109°C, recrystallized from benzene-hexane. ^{1}H-Nmr ($CDCl_3$)δ : 2.35 (3H, s, C-CH$_3$), 3.32 (3H, s, N-CH$_3$), 3.35 (3H, s, N-CH$_3$), 3.78 (2H, s, CH$_2$), 5.55 (1H, s, H-5), 7.06 (2H, d, J = 8.1 Hz, aromatic H), 7.16 (2H, d, J = 8.1 Hz, aromatic H). Ms *m/z* (%): 245, 12), 244 (M$^+$, 58), 227 (14), 130 (12), 105 (67), 82 (100). HRms: Anal. Calcd for $C_{14}H_{16}N_2O_2$: 244.1211. Found: 244.1230.

Photoreaction of 1 in *m*-Xylene (2b)-----Photoreaction was carried out under conditions describes above. The reaction mixture was passed through a short column of silica gel. The ethereal eluate was submitted to RP-LC with 38 % aqueous methanol to give **4b** (13 mg, 2.7 %), **5b** (5.4 mg, 1.1%), **3b** (19.5 mg, 4.0%) and **6b** (12 mg, 2.5%), together with the recovered **1** (199 mg, 57%).

1,3,8,10-tetramethylcyclooctapyrimidine-2,4-dione (**3b**) : Colorless crystals, mp 139-141°C (recrystallized from 2-propanol). ^{1}H-Nmr ($CDCl_3$)δ : 1.82 (3H, br s, C^8-CH$_3$), 1.93 (3H, d, J = 1.5 Hz, C^{10}-CH$_3$), 3.32 (3H, s, N^1-CH$_3$), 3.35 (3H, s, N^3-CH$_3$), 5.70 (1H, d, J = 4.0 Hz, H-7), 5.97 (1H, ddd, J = 1.5, 1.5, 1.1 Hz, H-9), 6.02 (1H, dddd, J = 11.4, 4.0, 1.5, 1.1 Hz, H-6), 6.26 (1H, d, J = 11.4, H-5). Ms *m/z* (%) 245 (21), 244 (M$^+$, 100), 229 (29), 172 (44), 159 (25), 158 (21), 144 (30). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.80; H, 6.51; N, 11.45.

6-methylene-4,9,11-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones (**4b**): Colorless crystals, mp 132-134 °C (recrystallized from benzene-hexane). Ms *m/z* (%): 244 (M^+, 43), 243 (100), 229 (54), 204 (36), 187 (26), 186 (14), 172 (22), 159 (31), 158 (49), 147 (38), 144 (38). HRms: Anal. Calcd for $C_{14}H_{16}N_2O_2$: 244.1235. Found: 244.1212.

5-methylene-3,9,11-trimethyl-9,11-diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane-10,12-diones (**5b**): Colorless oil. Ms *m/z* (%): 244 (M^+, 54), 243 (51), 229 (100), 186(23), 172 (66), 158 (30), 144 (32). HRms: Calcd for $C_{14}H_{16}N_2O_2$: 244.1211. Anal. Found: 244.1211.

1,3-dimethyl-6-(2,4-dimethylphenyl)uracil (**7b**): Colorless oil. Ms *m/z* (%): 245 (31), 244 (M^+, 88), 243 (39), 229 (100), 172 (63), 159 (43), 158 (66). ^{1}H-Nmr ($CDCl_3$)δ : 2.24 (3H, s, C-CH_3), 2.37 (3H, s, C-CH_3), 3.07 (3H, s, N-CH_3), 3.41 (3H, s, N-CH_3), 5.63 (1H, s, H-5), 7.03 (1H, d, J = 7.8 Hz, H-5'), 7.16 (1H, d, J = 7.8 Hz, H-6'), 7.11 (1H, s , H-3'). HRms: Anal. Calcd for $C_{14}H_{16}N_2O_2$: 244.1211. Found: 244.1186.

X-Ray Crystallography of 4a ---- The diffraction experiment was carried out using a colorless transparent prism with dimension of 0.45 x 0.35 x 0.35 mm. The diffract meter AFC/5 (RIGAKU) was used with graphite-monochromated CuKα radiation (λ = 1.5418 Å). The unit cell dimensions were determined from angular setting of 20 reflections (2θ values in the range of 35-60°), affording the following crystal data: $C_{14}H_{16}N_2O_2$, Mr = 244.29. a = 15.089(3), b = 14.652(2), c = 7.672(2) Å, β = 131.24(1)°, U = 1275.3(5)Å^3, monoclinic, $P2_{1/a}$, Z = 4, Dx = 1.27 g/cm^3, F(000) = 520, μ(CuKα) = 7.08 cm^{-1}. 1896 unique reflections (2$\theta \leq$ 120°) were measured, of which 1601 with $|Fo| \geq 2.67\ \sigma$ (Fo) were considered as observed. No absorption corrections were applied.

The structure was solved by a direct method using MULTAN 80[10] and difference Fourier method. The refinement of atomic parameters were carried out using block diagonal least-squares method with anisotropic temperature factors. Eight hydrogen atoms were located on the difference-Fourier maps and refined with isotropic temperature factors. The positions of the residual hydrogen atoms were assumed in the geometrically and fixed. Throughout the refinement, the function $\Sigma\ w(|Fo| - |Fc|)^2$ was minimized. The atomic scattering factors were taken from International Tables for X-Ray crystallography.[11] The final R factor is 0.067.

X-Ray Crystallography of 5a ---- The diffraction experiment was carried out using a colorless transparent prism with dimension of 0.2 x 0.2 x 0.1 mm. The diffract meter AFC/5 (RIGAKU) was used with graphite-monochromated CuKα radiation (λ= 1.5418 Å). The unit cell dimensions were determined from angular setting of 25 reflections (2θ values in the range of 70-90°), affording the following crystal data: $C_{14}H_{16}N_2O_2$, Mr = 244.29. a = 9.756(2), b = 14.898(2), c = 8.906(1) Å, β = 94.33(1)°, U = 1265.6(3)Å^3, triclinic, P $\bar{1}$, Z = 4, Dx = 1.28 g/cm^3, F(000) = μ(CuKα) = 7.04 cm-1. 3056 independent reflections (2$\theta \leq$ 130°) were measured. The structure was solved by a direct method using SHELXS-86[12] and difference Fourier method. The refinement of atomic parameters were carried out using full-matrix least-squares method(SHELXL-93)[13] with anisotropic temperature factors. The final R factor is 0.063.

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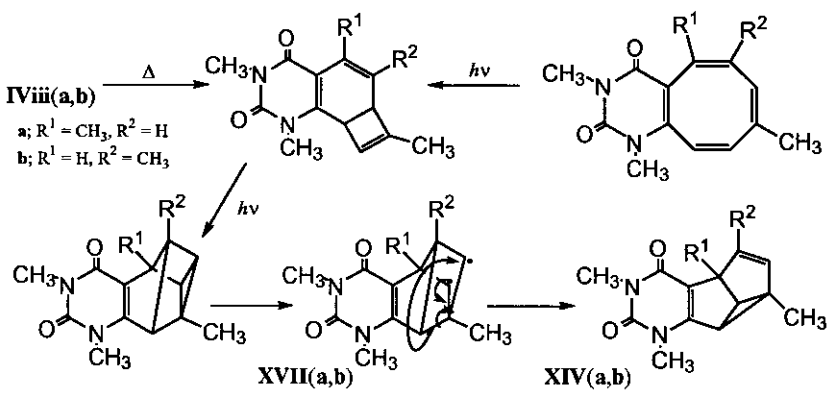
9. A possible transformation of **IViii** into **XIV** through the biradical intermediate **XVII** (Scheme 6) can be ruled out , since it has no substituents over which uncoupled electrons can be distributed.[14]



Scheme 6

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