HETEROCYCLES, Vol. 65, No. 11, 2005, pp. 2583 - 2586
Received, 25th July, 2005, Accepted, 8th September, 2005, Published online, 13th September, 2005

# PHOTOCHEMICAL SYNTHESIS OF BENZOPYRIMIDOSEMIBULLVALENES FROM BENZOPYRIMIDOBARRELENES

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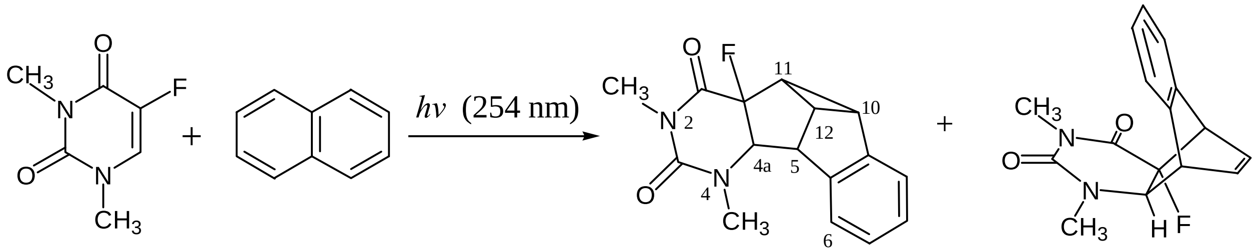
**Abstract**— UV irradiation (λ= 254 nm) of 5-fluoro-1,3-dimethyluracil with naphthalene afforded a novel benzopyrimidosemibullvalene derivative with H and F atoms remaining intact on the newly constructed moiety. It was found that the semibullvalene could be derived from the initially produced barrelene derivative during irradiation.

Photocycloaddition of naphthalenes with alkenes is well recognized as one of the useful procedures for constructing certain unique ring systems by way of 1,2-,[1,2] 1,4-,[1,2] 1,3-,[3] 1,8-[4] and [4 + 4] additions.[1,5] In our continuing studies on photochemical modification of the pyrimidine ring, we previously reported that UV-irradiation of 5-fluoro-1,3-dimethyluracil (5-FDMU) and naphthalene with a 500 W high-pressure mercury lamp in a degassed Pyrex tube (λ>300 nm) predominantly afforded the 1,4-adduct, namely barrelene derivative (**1a**) in high yield. [6] Application of this photoreaction to other naphthalenes also furnished the corresponding 1,4-adducts in fair yields.[7] Likewise, irradiation of 1,3-dimethyluracil and its derivatives with a substituent at C-5 similarly underwent cycloaddition to give the corresponding barrelene derivatives in fair yields.[8] During the course of our ongoing work, we recently found that the mode of the photoreaction was dramatically altered to give the 1,2-adduct upon irradiation of 5-FDMU and naphthalene in the presence of piperylene.[9] Thus, 1,2- and 1,4-adducts of the pyrimidine ring with naphthalene have been synthesized mode-selectively, whereas we have not yet obtained the other possible 1,3-adduct from 5-FDMU and naphthalene.

In order to further develop this new aspect of the photo-induced reaction of 1,3-dimethyluracils and naphthalene that would lead to the construction of new ring systems through the other possible processes including 1,3-cycloaddition, our attention was next shifted to the direct short-wave-length photolysis ($\lambda$= 254 nm) of 5-FDMU with naphthalene.

Direct irradiation of a solution of equimolar amounts of 5-FDMU and naphthalene in cyclohexane (1.1 mM) with a 60 W low-pressure mercury lamp ($\lambda$=254 nm) under an argon atmosphere for 1 h gave rise to the formation of a novel cycloadduct, benzopyrimidosemibullvalene (**2a**) in 20% yield together with a small amount of 1,4-adduct (**1a**) (7%) at the stage where 81% of 5-FDMU had been consumed (Scheme 1).



5-FDMU **2a** **1a**

Scheme 1

The structure of new compound (**2a**) [10] was assigned to be the 1,3-adduct of 5-FDMU with naphthalene consisting of a semibullvalene system on the basis of detailed MS and NMR spectroscopic studies. The FAB-MS spectrum showed the expected molecular ion peak $[M+H]^+$ at *m/z* 287, and the $^1$H-NMR ($CD_3OD$) spectrum displayed three proton singlets attributed to $N^2$-$CH_3$, and $N^4$-$CH_3$ at $\delta$ 2.47 and 3.14 (each 3H, s), respectively.

Three signals ascribable to the H-10, H-11 and H-12 methine protons on the three membered ring appeared at $\delta$ 2.74 (1H, dd, *J*=8.0, 6.3 Hz), 2.48 (1H, ddd, *J*=18.3, 8.0, 6.3 Hz), and $\delta$ 3.07 ppm (1H, ddd, *J*=6.3, 6.3, 6.3 Hz), respectively. Two signals due to the H-4a and H-5 protons on the five-membered-ring appeared at $\delta$ 4.44 (1H, dd, *J* =30.4, 6.9 Hz), and 4.07 (1H, ddd, *J*=6.9, 6.3, 1.7 Hz), respectively. The four aromatic protons were observed in the region between $\delta$ 6.85 and 7.22 ppm.

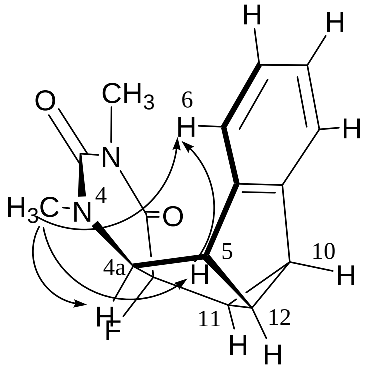


Figure 1. NOE Correlations for **2a**

The stereochemistry of **2a** was determined with the aid of NOE experiments. Irradiation of the $N^4$-$CH_3$ resonance significantly affected the H-5 proton, as well as H-4a, and H-6. Additional NOE results confirmed the structure assigned to **2a** (Figure 1).

From the mechanistic point of view, we investigated the time course of the present cycloaddition and the reaction was followed by $^1$H-NMR spectroscopy. As shown in Figure 2, prompt formation of **1a** occurred first, while the formation of **2a** was barely detectable at the initial stage. The formation of **1a** reached a maximum at 10 min. With the decrease of **1a**, formation of **2a** began to increase. These results indicate that 1,4-adduct (**1a**) may be converted to the formal 1,3-adduct (**2a**) during the irradiation.

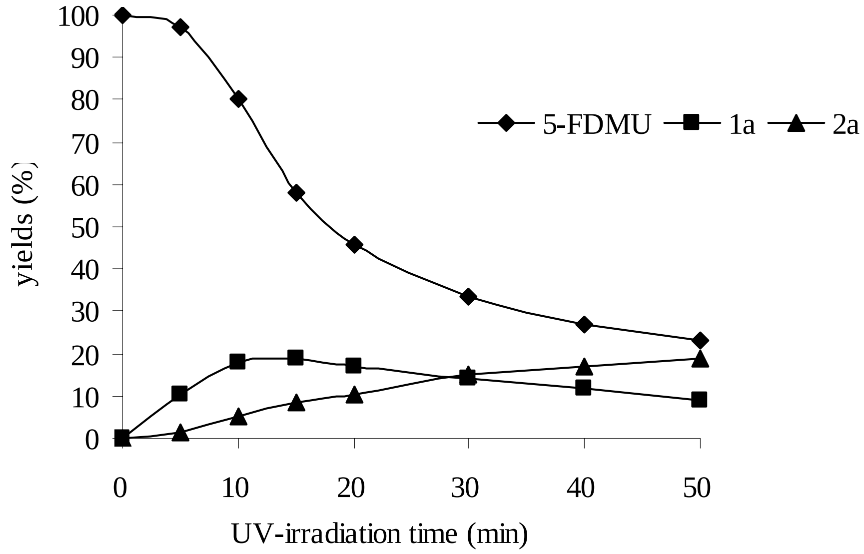
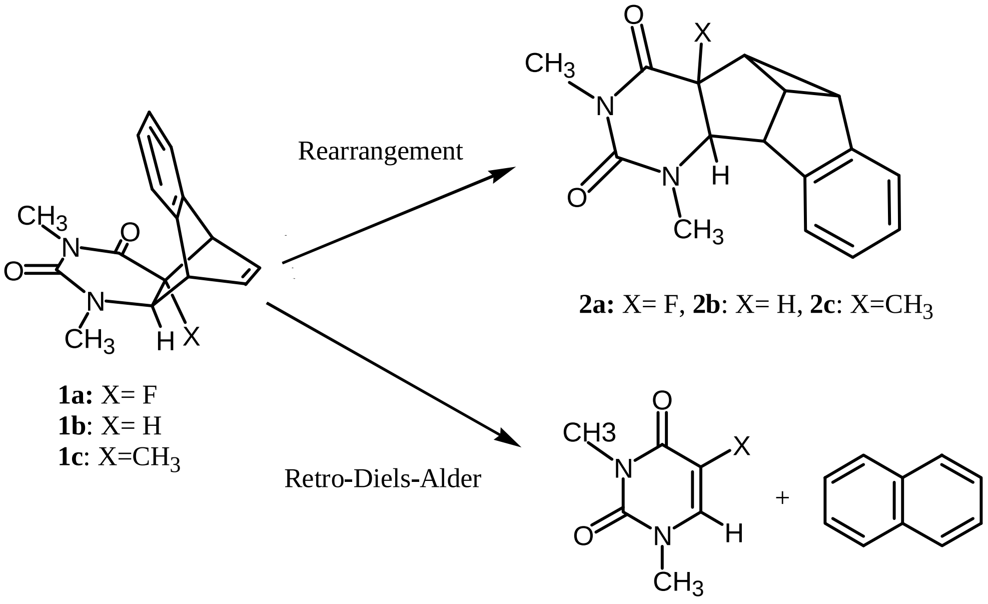


Figure 2

In order to examine whether the initially formed 1,4-adduct may be a direct precursor for **2a**, UV-irradiation of a cyclohexane solution of **1a** with 254 nm light was carried out for 15 min, to induce rearrangement to the expected **2a**. Indeed compound (**2a**) was formed in 30% yield in competition with the retro-Diels-Alder reaction restoring 5-FDMU and naphthalene (14%)(Scheme 2).



Scheme 2

We then applied the present reaction to 1,3-dimethyluracil (DMU) and 1,3-dimethylthymine (DMT) in the presence of naphthalene. The photoreaction was performed under the similar conditions employed for 5-FDMU, however, no cycloadduct formation was observed. Irradiation of the 1,4-adduct of 1,3-dimethyluracil (**1b**) afforded corresponding *cis*-oriented semibullvalene derivative (**2b**) [10] (60%) as well as DMU (40%). Similarly, photolysis of the 1,4-adduct of DMT (**2c**) produced semibullvalene derivative (**2c**)[10] predominantly (Scheme 2).

Thus, the UV-irradiation of 1,4-adduct barrelene derivatives smoothly underwent rearrangement to give rise to the formation of semivullbalenes. The present study is, to our knowledge, the first to demonstrate the formation of formal 1,3-adducts in the 1,3-dimethyluracil-naphthalene photoreaction system. It may be noteworthy that the present study demonstrates a mode selective synthesis[9] of three types of cycloadducts, 1,2-, 1,3-, *albeit* formally, and 1,4-adducts, by controlling reaction conditions appropriately.

## ACKNOWLEDGEMENTS

This study was partially supported by the “Academic Frontier” Project of the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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10. Selected data for **2a**: Colorless crystals, mp 215-217 °C. Anal. Calcd for $C_{16}H_{15}N_2O_2F$: C, 67.12; H, 5.28; N, 9.78. Found: C, 66.96; H, 5.44; N, 9.78. **2b**: Colorless crystals, mp 229-231 °C. Anal. Calcd for $C_{16}H_{16}N_2O_2 \cdot 1/3H_2O$: C, 70.05; H, 6.12; N, 10.21. Found: C, 69.81; H, 6.15; N, 10.33. **2c**: Colorless crystals, mp 184-185 °C. Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.17; H, 6.52; N, 10.12.