PHOTOREARRANGEMENT OF THE ORTHO-CYCLOADDUCT OF 6-CHLORO-1,3-DIMETHYLURACIL TO BENZENE THROUGH $[\pi 4s+\pi 2a]$ PHOTOCYCLOADDITION

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Abstract—Reaction pathway for the formation of the hydrogen chloride adducts of pyrimidosemibullvalene-2,4-dione derived from the photoreaction of 6-chloro-1,3-dimethyluracil in frozen benzene is interpreted by the mechanism involving the initial ortho-cycloaddition, not meta-cycloaddition, followed by the photochemical disrotatory cleavage of the cyclobutene moiety, and the successive intramolecular photo-Diels-Alder reaction of the resulting cyclooctatetraene ring.

In the previous paper, we have reported that UV-irradiation of 6-chloro-1,3-dimethyluracil (1) in frozen benzene in the presence of trifluoroacetic acid (TFA) (1 h) resulted in the formation of 1,3-dimethylcyclooctapyrimidine (2) (4.6%) and three novel cycloadducts, 7-chloro-1,3-dimethyl-4b,7,7a,8-tetrahydropentaleno[1,2-e]pyrimidine-2,4-dione (3), 5-chloro-1,3-dimethyl-4b,5,7a,8-tetrahydropentaleno[1,2-e]pyrimidine-2,4-dione (4), and 5-chloro-9,11-diazapentacyclo[6.4.0.0$^1$3.0$^2$6.0$^4$8]dodecane-10,12-dione (5), together with 1,3-dimethylbarbituric acid (6) (Scheme 1).1

By contrast to the photoreaction in a solution of benzene, wherein the ortho-cycloadduct (2) was formed
predominantly, the formation of these new compounds (3–5) could be superficially explained in terms of the initial meta-cycloaddition. However, the reason for the changes in the product distribution depending on the reaction conditions has remained unclear. In the course of our efforts to obtain these pentaleno derivatives (3–5) more effectively, we protracted the irradiation time, and found that the product distribution was changed significantly with the reaction time (Table 1).

Table 1. Photoreaction of 1 in Frozen Benzene in the Presence of TFA

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>Yields (%) of</th>
<th></th>
<th></th>
<th></th>
<th>Unreacted 1</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>4.3</td>
<td>2.1</td>
<td>2.8</td>
<td>5.9</td>
<td>24.5</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>1.3</td>
<td>2.8</td>
<td>8.8</td>
<td>41.0</td>
</tr>
<tr>
<td>3</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>7.5</td>
<td>50.0</td>
</tr>
</tbody>
</table>

These observations have drawn our attention and has encouraged us to obtain insight into the present reaction. In the present paper, we describe our findings that the formation of the pentaleno derivatives (3–5) can be interpreted by the mechanism involving the initial ortho-cycloaddition, not meta-addition, followed by the photochemical disrotatory cleavage of the cyclobutene moiety, and the successive intramolecular photo-Diels-Alder reaction of the resulting cyclooctatetraene ring.

Figure 1. Time course of the photoreaction of 1 in frozen benzene: ▼, 1(x1/10); □, 2; ◊, 3; ○, 4; ◆, 5; □, 3 + 4.
Time course of the photocycloaddition of 1 to benzene was investigated in frozen benzene in the presence of TFA in a Pyrex tube, using a high-pressure mercury lamp at -25 °C (Figure 1). The yields of the resulting cycloadducts were determined by the $^1$H-NMR spectra in benzene-$d_6$ with terephthalaldehyde as an internal standard.

Surprisingly the formation of 2 occurred smoothly at the initial stage of the reaction, to reach the top in ca. 10 min and then got decrease slowly. With the decrease of 2, formation of the pentaleno[1,2-ε]pyrimidines (3 and 4) began to arise. The yield of 3 reached the maximum in ca. 20 min and then gradually decreased, while the yield of 4 kept increasing. With gradual consumption of 3, formation of 5 got started. These results suggest that 2 is the precursor for 3 and 4, and that 3 is further converted into the ultimate cycloadduct (5) through [2+2] intramolecular photocycloaddition, whereas 4 is photochemically inactive.

Scheme 2
Conversion of 3 into 5 was confirmed by the fact that photolysis of 3 in frozen benzene in 10 min gave the pentacyclic compound (5) in high yield (86%), while no detectable transformation of 4 was observed by the similar photolysis. As the reactive intermediate for the transformation from 2 into the hydrogen chloride adducts (3 and 4), the pyrimidosemibullvalene (II) was invoked. However, no appreciable transformation of 2 was observed upon irradiation in the presence of TFA for 10 min. Hence, it was supposed that the thermally unstable isomer of 2 due to double bonds (I) might be produced prior to 2 at
low temperature according to the following pathway (Scheme 2); photocycloaddition of 1 to benzene in the mode of ortho gives rise to the formation of the cycloaduct with a cyclobutane ring, followed by the concomitant elimination of HCl. The photochemical disrotatory cleavage\(^3\) of the resulting cyclobutene moiety would lead to the formation of the key intermediate (I). The isomer (I) of 2 would readily isomerize into thermally stable 2 with the temperature rising to room temperature. At low temperature, photoexcitation of I would lead to the formation of II via symmetry allowed \([\pi4s + \pi2a]\) photo-Diels-Alder reaction process.\(^3\) Although the compound (I) is not isolated nor identified, the following results support the above basis. When 1 was photolyzed in frozen benzene at -25 °C for 5 min and then warmed up to room temperature (during this procedure, unreacted I is presumed to isomerize completely to inactive 2) and again photolyzed in frozen benzene for 5 min, the product ratio \((N)\) of 2 (16.2%) / [3 (1.1%) + 4 (0.6%)] \((N = 9.5)\) was found to be appreciably higher than that obtained from the reaction continuously irradiated for 10 min \((N = 3.5\): yields of 2, 3, 4 = 13.5, 2.9, and 1.0%), and rather closer to that obtained from the analogous reaction for 5 min \((N = 6.9\): yields; 2, 3, 4 = 6.6%, 0.6%, 0.36%).

Addition of piperylene to the present reaction was essentially ineffective on the formation of 2, but suppressed the formation of 3 and 4 significantly, suggesting that 2 may be produced via the excited singlet states, while the excited triplet states may participate in the pathway for the formation of 3 and 4. Although, alternative photochemical conversion leading to the formation of semibullvalene derivatives through di-\(\pi\)-methane rearrangement has been reported,\(^4\) these findings show that the present reaction may not involve analogous intermediates to benzobarrelene\(^4\) or cyclobutanaphthalene\(^5\) required for the rearrangement.

Thus, it is noteworthy that the present work provides a novel photochemical pathway into semibullvalene derivatives.

REFERENCES

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