

made in the sequence work on the PP site, and it is likely that the correct sequence for this site is the same as that for the FITC site.

We have previously reported that HSA has little, if any, catalytic activity with respect to the decomposition of MC, as compared to BSA.² Brown's sequence work on HSA⁵ indicates that the critical lysine 220 in BSA is replaced by an arginine in the homologous position (residue no. 221) in HSA. This provides a clear molecular proof for the critical importance of lysine 220 in the catalytic mechanism of BSA. It is likely that other albumins which do have this unusual activity will also have lysine at the homologous position.

Acknowledgments. It is a pleasure to acknowledge Ms. Claudia Bryner for expert technical assistance. Dr. Stacy Adrian is acknowledged for helpful suggestions. Financial support through the National Science Foundation is gratefully acknowledged.

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Received January 20, 1976

First Example of Photochemical Allowed $[4\pi + 2\sigma + 2\sigma]$ Cycloaddition¹

Sir:

Many more examples showing the application of the generalized selection rules for pericyclic reactions have been reported.^{2,3} It is surprising, however, that the photochemical allowed $[4\pi + 2\sigma (2\pi) + 2\sigma(2\pi)]$ cycloaddition has no precedent in chemical literature.⁴ Quadricyclane seems to be a good model for this purpose.⁵

We have investigated a photochemical reaction between aromatic hydrocarbons and quadricyclane and thereby found the first concrete evidence for photochemical allowed $[4\pi + 2\sigma + 2\sigma]$ cycloaddition between a 4π system and a pair of strained σ bonds.

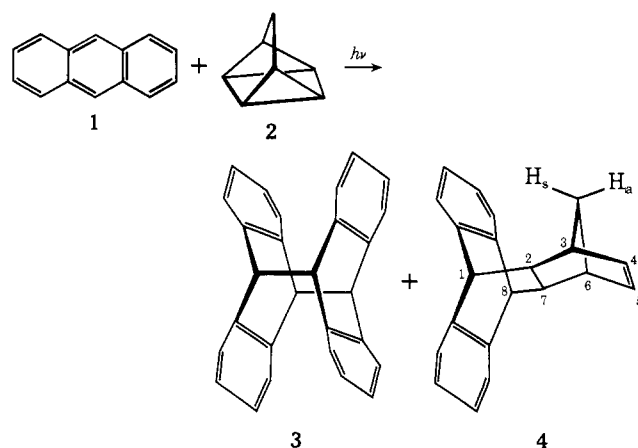
Murov and Hammond⁶ have reported that quadricyclane is a very effective quencher of the fluorescence of aromatic hydrocarbons such as anthracene and naphthalene, and suggested that the electronic energy of the aromatic hydrocarbons is efficiently transferred to vibrational energy of quadricyclane followed by isomerization to norbornadiene. Solomon et al.⁷ have described that the fluorescence quenching of aromatic hydrocarbons by quadricyclane could proceed via a charge-transfer complex. In spite of these efforts, the possibility of chemical product formation has not been excluded, since Yang et al.⁸ and authors⁹ have shown that some aromatic hydro-

carbons undergo highly efficient photocycloadditions with several cyclic diene and trienes resulting in the chemical product formations through a significant pathway for the decay of the exciplexes.

When a solution of anthracene (**1**) and a large excess of quadricyclane (**2**) in benzene was irradiated with a high-pressure mercury lamp (100 W) in a Pyrex vessel at 20° for 6 h, anthracene was rapidly consumed. After removal of the anthracene photodimer **3** (65%) precipitated during the irradiation, careful chromatography of the photolysis mixture on silica gel using benzene-*n*-hexane as eluent gave a 1:1 adduct **4** (mp 157–160°) in 45–50% yield. Interestingly, similar irradiation under the same conditions in the presence of methylene bromide resulted in the quantitative formation of the dimer **3**, conversion of norbornadiene (20%), and recovery of **2** (80%), and no 1:1 adduct was detected. The structure of the adduct **4** was deduced from elemental analysis (*Anal.* Calcd for C, 93.69; H, 6.31. Found: C, 93.43; H, 6.57), mass spectrum (M^+ 270), and its NMR data: the spectrum in CCl_4 exhibits signals of two bridged methylene protons at δ -0.19 (d, 1 H, syn H-13, $J = 10.5$ Hz), and 0.68 (d, 1 H, anti H-13, $J = 10.5$ Hz), methine protons at δ 2.02 (d, 2 H, H-2 and H-7, $J = 1.0$ Hz) and 2.41 (d, 2 H, H-3 and H-6, $J = 1.8$ Hz), benzylic methine protons at δ 4.04 (d, 2 H, H-1 and H-8, $J = 1.0$ Hz), olefinic protons at δ 6.03 (d, 2 H, H-4 and H-5, $J = 1.8$ Hz), and aromatic protons at δ 6.92–7.18 (m, 8 H). An appearance of the higher bridged methine proton signal was attributable to the anisotropy of benzene moiety which was to be expected for the exo isomer by molecular models. Thus, the adduct was concluded to be $exo[4\pi + 2\sigma + 2\sigma]$ cycloadduct **4**. It is to be noted that both the thermal and photochemical reactions of **1** and norbornadiene (**5**) gave no 1:1 adduct even under more drastic conditions. The external heavy-atom effect as described above suggests a singlet mechanism for the addition process. These results support the idea that the formation of photoproduct **4** may be rationalized as a concerted photoallowed $[\pi_4s + \sigma_2s + \sigma_2s]$ addition between singlet excited anthracene and quadricyclane.

On the other hand, the fluorescence of anthracene and naphthalene was efficiently quenched by **2** and linear Stern-Volmer plots were obtained for the quenching reactions. The rate constant for the quenching reaction of anthracene (3.1×10^9 l. mol⁻¹ s⁻¹) is about the same as that of naphthalene (3.2×10^9 l. mol⁻¹ s⁻¹). However, when a solution of naphthalene (**6**) and **2** in benzene was irradiated under the same conditions through a Corex filter, extensive isomerization of **2** to norbornadiene (**5**) was observed. One interesting implication comes from consideration of the fact that the chemical product could not be detected from quenching of naphthalene by **2** in comparison with the case of anthracene. It might be explained

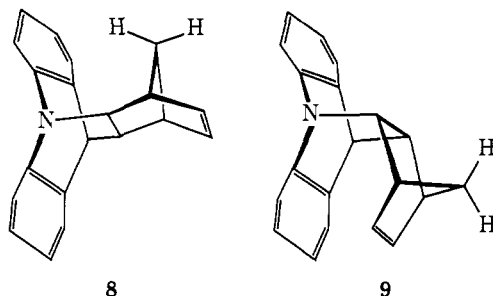
Scheme I



that the reactivity of excited naphthalene is much less than that of excited anthracene. Since the anthracene has a higher electron affinity than the naphthalene,¹¹ there is a difference in the charge-transfer character of the excited intermediates. Although a number of explanations are possible for the results, the reasons underlying these differences are not yet resolved at the present stage.

Similarly, the irradiation of acridine (**7**) and quadricyclane (**2**) in benzene afforded an isomeric mixture of 1:1 adducts **8** and **9** in a moderate yield. The NMR of the reaction mixture showed the ratio of 5:2. A pure sample of **8** was isolated by chromatography on alumina followed by recrystallization: colorless prisms, mp 135°. On the other hand, the isomer **9** decomposed slowly upon chromatography or the attempted purification. A crystalline material of about 95% purity was, however, obtained by crystallizing the crude reaction mixture: pale yellow prisms, mp 115–120°. The structures of the isomers were determined by the NMR data; a significant shielding effect by the anisotropy of the benzene moiety for the methylene bridge protons in **8** is observed at δ -0.08 (1 H, d, J = 9.0 Hz) and 0.90 (1 H, d, J = 9.0 Hz). By contrast, compound **9** showed methylene protons at δ 1.2–1.3 (2 H, multiplet). Thus, structures **8** and **9** were assigned to be exo and endo 1:1 adducts, respectively.

Chart I



The formation of the photoadducts might proceed via diradical intermediates, by the stabilization of a polar contributing structure by the electronegative nitrogen of an excited acridine molecule, rather than in a stereoselective concerted fashion, since quadricyclane does not quench appreciably the fluorescence of acridine by the fluorescence quenching experiments. Furthermore, the total yields of the 1:1 adducts of **8** and **9** are considerably decreased for the photoaddition re-

action in the presence of biacetyl which is known to a sensitizer of acridine.¹² In addition, the photoproduct formations are affected by the polarity of a solvent; upon irradiation with **2** in a protic solvent such as methanol and ethanol, acridine gave only the photoreductive products (acridan and biacridan)¹² and no 1:1 adducts were detected.^{13,14}

Acknowledgment. The authors wish to thank Dr. Keizo Aoki of the Department of General Education, Nagoya University, for measurement of fluorescence spectroscopy.

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- (13) During preparation of this paper, interesting photoadditions of 1,3-dienes to acridine were reported; see ref 8c.
- (14) The limitation of the photoreaction was that phenazine was inert to the photoaddition of quadricyclane.

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Received September 29, 1975

Book Reviews

Molecular Oxygen in Biology. Edited by O. HAYAISHI (Kyoto University). North-Holland Publishing Co., Amsterdam, and American Elsevier Publishing Co., Inc., New York, N.Y. 1974. xiii + 367 pp. \$36.50.

This book represents an ambitious undertaking designed to survey "neglected" aspects of the role of oxygen in biology. The editor has succeeded in assembling a diverse collection of reviews which include unusual topics such as "Molecular Oxygen and Evolution" as well as traditional topics such as the "Structure and Function of Hemoglobins". The references indicate literature coverage through 1973.

Chapter 1 ("The Physico-chemical Properties of Molecular Oxygen") summarizes the physical and chemical properties of oxygen but suffers under the burden of surveying too large an area of

research. It is doubtful whether there is sufficient detail for this summary to serve as an authoritative reference. It is certain that the reader will rarely refer to this chapter while reading later chapters. Chapter 2 ("The Electronic Structure of Coordinated Oxygen") covers a fascinating area of bioinorganic chemistry but contains an array of amusing as well as confusing errors. For example, a molecular orbital diagram (p 40) meant to illustrate the $^3\Sigma$ state of O_2 results from combining one oxygen atom possessing six electrons with another oxygen atom possessing seven electrons. Chapter 3 ("Molecular Oxygen and Evolution") is a fascinating account of evolution as a function of atmospheric composition. Hypotheses concerning the effect of oxygen pressure variation on evolution are well described and critically evaluated. Chapter 4 ("Oxygen Effects in Radiobiology") is a brief account of the effects of oxygen