

- tenfold excess of $p\text{-IC}_6\text{H}_4\text{CO}_2\text{Me}$ to produce I_2NiL_2 , which is, however, not observed immediately after reaction. The same reaction in the presence of excess $n\text{-Bu}_4\text{NBr}$ will produce Br_2NiL_2 within 20 min due to the enhanced reactivity of nickel(I) species with the aryl iodide, presumably by formation of the dibromonickelate(I) species, $\text{Br}_2\text{NiL}_2^-$. In the absence of excess aryl halide, no X_2NiL_2 was observed. The dihalonickel(II) complex $\text{Cl}_2\text{Ni}(\text{PEt}_3)_2$ has been isolated in the reactions of $\text{Ni}(\text{PEt}_3)_4$ with 3-chloro-2-norbornane and hexachlorobenzene,¹⁵ but in both cases excess chloro compound was used. (c) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, in press.
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Photochemical Oxidation and Rearrangement of Dibenzobarrelele and Dehydrojanusene

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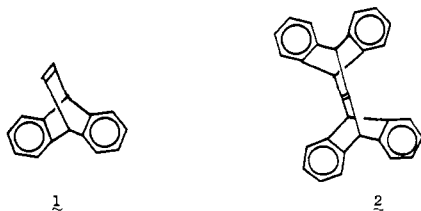
Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129. Received January 11, 1979

Abstract: Dibenzobarrelele (**1**) and dehydrojanusene (**2**) are unreactive toward singlet oxygen under photosensitization with tetraphenylporphyrin (TPP), methylene blue (MB), or rose bengal (RB) in visible light. With a medium-pressure mercury vapor lamp, **2** gives a minor amount of epoxide and extensive di- π -methane rearrangement into **6**, whose structure was established by X-ray diffraction analysis. **6** was obtained in high yield by photosensitization with benzophenone or acetone; with acetone as solvent an addition product of ketone to hydrocarbon **6** (but not to **2**) was also formed, for which structure **10** is suggested. In mixtures, the rearrangement of **2** was 1.5–2.0 times as fast as the known rearrangement of **1** to **8**. Biacetyl and benzil photosensitize the epoxidation of both **1** and **2** to photounstable epoxides. Under the epoxidation conditions, the epoxide from **1** is converted into substantial amounts of anthraquinone. Under the conditions of photoepoxidation, anthracene (also observed in these reactions) is oxidized to anthraquinone along with some carboxylic and phenolic products.

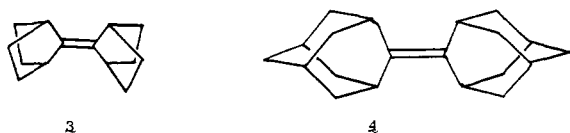
Introduction

The known compounds dibenzobarrelele (**1**)^{2a} and dehydrojanusene (**2**)^{2b} belong to a general class of hydrocarbons

that have proved important in the study of photooxidation. Along with 7,7'-binorbornylidene (**3**) and biadamantylidene (**4**), these hydrocarbons possess special hindrance to any re-



action involving their allylic hydrogens, since these hydrogens are all at bridgeheads; for this reason **3** and **4**, atypically for

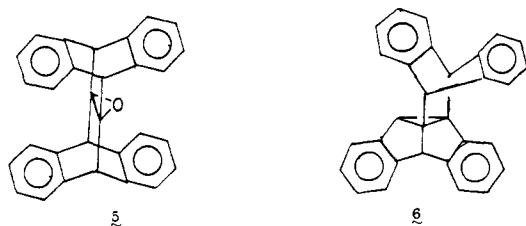


hydrocarbons, react with singlet oxygen to yield dioxetanes which are, incidentally, remarkably stable thermally.^{3,4} The latter hydrocarbons have the additional property of yielding, on photosensitization with rose bengal and certain other sensitizers, mixtures of dioxetanes and epoxides,⁴ the latter arising in a competitive mechanism or mechanisms not yet understood. In a program to characterize these processes we have examined the photooxidations of **1** and **2**.

Results

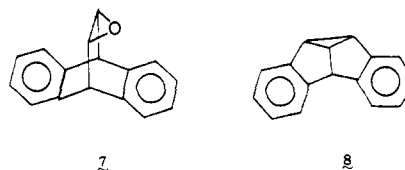
Under singlet oxygen forming conditions (methylene blue or tetraphenylporphin in methylene chloride, irradiated by a 500-W tungsten projection lamp) neither **1** nor **2** formed any dioxetane in times up to 20 h, conditions under which the oxidation of 7,7'-binorbornylidene would be complete. **1** and **2** are accordingly at least two orders of magnitude less reactive toward singlet oxygen than **3**, which in turn is less reactive than **4** by a factor of at least 5.⁶

In the case of **2**, when the light source was a Hanovia 450-W medium-pressure mercury lamp, a slow epoxidation was observed and a more rapid photoisomerization of the hydrocarbon, still with no dioxetane being produced. Irradiation for 1 h with 5 mol % of methylene blue led to bleaching of the solution to a pale green and the consumption of 67% of the hydrocarbon. The epoxide **5** was found in 3.8% yield, and the hydrocarbon **6** in 21% yield. The structure of **6** as a di- π -



methane rearrangement product was shown by X-ray determination of its crystal structure; its ¹H and ¹³C NMR spectra were in accord with this structure. Similar irradiation of **2** for 3 h with tetraphenylporphine led to consumption of the sensitizer. 74% reaction of **2**, 7.6% of the epoxide, and 38% of the rearrangement product **6**.

Epoxides are generally more favorably formed by sensitization with biacetyl or benzil,⁷ and this proved to be true of **1** and **2**. Dehydrojanusene, on photosensitized oxidation with biacetyl for 1 h, yielded 49% of its epoxide along with several other products. Irradiation with benzil for 0.5 h gave 48% of the epoxide. In both cases the epoxide disappeared on further irradiation and anthraquinone was formed in increasing amounts. Dibenzobarrelene (**1**) on irradiation in the presence of oxygen with 1.25 equiv of biacetyl for 0.5 h gave about 20% of epoxide **7**, 5.5% of anthracene, and 20% of anthraquinone. Although anthracene was involved in the original preparation of **1**, its absence in the starting material of these experiments



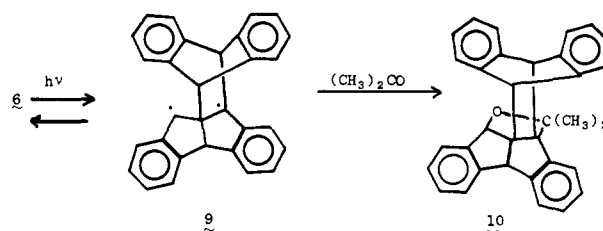
was confirmed by NMR and TLC analysis. Epoxide **7** was quickly destroyed under the conditions of its formation; a sample prepared from **1** with *m*-chloroperbenzoic acid underwent rapid decomposition even on irradiation in chloroform in the absence of oxygen, although no anthracene was formed in this process. Anthracene, on the other hand, was rapidly converted by photooxidation in the presence of biacetyl into anthraquinone (52%), aromatic carboxylic acids, and phenols. The lability of the epoxides to irradiation, and the number of products formed, accounts for poor material balances in the sensitization experiments with methylene blue and tetraphenylporphine with the mercury lamp.^{7b}

In 1 h of irradiation of dehydrojanusene in methylene chloride with benzophenone as sensitizer, 53% of the di- π -methane rearrangement product (**6**) was obtained, with 6.9% of epoxide **5**. In the case of dibenzobarrelene, under the same conditions the reaction was slower (only 79% reaction instead of 95% with dehydrojanusene) and the 29% of the known^{8c} rearrangement product **8** was accompanied by 50% of unidentified products including no detectable amount of epoxide.

Many di- π -methane rearrangements are best carried out by irradiation of acetone solutions. Indeed, in the case of **1**, the rearrangement occurs in 96% yield on 1-h irradiation of an acetone solution. In the case of **2**, direct irradiation of a methylene chloride solution under argon for 3 h afforded a 74% yield of the rearrangement product **6**. However, the sensitization of this reaction by acetone was complicated by formation of an acetone adduct. After 3 h of irradiation of a solution of dehydrojanusene (**2**) in 1:2 acetone-methylene chloride, a 29.6% yield of the rearrangement product was accompanied by 19.9% of a crystalline compound whose ¹H NMR spectrum showed two different methyl singlets at 0.12 and 0.58 ppm, along with four well-separated methine singlets and the expected aromatic multiplet. This lack of symmetry shows that the acetone adduct cannot be an oxetane formed by direct addition of acetone to **2**, but it could be easily derived from a biradical intermediate in the di- π -methane rearrangement. However, when a similar irradiation was carried out for only 1 h, only **6** was obtained, and in 85% yield. Therefore the acetone adduct is formed, not on the way to **6**, but as a product of further irradiation of **6** itself. The fact that the three-membered ring of **6** could open to a doubly benzylic biradical makes the mechanism of Scheme I appear likely. The biradical (**9**) depicted in this scheme has more electron delocalization than is possible for the isomeric biradical immediately preceding **6** in the di- π -methane rearrangement. The orientation shown for the acetone moiety in **10** is based only on an expected preference for attachment of the O atom of acetone at the secondary site in **9**.

An equimolar mixture of **1** and **2** was irradiated in methylene chloride-acetone for 14 min. In that time, NMR analysis

Scheme I



showed that total conversion was less than 50%, and that the rearrangement of **2** was the faster by a factor of 1.5–2.0.

Discussion

A purpose in examining the photooxidations of **1** and **2** was to search for special rate effects that might be diagnostic of the nature of the intermediates in photoepoxidation. The only such effect in these compounds is their failure to give dioxetanes with singlet oxygen under conditions where in general dioxetanes are not rapidly photolyzed. Since there is no hindering structure near the double bond, we conclude that this unreactivity is due to the decreased electron-donor character of the double bond, which is the most common reason for low reactivity toward singlet oxygen. It has been noted previously⁹ that singlet oxygen is among the reagents most sensitive to this property, while photoepoxidation with α -diketones⁷ is very much less so. Cristol and Imhoff have reported² reactivity ratios for **2**/**1** of 20 toward *m*-chloroperbenzoic acid and of 1.5 toward bromine. The great instability of the epoxides under the conditions of their formation and the complexity of the competitive reactions and of the product mixtures made it impossible to obtain a reliable reactivity ratio for photoepoxidation.

In previous comparisons of reactivity toward singlet oxygen, 7,7'-binorbonylidene (**3**) has been observed to be about five times less reactive than biadamantylidene (**4**).⁶ With the substituents flanking the double bond being as similar as they are, this difference must be correlated directly with the rehybridization at the doubly bonded carbon atoms associated with the small differences in bond angles forced by the attached rings. Anything that makes the angle at the doubly bonded carbon atoms other than 120° disturbs the p character of the orbital available at that atom and makes the π character of the double bond less than optimal.

In contrast to **3** and **4**, the angle constraint acting on the olefinic carbons of **1** and **2** is similar in both cases, and would not be expected to make **1** less reactive than **2** for reasons of rehybridization. The rather clear case of peracid epoxidation shows that here, as usual, the tetrasubstituted double bond is more active than the disubstituted one toward an electrophilic reagent. The results here seem to be largely determined by competition between energy donation by the sensitizer to the hydrocarbon and to oxygen, or alternatively between different sequels to energy acceptance by the hydrocarbon. Thus, while the present results appear quite negative with respect to steric effects in photoepoxidation, they are consistent with hypotheses⁵ that energy transfer to the substrate is involved in the process. This aspect of substrate reactivity is currently under investigation.

The photochemical di- π -methane rearrangements of **1** into **8** and **2** into **6** are quite distinct from the rearrangements of **2** into isojanusenes¹⁰ repeatedly observed in thermal ionic reactions, or even in photolysis of certain bromides. Whereas a cationic center induces migration of an aromatic group to an adjacent position resulting in the isojanusene structure, the three-membered ring forms with great readiness from an excited state of the structure of **1** or **2**. As far as present evidence goes, the products from these two processes seem to be mutually exclusive.

Crystal Data and Refinement. Tetrabenzopentacyclo[6.2.2.2^{2,6}.0^{2,7}.0^{3,7}]tetradecatetraene-4,5,9,10,11,12,13,14 (**6**) was recrystallized from a methanol-chloroform mixture, and a crystal of dimensions 0.1 × 0.3 × 0.35 mm was used to collect all X-ray data. The unit cell was found to be orthorhombic (*Pbca*) and room temperature cell dimensions were obtained by a least-squares fit to 15 medium-angle reflections yielding $a = 21.186$ (9) Å, $b = 16.865$ (9) Å, $c = 11.298$ (5) Å, $V = 4037$ (4) Å³, $Z = 8$, and $d_c = 1.252$ g cm⁻³. Intensity data for $2\theta < 120^\circ$ were collected on a Syntex P2₁ diffrac-

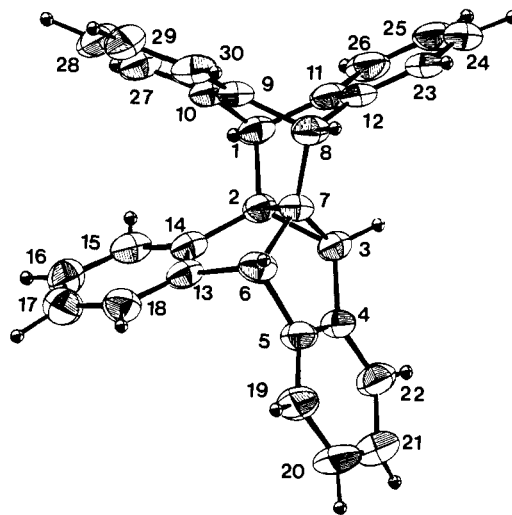


Figure 1.

tometer by the θ - 2θ scan technique using a graphite monochromator and a variable scan speed. A periodically monitored reflection showed no significant crystal deterioration. Of the 2939 independent reflections measured, 1644 had intensities greater than $3\sigma(I)$ where $\sigma(I)$ was estimated from counting statistics. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The structure (Figure 1) was solved by direct methods using MULTAN¹³ and refined by full-matrix least-squares techniques with anisotropic thermal parameters for carbon atoms and isotropic thermal parameters for hydrogen atoms. Hydrogen atoms were located in a difference map, and were included during the final stages of refinement. Refinement with 1644 reflections was terminated at a residual of 0.068 where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. The function minimized was $\sum \omega (|F_o| - |F_c|)^2$ where $\omega = 1/\sigma(F)^2$. All parameter shifts during the final cycle were less than 0.4σ and a final difference map showed no peak larger than 0.24 e/Å³. Atomic positional parameters are given in Table I, while bond lengths, valence angles, and torsion angles are given in Tables II and III.¹⁴

The two five-membered rings 3-4-5-6-7 and 2-7-6-13-14 exhibit flattened half-chair conformations, although most

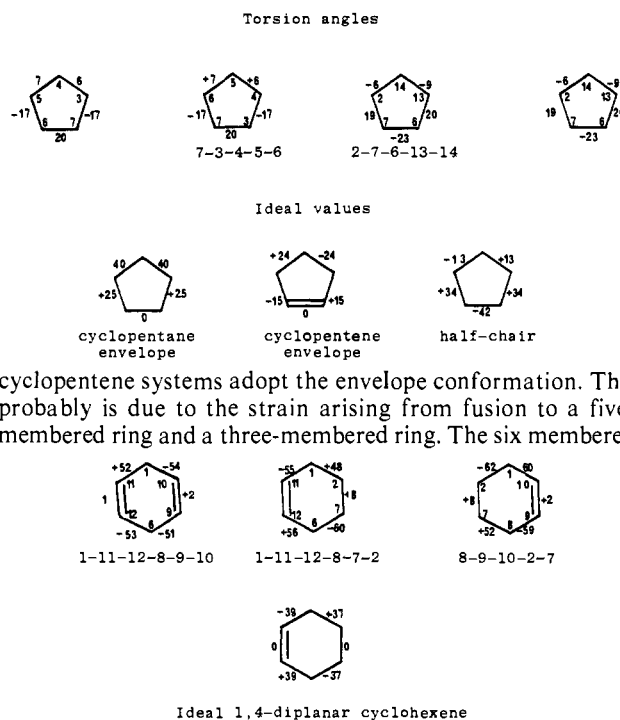


Table I. Atomic Positional Parameters $\times 10^4$ ($H \times 10^3$)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(1)	1352(2)	9932(3)	5459(4)
C(2)	2069(2)	9762(3)	5638(4)
C(3)	2501(2)	10 398(3)	6256(4)
C(4)	3200(2)	10 283(3)	6304(4)
C(5)	3352(2)	9562(3)	6847(4)
C(6)	2750(2)	9080(3)	7077(4)
C(7)	2218(2)	9714(3)	6957(4)
C(8)	1619(2)	9726(3)	7743(4)
C(9)	1211(2)	9064(3)	7206(4)
C(10)	1065(2)	9187(3)	6021(4)
C(11)	1156(2)	10 611(3)	5254(5)
C(12)	1289(2)	10 506(3)	7461(5)
C(13)	2666(2)	8588(3)	5942(4)
C(14)	2325(2)	9020(3)	5097(4)
C(15)	2196(2)	8709(3)	3995(4)
C(16)	2415(2)	7929(3)	3762(4)
C(17)	2760(2)	7513(4)	4590(5)
C(18)	2892(2)	7834(3)	5687(4)
C(19)	3973(2)	9350(3)	7064(5)
C(20)	4445(2)	9886(4)	6700(6)
C(21)	4302(2)	10 604(4)	6171(6)
C(22)	3667(2)	10 807(3)	5936(5)
C(23)	1135(2)	11 076(3)	8303(5)
C(24)	0838(2)	11 774(4)	7888(7)
C(25)	0702(2)	11 875(4)	6700(6)
C(26)	0858(2)	11 301(3)	5851(5)
C(27)	0713(2)	8628(3)	5370(5)
C(28)	0541(2)	7921(3)	5954(5)
C(29)	0696(2)	7801(3)	7126(5)
C(30)	1038(2)	8366(3)	7786(5)
H(1)	128(2)	1001(2)	448(3)
H(3)	233(2)	1097(3)	631(4)
H(6)	279(2)	882(3)	796(4)
H(8)	171(2)	967(2)	870(3)
H(15)	186(2)	899(3)	341(4)
H(16)	232(2)	772(2)	300(4)
H(17)	299(3)	696(3)	440(5)
H(18)	314(2)	755(3)	631(4)
H(19)	409(2)	884(3)	766(5)
H(20)	490(2)	977(3)	687(4)
H(21)	455(3)	1100(4)	558(6)
H(22)	357(2)	1136(2)	551(3)
H(23)	123(2)	1099(2)	926(3)
H(24)	076(3)	1217(3)	856(5)
H(25)	049(3)	1246(4)	633(5)
H(26)	074(2)	1141(3)	484(4)
H(27)	061(2)	868(2)	443(3)
H(28)	029(2)	751(3)	546(5)
H(29)	061(2)	725(3)	758(5)
H(30)	118(2)	826(2)	873(4)

Table II. Intramolecular Distances (Å) and Valence Angles (deg)

C(1)–C(2)	1.559(6)	C(15)–C(16)	1.420(8)
C(2)–C(3)	1.573(7)	C(16)–C(17)	1.379(8)
C(2)–C(7)	1.526(6)	C(17)–C(18)	1.381(7)
C(3)–C(7)	1.522(7)	C(18)–C(13)	1.390(7)
C(3)–C(4)	1.495(6)	C(5)–C(19)	1.387(7)
C(4)–C(5)	1.399(7)	C(19)–C(20)	1.408(8)
C(5)–C(6)	1.534(6)	C(20)–C(21)	1.385(9)
C(6)–C(7)	1.559(6)	C(21)–C(22)	1.411(7)
C(7)–C(8)	1.550(6)	C(22)–C(4)	1.391(7)
C(8)–C(9)	1.536(7)	C(12)–C(23)	1.391(7)
C(9)–C(10)	1.390(7)	C(23)–C(24)	1.416(8)
C(10)–C(1)	1.533(7)	C(24)–C(25)	1.383(10)
C(1)–C(11)	1.515(7)	C(25)–C(26)	1.402(9)
C(11)–C(12)	1.404(7)	C(26)–C(11)	1.399(7)
C(12)–C(8)	1.523(7)	C(10)–C(27)	1.409(7)
C(6)–C(13)	1.538(7)	C(27)–C(28)	1.411(8)
C(13)–C(14)	1.401(6)	C(28)–C(29)	1.379(8)
C(14)–C(2)	1.495(7)	C(29)–C(30)	1.410(8)
C(14)–C(15)	1.377(6)	C(30)–C(9)	1.398(7)
C(1)C(11)C(12)	115.1(5)	C(13)C(14)C(15)	121.4(5)
C(11)C(12)C(8)	113.9(5)	C(14)C(15)C(16)	117.1(5)
C(12)C(8)C(9)	106.7(5)	C(15)C(16)C(17)	121.2(5)
C(8)C(9)C(10)	113.5(5)	C(16)C(17)C(18)	121.2(5)
C(9)C(10)C(1)	115.6(5)	C(17)C(18)C(13)	118.4(5)
C(10)C(1)C(11)	105.4(5)	C(18)C(13)C(14)	120.7(5)
C(11)C(1)C(2)	109.2(5)	C(4)C(5)C(19)	121.3(6)
C(1)C(2)C(7)	109.7(5)	C(5)C(19)C(20)	117.2(6)
C(2)C(7)C(8)	112.9(5)	C(19)C(20)C(21)	122.1(6)
C(7)C(8)C(12)	105.5(5)	C(20)C(21)C(22)	120.1(6)
C(7)C(8)C(9)	103.0(5)	C(21)C(22)C(4)	117.9(6)
C(2)C(1)C(10)	100.6(5)	C(22)C(4)C(5)	121.3(6)
C(2)C(3)C(7)	59.1(4)	C(11)C(12)C(23)	122.0(6)
C(3)C(7)C(2)	62.1(4)	C(12)C(23)C(24)	116.9(6)
C(7)C(2)C(3)	58.8(4)	C(23)C(24)C(25)	121.1(7)
C(7)C(3)C(4)	105.9(5)	C(24)C(25)C(26)	122.0(7)
C(3)C(4)C(5)	110.8(5)	C(25)C(26)C(11)	117.3(6)
C(4)C(5)C(6)	110.1(5)	C(26)C(11)C(12)	120.8(6)
C(5)C(6)C(7)	102.9(5)	C(9)C(10)C(27)	121.4(5)
C(6)C(7)C(3)	106.3(5)	C(10)C(27)C(28)	117.3(5)
C(6)C(7)C(2)	105.7(5)	C(27)C(28)C(29)	120.8(5)
C(2)C(3)C(4)	120.3(5)	C(28)C(29)C(30)	122.1(5)
C(7)C(2)C(14)	106.2(5)	C(29)C(30)C(9)	117.2(5)
C(2)C(14)C(13)	110.0(5)	C(30)C(9)C(10)	121.3(5)
C(14)C(13)C(6)	110.4(5)	C(10)C(11)C(26)	124.1(6)
C(13)C(6)C(7)	102.3(5)	C(1)C(10)C(27)	122.8(5)
C(1)C(2)C(14)	117.0(5)	C(8)C(12)C(23)	124.1(6)
C(8)C(7)C(6)	123.5(5)	C(8)C(9)C(30)	125.1(5)
C(1)C(2)C(3)	120.0(5)	C(6)C(13)C(18)	128.9(5)
C(8)C(7)C(3)	127.6(5)	C(3)C(2)C(14)	122.8(5)
C(5)C(6)C(13)	103.9(5)	C(6)C(5)C(19)	128.5(6)
C(2)C(14)C(15)	128.0(5)	C(3)C(4)C(22)	127.8(6)

rings 1-11-12-8-9-10, 1-11-12-8-7-2, and 8-9-10-1-2-7 can be described as more strongly bent (as opposed to flattened) 1,4-diplanar forms (boat).

Experimental Section

Dibenzobarrelele, janusene, and dehydrojanusene were prepared as described by Cristol and co-workers.^{2a,b}

Dibenzobarrelele was obtained from the trans dichloride, mp 118–119.5 °C (lit. 119.5–120 °C), in 90% yield.

Addition of anthracene gave janusene in 58% yield, mp 233–235 °C, from alumina column chromatography (lit. 236–237 °C).¹¹

Dehydrojanusene was obtained from dibromojanusene and zinc-copper couple in 73% yield, mp 361–362 °C dec. Recrystallization from methylene chloride raised the melting point to 394–395 °C dec (lit. 360–361 °C dec).^{2b}

Epoxyjanusene. To a solution of 283 mg (0.74 mmol) of **2** in 30 mL of methylene chloride was added 162 mg (8 mmol) of 85% pure *m*-chloroperbenzoic acid in 25 mL of methylene chloride. This mixture was stirred in the dark at room temperature for 2 days. It was washed

with two 50-mL portions of ferrous ammonium sulfate, two 5-mL portions of sodium carbonate, and two 50-mL portions of water and dried with MgSO₄. The methylene chloride was removed and the crystalline residue was purified by preparative TLC (benzene as eluent). The purified product weighed 250 mg (85%), mp 295–297 °C dec (lit. mp 283–285 °C dec).^{2b}

Dibenzobarrelele Oxide (7). A solution of 408 mg (2 mmol) of **1** and 447 mg (2.2 mmol) of 85% pure *m*-chloroperoxybenzoic acid in 100 mL of CH₂Cl₂ was allowed to stand at room temperature for 1 week. The mixture was washed four times with 10% NaOH and then with water and dried. The methylene chloride was evaporated and the residue was recrystallized from CHCl₃–hexane to give 300 mg (68%) of **7**, mp 153–157 °C (lit.¹² mp 154–165 °C).

Treatment of Dehydrojanusene (2) under Singlet Oxygen Conditions. Dehydrojanusene was exposed to singlet oxygen under the following conditions: a) a 2×10^{-3} M solution of dehydrojanusene in methylene chloride, with oxygen bubbling through the solution, was irradiated (a) for 16 h in the presence of 10^{-4} M tetraphenylporphine; (b) for 24 h with 10^{-4} M methylene blue; (c) a 10^{-3} M solution of **2** in 1:1 methylene chloride–acetone, 5×10^{-5} M in rose bengal, was irradiated

Table III. Selected Torsion Angles (deg)

1-11-12-8	1	1-11-12-8	1	8-9-10-1	2
11-12-8-9	-53	11-12-8-7	56	9-10-1-2	60
12-8-9-10	51	12-8-7-2	-60	10-1-2-7	-62
8-9-10-1	2	8-7-2-1	8	1-2-7-8	8
9-10-1-11	-54	7-2-1-11	48	2-7-8-9	52
10-1-11-12	52	2-1-11-12	-55	7-8-9-10	-59
7-3-4-5	6	7-2-14-13	-6	4-3-2-14	1
3-4-5-6	7	2-14-13-6	-9	7-2-3-4	91
4-5-6-7	-17	14-13-6-7	20	6-7-2-3	-100
5-6-7-3	20	13-6-7-2	-23	3-7-2-14	119
6-7-3-4	-17	6-7-2-14	19	8-7-2-14	-119
5-6-13-18	91	8-12-23-24	179	2-14-15-16	170
4-5-6-13	90	1-10-27-28	172	6-13-18-17	-179
1-11-26-25	180	8-9-30-29	-176	3-4-22-21	174
				6-5-19-20	176

ated for 17 h, all with a 500-W projection lamp. On workup the dehydrojanusene was recovered in yields of 82, 89, and 89%, respectively, and no oxidation product was detected.

Experiments similar to (a) and (b) were carried out with a Hanovia 450-W medium-pressure mercury light source instead of the projection lamp. The tetraphenylporphine turned dark green in 3 h and the methylene blue turned pale green in 1 h under this illumination. Preparative TLC of the TPP product yielded 26% of recovered **2**, 7.6% of epoxide **5**, and 38% of rearrangement product **6**. From methylene blue the yields were 33% recovered **2**, 3.8% **5**, and 21% **6**. In neither case was any singlet oxygen product observed, although there were a number of unidentified products in small amounts.

Dibenzobarrelene (**1**) was recovered quantitatively after irradiation in methylene chloride with the projection lamp for 21 h in the presence of oxygen and methylene blue.

α -Diketone-Sensitized Oxidation of Dehydrojanusene (2). A solution of 152 mg (0.4 mmol) of **2** and 43 mg (0.5 mmol) of biacetyl was saturated with oxygen and irradiated with a Hanovia 450-W medium-pressure mercury lamp for 0.5 h, oxygen being bubbled through the solution. The mixture was washed with sodium bicarbonate solution and then with water and dried. After removal of the methylene chloride the residue was subjected to preparative TLC. Elution with benzene gave six fractions. One, weighing 78 mg, was identified as dehydrojanusene oxide (**5**, 49%), accompanied by a small amount of anthraquinone (mp and mmp 285–287 °C). The other five fractions were less than 5 mg each.

The same treatment of **2** (152 mg, 0.4 mmol) with benzil (84 mg, 0.4 mmol) for 0.5 h led to recovery of **2** (trace), benzil (55%), dehydrojanusene oxide (48%), and 13 mg of anthraquinone. When the irradiation was continued for 1 h, only benzil (30 mg, 36%) and anthraquinone (22 mg) were recovered in appreciable amounts. The epoxide is obviously unstable under the conditions of irradiation.

Benzophenone-Sensitized Oxidation of Dehydrojanusene (2). A solution of 152 mg (0.4 mmol) of **2** and 73 mg (0.4 mmol) of benzophenone in 20 mL of methylene chloride was irradiated for 1 h with oxygen bubbling through the solution. After removal of the solvent the viscous, oily residue was subjected to preparative TLC. Elution with methylene chloride gave recovered **2** (7 mg, 4.6%), benzophenone (73 mg, 100%), anthraquinone (3 mg, 3.6%) dehydrojanusene oxide (**5**, 11 mg, 6.9%), and the rearranged hydrocarbon **6** (81 mg, 53%).

Benzophenone-Sensitized Rearrangement of 2. A solution of 76 mg (0.2 mmol) of **2** and 36 mg (0.2 mmol) of benzophenone in 10 mL of methylene chloride in a 20-mL Pyrex test tube was saturated with argon and irradiated with the mercury lamp for 1 h. Preparative TLC yielded, on elution with benzene, 64 mg (84%) of **6** and 34 mg (94%) of recovered benzophenone.

Characterization of the Di- π -methane Rearrangement Product 6. A sample of **6** recrystallized from CH₂Cl₂-MeOH formed colorless needles: mp 247–249 °C with some decomposition; ¹H NMR (δ in CDCl₃) 2.63 (s, 1 H), 4.31 (s, 1 H), 4.58 (s, 1 H), 4.99 (s, 1 H), and 6.6–7.3 (m, 16 H); ¹³C NMR (ppm, CDCl₃) 154.96, 152.95, 144.69, 142.81, 142.49, 140.08, 139.50, and 137.29 (benzene ring carbons carrying no hydrogen), 126.31, 126.05, 125.14, 124.68, 124.16, 123.77, and 120.98 (benzene ring carbons carrying hydrogen), 66.47 and 52.95 (quaternary carbon), 56.14, 50.48, 48.99, and 47.23 (methine carbon).

Anal. Calcd for C₃₀H₂₀: C, 94.70; H, 5.30. Found: C, 94.63; H, 5.33.

Acetone-Sensitized Rearrangement of 2. A solution of 152 mg (0.4 mmol) of **2** in 30 mL of a mixture of acetone and methylene chloride (1:2) in a 50-mL Pyrex test tube was saturated with argon and irradiated for 3 h. The pale yellow mixture was evaporated and the residue subjected to preparative TLC. Elution with CH₂Cl₂-CCl₄ (1:4) gave 45 mg (29.6%) of **6** and 35 mg (19.9%) of crystalline acetone adduct. The latter was further purified by preparative TLC with benzene as eluant: ¹H NMR (δ , CDCl₃) 0.12 (s, 3 H, methyl), 0.58 (s, 3 H, methyl), 3.28 (s, 1 H, methine), 3.95 (s, 3 H, methine), 4.23 (s, 1 H, methine), 4.65 (s, 1 H, methine), and 6.8–7.6 (m, ca. 16 H, aromatic).

In the same length of irradiation, in methylene chloride without acetone, 76 mg of **2** in 10 mL of methylene chloride yielded 74% of the rearrangement product **6**.

One-hour irradiation of a solution of 76 mg (0.2 mmol) of **2** in 12 mL of a mixture of acetone and methylene chloride (1:5) gave 65 mg (85%) of **6** as the sole product. Any acetone adduct of **6** could have been detected by NMR.

Acetone-Sensitized Rearrangement of Dibenzobarrelene (1). A solution of 164 mg (0.8 mmol) of **1** in 20 mL of acetone was irradiated for 1 h.^{8b} The crystalline residue after evaporation was purified by preparative TLC to give 158 mg (96%) of **8**, mp 99–100 °C from methanol (lit. mp 105 °C).^{8c}

Photoepoxidation of Dibenzobarrelene with Biacetyl. A solution of 82 mg (0.4 mmol) of dibenzobarrelene (**1**) and 43 mg (0.5 mmol) of biacetyl in 20 mL of methylene chloride in a Pyrex test tube was saturated with oxygen and irradiated with the mercury lamp for 0.5 h, oxygen being bubbled through the solution. The resulting yellowish-orange mixture was washed with sodium bicarbonate and water and dried. The methylene chloride was evaporated. The NMR spectrum of the solution indicated about 20% each of **1** and its epoxide **7**, along with other products. By silica gel column chromatography 4 mg (5.5%) of anthracene and 17 mg (20%) of anthraquinone were isolated (mp of anthraquinone, recrystallized from benzene, 285–287 °C).

Irradiation of a sample of **7** in chloroform for 0.5 h caused considerable decomposition to a complex mixture, in which it was not possible to identify any anthracene.

Sensitized Oxidation of Anthracene. A solution of 178 mg (1 mmol) of anthracene and 86 mg (1 mmol) of biacetyl in 20 mL of methylene chloride was saturated with oxygen and irradiated for 0.5 h with the Hanovia medium-pressure mercury lamp. Workup in stages gave a total of 110 mg (52%) of anthraquinone along with 18 mg of phenolic material and some insoluble aromatic carboxylic acids.

Competitive Di- π -methane Rearrangement of 1 and 2. A solution of 41 mg (0.2 mmol) of **1** and 76 mg (0.2 mmol) of **2** in 10 mL of methylene chloride and 2 mL of acetone was irradiated for 15 min. The faintly yellow mixture was evaporated under reduced pressure to leave a crystalline residue, which was analyzed by NMR. The amounts of the two rearrangement products were determined by comparing the intensities of the cyclopropane signals of **8** (2 H) and **6** (1 H). The results indicate that **2** rearranged faster than **1** by a factor between 1.5 and 2.0.

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Supplementary Material Available: Anisotropic thermal parameters, selected torsion angles, and structure factor tables (15 pages). Ordering information is given on any current masthead page.

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- ratory has observed that, if the light from this source is filtered through a solution of 75 g of sodium nitrite per 100 mL of water, 1 can be epoxidized with as little as 10% photodestruction of the epoxide, while epoxidation with light from a G.E. sodium lamp proceeds in good yield with no more than traces of anthracene and anthraquinone being formed.
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Photochemical Electron Transfer in Monolayer Assemblies. 1. Spectroscopic Study of Radicals Produced in Chlorophyll *a*/Acceptor Systems

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Abstract: Chlorophyll monolayers together with an acceptor species such as sublimed chloranil cause a light-induced electron paramagnetic resonance (EPR) signal. Under steady-state illumination, the rise and decay of this signal were of the order of minutes. Under flash illumination, the decay time of this signal was 0.6 ms and was temperature independent. An experiment using deuterated chlorophyll monolayers with bromanil resulted in a narrow light-induced signal with a *g* factor of 2.0025 and a broad signal with a *g* factor near 2.009. These signals were attributed to the chlorophyll radical cation and the bromanil anion, respectively. In a separate experiment we generated the chlorophyll radical cation in monolayers using iodine vapor. The resulting EPR signal had a *g* factor of 2.0025 and the life width indicated that the signal was due to monomeric chlorophyll species. We also measured the magnetic circular dichroism (MCD) spectrum of monolayer assemblies of chlorophyll with surface-active acceptor species. We found light-induced bleaching at 680 nm with enhancement occurring at 660 and 672 nm.

Introduction

Although the details of photosynthesis are not yet fully understood, the concept of a functional unit, such as a reaction center, containing a donor and an acceptor is central to the mechanism of photosynthesis. Monolayers are often studied in an attempt to mimic the aggregation states of chlorophyll (Chl) and the donor-acceptor functional unit of photosynthesis. It is believed that thin barriers of less than 100 Å in thickness are instrumental in mediating the primary charge separation.^{1,2} The monolayer model systems are attempts to mimic such a barrier. A number of studies have characterized the surface properties of the Chl monolayer,³⁻⁵ as well as its spectroscopic properties.^{6,7}

In this paper, we have constructed monomolecular films of Chl together with acceptors in an attempt to model the donor-acceptor electron transfer reaction found in photosynthesis. In part 1, we describe the electron paramagnetic resonance (EPR) results and the magnetic circular dichroism (MCD) results of this study. In part 2,⁸ we describe the photoelectric phenomena in these monolayer assemblies.

Experimental Section

Monolayer Preparation. Great care is required in the preparation of monolayer systems, particularly in Chl monolayer systems.^{5,9,10} To eliminate vibrations, the film balance was placed below ground level in the basement of the building; elsewhere in the building vibrations were too disruptive. The balance was covered with a Plexiglas box at all times to prevent dust contamination. Nitrogen gas was admitted to the balance chamber in an attempt to minimize degradation

of the chlorophyll film by atmospheric oxygen. The film balance was a Cenco torsion balance. The trough, coated with Bakelite, was carefully washed with Decon 75 (BDH) detergent, rinsed thoroughly with doubly distilled water, and dried. The entire surface was coated with a film of paraffin wax dissolved in benzene to leave the surface hydrophobic. The torsion barrier was made of Teflon with flexible Teflon tape closing off the ends. The subphase was triply distilled water. House distilled water was further distilled from KMnO₄, then from glass. The pH of the subphase was adjusted to 7.5 by adding phosphate buffer (10⁻⁴ M).

The pressure-area curve of the chlorophyll *a* monolayer is shown in Figure 1. This curve agrees well with that reported in the literature by Hirsch et al.¹¹ The experiments involving Chl were carried out in a dim green light, just bright enough to permit the manipulation of the apparatus. The Chl was spread with a benzene solvent.⁴ After the benzene had evaporated, the surface pressure was very gently increased to 20 dyn cm⁻¹, which is below the collapse point of the Chl monolayer.⁹ Then the sample slides were dipped. After the downward dip, the surface pressure was readjusted and the upward dip proceeded. In this way, we attempted to eliminate random fluctuations in the surface pressure during the dipping procedure. The Chl thus was deposited in the pressure range of 17.5–20 dyn cm⁻¹. The glass substrates used were relatively small, less than 5% of the water surface area covered with Chl.

The monolayers were deposited on Corning microscope slide covers. These were first cut to size to fit into the EPR cavity (10 × 22 mm). They were washed in ethanol or acetone, then boiled in concentrated nitric acid for 3–4 h. The slides were then washed with doubly distilled water repeatedly, then with absolute ethanol, and were then dried. The substrates were then placed in a chloroform solution containing dimethyldichlorosilane¹² for a period of 15 min. After further washing with chloroform, the slides were dried. Only those slides which shed water perfectly were used for depositing monolayers. The slides were then suspended vertically from a system of levers driven by a phase tracking motor via a cardiodal cam resulting in an approximately

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