Acid-Catalyzed Photoreaction of 6-Chloro-1,3-dimethyluracil in Frozen Benzene: Formation of Novel Cycloadducts, Tetrahydropentaleno[1,2-e]pyrimidine-2,4-dione Derivatives

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Contrasting to the photoreaction of 6-chloro-1,3-dimethyluracil in benzene at ambient temperature in the presence of trifluoroacetic acid, whereby 1,3-dimethylcyclooctapyrimidine was produced as a sole cycloadduct, the similar photoreaction in frozen benzene at -15 ~ -20 °C proceeded quite differently to give three novel photocycloadducts, 7-chloro-1,3-dimethyl-4b,5,7a,8-tetrahydropentaleno[1,2-e]pyrimidine-2,4-dione, 5-chloro-1,3-dimethyl-4b,7,7a,8-tetrahydropentaleno[1,2-e]pyrimidine-2,4-dione, and 6-chloro-10,12-diazapentacyclo[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]-dodecane-9,11-dione.

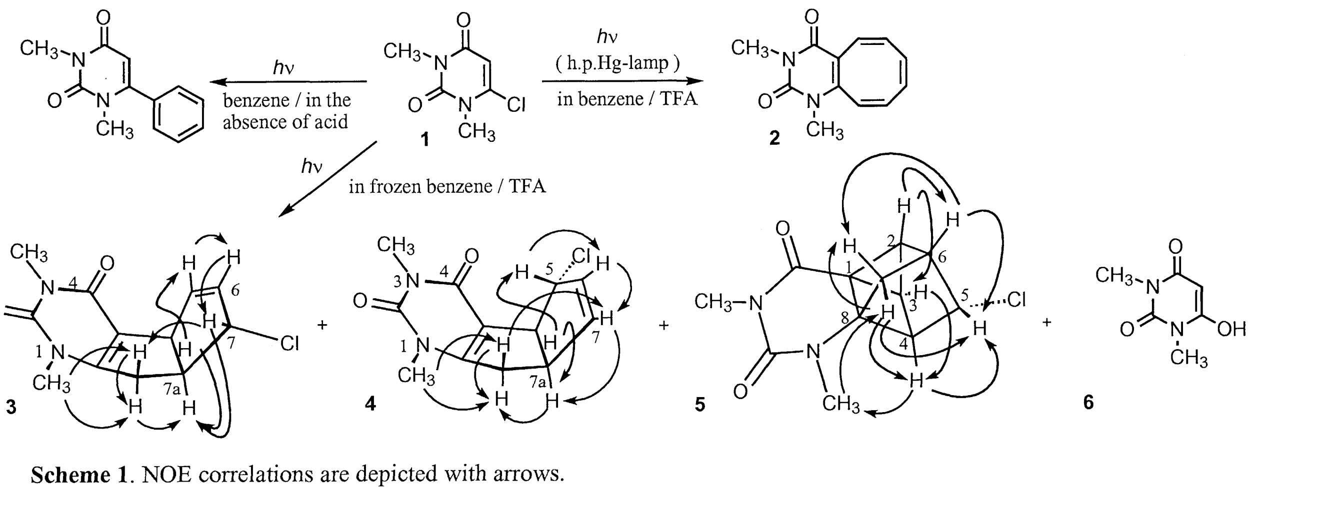
It is well known that photoreactions in frozen solutions proceed in a different manner from those in liquid solutions, as demonstrated in the photodimerization of pyrimidine bases[1] or photocoupling of 5-bromouracil and 5-bromouridine to tryptophan.[2] We have reported that the photolysis of 6-chloro-1,3-dimethyluracil (**1**) in benzene[3] and its mono-substituted derivatives[4] in the presence of trifluoroacetic acid (TFA) gave 1,3-dimethylcyclooctapyrimidine-2,4-dione (**2**) and its derivatives, presumably *via ortho*-cycloaddition. Similar photolyses of *p*- and *m*-xylene were found to produce pentacyclic compounds, 6-methylene-9,11,n-trimethyl-9,11-diazapentacyclo-[6.4.0.0^{1,3}.0^{2,5}.0^{4,8}]dodecane-10,12-diones, together with cyclooctapyrimidine derivatives.[5]

With a view to explore the scope of the acid-catalyzed photoreaction[6] for the construction of new ring systems, we have conducted the above photoreaction in frozen 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**) and a diazapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}] dodecane derivative (**5**) as the major cycloadducts.

UV-irradiation of **1** in frozen benzene in the absence of TFA gave no detectable amounts of photoproducts, while the reaction in the presence of TFA[7] resulted in the consumption of 93% **1** to give **2** (4.6%) and three cycloadducts, 7-chloro-1,3-dimethyl-4b,5,7a,8-tetrahydropentaleno[1,2-e]pyrimidine-2,4-dione (**3**) (2.8%), 5-chloro-1,3-dimethyl-4b,7,7a,8-tetrahydropentaleno-[1,2-e]pyrimidine-2,4-dione (**4**) (3.4%) and 5-chloro-9,11-di-azapentacyclo[6.4.0.0^{1,3}.0^{2,6}.0^{4,8}]dodecane-10,12-dione (**5**) (9.1%), together with a large amount of 1,3-dimethylbarbituric acid (**6**)[8] (43%) (Scheme 1).[9] Similarly, the photoreaction in the presence of methanesulfonic acid (CH_3SO_3H, 2 equiv. molar) resulted in a 58% conversion of **1** with the formation of photoproducts, **2**, **3**, **4** and **5** in yields of 1.0, 4.3, 2.1 and 1.9%, respectively. Some changes in the product distribution were observed: the ratio of the yields of **2** *vs*. total yields of cycloadducts (**2** + **3** + **4** + **5**) was appreciably suppressed in comparison with those from the reaction with TFA. The structures[10] of **3**,[11] **4**,[12] and **5**[13] were deduced essentially on the basis of the ^{1}H-NMR spectra and the NOE experiments (Scheme 1). UV-irradiation of a solution of **3** in benzene, whereby **3** was converted into **5** in high yield (86%) supported the structures of **3** and **5**.

The formation of **3**, and **4** may result from the addition of hydrogen chloride (HCl) to the intermediate **II**. Subsequent [2+2]-intramolecular photocycloaddition of **3** results in the formation of the pentacyclic compound **5** (Scheme 2).

Thus, the formation of the intermediate (**II**), which might be derived from the *meta*-adduct (**I**)[14] (Scheme 2), is suggested by the isolation of the cycloadducts **3** and **4**. The reasons for the changes in the product distributions in the presence of TFA and CH_3SO_3H are unclear. It is noteworthy that in liquid benzene, **2** was the predominant product,[3] whereas in frozen benzene, the reaction proceeded quite differently to give novel cycloadducts con-



Scheme 1. NOE correlations are depicted with arrows.

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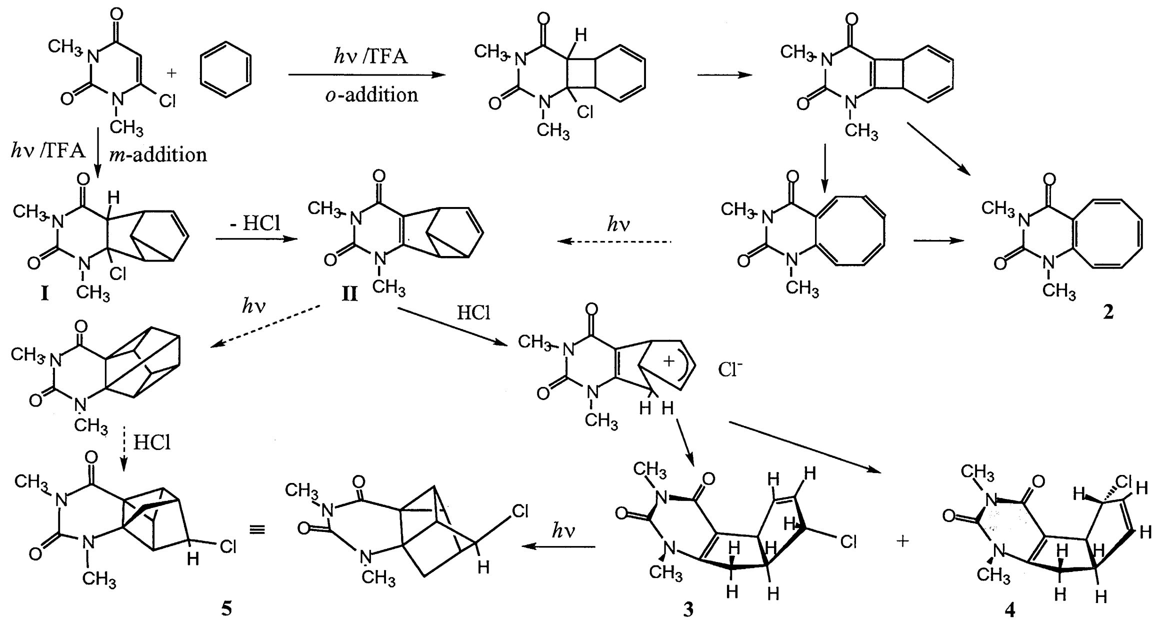

Scheme 2.

sisting of a pentalene ring fused to a pyrimidine skeleton (**3**, **4**) and their derivative (**5**) through [2+2]-intramolecular photocycloaddition.

References and Notes

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6 A solution of a mixture of **1** (0.025 mmol) and an acid (0.05 mmol) in frozen benzene (5 ml) was irradiated with a high pressure mercury lamp in a degassed Pyrex tube for 1 h at -15~-20 °C.

7 Spectroscopic studies on the effects of the added acids have been reported .[4, 5]

8 Details of the mechanism for the formation of **6** are not elucidated.

9 Yields were determined by ^{1}H-NMR spectra.

10 All new compounds gave satisfactory elemental analyses.

11 ^{1}H-NMR (400 MHz, benzene-d_6) data for **3** (position number): 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), 6.26 (1H, m, J = 5.2, 2.4, and 0.8 Hz) (5), 5.49 (1H, m, J = 5.2, 2.4, and 2.4 Hz) (6), 4.25 (1H, m, J = 2.4, 2.4, 2.0, and 0.8 Hz) (7),2.79 (1H, m, J = 10.4, 7.7, 5.0, and 2.4 Hz) (7a), 1.41 (1H, m, J = 17.6, 5.0, and 1.8 Hz) (8-H^a), 1.82 (1H, dd, J = 17.6, 10.4 Hz) (8-H^b). ^{13}C-NMR(benzene-d_6) (position number): δ 27.64 (3-CH_3), 31.59 (1-CH_3), 36.32 (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).

12 ^{1}H-NMR (400 MHz, $CDCl_3$) data for **4** (position number): 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), 5.19 (1H, m, J = 2.0, 1.8, and 0.6 Hz) (5), 5.91 (1H, m, J = 5.6, 2.0, and 2.0 Hz) (6), 5.84 (1H, dd, J = 5.6 and 2.0 Hz) (7), 3.81 (1H, m, J = 9.2, 6.8, 2.0, 2.0, 2.0, and 1.8 Hz) (7a), 2.66 (1H, m, J = 17.6, 2.0, and 2.0 Hz) (8-H^a), 3.11 (1H, m, J = 17.6, 9.2 and 2.0 Hz) (8-H^b). ^{13}C-NMR ($CDCl_3$) (position number): 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).

13 ^{1}H-NMR (400 MHz, $CDCl_3$) data for **5** (position number): δ 3.15 (1H, m, J = 5.2, 3.6 and 1.2 Hz) (2), 3.22 (1H, dd, J = 5.2 and 2.4 Hz) (3), 2.70 (1H, m, J = 2.4, 2.4, 2.4 and 1.2 Hz) (4), 3.82 (1H, dd, J = 2.4 and 0.8 Hz) (5), 2.86 (1H, m, J = 3.6, 4.4, and 0.8 Hz) (7a), 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 ($CDCl_3$) (position number): 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; H-2 with C-4, C-5, C-6; H-3 with C-1, C-7, and C-8; H-4 with C-6; H-5 with C-2 and C-3; H-6 with C-4 and C-8; 7-H^a with C-1, C-4, C-5, and C-6; 7-H^b 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).

14 *Meta*-cycloaddition of arenes to olefins has been investigated for long time; *J. Photochem.*, J. Mattay, **37**, 167 (1987), and references therein.