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BIS-DECARBONYLATION AND BENZYNE FORMATION IN LOW TEMPERATURE PHOTOLYSIS OF BENZOCYCLOBUTENEDIONE.

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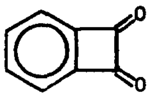
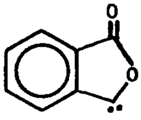
Room temperature photolysis of benzocyclobutenedione (I) has been studied in considerable detail.[1-3] Low temperature (-196°) photolysis of I in a thin film without solvent has also been reported recently.[4] Both room and low temperature studies agree on the presence of the carbene intermediate (II) during the process. The diketene (III) has also been considered as a possible intermediate at ambient temperature work. No indication of the presence of benzyne (IV) as an intermediate in the photochemistry of I has been reported in the literature. Formally, IV would be formed by bis-decarbonylation of I. Photolytic bis-decarbonylation of cyclic α-diketones, a relatively infrequent process in the photochemical literature, has been reported a few times during the past years,[5-8] mostly for six-membered cyclic α-diketones.


I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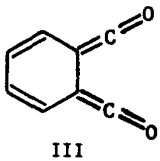
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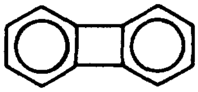
V

We have observed photolytic bis-decarbonylation of I to IV on irradiation in EPA[9] matrix at -196° (2 mm Suprasil cell, optical dewar with Suprasil windows, and 200 W high-pressure mercury arc were used throughout). Upon subsequent warming to room temperature, benzyne (IV) dimerized to biphenylene (V), which could be easily seen in absorption spectrum due to its characteristic structured band in the spectral region where none of the other components of the reaction mixture exhibit any comparably strong bands. The experiment can be most easily followed in Figure 1.

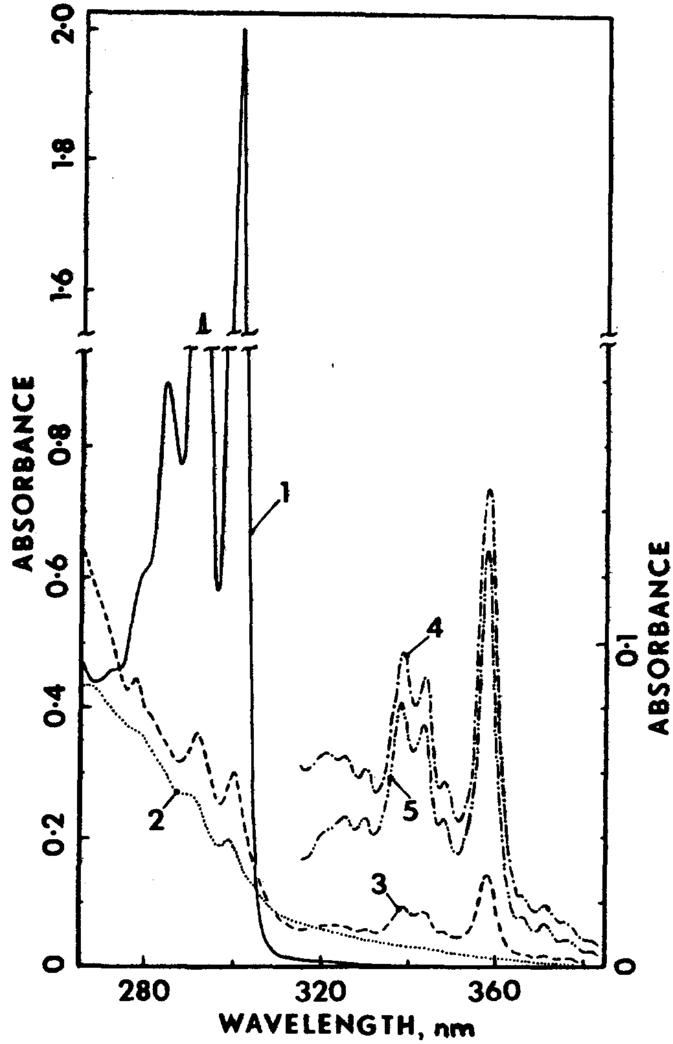

Figure 1. 1) I in EPA before irradiation; 2) after irradiation with 200 W high-pressure mercury arc at -196° for 40 minutes; 3) the irradiated sample after warming to room temperature and recolling to -196°; 4) part of the curve 3 recorded with the instrument sensitivity increased five times; 5) authentic biphenylene in EPA for comparison. All spectra were taken at -196°; absorbance scale on the left side is pertinent to curves 1-3, the scale on the right side to curves 4 and 5.

In the Figure 1, curve 1 represents a second absorption band of the starting diketone I (concentration ca. 1.1 × 10^{-3}M in EPA; the first band of I, located near 425 nm[10], is too weak to be observed at this concentration in 2 mm cell). After irradiation the diketone band was practically eliminated (curve 2). On warming to room temperature and subsequent recooling, the characteristic spectrum of biphenylene was observed in the region 320-380 nm (curves 3 and 4). It matches the spectrum of authentic biphenylene taken under the same experimental conditions (curve 5).

The efficiency of biphenylene formation was observed to be 12-15% of the highest possible theoretical value (calculated assuming [a] bis-decarbonylation to be the only photochemical reaction of I, [b] the complete dimerization of benzyne to biphenylene)*. Therefore, under our experimental conditions the formation of benzyne must be classified as one of the major photolysis pathways.

No absorption due to biphenylene was seen after photolysis of I in EPA solution at room temperature. In this case the spectral region between 300 and 400 nm developed an intense, poorly structured absorption, which would obscure spectrum of V unless present in very large amounts.

The low-temperature photolysis of I in non-polar matrix of 3-methylpentane gave a completely different picture than irradiation in polar EPA matrix. Diketone I disappeared even faster than in EPA, but there was no sign of benzyne being formed. A broad, unstructured band developed in 320-420 nm region (maximum ca. 365 nm). The band did not disappear on warming to room temperature, and no new bands could be observed. While the nature of the photoproduct is subject to further investigation, there is no doubt that the photolysis of I in the two matrices of different polarity takes a completely different course. This together with results of low-temperature photolysis in thin film without solvent[4] clearly shows an interesting case of a very high sensitivity of photochemical reaction to matrix effects. This may be a much more general feature of low-temperature matrix photolysis than is currently realized (cf. also 11). We are continuing to search for other examples of photochemistry strongly influenced by matrix effects.

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*The sharp peak of I at 298.5 nm (ε = 9680 in EPA at -196°) served to monitor the consumption of I. A sharp peak of V at 357.5 nm (ε = 12700 in EPA at -196°) was employed to measure its formation.

Acknowledgment

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