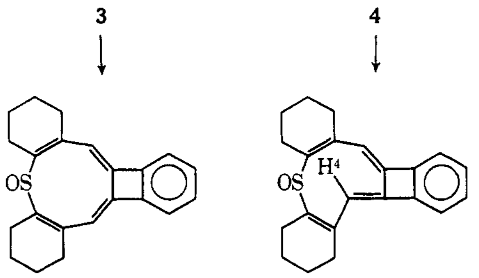
due to the configurational change induced by the *trans* double bond.

The fact that **3** and **4** differ only in the stereochemistry is supported by the results of Raney nickel desulfurization. Treatment of **3** in refluxing ethanol wtih a large excess of Raney nickel gave a mixture (~2:1) of **5** (*m/e* 296) and **6** (*m/e* 298) in 50% yield. Similar desulfurization of **4** led to a mixture (~4:1) of **5** and **6** in 40% yield, the identity of the compounds being established by glc and mass spectral comparison.

Oxidation of **3** with 6% hydrogen peroxide in acetic acid gave the sulfoxide **7** (67%, mp 252–254°), characterized by molecular composition[8] and spectral properties. Similar oxidation of **4** gave **8** (40%, mp 190–193°).[8] The nmr spectrum (CCl_4) of **7** showed signals at τ 2.91 (broad s, 4 H, aromatic), 4.26 (broad s, 4 H, olefinic), 6.8–7.7 (m, 8 H), and 7.7–8.8 (m, 8 H), and that of **8** had signals at τ 2.90 (broad s, 4 H, aromatic), 4.02 (broad s, 1 H, olefinic), 4.15 (s, 1 H, olefinic), and 7.0–8.8 (m, 16 H). The signal at τ 4.15 in **8** is assigned to H-4, again on the basis of solvent dependence.[10] The uv spectrum of **7** [λ_{max}^{EtOH} 267 nm (ϵ 37,700), 359 (8000)] is that expected for a 1,2-dimethylenebenzocyclobutene derivative,[9] whereas that of **8** [λ_{max}^{EtOH} 225 nm (ϵ 16,500), 315 (9500)] resembles **4**.



7 **8**

The nmr spectra of both **3** and **4** clearly indicate that these compounds do not have delocalized, aromatic thionin rings, but that this system has a buckled, nonplanar conformation. The absence of delocalization in these systems is further supported by the finding that the chemical shifts of the aromatic protons are virtually unaltered when **3** or **4** is oxidized to the corresponding sulfoxide, in contrast to the behavior of 2-thianorbiphenylene on oxidation.[1c] The properties of **3** and **4** suggest strongly that thionin, like oxonin,[5,11] is not an aromatic system.[12]

Acknowledgments. One of us (A. B. H.) thanks the Shell Company of Australia for a Postgraduate Scholarship, and we are also indebted to the Royal Society (London) for generous financial support.

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Photochemical and Thermal Reactions of Tricyclo[$3.3.1.0^{2,8}$]nona-3,6-dien-9-one[1]

Sir:

The decarbonylation of cyclic unsaturated ketones by irradiation or heating has been studied experimentally by several investigators and also discussed from a theoretical point of view.[2] Examples are the photochemical decarbonylation of cyclohepta-3,5-dienone[3] and 7,8-benzobicyclo[4.2.1]octa-2,4,7-trien-9-one[4] and the thermal decarbonylation of norbornadienone,[5] a dimer of cyclopentadienone[6] and tropones.[7] In connection with such decarbonylation of cyclic unsaturated ketones, we have studied the photochemically and thermally induced reactions of tricyclo-[$3.3.1.0^{2,8}$]nona-3,6-dien-9-one (I)[8] and have discovered that I behaves in a sharply contrasting manner in the two processes.

When I was irradiated in tetrahydrofuran or carbon tetrachloride using a high-pressure mercury lamp (Toshiba H 400-p), a clean reaction occurred to give a single oily product (II). The product was confirmed as cyclooctatetraene on the basis of its nmr spectrum, showing a singlet at τ 4.26, and formed an adduct, mp 170°,[9] with maleic anhydride. Neither sensitizing nor quenching effects were observed when the irradiation was carried out in the presence of benzophenone, fluorenone, anthracene, or piperylene. The decarbonylation also took place by irradiation with filtered 307-nm light,[10] where I has an absorption maximum due to n–π^* excitation. These facts indicate that the photoreaction of I proceeded *via* the n–π^* singlet state and that cyclooctatetraene (II) did not originate from semibullvalene (uv max in ethanol 225–235 nm, sh) which was considered to be a possible intermediate resulting from the decarbonylation of I.[11] In addition, no ester was formed by irradiation of I in methanol and no effect was observed when I was irradiated in the presence of a radical scavenger such as 2,6-di-*t*-butylphenol or toluene.

In contrast with such a lability to light, I was so stable to heat that attempted pyrolysis through a quartz column heated at 200° resulted in its complete recovery. However, upon pyrolysis at 500° I afforded two oily products, III and IV, in 28 and 26% yields, respectively, with the recovery of I in a 26% yield. The

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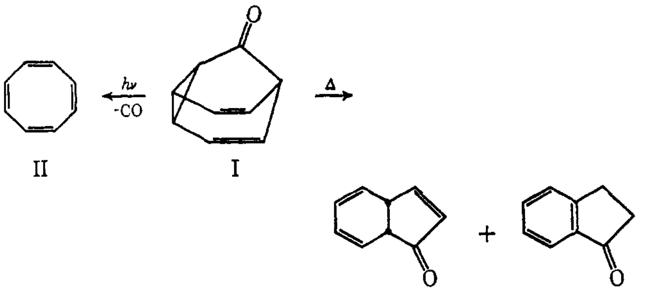
product III was found to be identical with *cis*-dihydroindenone by means of vpc analysis and nmr spectroscopy and by the formation of an adduct, mp 241°,[12] with maleic anhydride. The structure of IV was assigned as indanone on the basis of the formation of a semicarbazone, mp 236°, in addition to the spectral data. As is well known, the product IV was a secondary thermal product of III.

On electron impact, I exhibited the following peaks (*m/e*): 132 (M, 42%), 131 (M − 1, 71%), 104 (M − CO, 100%), and 78 (M − CO − C_2H_2, 69%). This spectrum seems to resemble more closely that which would be expected as a result of the photolysis rather than that of the pyrolysis of I.



II I III IV

The mechanistic pathways for both photolysis and pyrolysis of I are intriguing, especially when these reactions are compared with the photochemical and thermal reactions of bullvalene (V) or with the photolysis of the bicyclo[4.1.0]hept-4-en-2-one system (VI).[13] The compound I is considered to be a keto analog of V, that is, I differs from V by bearing a keto group in the place of an ethylene group. It has been reported that the irradiation of V gave bicyclo[4.2.2]deca-2,4,7,9-tetraene,[14] whereas the pyrolysis of V at 350° afforded dihydronaphthalene.[15] On the assumption that the photolysis of I behaves in a way similar to that of V, bicyclo[4.2.1]nona-2,4,7-trien-9-one comes out as a possible intermediate for the formation of II. It should also be noted that, although I has a structure partially common to VI, the irradiation of a bicyclo[4.1.0]hept-4-en-2-one derivative afforded a penta-2,4-dienylketene derivative *without decarbonylation.*[13] The mechanism of the photodecarbonylation of I is ambiguous at present, but it should add a new example to the photocheletropic decarbonylation of cyclic unsaturated ketones if it occurs as a concerted process.[16] On the other hand, the mechanistic pathway for the pyrolysis of I as well as that of bullvalene would be complicated, because the reaction was carried out at a high temperature. However, one of the possible paths from I to III is *via* cyclohepta-1,3,5-trienylketene and its valence isomer.[17] In order to clarify these ambiguities, we are continuing the studies on the photochemical and thermal reactions of I and its related compounds.

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(16) Although our trapping experiments do not completely rule out nonconcerted processes such as α cleavage of the carbonyl group followed by ring opening and decarbonylation, the decarbonylation of I could also be explained by a concerted mechanism on the basis of the molecular orbital consideration (private communication from Professor K. Fukui). Details will be reported in our full paper.

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Book Reviews

Topics in Phosphorus Chemistry. Volume 6. By K. Darrell Berlin, G. M. Blackburn, J. S. Cohen, D. E. C. Corbridge, and D. Michael Hellwege. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. vii + 309 pp. 15.5 × 23 cm. $27.50.

The sixth volume of "Topics in Phosphorus Chemistry" is as welcome as were the first five. The editors and contributors are to be congratulated for their continued diligence in providing timely reviews in a rapidly expanding subject.

The first chapter by Berlin and Hellwege covers carbon–phosphorus heterocycles. The review is extensive and thorough. An appendix containing Tables of Compounds will be of considerable value to investigators who wish to find out which compounds have been prepared. The review is organized on the basis of the syntheses of the heterocycles starting with three-membered ring compounds and proceeding to large-ring heterocycles. The second section discusses reactions, stereochemistry, and spectral properties.

The following chapter by Blackburn and Cohen covers chemical oxidative phosphorylation. This is a subject which has received considerable mechanistic study, and the authors do a good job in discussing the various pros and cons of the proposed mechanisms. Of particular interest is the section on quinol phosphates, both because of the mechanistic complexity and the possible relationship to oxidative phosphorylation in biological systems. The authors note, however, "that there may be *no actual phosphorylation* of quinones during the complex of biological processes grouped under the term oxidative phosphorylation."

The third and final chapter by Corbridge reviews the infrared spectra of phosphorus compounds. The review is broad in scope, and it covers all of the multitude of types of known phosphorus compounds. There is an extensive series of tables which cover the total fundamental frequencies of simple molecules such as phosphine and phosphorus trichloride. They also cover particular group frequencies. The review covers theory and vibrational studies of simple molecules and then turns its attention to spectra–structure correlation. There is no question that this chapter and the others will be of considerable value to organophosphorus chemists.

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