188. The Irreversible Photochemistry of Bianthrone

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Summary. A 4a,4b-dihydrophenanthrene-type cyclic photoisomer, the **C** isomer, is the major primary photoproduct of bianthrone in protic and aprotic polar solvents, and undergoes solvent-dependent secondary reactions, including the formation of dihydrohelianthrone in protic solvents. The **C** isomer was shown to be formed through the singlet excited state while the **B** isomer is formed *via* the triplet manifold.

Introduction. – The photochemistry of bianthrone, I, and of its derivatives involves both reversible and irreversible reactions [1a] [2]. At low temperatures these molecules photoisomerize to the **B** modifications (*e.g.* Fig. 2, curve B) which revert thermally to the starting fundamental forms (denoted as **A**) upon heating. At high temperatures those derivatives not substituted at the 1,1′ positions undergo irreversible photoreactions competing with the formation of the **B** isomer [1a]. Derivatives substituted at the 1 and 1′ positions do not undergo irreversible photoreactions, but in several of these one observes the additional formation of another photoisomer denoted as **C**, which also reverts thermally to **A**. The [**C**]/[**B**] ratio is much higher in polar or strongly polarizable solvents. It falls off at lower temperatures so that eventually **B** becomes the sole photoproduct [1a] [2]. A cyclic structure, similar to II, was assigned to the **C** isomers on the basis of low-temperature ^{1}H-NMR. spectra [1a] [3]. The structure of the **B** isomer was found to involve torsion of *ca.* 57° about the central double bond (see [4]). Here too the structure determination was based both on low-temperature ^{1}H-NMR. measurements and on minimum-strain-energy-type conformational analysis [4]. **B** was shown to be formed *via* the triplet manifold [1] [5] [7]¹).

The irreversible photochemistry of bianthrone has been extensively studied by *Brockmann & Mühlmann* [8]. They observed the following processes:

(i) $2\ \mathrm{IV} \xrightarrow{h\nu} \mathrm{III} + \mathrm{VI}$

(ii) $3\ \mathrm{I} \xrightarrow{h\nu} 2\ \mathrm{V} + \mathrm{VI}$

(iii) $\mathrm{III} + O_2 \longrightarrow H_2O_2 + \mathrm{IV}$

(iv) $\mathrm{V} + O_2 \longrightarrow H_2O_2 + \mathrm{I}$

(v) $\mathrm{III} + \mathrm{I} \longrightarrow \mathrm{IV} + \mathrm{V}$

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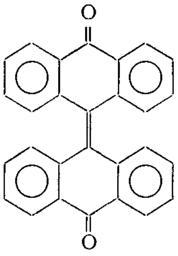
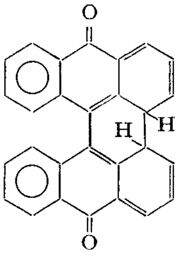
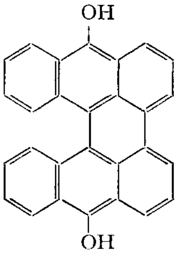
¹) In [5b] the controversy with the Swiss authors [6] is resolved.



I ≡ *A*



II ≡ *C*-type isomers



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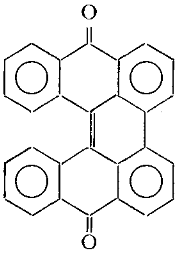

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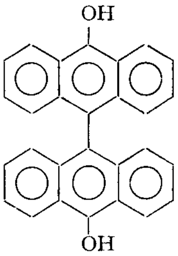

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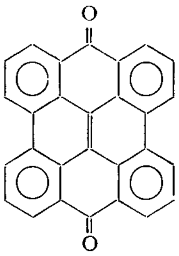

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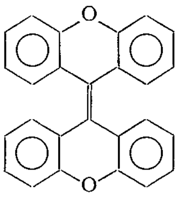

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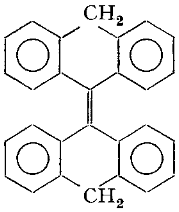

VIII

Flash-photolytic techniques were applied to the dianthrones by *Dombrowski* [7] and by *Becker* [9]. The latter postulated a detailed mechanism of the I → IV photoreaction, involving also the **B** isomer. The involvement of **B** was challenged [1], as this isomer is not dehydrogenated by oxygen neither thermally nor photochemically.

In an effort to establish common reaction mechanisms for bianthrone and its 1,1'-disubstituted derivatives, we have performed a flash-photolytic search for a cyclization product II, similar to the **C** isomer observed with the 1,1'-dimethyl and the 1,1', 3, 3'-tetramethyl-derivatives of I. This cyclic form could act as a primary photoproduct in the course of the photocyclodehydrogenation I → IV. In this context we also reinvestigated the photobehavior of I in a wide range of solvents and temperatures, employing static low temperature methods. These results will be described first.

Results. – Dihydrohelianthrone, III, whose structure was suggested and proven by *Brockmann* [8], is tautomeric with the postulated **C** isomer, II. III is formed photochemically from I only in deaerated polar solvents such as propanol or 2-methyltetrahydrofuran. III is stable even at room temperature in the absence of oxygen or other oxidizers. It is characterized by absorption peaks at 610 and 575 nm (curves 2–5 in Fig. 1), and is formed at temperatures from – 100° to + 20°, the quantum

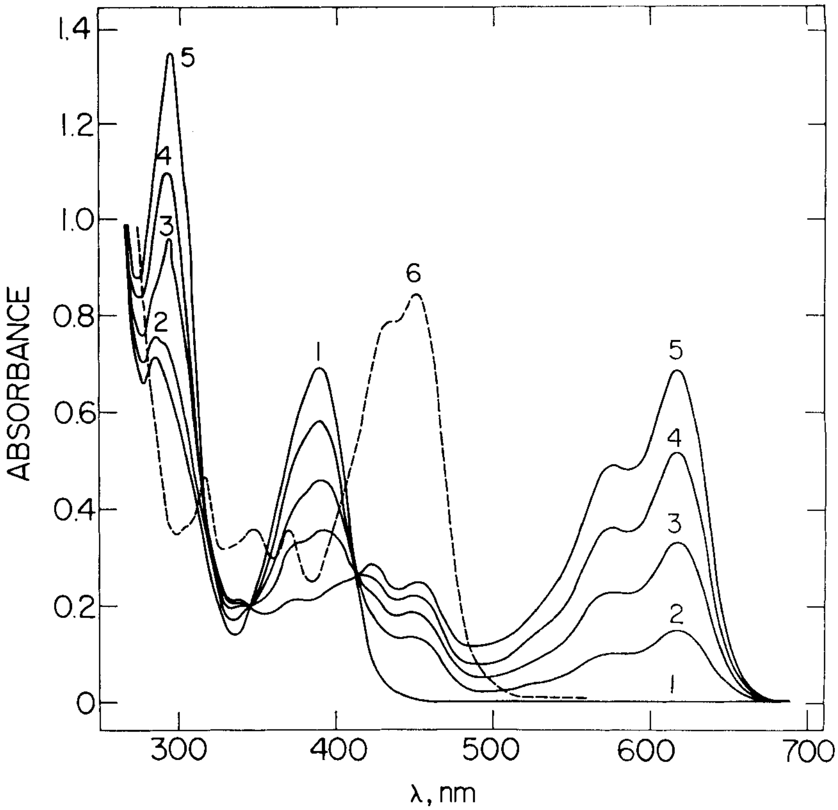

Fig. 1. *Bianthrone in 2-propanol* (–75°, 5 × 10^{-5} M). *Curve 1:* before irradiation. *Curves 2–5*: progressive irradiations at 405 nm. *Curve 5* is the absorption spectrum of pure dihydrohelianthrone (III). *Curve 6* is the absorption spectrum of helianthrone (IV) formed on admission of air into the cell.

yield being around 0.4. At lower temperatures its formation is less efficient, and it virtually stops below – 130°, where photoisomer **B** is formed instead. In the intermediate region, between – 100° and – 130°, a mixture of III and the **B** isomer is obtained. Typical absorption changes occurring during the photoconversion I → III at – 75° are shown in Fig. 1, curves 1–5. Isosbestic points exist at 413 and 345 nm and suggest a two-component system, or at least a system whose composition is determined by a single parameter. Almost complete conversion I → III can be obtained. Flushing with air causes rapid oxidation to helianthrone, IV, even at – 75° (Fig. 1, curve 6). As long as the photoconversion I → III is incomplete, or when I and III are mixed, a slow thermal oxidation-reduction takes place, resulting in the formation of helianthrone, IV, and bianthranol, V (equation [v]).

This process can be disregarded if the photoconversion I → III is carried out rapidly. At the concentrations studied, ($[I] = 2 \times 10^{-5}$M; $[III] = 3.2 \times 10^{-5}$M) the half-life time, $\tau_{1/2}$, for reaction (v) is 10 min at 20°. III was found to be light stable. $\tau_{1/2}$ for oxidation of III in air-saturated solutions as given by reaction (iii) was ∼3 min at – 75°. The question if the air-oxidation proceeds by a free radical $HO_2^{\cdot}$ chain mechanism [12] was studied by employing the strong $HO_2^{\cdot}$ inhibitor 2,6-di-*t*-butyl-4-methyl-phenol. Under the usual conditions, $[I] = 5.2 \times 10^{-5}$M at a concentration of 1.8×10^{-1}M of the inhibitor, no significant effect on the $\tau_{1/2}$ values could be observed. Thus significant oxidation through the $HO_2^{\cdot}$ chain can be ruled out.

Photosensitization experiments with biacetyl in propanol solution at – 75° indicate that the **B** isomer is the only photoproduct formed (Fig. 2, curve B). At this

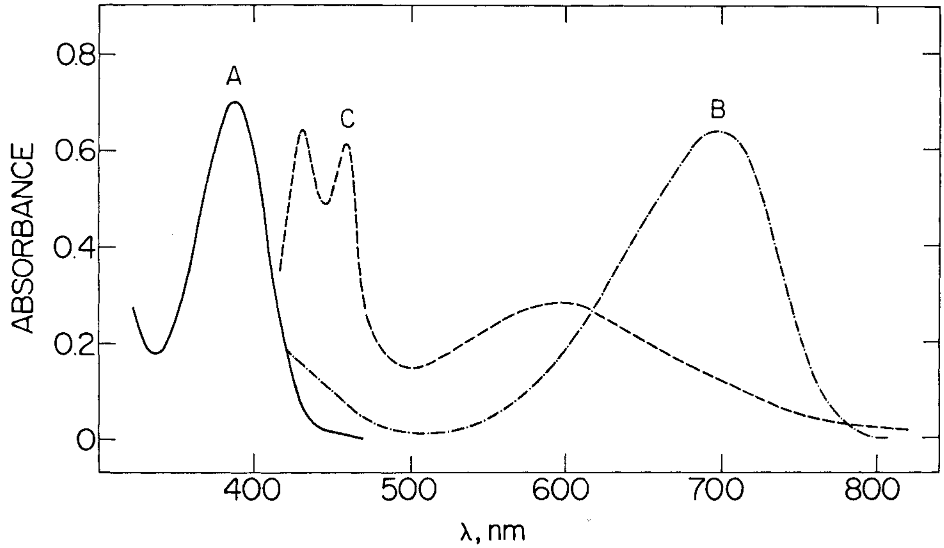

Fig. 2. *Absorption spectra of bianthrone* (*I*≡**A**) *and its* **B** *and* **C**(≡*II*) *isomers in 2-propanol* (–75°, 5×10^{-5} M). *Curve A*: before irradiation (absorption spectrum of **A** isomer); *curve B*: the absorption spectrum of the **B** isomer obtained by direct irradiation at –160°, with 405 nm light. The same spectrum is obtained by photosensitization with biacetyl (1.3×10^{-2} M) at –75°; excitation with 436 nm light. *Curve C*: primary transient in the absence of biacetyl.

temperature the **B** isomer is stable, the $\tau_{1/2}$ value for its thermal decay at $-60°$ being ~ 140 minutes. Irradiation under similar conditions in the absence of biacetyl results in III as the sole product. We therefore conclude that **B** and III are formed in competing photoreactions. Since **B** is known to be formed through the triplet manifold, III must be formed from the singlet excited state through a different path.

The mechanism of the formation of III was examined by flash photolysis experiments performed under the conditions of the steady irradiations described above. The spectrum of the transient which appears within 20 µs is given in Fig. 2, curve C. This first intermediate undergoes a complex reaction, with $\tau_{1/2} \sim 0.08$ s at $-75°$, leading to III. We suggest that this transient, whose absorption spectrum closely resembles that of the **C** photoisomer of 1,1′-dimethyl-bianthrone, is indeed II as postulated above. Neither II or III were observed in solutions of I in either aliphatic or aromatic hydrocarbon solvents. In the latter, *e.g.* benzene and toluene, **B** seems to be a major photoproduct even at 25° [7], besides the other products of irreversible photoreactions. In saturated hydrocarbon solvents, *e.g.* methylcyclohexane, IV and V are the main final photoproducts, but the mechanism of their formation could not be elucidated.

Since it was shown [1] [2] that in the 1,1′-dimethyl- and the 1, 1′, 3, 3′-tetramethyl-derivative of I the ratio [C]/[B] increases with solvent polarity, it was of interest to observe the photobehavior of solutions of I in the aprotic polar solvent acetonitrile which, unlike alcoholic solvents, may be expected not to take part in the hydrogen shift during II → III. Indeed, flash experiments in acetonitrile solutions showed the photoformation of II as a primary product, just as in 2-propanol solutions. However, no III was detected, and II disappears through other, mostly irreversible, paths.

We conclude that II is a major primary photoproduct of I in solutions in both protic and aprotic polar solvents, and undergoes rapid irreversible solvent-dependent secondary reactions, in protic solvents the major one being hydrogen shift, to form III, with direct participation of the solvent molecules.

The general mechanism for all bianthrones would thus be as follows:

$$\begin{tikzcd}
A \arrow[r] & {}^{1}A^{*} \arrow[rr] \arrow[d] & & C(\rightarrow \text{irreversible products}) \arrow[d] \\
& {}^{3}A^{*} \arrow[r] & B \arrow[r] & A
\end{tikzcd}$$

The reactions in parentheses take place only in bianthrones not substituted in the 1,1′-positions. **C**-type photoisomers were also observed in the bianthrone-like compounds bixanthylidene (VII) [10] and dihydrobianthrylidene (VIII) [11] and their derivatives. In these compounds the **C** photoisomer can be stabilized at low temperatures, whereas in bianthrone itself it could be observed only as a transient, because of efficient hydrogen shifting processes. Both ground- and excited-state abstractions by the carbonyl groups of bianthrone and of II could be involved.

Experimental Part

Bianthrone (*Koch-Light*) was used after recrystallisation under N_2; spectroscopic grade 2-propanol and acetonitrile were used without further purification; 2-methyltetrahydrofuran (*pur., Fluka*) was distilled *in vacuo* from *Woelm* basic alumina onto the solute in the cells used, which were then fused-off.

Spectrophotometry, photochemical techniques, and flash photolysis, all over a wide temperature range, were applied as described earlier [13].

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