

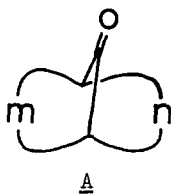
PHOTOCHEMICAL AND THERMAL BEHAVIOR OF BICYCLO[4.2.1]-
NONA-2,4,7-TRIEN-9-ONE¹

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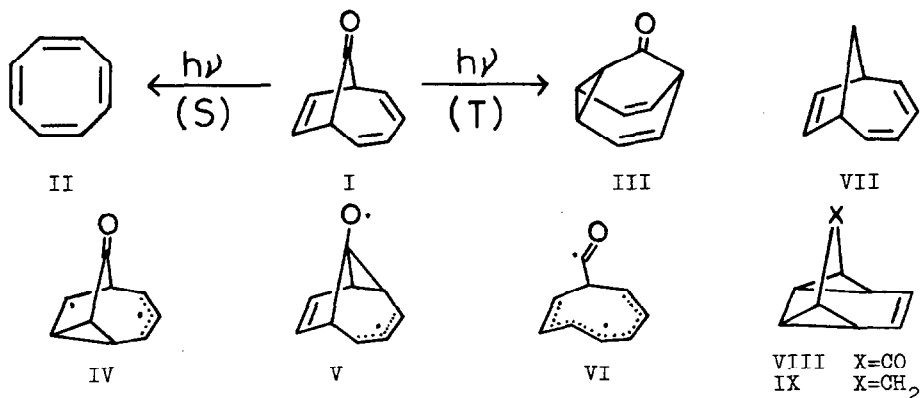
In connection with the recent development of orbital symmetry theory (2), it seems of interest to study the course of the photochemical and thermal decarbonylation of cyclic unsaturated ketones. The photolysis of the 3,5-cycloheptadienone system leading to the hexatriene system (3), and thermolysis of the 3-cyclopentenone system to the butadiene system (4), although with some ambiguities (5), are noteworthy examples of cheletropic reactions (2). In order to derive more information on this series of reactions, we studied the photochemical and thermal reactions of bicyclo[4.2.1]nona-2,4,7-trien-9-one (I) (6), which belongs to the system A consisting of $m=4q$ and $n=4q + 2 \pi$ electrons.



For instance, it seems of interest to know which one among the m, n and $m + n + 2 \pi$ electron systems controls the reaction path of I. In addition, the photochemical behavior of I is also intriguing in connection with the photodecarbonylation of barbaralone (7), because of the possibility of the intermediacy of I in the latter photoreaction.

When the compound I (8), which shows uv maxima in n-hexane at 270 nm ($\log \epsilon$ 3.41), 280 (3.43) and 320 (2.75), was irradiated in tetrahydrofuran using a Rayonet Photoreactor (300 nm), decarbonylation took place in a clean reaction and cyclooctatetraene (II) was obtained in 82% yield. On the other hand, when I was irradiated with 350 nm light in the presence of benzophenone or fluorenone, barbaralone (III), mp 53° (9), was obtained in 78 and 72% yields respectively. The structures of II and III were assigned on the basis of their spectral data. These facts indicate that the formation of II proceeded via

a $n-\pi^*$ singlet state whereas III was formed from the triplet state of I. The photochemical behavior of I is similar to that of 3,5-cycloheptadienone, which also exhibits different reactions depending on the multiplicity of the excited states (3c). The fact that both compounds undergo decarbonylation via the singlet state suggests a similarity in the reaction mechanism, i.e., a cheletropic process. Evidence presently available does not allow a decision between a concerted or a stepwise triplet reaction. If a concerted process is involved, the formation of III could be explained by a $[\sigma_{2a}^2 + \pi_{2a}^2]$ change in the cycloheptadienone system (2,10), or by a $[\sigma_{2s}^2 + \pi_{2s}^2 + \pi_{2a}^2 + \pi_{2a}^2]$ change, i.e., the homotrienylyl-1,7-carbon shift from the C_1 to C_2 position. It is also conceivable that III is formed from the diradical IV resulting from a di- π -methane interaction (11), or a diradical such as V or VI, arising from the excitation of the carbonyl group (10). However, it should be noted that the same type of isomerization is also observed in the photoreaction of the triplet state of bicyclo[4.2.1]nona-2,4,7-triene (VII)(12) and bicyclo[4.2.2]deca-2,4,7-triene and 2,4,7,9-tetraene derivatives (13). These facts may deny the participation of the carbonyl group in the formation of III, that is, the reaction path via the radical V or VI would be ruled out.



In contrast with the lability towards light, I was so stable to heat that it was recovered unchanged after heating at 150–200°, at which temperatures most 7-ketonorbornene derivatives (4,14) undergo decarbonylation. Furthermore, attempted pyrolysis of I by passing it through a column containing quartz helices heated at 400° resulted in recovery of 86% of I. Such stability of I to

heat may partly be attributed to the thermal stability of the valence isomer VIII in addition to that inherent in I, which may be ascribed to the antiaromaticity of planar cyclooctatetraene formed in the transition state. Recently it was found that the corresponding hydrocarbon (VII) is stable to heat but is rearranged to dihydroindene on heating over 300° (15). The migration of the C₉-hydrogen of valence isomer IX has an important role in the rearrangement of VII (15). However the ketone VIII seems to regenerate only I, because of the lack of such a hydrogen.

On electron impact, I exhibited the following peaks (m/e); 132 (M, 49%), 131 (M-1, 48%), 104 (M-CO, 100%) and 78 (M-CO-C₂H₂, 45%).

Thus, it can be concluded that the photo-cheletropic decarbonylation of I takes place as a linear, disrotatory process in the 3,5-cycloheptadienone system of I (16,17), but the thermal decarbonylation, expected to occur in the 3-cyclopentenone system, does not take place. Such behavior of I can be explained as follows. Inspection of a Dreiding model of I shows that the angle between the C₁-C₉-C₆ and C₁₍₆₎-C₇-C₈ planes is ca. 155° whereas that between the C₁-C₉-C₆ and C₁₍₆₎-C₂₍₅₎-C₃₍₄₎ planes is ca. 100°. This suggests that the developing p-orbitals at the C₁ and C₆-positions have a great advantage in overlapping with the π-orbitals of the diene system rather than with the π-orbitals of the ene system.

Concerning the photoreaction from the singlet state of both I and III, it should be noted that the formation of II is much faster from I than from III. However it is still not possible to determine whether I is an intermediate in the photolysis of III, since I has a more intense absorption around 300 nm region in the uv spectrum. Further study is in progress in this regard.

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