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Synthetic Photochemistry. V.[1] Azulene Derivatives from the Photoadducts of Methyl Acetopyruvate with Cycloheptatriene

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Synopsis. Two azulene derivatives, 1-methoxycarbonyl-3-methylazulene (III) and 1-methoxycarbonyl-2-methylazulene (IV), were obtained by the pyrolysis of the photoproducts of methyl acetopyruvate–cycloheptatriene. IV was understood to be derived from a subsequent photopinacolization of an unisolable [2+2]π photoadduct (VIII).

In the course of our studies of the photocycloaddition reaction of methyl acetopyruvate (I) with cycloheptatriene (II),[2] we noticed a characteristic coloration which should indicate a formation of azulene derivatives during the work-up. This paper will discuss the structures and mechanism of the formation of the azulene derivatives.

When the reaction mixture was heated *in vacuo*, a dark colored fraction was obtained after the distillation of most of the volatile fraction. The subsequent silica gel chromatographic separation of this afforded two azulene derivatives, III (blue needles) and IV (blue violet solids).[3] Both III and IV were analyzed to be $C_{13}H_{12}O_2$ arising from 1:1 adducts of I and II. Since III and IV both have the aromatic methyl group [δ: 2.61 (III), and 2.85 (IV)] and the methoxycarbonyl group [δ: 3.87 (III), and 4.01 (IV), $\nu_{C=O}$: 1675 (III), and 1677 cm^{-1} (IV)] on the five-membered ring [1H singlet at δ: 8.09 (C_2–H of III), and 7.17 (C_8–H of IV)], the determination of the position of either of the substituents should clarify their structures. In the NMR spectra, III [δ: 9.52 (dd, J=9.5, 2.0 Hz)] and IV [δ: 9.63 (dd, J=10.0, 2.0 Hz)] both have C_8–H signals at a very low field, disclosing the presence of a methoxycarbonyl group at the C_1–position for these compounds. Therefore, by the use of Plattner's well-known rule on the UV- and visible absorption maxima of azulenes[4] [λ_{max}^{MeOH}: 564 (III), and 530 nm (IV). $\lambda^{predict}$: 557 (III), and 519 nm (IV)], their structures have been deduced to be as shown.

Chart 1.

Since the absence of the azulenes in the original reaction mixture has been ascertained by a careful inspection of the NMR spectra of the fractions obtained by silica gel chromatography prior to the distillation, the azulenes must be formed during the distillation.

When the photoadducts of I and II[2] were pyrolyzed, only the ene-reaction product (V) was shown to develop a coloration due to the azulenoid compound, which consisted solely of a blue isomer (III). On the other hand, the most polar fraction of the photoproducts of I and II was also shown to give a coloration due to azulene derivatives by pyrolyzing under a nitrogen atmosphere; indeed, the presence of III and IV in the product mixture was proved by direct comparisons. We failed to isolate azulene-precursors due to the extreme instability and the limited quantity available,[5] but it seems reasonable to consider the precursors of the azulenes as glycol derivatives (VI and VII), which may be supposed to come from a further photochemical reaction of their primary products (V and VIII). Therefore, the following scheme may be proposed:

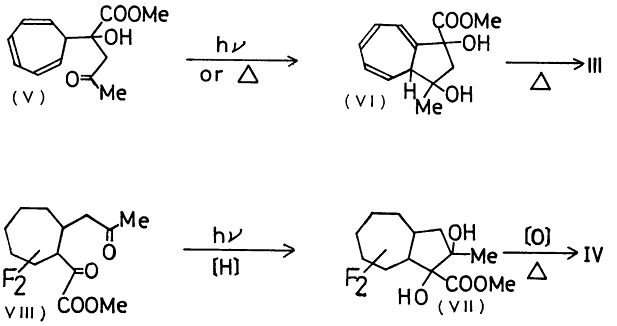
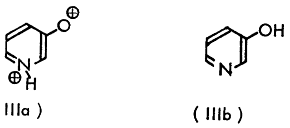


Chart 2.

VI (a 1,3-glycol) can be formed by an intramolecular hydrogen abstraction with the excited carbonyl group of V, and its aromatization needs the elimination of only two moles of water. On the other hand, VII (a 1,2-glycol) corresponds to a photo-reductive pinacolization product of VIII, being a (2+2)π cycloadduct. Although VIII has not been detected in the products of I and II, an analogous reaction was reported in the literature;[6] furthermore, the presence of excess II may facilitate the reduction process. The dehydration of VII should give a dihydroazulene derivative, whose type of compounds undergoes a spontaneous aromatization.

It is worthwhile to note that it seems superficially that the formation of III and IV could be interpreted in terms of an "oxabicyclobutane" intermediate.[7] The concept has been frequently mentioned, but never verified.[8] The present results, either, since no product directly linked to compound (IX) has been detected, and since it would be improbable to assume that all the photo-products of IX with II are too unstable to be characterized, do not seem to favor the concept.



(IIIa) (IIIb)

Chart 3.

To date, there have been considerable interests in the non-dehydrogenative preparation of the azulene skeleton by various cyclizations of propenyl-substituted seven-membered derivatives. Indeed, two successful experiments have been reported; Tsuruta *et al.*[9] have obtained 1,2-dicyanoazulene by a thermal rearrangement of 8-(2,2-dicyanovinyl)-heptafulvene, and Watanabe *et al.*[10] have used an acid-induced cyclization of 2-(7-tropyl)-benzaldehyde to afford benz[a]azulene, although uncondensed azulene was not obtained by this method. The formation of III from V thus constitutes a facile synthesis of azulene derivatives; according to one view of the initial photochemical step, this could be a rather general method for the preparation of 1-carboxy-2-, and/or -3-alkyl azulenes.[11] Although the yields, in the present stage, are insufficient, an improvement for the aromatization of V may not be difficult.

Experimental

Pyrolysis of the Whole Photoproduct Mixture of I and II. I (6.00 g) was dissolved in II (100 ml) and dioxane (200 ml), and the mixture was irradiated by means of a 450 W high pressure mercury lamp for 95 hr until it showed a negative ferric chloride test. Then the mixture was distilled under reduced pressure to remove a polymeric material. The higher boiling fraction (bp 172—184 °C/4 mmHg, 3.67 g) developed a dark-coloration by cooling. Silica gel column chromatography of the above afforded blue needles (III, mp 61—62 °C, 85 mg) (Found: C, 78.29; H, 6.13%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%) and a blue-violet solid (IV, 115 mg) (Found: C, 77.86; H, 6.11%) in addition to the previously-reported products,[2] methyl tropylglyoxalates (140 mg), ene-product (V, 105 mg), $(4+2)\pi$-cycloadduct (102 mg), and $(6+2)\pi$-cycloadduct (34 mg). The most polar fraction (75 mg) eluted with methanol–ether showed a strong ν_{OH} in the IR spectrum.

Pyrolysis of V; Formation of III. V (300 mg) was sealed in a glass tube and heated at 190 °C for 3 hr. The subsequent fractionation of the mixture afforded III (~3 mg) and methy ltropylglyoxalate (20 mg), together with recovered V (80 mg).

Pyrolysis of the Polar Fractions of Photoproducts; Formation of III and IV. The most polar portion of eluate (0.3 g) of the chromatography was heated in a sealed tube at 190 °C for 30 min. The mixture was then chromatographed through silica gel, and the blue fractions were collected to give III (~1 mg) and IV (~1 mg).

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References

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3) Spectral (NMR, UV) properties of this compound are in well accord with the reported data of 1-ethoxycarbonyl-2-methylazulene. *cf.* T. Nozoe, K. Takase, T. Nakazawa, and S. Fukuda, *Tetrahedron.*, **27**, 3357 (1971).

4) Pl. A. Plattner, A. Fürst, A. Müller, and A. R. Somerville, *Helv. Chim. Acta*, **34**, 971 (1951).

5) Unless the freshly prepared fraction was used, no IV was obtained from the pyrolyzate, thus the precursor of IV is much unstable than that of III.

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7) *e.g.*, a) E. J. Corey, J. D. Bass, R. LaMahien, and R. B. Mitra, *ibid.*, **86**, 5574 (1964); b) N. Furutachi, Y. Nakadaira, and K. Nakanishi, *ibid.*, **91**, 1028 (1969).

8) L. E. Friedlich and G. B. Schuster, *ibid.*, **94**, 1193 (1972).

9) H. Tsuruta, T. Sugiyama, and T. Mukai, *Chem. Lett.*, **1972**, 185.

10) T. Watanabe and N. Soma, *Chem. Pharm. Bull.*, **20**, 2215 (1971).

11) An extention of the reaction is presently undergoing. Homologs of I have shown the formation of azulenes, but acetylacetone or other simple β-diketones gave no azulene derivatives.