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Photochemical Additions of Conjugated Dienes to Anthracene

Sir:

Electronically excited molecules are susceptible to molecular complex formation, and such complexes are commonly known as excimers and exciplexes.¹ Electron transfer may occur following the complex formation which will lead to a number of interesting physical phenomena and chemical reactions. Contributions by Hammond and his coworkers showed that conjugated dienes quenched the fluorescence of naphthalene and other aromatic hydrocarbons and suggested that exciplexes were the intermediates in the quenching processes.^{2,3} Although the possibility of chemical product formation had been mentioned,² no chemical products were characterized in these processes. Kraft and Koltzenburg reported that the photochemical reactions of benzene, alkylated benzenes and naphthalene with 1,3-butadiene or isoprene gave a complex mixture of products.⁴ Anthracene has a higher electron affinity than naphthalene and benzenes⁵ and may be more reactive than the simpler analogs in its excited state. The current communication deals with the photochemical 1,4 cycloaddition of conjugated dienes to anthracene and the formation of the novel 7,8,9,10-dibenzobicyclo[4.2.2]-7,9-*trans*-3-decatrienes (**1**) from acyclic 1,3-dienes and anthracene.

When a solution of anthracene (280 mg) and 1,3-cyclohexadiene (10 ml) in benzene (120 ml) was ir-

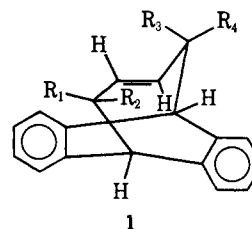
(1) For reviews on excimers and exciplexes, see: (a) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, New York, N. Y., 1970; (b) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

(2) L. M. Stephenson and G. S. Hammond, *ibid.*, **16**, 125 (1968); *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969); L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665, 3893 (1966).

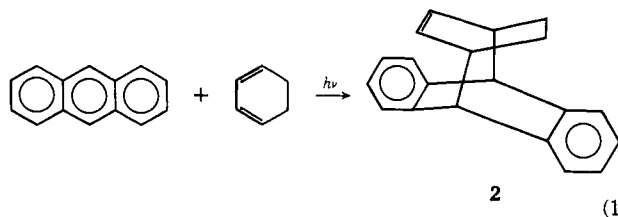
(3) T. R. Evans, *ibid.*, **93**, 2081 (1971).

(4) K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4357, 4723 (1967).

(5) Reference 1a, p 462.



radiated with a Hanovia 450-W lamp through a Pyrex filter, anthracene was rapidly consumed. The quantum yield of anthracene consumption at 313 nm was found to be 0.26. The nmr of the reaction mixture showed the presence of only one 1:1 adduct and the dimers of cyclohexadiene (170 mg). The yield of the adduct was estimated to be 96%, a pure sample of which was isolated by chromatography on alumina followed by recrystallization:⁶ mp 197–200° dec (CH₂Cl₂-petroleum ether); uv max (cyclohexane) 279 (ε 2460), 276 (ε 1425), and 272 nm (ε 1635); ir (KBr) 718 cm⁻¹; nmr (CDCl₃) δ 1.42 (m, 4, CH₂), 3.08 (m, 2, CHCH=CH), 4.16 (d, 2, J = 10 Hz, ArCHAr), 5.62 (sextet, 2, CH=CH), and 7.08 ppm (m, 8, ArH). The olefinic protons exhibit a sextet with the two outer peaks of very low intensity and the four inner peaks of almost equal intensity which is characteristic of an A₂X₂ system similar to that in bicyclo[2.2.2]-octenes.⁷ First-order analysis gives the following coupling constants: J_{CH=CH} = 8.7 Hz, J_{C=CHCH} = 7.0 Hz, and J_{CH=CCH} = 1.4 Hz.⁸ The adduct is therefore identified to be the 1,4 adduct **2** (reaction 1). The reaction was extended to 9,10-dimethyl-



anthracene and 9-cyanoanthracene, and crystal line adducts were isolated in good yields in both cases (66 and 87%).

When the irradiation of anthracene was carried out with 2,5-dimethyl-2,4-hexadiene under similar conditions, an adduct was again formed in high yield. In contrast to the adduct formed from cyclohexadiene, this adduct decomposes rapidly upon chromatography or other attempted purification.^{9,10} A crystalline material of about 90% purity was, however, obtained by crystallizing the crude reaction mixture from ethanol: 87–95°; uv max (cyclohexane) 275 (ε 909), 266 (ε 1020), and 258 nm (ε 1150); ir (CCl₄) 1005 cm⁻¹;¹¹ nmr (CCl₄)

(6) All crystalline new products in this communication gave satisfactory elemental analyses.

(7) K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

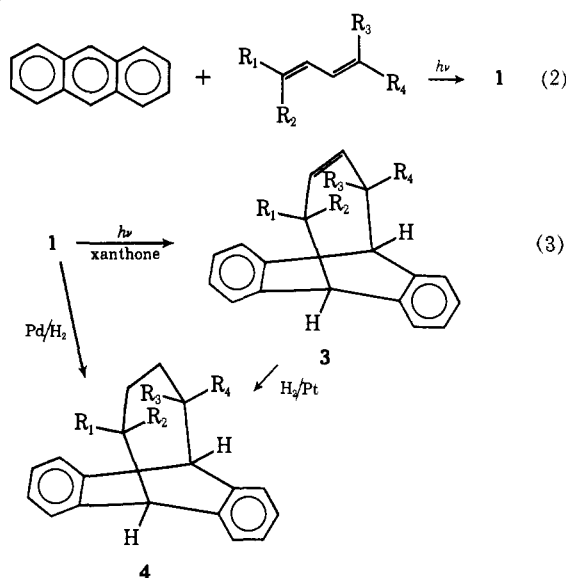
(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Can. J. Chem.*, **35**, 1060 (1957).

(9) A major decomposition product appears to be the corresponding epoxide which was detected as the only contaminant in our crude product. The epoxide was characterized by its elemental analysis, molecular weight, uv, ir, and nmr spectra. The mechanism of its formation will be investigated.

(10) Neither **1a** nor **1b** showed any tendency to dimerize under our experimental conditions.

(11) The ir spectra of *trans*-cyclooctenes and *trans*-cycloheptenone exhibit a band between 9.9 and 10.1μ: A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953); P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964); **87**, 2052 (1965).

δ 1.04 (s, 6, CH_3), 1.37 (s, 6, CH_3), 3.26 (s, 2, ArCHAr), 5.30 (s, 2, $\text{CH}=\text{CH}$), and 7.12 ppm (broad s, 8, ArH). Under the influence of light and xanthone as the sensitizer, the adduct was rapidly converted into a stable isomer **3a**: mp 139–141° (petroleum ether–methanol); uv max (cyclohexane) 272 (ϵ 1190), 266 (ϵ 1020), and 248 nm (ϵ 690, shoulder); ir (KBr) 709 cm^{-1} ; nmr (CCl_4) δ 1.20 (s, 12, CH_3), 3.68 (s, 2, ArCHAr), 4.45 (s, 2, $\text{CH}=\text{CH}$), and 7.12 ppm (m, 8, ArH). Both isomers upon hydrogenation gave the same dihydro derivative **4a**, mp 156–158°, which exhibited spectral properties in accordance with its structure. The results suggest the labile adduct to be **1a** ($\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{CH}_3$) with the newly formed double bond in the strained trans configuration which may be isomerized to the more stable cis isomer **3a** by photosensitization (reaction 3).



Similarly, upon irradiation with *trans,trans*-2,4-hexadiene, anthracene gave the metastable 1,4 adduct (**1b**, $\text{R}_1 = \text{R}_4 = \text{CH}_3$; $\text{R}_2 = \text{R}_3 = \text{H}$) in excellent yield, which failed thus far to crystallize: uv max (cyclohexane) 260, 267, and 275 nm; ir (CCl_4) 1005 cm^{-1} ; nmr (CCl_4) δ 1.28 (d, 6, $J = 7$ Hz, CHCH_3), 2.45 (m, 2, CHCH_3), 3.56 (s, 2, ArCHAr), 4.93 (sextet, 2, $\text{CH}=\text{CH}$),¹² and 7.12 ppm (s, 8, ArH). The compound was isomerized to a more stable isomer **3b** by photosensitization: mp 110–113°; uv max (cyclohexane) 270 (ϵ 1255), 263 (ϵ 1160), and 255 nm (ϵ 775); ir (KBr) 720 cm^{-1} ; nmr (CCl_4) δ 1.18 (d, 6, $J = 7.5$ Hz, CHCH_3), 2.92 (m, 2, CHCH_3), 3.82 (d, 2, $J = 3.0$ Hz, ArCHAr), 4.68 (d, 2, $J = 1.2$ Hz, $\text{CH}=\text{CH}$), and 7.12 ppm (m, 8, ArH). Both isomers **1b** and **3b** upon hydrogenation gave the same dihydro derivative **4b**, mp 78–80°, which exhibited spectral properties in accordance with the structure. These results indicate that the addition proceeds in a stereospecific manner.

The light-induced addition of 1,3-dienes to anthracene may be visualized as a photochemical electrocyclic $4_\pi + 4_\pi$ addition reaction.¹³ The stereospecificity of

(12) The sextet was analyzed to be a characteristic A_2X_2 pattern, and the first-order analysis (ref 8) gives the following coupling constants: $J_{\text{CH}-\text{CH}} = 8.8$ Hz, $J_{\text{CHCH}-\text{CH}} = 7.8$ Hz, and $J_{\text{CHCH}-\text{CH}} = 0.9$ Hz.

(13) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y. 1971.

the addition suggests that the reaction proceeds in a concerted manner and that the diene assumes the *s-trans* conformation in the transition state. Since the *trans* adduct **1** may be isomerized by photosensitization to give the more stable *cis* adduct **3**, it is probable that the various products from the benzene-1,3-diene photo-reactions may be formed from the bicyclo[4.2.2]deca-7,9-*trans*-3-trienes as the intermediate.⁴

It is known that 1,3-cyclohexadiene quenches the fluorescence of anthracene efficiently with a rate approximately equal to one-half of that of a diffusion-controlled process,² and we have found that the quantum yield of consumption of anthracene in the presence of 1 *M* 1,3-cyclohexadiene is comparable to that of anthracene fluorescence. Traces of anthracene dimer were detected in the reaction mixture; however, the dimer was formed in 10–15% yield at higher anthracene concentrations. If the mechanism of fluorescence quenching of anthracene by cyclohexadiene involves exciplex formation, the principal mode of decay of the exciplex is the formation of the adduct **2**. It is not certain at this moment whether the exciplex would dissociate appreciably back to the excited state of anthracene once it is formed.

The formation of cyclohexadiene dimers from the irradiation of anthracene in the presence of cyclohexadiene may be due to energy transfer from the upper triplet state of anthracene to cyclohexadiene,¹⁴ but the quantum efficiency for the dimer formation is much higher than that for the anthracene-sensitized *cis-trans* isomerization of 1,3-pentadiene. The mechanism of cyclohexadiene dimer formation in this reaction is being examined.

Acknowledgment. The authors wish to acknowledge the National Institutes of Health, Grant No. AM-11,676, and the National Science Foundation, Grant No. GP-16,347, for the support of this work.

(14) R. S. H. Liu, *J. Amer. Chem. Soc.*, **90**, 1899 (1968); R. S. H. Liu and J. Erdman, *ibid.*, **90**, 213 (1968); **91**, 1492 (1969); R. S. H. Liu and R. E. Kellogg, *ibid.*, **91**, 250 (1969).

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Photochemical Addition of Acyclic 1,3-Dienes to 9-Cyanoanthracene and 9-Anthraldehyde, a $4_\pi + 2_\pi$ Stereospecific Photochemical Cycloaddition

Sir:

In the accompanying communication,¹ we reported the 1,4 photocycloaddition of 1,3-dienes to anthracene. Since the diene may act as an electron donor in its interaction with the excited anthracene,² we investigated the effect of electron-withdrawing substituents on anthracene in this reaction. This communication deals with the stereospecific 1,2 photocycloaddition of acyclic 1,3-dienes to 9-cyanoanthracene (**1a**) and 9-anthraldehyde (**1b**) to give 9,10-ethanoanthracene derivatives **2** (reaction 1). This result suggests that the course of a photochemical addition reaction may be controlled by the configuration of the two components in the exciplex intermediate.

(1) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **94**, 1405 (1972).

(2) T. R. Evans, *ibid.*, **93**, 2081 (1971).