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INTERMOLECULAR PHOTOADDITION INVOLVING 1,4-TRANSFER OF CYANO GROUP. 2. PHOTOADDITION OF 6-CYANO-1,3-DIMETHYLURACIL WITH ACETYLENIC COMPOUNDS[1]

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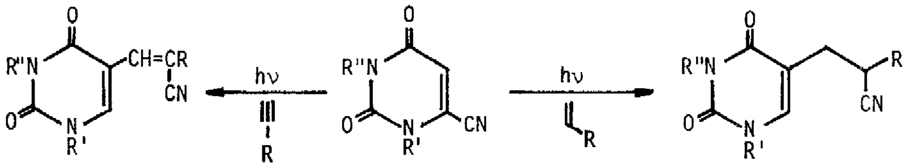
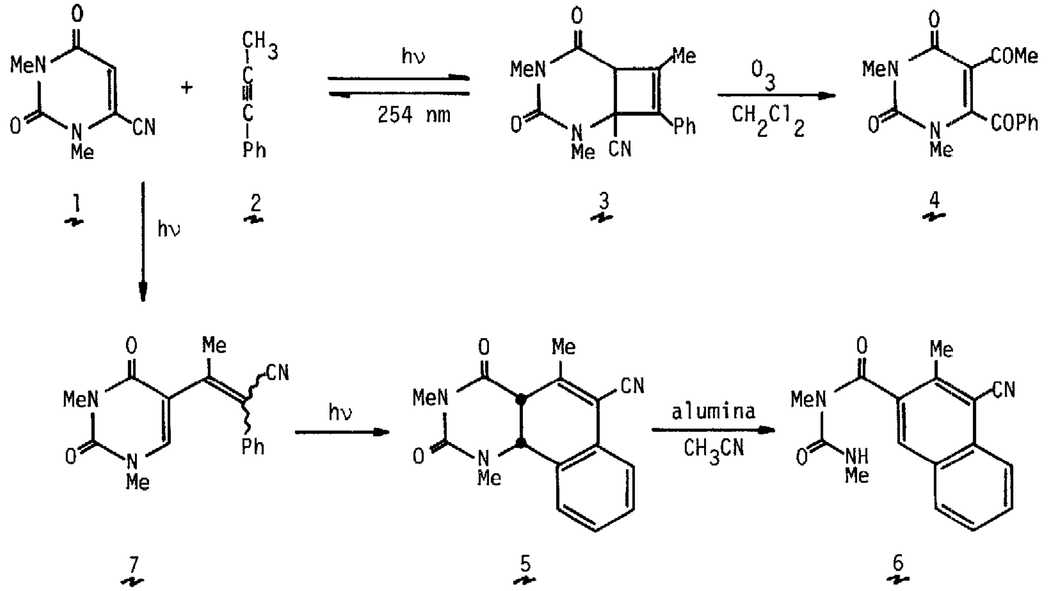
Summary: Wavelength dependent photoadditions of 6-cyano-1,3-dimethyluracil to phenylacetylenes are described. Photolysis with Pyrex-filtered light gave the fused cyclobutenes (3, 9), whereas irradiation with 254-nm light afforded the rearranged adducts (5, 11). The structures of the adducts were established by X-ray analyses.

Photochemical [2 + 2] cycloadditions of α,β-unsaturated ketones to olefins have been extensively utilized in organic synthesis.[2] Recently, we have found a new type of photoaddition in which an α,β-unsaturated nitrile undergoes addition with alkenes and alkynes through a 1,4-transfer of the cyano group as exemplified in Scheme I.[3] In connection with our interest in the synthesis of fused pyrimidine bases, we have investigated the photoreaction of 6-cyano-1,3-dimethyluracil (1) with aryl-substituted acetylenes. We report herein additional examples of this novel type of photoadditions.

Scheme I

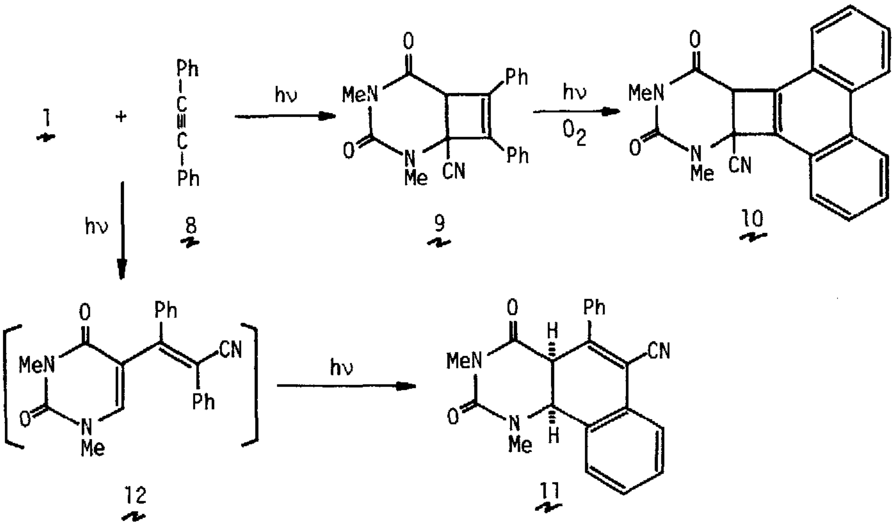


Irradiation of 1 (1 mmol) and 1-phenyl-1-propyne (2, 2 mmol) in benzene with a high-pressure mercury lamp (Pyrex filter) gave the cyclobutene 3 (43%) as the major product.[4,5] The long range coupling (J = 1.5 Hz) between methine and methyl protons in the NMR spectrum of 3[6] confirmed the regiochemistry of 3. Further support for the structure was obtained from the ozonolysis of 3 yielding 4[6] (55%). In contrast, photolysis of 1 and 2 with 254-nm light (lowpressure mercury lamp, Vycor filter) under the same conditions produced a different product, 5[6] (36%), together with considerable amounts of polymeric products; 3 has never been detected. Treatment of 5 with basic alumina gave the naphthalene derivative 6.[6] The structure of 5 was tentatively assigned on the basis of spectral data and finally confirmed by X-ray analysis.[7]



As evident from the structure of 5, the cyano group of 1 must undergo migration during the photoaddition. In order to know the multiplicity of the excited states of 1 we have examined the triplet-sensitized reaction. Xanthone-sensitized irradiation[8] of 1 (1 mmol) and 2 (2 mmol) in benzene resulted in the formation of 3 (30%) and a 1 : 1 *E/Z* mixture of 7.[6] Under the irradiation conditions both isomers of 7 are interconvertible. However, direct irradiation of 7 with 254-nm light resulted in a rapid photocyclization to 5 in almost quantitative yield, indicating that 7 is the precursor for 5.[9] The sensitization experiment strongly suggests a common triplet precursor for both 3 and 7. The formation of 3 and 7 from the triplet state of 1 can be reasonably explained by the mechanism involving a 1,4-biradical intermediate as has already been proposed in the previous paper.[3] The observed wavelength dependent reaction[10] can be ascribable to the secondary photoreaction of the cyclobutene 3. In fact, irradiation of 3 with 254-nm light resulted in a cycloreversion giving 1 and 2, being accompanied with the formation of 5 on prolonged irradiation.

Similar results were obtained in the photoaddition of 1 to diphenylacetylene (8). Irradiation of 1 (1 mmol) and 8 (2 mmol) in acetonitrile with Pyrex-filtered light under oxygen-free nitrogen stream afforded the cyclobutene 9[6] (60%). In the presence of oxygen 9 was readily converted to 10[6] under the irradiation conditions. Likewise, irradiation with 254-nm light produced 10[6] (40%) and 11[6] (20%). The structure of 11 was established by X-ray analysis (Fig. 1).[7] In this case, however, isolation of 12 on direct or sensitized irradiation has been fruitless presumably because of its rapid photocyclization to 11.



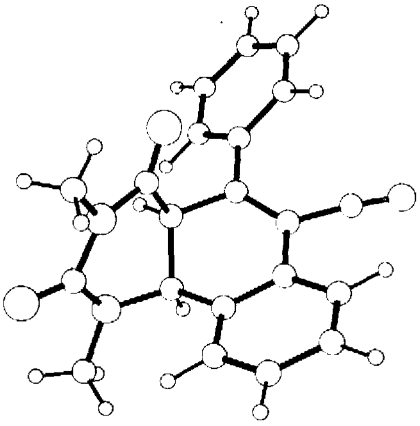


Figure 1. A computer generated perspective drawing of the compound 11.

Mechanistic details of this novel photoaddition will be published in a forthcoming paper.

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References and Notes

1. Photoinduced Reactions. 122.
2. (a) P. G. Bauslaugh, *Synthesis* 287 (1970); (b) P. de Mayo, *Acc. Chem. Res.* **4**, 41 (1971).
3. I. Saito, K. Shimozono, and T. Matsuura, *J. Am. Chem. Soc.* in press.
4. Photoproducts were isolated by preparative TLC (silica gel). Yields are isolated yields. Under the irradiation conditions more than 95% of the incident light was absorbed by **1**.
5. For the uracil-acetylene cycloadducts, see R. N. Comber, J. S. Swenton, and A. J. Wexler, *J. Am. Chem. Soc.* **101**, 5411 (1979).
6. All new compounds gave satisfactory elemental analyses and spectral data (^{1}H and ^{13}C NMR, UV, IR, MS). Selected data: **3**, mp 158 - 160 °C, ^{1}H NMR ($CDCl_3$) δ 2.08 (d, J = 1.5 Hz, 3 H), 3.16 (s, 3 H), 3.25 (s, 3 H), 4.10 (q, J = 1.5 Hz, 1 H), 7.45 (br s, 5 H); **4**, mp 134 - 140 °C; **5**, mp 156 - 157 °C; **6**, mp 155 - 156 °C; (E)-**7**, ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 3 H), 3.12 (s, 3 H), 3.30 (s, 3 H), 6.60 (s, 1 H), 7.22 (br s, 5 H); (Z)-**7**, ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 3.40 (s, 3 H), 3.45 (s, 3 H), 7.35 (br s, 5 H), 7.45 (s, 1 H); **9**, mp 181 - 185 °C, ^{1}H NMR ($CDCl_3$) δ 3.02 (s, 3 H), 3.20 (s, 3 H), 4.62 (s, 1 H), 7.20 - 7.80 (m, 10 H); **10**, mp 221 - 223 °C, UV (CH_3CN) 305 nm (log ε 4.07), 292 (4.00), 282 (4.02), 258 (4.76), 250 (4.76); **11**, mp 190 - 192 °C.
7. **5**, Monoclinic space group P$\bar{1}$ with a = 9.277, b = 10.513, c = 8.446 Å; α = 82.58, β = 121.52, γ = 83.29°; R = 0.05. **11**, Monoclinic space qroup P2_1/c with a = 7.960, b = 12.780, c = 16.893 Å; β = 92.05°; R = 0.04. Details will be published in a full paper.
8. Irradiation was done with a high-pressure Hg lamp through an aqueous $CuSO_4$ filter solution at a sufficient sensitizer concentration to absorb more than 95% of the incident light.
9. Analogous photocyclizations of [6π] systems leading to more stable *cis*-fused products, see (a) I. Ninomiya, S. Yamauchi, T. Kikuchi, A. Shinohara, and T. Naito, *J. Chem. Soc. Perkin I*, 505 (1973); (b) Y. Kanaoka, S. Nakano, and Y. Hatanaka, *Heterocycles*, **5**, 261 (1976).
10. For a review, see N. J. Turro, V. Ramamurthy, W. Cherry, and W. Farneth, *Chem. Rev.*, **78**, 125 (1978).

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