Tetrahedron. Vol. 28, pp. 3191 to 3201. Pergamon Press 1972. Printed in Great Britain

PHOTODIMERIZATION OF HALOGENATED ANTHRONE DERIVATIVES

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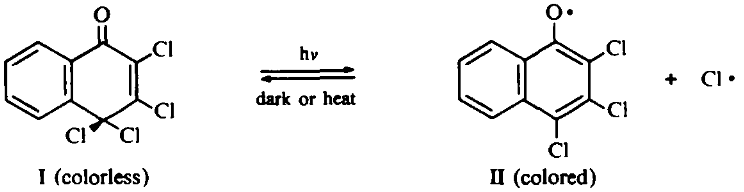
(*Received in Japan* 5 *August* 1971; *Received in the UK for publication* 6 *March* 1972)

Abstract—The photochemistry of 10-bromoanthrone (IV), 10,10-dibromoanthrone (III) and 10,10-dichloroanthrone (IX) in dioxane has been investigated. Short time irradiation in the absence of oxygen at wavelengths above 3900 Å or 4200 Å led to 10,10'-bianthrone (VII), 10,10'-dibromobianthronyl (VI), and 10,10'-dichlorobianthronyl (X), respectively. Further irradiation of 10-bromoanthrone (IV) and 10,10-dibromoanthrone (III) gives quantitatively mesonaphthobianthrone (V). Fluorescence emission spectra indicate that bianthrone (VIII) is the second intermediate in the conversion of 10-bromoanthrone (IV) and 10,10-dibromoanthrone (III) to mesonaphthobianthrone (V). The mechanism of the first step is discussed in detail. Evidence was found that formation of VI and VII proceeds by a mechanism involving the 9-anthryloxy (XIa) and 9-bromo-10-anthryloxy (XIb) radicals from the respective $^3(n,\pi^*)$. By analogy, a similar mechanism is proposed for the conversion of VI to VIII.

Recent studies on the photochemistry of halogenated carbonyl compounds have been restricted to investigations made in the gas phase,[2] whereas condensed phase photolysis has so far attracted little attention. Only a few cases have been investigated in connection with their behavior as photochromic systems. Scheibe *et al.*[3] noted that photodissociation occurs for a large number of substituted quinols in carbon tetrachloride solution. The reversible formation of naphthoxy radicals (II) from tetrachloro-1(4H)naphthalenone (I) is represented as follows:



The existence of free radicals was demonstrated by the photopolymerization of vinyl acetate induced by chlorine atoms and the fading of a solution of the triphenylmethyl radical. The photochemical behavior of halogenated anthrone derivatives when irradiated at their long-wavelength and low-intensity absorption bands seemed an interesting subject for detailed investigation.

RESULTS

Irradiation of 10,10-dibromoanthrone (III) ($n \rightarrow \pi^*$ band: λ_{max} 387 mμ, ε 40) and 10-bromoanthrone (IV) ($n \rightarrow \pi^*$ band: λ_{max} 415 mμ, ε 8) in purified dioxane (99·9%) for 24

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† One (W.K.) of the authors gratefully acknowledges financial support by the Japan Society for the Promotion of Science (Tokyo) and the "Stiftung für Stipendien auf dem Gebiete der Chemie" (Zurich, Switzerland). Present address: Sandox Ltd., Basle, Switzerland.

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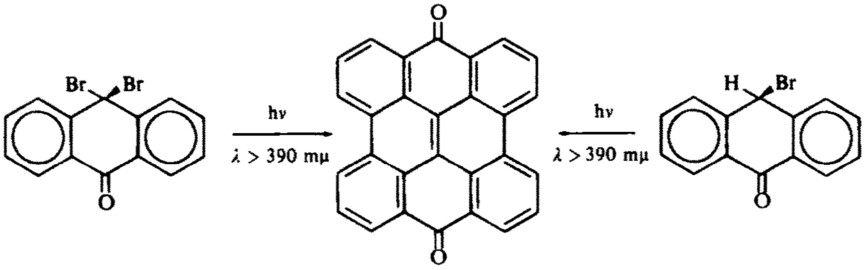
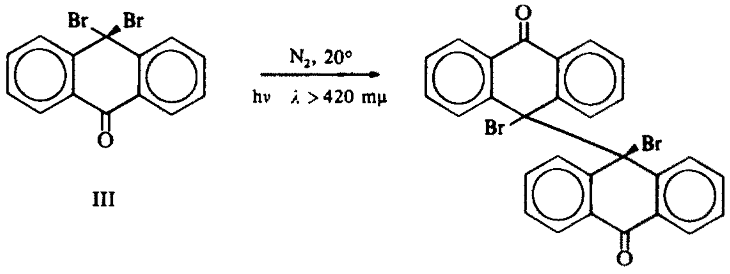
hr, using a high pressure mercury lamp (Taika Kōgyō 500 Watt—Sansui 100 Volt stabilizer) as the external light source (Glass filter transmitting above 390 mμ), gave in a 95–100% yield mesonaphthobianthrone (V), which precipitates from solution. The reactions were carried out in a cylindrical thermostated double compartment quartz cell at 20 ± 1° under purified nitrogen.



III V IV

The identity of V could be proved with the help of an authentic sample obtained by the irradiation of bianthrone.[4] Chemical and UV spectral[5] properties of the two samples were identical. The IR spectrum in KBr had a strong carbonyl peak at 1657 cm^{-1}, a value typical for polycyclic quinones with the two quinonoid carbonyls in different rings.[6] Irradiation of III in the same solvent for a much shorter time (30–90 min), using a glass filter transmitting above 420 mμ, permitted the isolation of a photodimer containing two halogen atoms and identified as 10,10′-dibromobianthronyl (VI).



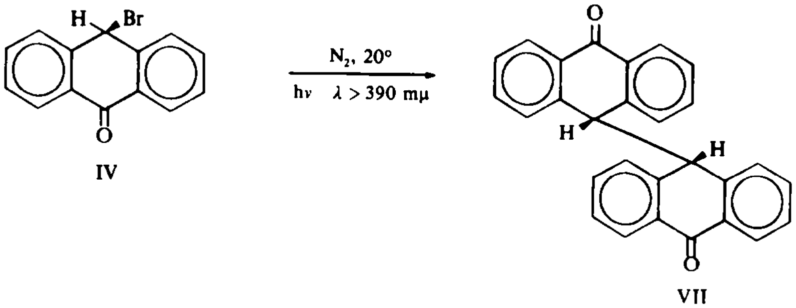
III VI

Further irradiation of VI led, as before, to mesonaphthobianthrone (V).

The structure of VI, m.p. 188° (darkens at 175°), believed to be a new compound, could be assigned by its elemental analysis and spectral (NMR and IR) data. The dimeric structure of VI was established by degradative evidence, i.e. its oxidative cleavage in 96% sulfuric acid to anthraquinone ($0\cdot963 \times 10^{-5}$ mole of VI gave $1\cdot928 \times 10^{-5}$ moles of anthraquinone).

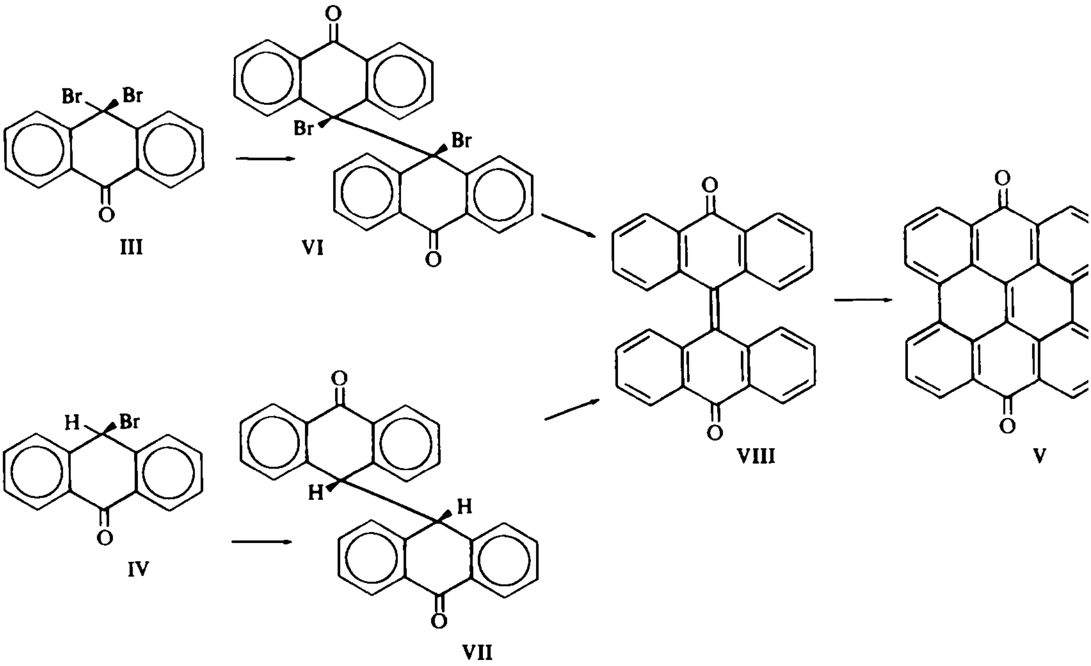
Likewise, short time irradiation of IV, using a glass filter transmitting above 390 mμ, gave photodimer VII, 10,10′-bianthrone, identified by comparison with an authentic sample.[7]

The same dimerizations were observed in $CHCl_3$ and benzene as solvents, where VI precipitates quantitatively at room temperature. Careful VPC-analysis of the recovered solvent (dioxane or benzene) demonstrated the presence of impurity peaks due to



partially brominated solvent molecules, beside HBr formation. The absence of any side reactions was confirmed by the quantitative conversion of both III and IV to mesonaphthobianthrone (V) and by liquid phase chromatography experiments, using Mallinckrodt silicic acid (100 Mess) as the stationary phase. The pH-value of the solutions, measured before and after irradiation, remained essentially constant within experimental error. It seemed reasonable to postulate that bianthrone (VIII) might be the second intermediate in the course of the photodimerization of III and IV, both giving the insoluble product V.

This fact was established by spectral evidence. The fluorescence emission spectra† of fresh samples of III, IV, VI, VII and VIII were measured in the solvent (dioxane) used for the irradiations. III, IV, VI and VII, excited between 360 and 450 mμ, did not show significant fluorescence for short irradiations (Xenon lamp 500 Watt).



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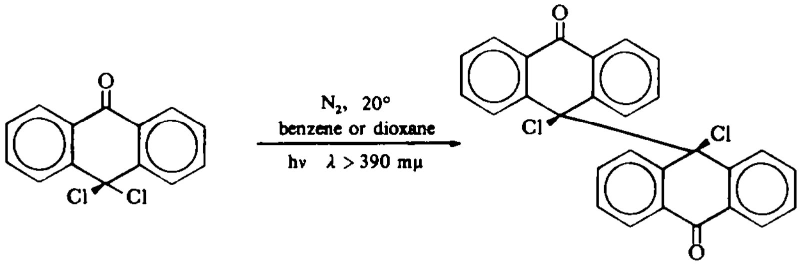
† We thank Mr. F. Takabayashi (Teijin Limited, Fiber and Textile Research Institute, Ibaraki-shi, Osaka) for recording these spectra.

After a few minutes, however, time-dependant fluorescence maxima were detected identical with the time-dependant spectrum of bianthrone.

A dimer (X) corresponding to VI was obtained quantitatively upon irradiation of 10,10-dichloroanthrone (IX) under our reaction conditions.



IX X

By using 4365 Å light no detectable amounts of mesonaphthobianthrone (V) and bianthrone (VIII) were formed upon irradiation of III at 20°, so that the first step could be followed spectrophotometrically for periods shorter than 90 min. At this point, less than 10% of III was converted. The same technique was applied for the conversion of IV to VII, using this time 4049 Å light. The light intensities were monitored with ferrioxalate and uranyl oxalate actinometers and found to be $1{\cdot}05 \times 10^{18}$ quanta/sec for 4049 Å light and $0{\cdot}80 \times 10^{18}$ quanta/sec for 4365 Å light, respectively (Experimental). The quantum yields for the conversion of starting material versus the concentration of both III and IV in dioxane at 20° are given in Fig. 1.

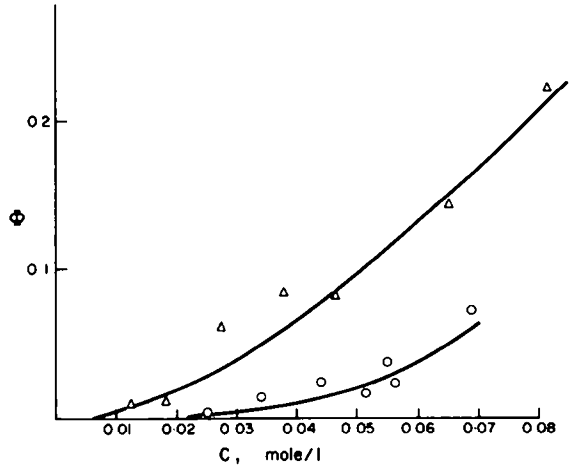


FIG. 1. Quantum yields (Φ) vs. concentration of starting material (mole/l): open circles, 10-bromoanthrone; open triangle, 10,10-dibromoanthrone.

DISCUSSION

There seem to be two alternative mechanistic routes to describe the process.

(a) Simple photodecomposition (photocleavage): The energy associated with light of 4049 Å is 70·1 kcal/mole, an amount of energy large enough for a simple photodecomposition, the C—Br bond dissociation energy being estimated in the order of 50–70 kcal/mole. The fragments would still carry excess energy. Bond cleavage, as reported by Miller *et al.*[8] and by Kharasch *et al.*[9] for bromo aromatics, plausible here on thermochemical grounds, followed by the dimerization of the fragments, is unlikely to occur on the basis of the results obtained with 10,10-dichloroanthrone (IX). The C—Cl bond dissociation energy may be of the order of 80 kcal/mole.[10], compared with 70·1 kcal of an einstein light of 4049 Å. The absence of any reaction with the solvent and the very small quantum yields for concentrations of III and IV smaller than 2×10^{-2} M (Fig. 1) cannot be rationalized in terms of the suggested photocleavage.

(b) n-π^* Excitation: This process seems to be consistent also with the spectral data given in Table 1.

TABLE 1. LONG WAVELENGTH ABSORPTION BANDS OF 10,10-DIBROMOANTHRONE (III) AND 10-BROMOANTHRONE (IV) IN DIFFERENT SOLVENTS AT 20°

	Solvent	λ_{max}	ε
III	dioxane[a]	388 mμ	40
	benzene[a]	390 mμ	43
	cyclohexane[b]	398 mμ	36
IV	dioxane[a]	415 mμ	8
	benzene[c]	416 mμ	5
	chloroform[c]	418 mμ	5

[a] Well resolved shoulder. [b] Band. [c] Slight shoulder.

Since the long-wavelength and low-intensity absorption bands of III and IV are shifted to the blue with increasing solvent polarity, both bands are assigned to the n-π^* bands. It is assumed, therefore, that the excitation responsible for the reaction is localized in the carbonyl group and is n,π^*. A quantitative formulation could at this point be attempted (Chart 1).

The fact that III and IV do not fluoresce (*vide supra*) makes it likely that transition from the excited singlet S_1 (n,π^*) to the triplet occurs with the high efficiency. The multiplicity of the reactive state is suggested furthermore by quenching the reaction with oxygen, flushed through the system. That oxygen might act as a triplet- and not as a radical quencher is supported by the fact that unchanged material is recovered in the case of III.

One additional factor is that the shape of the curves obtained by plotting the quantum yields versus the concentrations of III and IV (Fig. 1) and the strong non-linear increase of the quantum yields with increasing concentrations,† is most conveniently described in terms of a chain process. This hypothesis could be confirmed by irradiating III in benzene, where the presence of a chain process is demonstrated by the observed quantum yield being slightly higher than unity (Experimental). Whereas the photochemical isomerization of sodium 9-anthroate in aqueous solution involves the anthrol anion,[11]

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† The reciprocal of the quantum yields vs. the reciprocal of the concentrations of III and IV does not fit a straight line.

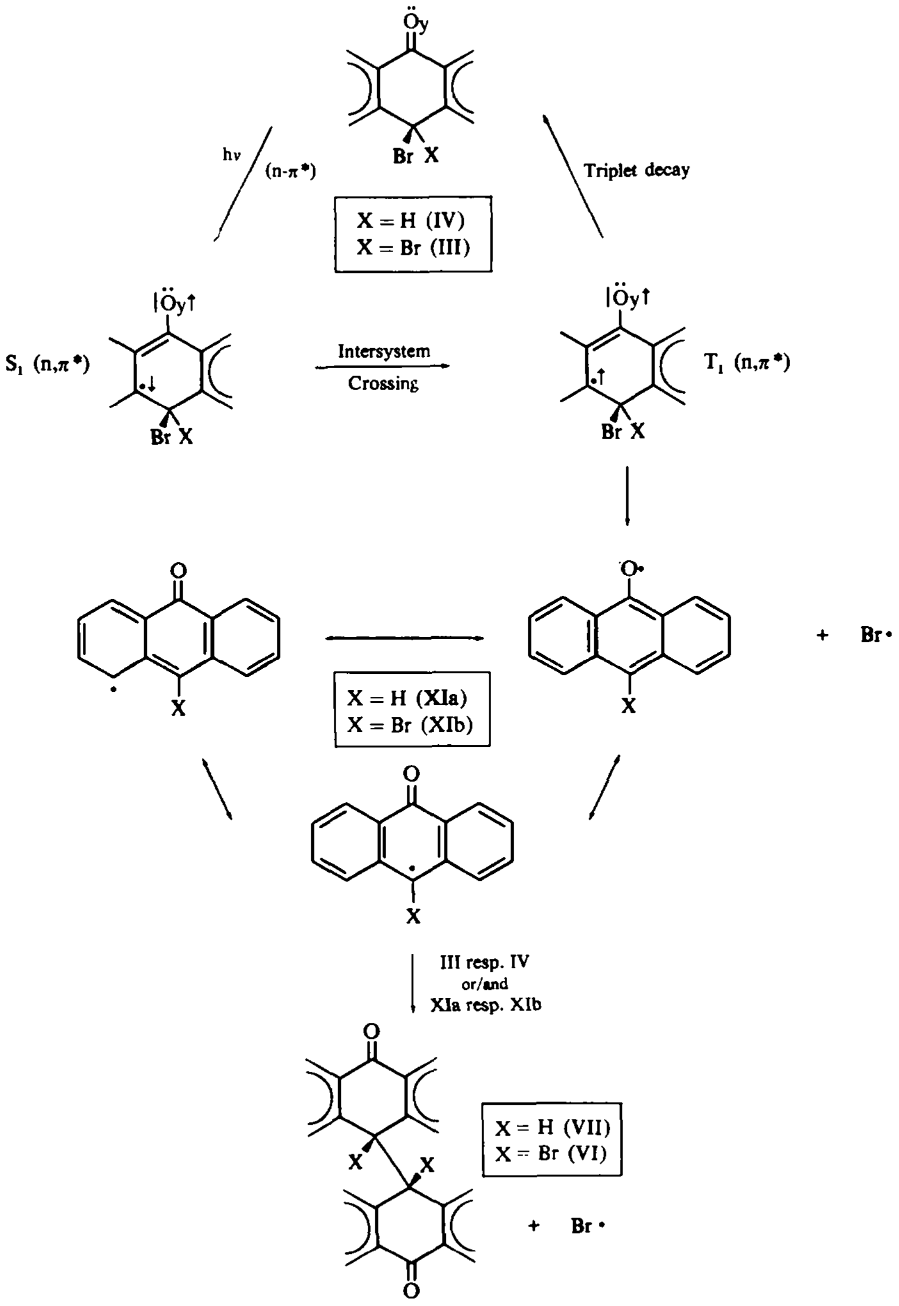
hν
(n-π*)
Br X
X = H (IV)
X = Br (III)
Triplet decay
S₁ (n,π*)
Intersystem
Crossing
T₁ (n,π*)
+ Br•
X = H (XIa)
X = Br (XIb)
III resp. IV
or/and
XIa resp. XIb
X = H (VII)
X = Br (VI)
+ Br•

CHART 1

the dimerization of 9-anthryloxy radicals (XI) to 10,10′-bianthrone (VII) has been described recently by Chapman.[12] In the irradiation of 9-nitroanthracene in acetone, by sweeping out nitrogen (II) oxide with an inert gas, high yields of dimer had been obtained, in excellent agreement with our present results. The formation of 10,10′-dibromobianthronyl (VI) and 10,10′-bianthrone (VII) might be due partly to the attack of the anthryloxy radicals XIa and XIb on III or IV as well as to dimerization of these radicals (Chart 1). The following scheme is, in a first approximation, consistent with the existing data:

$$\mathrm{A} \xrightarrow{h\nu} {}_1\mathrm{A}^* \quad \text{(excitation of reactant to singlet)} \tag{1}$$

$${}_1\mathrm{A}^* \xrightarrow{k_1} {}_3\mathrm{A}^* \quad \text{(intersystem crossing)} \tag{2}$$

$${}_3\mathrm{A}^* \xrightarrow{k_2} \mathrm{A} + h\nu' \quad \text{(phosphorescent decay)} \tag{3}$$

$${}_3\mathrm{A}^* \xrightarrow{k_3} \mathrm{A_R} + \mathrm{Br} \quad \text{(primary process of rad. form.)} \tag{4}$$

$$\left.\begin{array}{ll} \mathrm{A_R} + \mathrm{A} \xrightarrow{k_4} \mathrm{D} + \mathrm{Br} & (5) \\ 2\mathrm{A_R} \xrightarrow{k_5} \mathrm{D} & (6) \end{array}\right\} \text{(dimer formation)}$$

$$\mathrm{A} + \mathrm{Br} \xrightarrow{k_6} \mathrm{A_R} + \mathrm{Br_2} \quad \text{(radical propagation)} \tag{7}$$

It seems reasonable to assume that the bromine radicals liberated in the primary process (Eq. 4) and the secondary process of radical recombination (Eq. 5) will propagate the chain process (Eq. 7).† This chain process appears to be responsible for the higher quantum yields observed for the complete conversions of III and IV to mesonaphthobianthrone (V) (Experimental). A question arises as a result of the observation described above (Fig. 1). By the attachment of a second bromine substituent, the C—Br bond dissociation energy in the excited species (${}_3\mathrm{A}^*$) might be significantly lowered to account for the high quantum yield of III compared with IV.[13] The higher extinction coefficient of III might be another important factor. Last, phosphorescence emission (Eq. 3) or collisional self-quenching (Eq. 8) of the more stable triplet may decrease the quantum efficiency of the reaction. Since no enolization was observed, dimerization of XIa and XIb (Eq. 5 and 6) occurs in both cases with high efficiency, more rapidly than hydrogen abstraction.

$${}_3\mathrm{A}^* + \mathrm{A} \longrightarrow 2\mathrm{A} \quad \text{(self-quenching)} \tag{8}$$

A brief comment seems in order regarding the formation of radicals XIa and XIb. The C—H bond and not C—H bond cleavage in the triplet of IV indicates that the β carbon is not electron deficient[14] and is suggestive that the n-π* triplet is the species involved.

The hydrogen abstraction of 10,10′-bianthrone (VII) with bromine radicals liberated by Eqs. 4 and 5 might be responsible for the formation of VIII from VII.

It proves impossible to obtain direct mechanistic evidence for the conversion of 10,10′-dibromobianthronyl (VI) to bianthrone (VIII). Fig. 2 illustrates the measured quantum yields[8] (for formation of mesonaphthobianthrone) at 20° in dioxane for the conversions of VI and VIII to mesonaphthobianthrone (V), using in both cases a filter

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† From Eq. 1 through 7, by making the usual stationary state assumptions, it can be derived that $\phi_A \equiv a[1 + (3k_3A - k_2)/(k_2 + K_3A) + (8k_3k_4^2A^3)/k_5(k_2 + k_3A)^{\frac{1}{2}}$, ϕ_A = quantum yield for the conversion of starting material. The function $1/\phi_A = f(1/A)$ cannot be linearized.

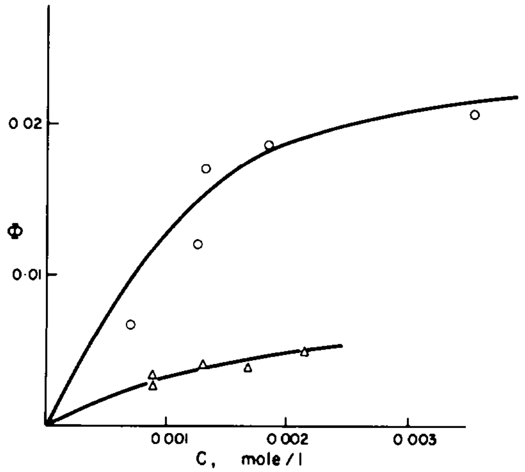

FIG. 2. Quantum yields (Φ) for photoproduct (mesonaphthobianthrone) vs. concentration of starting material: open circles, branthrone; open triangles. 10, 10′-dibromobianthronyl.

transmitting above 420 mμ. Since bianthrone (VIII) was not directly detected (*vide supra*), a positive difference would have provided us with some useful data regarding the second step, i.e. the conversion of VI to VIII. The complexity of the species[15] and processes (quenching, sensitization) involved and the lack of information on the photochromic bianthrone (VIII)[16] limits the value of a more detailed discussion. Nevertheless and by analogy, since no fluorescence was detected (*vide supra*), the irradiation of VI in the long wavelength region can be rationalized on the basis of the mechanism given in Chart 2. The low quantum yields observed (Fig. 2) indicate the absence of a chain process. Accordingly the formation of VIII from VI seems to occur by an intramolecular stepwise bromine elimination from the excited species (n,π*triplet) as shown in Chart 2.

EXPERIMENTAL

IR (KBr pellets) were recorded on a Jasco Model DS-402G spectrometer and UV spectra on a Shimadzu model SV-50 spectrometer. NMR spectra were recorded on a Jeolco CH-60 spectrometer. The fluorescence measurements were carried on a Shimadzu fluorescence spectrometer (Light source: 500 Watt Xenon lamp). VPC analyses were done on a Shimadzu Model 2C chromatograph using the columns described below. M.ps are uncorrected. Microanalyses were performed by the Elemental Analysis Center of Kyoto University.

Materials. C_6H_6, cyclohexane and $CHCl_3$ (Merck Reagents) were used without further purification. Dioxane (Wako Pure Chemical Industries Ltd.), was purified following in parts the procedure described in the literature.[17] The commercially available solvent was distilled twice under atmospheric pressure (60 cm Rasching column), kept over KOH pellets for 10 hr, and distilled over metallic Na. The purity, tested by VPC at 200° using an analytical silicone column (3 m), was found to be at least 99·9%. The preparation of 10-bromoanthrone (IV) (m.p. 148°), 10,10-dibromoanthrone (III) (m.p. 157°), and 10,10-dichloroanthrone (IX) (m.p. 133°) from anthrone (Merck) has been described.[18] Bianthrone (VIII), 10,10′-bianthrone (VII) and mesonaphthobianthrone (V) were identified by direct comparison with authentic samples synthesized by unambiguous methods.[4, 7]

Analytical procedure. Mallinckrodt silicic acid (100 mesh), predried for 24 hr at 100°, was slurried with benzene and introduced into two identical columns (length 420 mm, diameter 25 mm) containing the same solvent. Irradiated and non-irradiated samples (250–300 mg) of 10-bromoanthrone (IV) and 10,10-dibromoanthrone (III), taken up in the minimum amount of dioxane, were eluted at the same time with benzene followed by $CHCl_3$ then C_6H_6–MeOH mixtures of increasing polarity (1 : 0, 6 : 1, 5 : 1, 4 : 1, etc.)

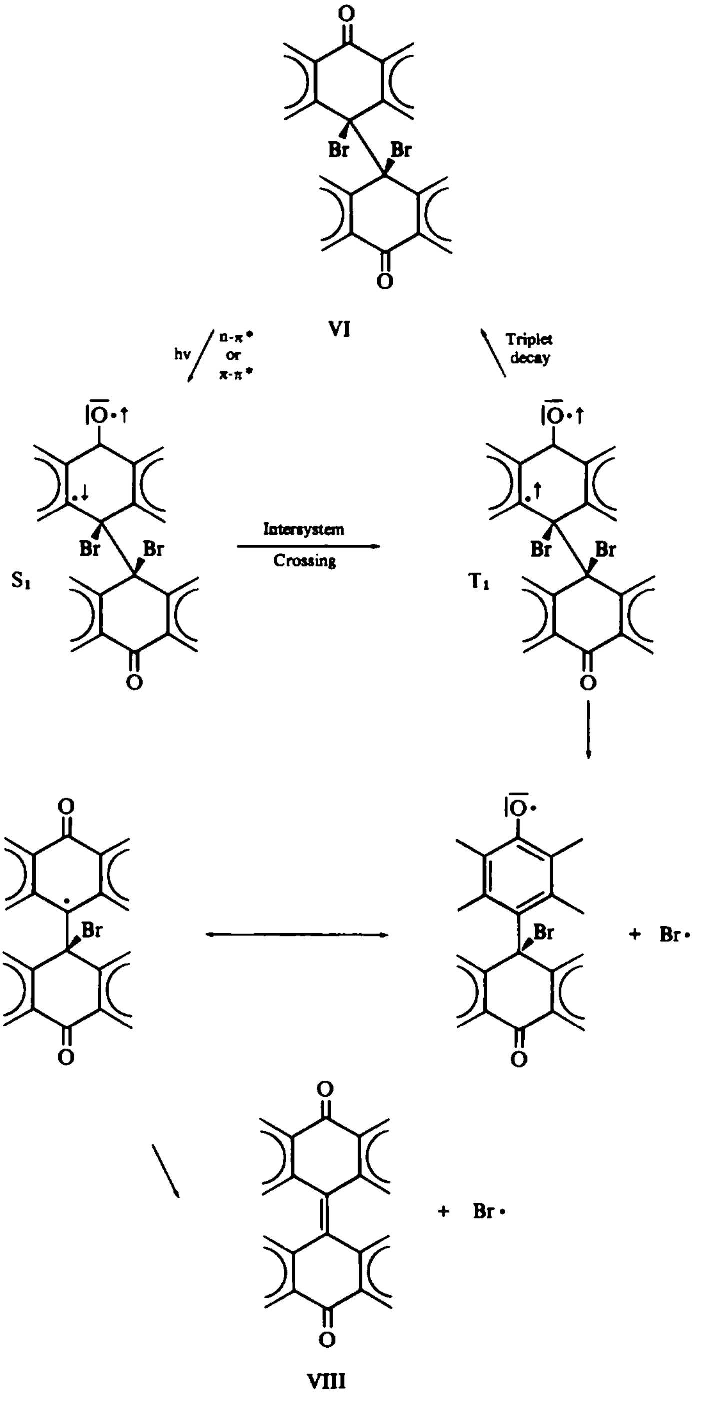
VI
hv
n-π* or π-π*
Triplet decay
S₁
Intersystem Crossing
T₁
Br
+ Br•
+ Br•
VIII

CHART 2

under N_2. Elution with pure C_6H_6 gave unreacted products and demonstrated the presence of free bromine (front), analyzed spectrophotometrically, in the irradiated samples. Elution with $CHCl_3$ or C_6H_6/MeOH mixtures gave 10,10′-bianthrone (VII) and 10,10′-dibromebianthronyl (VI) respectively. Elution with pure MeOH asserted the absence of by-products.

Apparatus and quantum yield procedures. Experiments were carried out in a horizontally disposed cylindrical double-compartment apparatus with quartz windows. The smaller reaction cell was equipped with an inlet for external temperature control (thermoelement). Dimensions of the reaction cell: volume 31·4 ml (length 200 mm; diameter 44 mm). Dimensions of the actinometric cell: volume 190·8 ml (length 125 mm; diameter 44 mm). Cooling was by a copper jacket surrounding both the reaction and actinometric cells, through which ice water circulated. The temperature of the irradiations was, if not otherwise mentioned, 20 ± 1°. Agitation was by a dried (conc. H_2SO_4 and $CaCl_2$) and purified (Fieser solution) N_2 stream during irradiation. The solutions were usually flushed with N_2 prior to irradiation. All quantum yield determinations were carried out at 20 ± 1° with appropriate glass filters (*vide infra*), using a 500 Watt Taika Kōgyō high-pressure mercury lamp (100 Volt Sansui stabilizer) as the external light source. Uranyl oxalate, potassium ferrioxalate[19] and chromium complex[20] actinometries were used. Results obtained by ferrioxalate and chromium complex actinometry agreed within 2%. The quantum yield of the more convenient uranyl oxalate solution (0·05 M) was determined for both glass filters transmitting above 390 mμ and 420 mμ (permanganate titration). The data obtained with the chromium complex actinometer were corrected, since the emission bands of the 500 Watt lamp at 547·9 mμ, 579·6 mμ and 581 mμ are neglected by using the uranyl and ferrioxalate solutions which do not absorb in this spectral region. The light intensities were found to be $1·05 \times 10^{18}$ quanta/sec for Å light, $0·80 \times 10^{18}$ quanta/sec for 4365 Å light and $1·17 \times 10^{18}$ quanta/sec for the filter transmitting between 300 and 500 mμ. The concentration range of the quantum yield determinations were $10^{-2} \sim 7 \times 10^{-2}$ mole/l. for IV and $10^{-2} \sim 8 \times 10^{-2}$ mole/l. for III (Fig. 1). The dioxane solutions exhibiting maxima at different wavelengths, the conversions of both III (λ_{max} 295 mμ, ε 25400) to VI (λ_{max} 253 mμ, ε 84700 and IV (λ_{max} 254·5 mμ, ε 22200) to VII (λ_{max} 262 mμ, ε 153000) could be followed by spectrophotometry. The conversions of VI to V and VIII to V were monitored by careful gravimetric analysis, mesonaphthobianthrone (V) being insoluble in most solvents.

Fluorescence measurements. Whereas bianthrone (VIII) (230·3 γ/10 ml) showed intense greenish blue fluorescence with a strong emission band at 525 mμ when excited at 350 mμ in dioxane at 20°, compounds III (323·0 γ/10 ml), IV (308·0 γ/10 ml), VIII (374·6 γ/10 ml) and VI (209·4 γ/10 ml) did not fluoresce. After a few min, compounds III, VI and VIII gave time-dependent spectra (intense light blue fluorescence) with a common emission band at 475 mμ. Compounds III, VI, and especially IV showed in addition maxima or shoulders at 413 and 395 mμ, characteristic for the time-dependant spectrum of anthraquinone recorded in the same solvent. Due to the small concentrations used for the measurements, partial oxidation to anthraquinone by traces of oxygen in the solvent had to be expected. Compounds IV, VI and VII did not fluoresce in C_6H_6 when excited between 280 and 480 mμ; furthermore, no time dependance was detected. III showed blue fluorescence with a strong band at 560 mμ remaining unchanged over 1 hr. V showed greenish blue time dependent fluorescence with a maximum being shifted from 495 mμ to two new peaks at 465 and 450 mμ within a few min. The fact that IV did not fluoresce in C_6H_6 and dioxane strongly suggested that the enol is never present in significant amounts.

Preparation of 10,10′-*dibromobianthronyl* (VI). (a) A saturated solution of 0·9 g of 10,10-dibromoanthrone (III) in 31·4 ml of dioxane was irradiated under N_2 at 20° for 30 min in the apparatus described ($\lambda > 420$ mμ). The solution was filtered (traces of mesonaphthobianthrone) and cooled to 13–13·5°. III remained in solution whereas VI precipitated in pure form as colorless crystals, m.p. 188° (darken at 175°). After washing with solvent, VI was dried *in vacuo* (0·140 g, 20%). (b) More convenient was the preparation in C_6H_6 where VI precipitated at room temp. A saturated solution of 2·07 g of III in 31·4 ml C_6H_6 was irradiated under N_2 at 20° for 25 min in the apparatus described (Filter $\lambda > 420$ mμ). 0·570 g of pure VI were isolated by filtration (36%). The calculated quantum yield for the conversion of III was 1·060, demonstrating a chain process. The IR spectrum in KBr showed a strong carbonyl band at 1672 cm^{-1}. The UV spectrum in dioxane showed λ_{max} 253 mμ (ε 84470). NMR in $AsCl_3$: complex ABB′D-system at $\tau = 1·45–2·75$ ppm, the 4 equivalent protons in peri-position to the carbonyl groups as multiplet at $\tau = 1·45–1·75$ ppm. Oxidative cleavage in 96% H_2SO_4 at room temp for 60 hr: $0·963 \times 10^{-5}$ mole of VI gave $1·928 \times 10^{-5}$ moles of anthraquinone. Irradiation of VI ($\lambda > 420$ mμ) gave mesonaphthobianthrone (V). (Calc. for $C_{28}H_{16}O_2Br_2$: Br, 29·43. Found: Br, 29·54%).

Preparation of 10,10′-*dichlorobianthronyl* (X). The method described for the preparation of VI was applied. The product precipitated in colorless crystals, m.p. 214° (darkens 183°), from an irradiated

($\lambda > 420$ mμ) saturated solution (31·4 ml) of IX in C_6H_6 at 20°. After 5–6 hr, conversion was 100%. X was washed with fresh solvent and dried *in vacuo*. IR (KBr); carbonyl stretching band at 1672 cm^{-1}. NMR ($AsCl_3$) ABB′D-system at $\tau = 1{\cdot}4$–$2{\cdot}6$, the 4 equivalent protons in peri-position to the carbonyl groups as well resolved multiplet at $\tau = 1{\cdot}40$–$1{\cdot}75$. $6{\cdot}60 \times 10^{-6}$ moles of X gave $1{\cdot}31 \times 10^{-5}$ moles of anthraquinone in 96% H_2SO_4 for 96 hr at room temp. (Calc. for $C_{28}H_{16}O_2Cl_2$: C, 73·85; H, 3·52; Cl, 15·49. Found: C, 73·71; H, 3·50; Cl, 15·32%).

Conversion of III *and* IV *to mesonaphthobianthrone* (V). 0·630 g of III was irradiated ($\lambda > 390$ mμ) under N_2 at 20°. After 18 hr 0·320 g mesonaphthobianthrone (V) was obtained by filtration (96%). The crude product, m.p. > 300°, was taken up in 96% H_2SO_4 and precipitated with water. Identification by comparison with an authentic sample.[4] The UV spectrum of the red-carmin solution of V in 96% H_2SO_4 showed maxima at 257·5 mμ (ε 51000), 306 mμ (ε 28000), 321 mμ (ε 30500), 513 mμ (ε 43500) and 575 mμ (ε 18400). IR (KBr) strong carbonyl band at 1657 cm^{-1}. IV, when irradiated under the same conditions for 24–30 hr, yielded mesonaphthobianthrone (95–100%).

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