Photoinduced Reactions. Part 147.[1] Photochemistry of 1-Isopropylanthrone

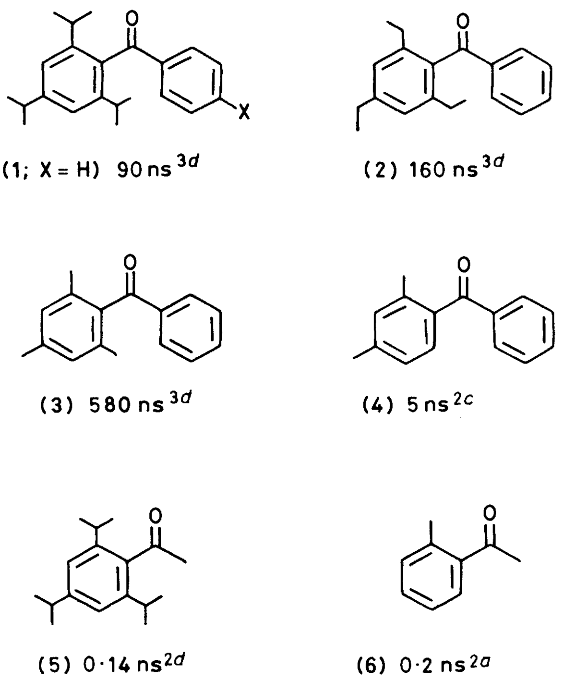
Yoshikatsu Ito,* Norio Inada, and Teruo Matsuura
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

The triplet state of 1-isopropylanthrone (8) was found to be very short-lived (45 ± 25 ps) in view of its effect on the triplet-sensitized isomerization of *cis*-piperylene. This result agrees with our previous conclusion that the triplet lifetime of 2,4,6-tri-isopropylbenzophenone (1) is controlled by hindered rotation in the excited state. Measurement of absorption and emission spectra for (8) has revealed that the keto–enol equilibrium for (8) is overwhelmingly on the side of the keto-form even in ethanol.

Triplet states of *o*-alkylphenyl ketones are very short-lived due to the facile intramolecular abstraction of a benzylic hydrogen atom.[2] Scheme 1 summarizes some data for the lifetimes (τ_T) of the triplets which are directly responsible for the intramolecular hydrogen abstraction.

We have recently demonstrated that the triplet lifetimes of highly hindered 2,4,6-tri-isopropylbenzophenones (1; X = OMe, Me, H, or CF_3) are determined by restricted rotation around bond a (Scheme 2): the hindered rotation ensures that the twisted conformation (the most strain-free conformation in the ground state) of the molecule (1) is planar, and thus rapid intramolecular hydrogen abstraction takes place.[3] However, since the less hindered 2,4,6-trialkylbenzophenones (2) and (3) are longer-lived than (1; X = H) (Scheme 1), similar restricted rotation does not seem important in determining τ_T of (2) and (3). Furthermore, although ketones (3), (5), and (6) were found to have a kinetically distinct triplet which is thought to be conformationally different from that responsible for intramolecular hydrogen abstraction,[2a,b,d,3] the situation for 2-methylbenzophenone is uncertain.[2a,c,e,4]

We considered it desirable to study the photochemistry of 1-isopropylanthrone (8). We expect that the π-system of (8) is approximately planar and hence intramolecular hydrogen abstraction is geometrically more feasible than in (1). In fact, as shown later, the triplet lifetime of (8) was found to be very short. Also the anthrone–anthranol equilibrium for (8) is overwhelmingly shifted towards the keto-form even in a polar solvent such as ethanol.



(1; X = H) 90 ns[3d]
(2) 160 ns[3d]
(3) 580 ns[3d]
(4) 5 ns[2c]
(5) 0·14 ns[2d]
(6) 0·2 ns[2a]

Scheme 1.

Results and Discussion

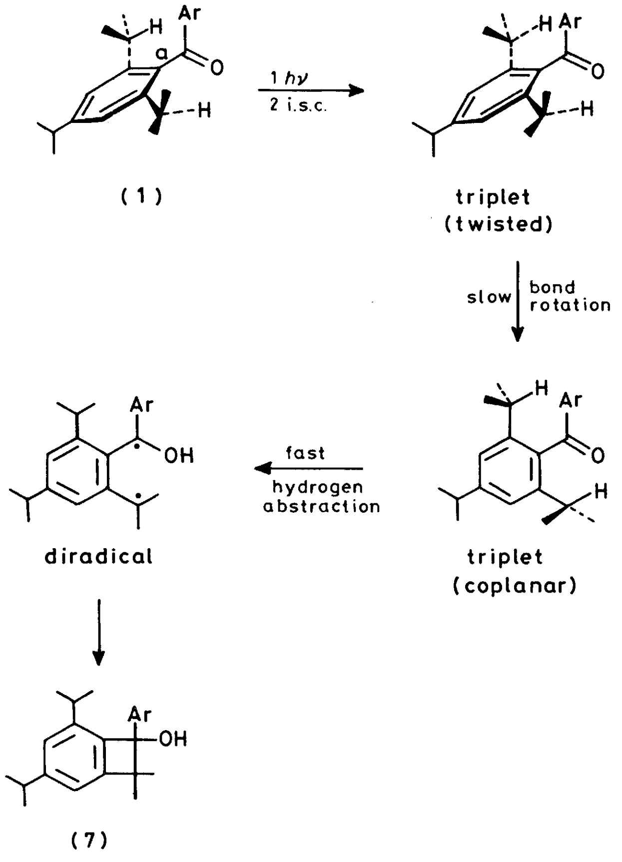
Preparation of 1-*Isopropylanthrone* (8).—As outlined in Scheme 3, this compound was prepared by tin(II) chloride reduction of 1-isopropylanthraquinone (11) which was synthesized by two independent methods. The isomer, 4-isopropylanthrone (9), was simultaneously produced in a somewhat lower yield [(8) : (9) = 4 : 3].

Irradiation of (8).—While photolysis of the benzophenone (1) in benzene gave the cyclobutenol (7) in high quantum yield (Φ 0.60),[3] the anthrone (8) afforded no photoproducts under the same reaction conditions. Probably, cyclization to the corresponding cyclobutenol (13) requires too much bond strain and the diradical intermediate disproportionates back to the parent ketone (8) without producing (13) [equation (1)]. It has been reported that 6-benzylbenzanthrone exhibits similar photochemical behaviour.[5]

The unsubstituted anthrone (10), upon photolysis in hydrogen-donating solvents, produces a variety of products (anthrapinacol, dianthranol, anthranol, *etc.*) *via* the anthrone ketyl radical [equation (2)].[6] Similarly 4-isopropylanthrone (9) underwent readily a photochemical decomposition in MeOH. However, photolysis of (8) in MeOH resulted in more than 90% recovery under the photolysis conditions where 80% of (9) disappeared. This photochemical stability of (8) is probably because the reversible intramolecular hydrogen abstraction [equation (1)] is rapid.

Photosensitized cis–trans *Isomerization of* cis-*Piperylene by* (8).—In order to obtain photokinetic data for the anthrone (8), the quantum yield ($\Phi_{c \rightarrow t}$) for sensitized isomerization of *cis*-piperylene using (8) as a photosensitizer was measured.[7] From a plot of $0.55/\Phi_{c \rightarrow t}$ *versus* the reciprocal of the *cis*-piperylene concentration (Figure 1), we estimated that the intercept ($1/\Phi_{\text{i.s.c.}}$) is 1—3 and the intercept/slope ratio ($k_{T\text{-}T}\tau_T$) is 0.095—0.35. Assuming that the rate for triplet energy transfer from (8) to *cis*-piperylene ($k_{T\text{-}T}$) is nearly diffusion-controlled, *i.e.*, $k_{T\text{-}T}$ 5×10^9 l mol^{-1} s^{-1} in benzene,[8] the triplet lifetime (τ_T) of (8) is 45 ± 25 ps.

The $S_1 \longrightarrow T$ intersystem crossing rate of the unsubstituted anthrone (10) is similar to that for benzophenone ($\geqq 10^{11}$ s^{-1})[9] and τ_T is *ca.* 260 μs in CCl_4 at 25 °C.[10] The very short triplet lifetime of (8) is ascribable to rapid intramolecular hydrogen abstraction, since in entropically favourable cases intramolecular hydrogen abstraction by the *n*,π* carbonyl group is



Scheme 2.

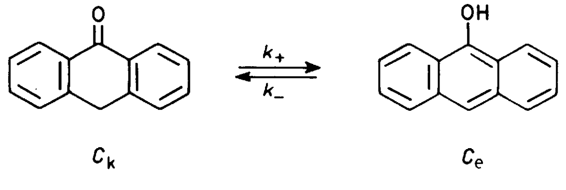
very rapid (*ca.* 10^{10} s^{-1}).[2,11] This, in turn, confirms the previous conclusion [3] that τ_T for (1) (90 ns) is determined by hindered rotation about bond a, not by intramolecular hydrogen abstraction (see Scheme 2).

Absorption and Emission Spectra of (8) *and* (9).—The keto-enol equilibrium of anthrone (10) was studied by various physical and chemical methods, including absorption and fluorescence spectroscopy.[12] As a result of these studies it was established that (10), when dissolved in solvents, slowly isomerizes to anthranol and reaches an equilibrium in favour of the keto-form (Table). Both the rate (k_+) and the equilibrium constant ($K = C_e/C_k$) are greater in polar solvents than in hydrocarbon solvents.

We have found that the absorption and emission spectra of 4-isopropylanthrone (9) are quite similar to those of (10).[12a,13] Thus, the absorption shoulder at 404 nm (Figure 2a) and the fluorescence maxima at 427, 452, 479, and 515sh nm (Figure 3), both of which were observed in ethanol solution, are characteristic [12a] of the corresponding anthranol, whereas in hydrocarbon solvents (cyclohexane or methylcyclohexane) only the anthrone n,π^* absorption (Figure 2a) [12a] and the anthrone phosphorescence (Figure 4a) [13] were observable.

The electronic spectra of 1-isopropylanthrone (8) were quite different from those of (9), since anthranol absorption and fluorescence were not detected in ethanol. The observed structureless absorption band at $\lambda_{max.}$ 360 nm in cyclohexane was only blue-shifted upon changing the solvent to ethanol, with no significant increase in the absorption coefficient at *ca.* 404 nm (Figure 2b). In both methylcyclohexane and ethanol no emission was detectable at room temperature. In ethanol glass at 77 K, however, a fluorescence spectrum ($\lambda_{max.}$ 430, 455, and 482 sh nm) similar to that of (9) (Figure 3) was observed, although it was very weak.

Table. Keto-enol equilibrium for anthrone (10)



Solvent	$K (= k_+/k_-)$	k_+/min^{-1}	Temp. (°C)	Ref.
Iso-octane	2.07×10^{-3}	very slow	20	12*a*
Benzene	2.30×10^{-3}		16	12*a*
MeOH	0.14	6.9×10^{-4}	20	12*b*
EtOH	0.11	3.6×10^{-4}	20	12*b*

These spectral properties for (8) indicate that, in contrast to the situation for (9) and (10), the keto–enol equilibrium for (8) is overwhelmingly on the side of the keto-form even in ethanol. The steric effect of the bulky 1-isopropyl group should be responsible for this discrepancy.

The compound (8) was slightly phosphorescent in methylcyclohexane glass at 77 K (Figure 4b). Although this weak phosphoresence (near the lower limit of detection) may be due to impurities, since the corresponding phosphorescence excitation spectrum did not agree with the absorption spectrum (Figure 2b), the relative phosphorescence intensities for (8)—(10) were estimated to be 0.6 : 37 : 100. The weak phosphorescence for (8) is probably due to the rapid intramolecular hydrogen abstraction [equation (1)] or to triplet decay *via* *T–S* surface crossing before the occurrence of hydrogen abstraction.[14]

Experimental

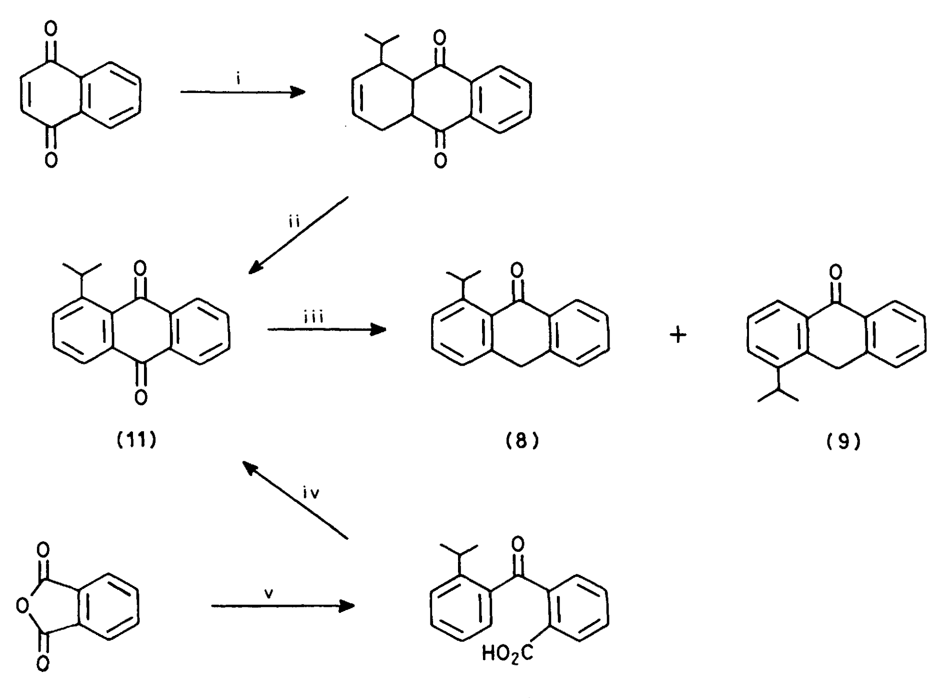
M.p.s are uncorrected. N.m.r., i.r., and u.v. spectra were recorded on Varian T-60, JASCO IRA-1, and Shimadzu UV-200 spectrometers, respectively. Emission spectra were measured with a Shimadzu RF-500 spectrometer, equipped with accessories for phosphorescence measurements (PHA-1).

Materials.—Anthrone (10) (Wake Chemicals; guaranteed reagent) was purified by column chromatography on silica gel, followed by recrystallization from benzene–light petroleum. Commercial spectrograde solvents were used without further purification for u.v. and emission measurements.

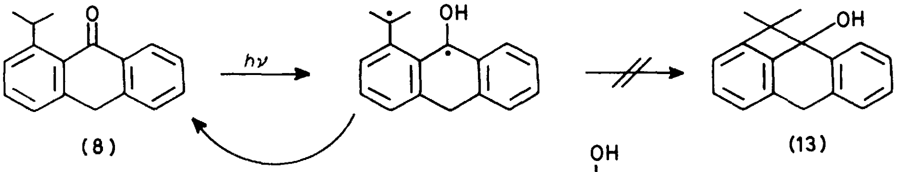
Preparation of 1-*Isopropylanthraquinone* (11).—Of the two methods A and B employed, method A gave better results.

A. A solution containing 5-methylhexa-1,3-diene (15.4 g, 0.16 mol) and 1,4-naphthoquinone (15.8 g, 0.1 mol) in ethanol (50 ml) was refluxed with stirring for 46 h. The solution was cooled and placed in a refrigerator for 12 h to afford crystals (13.0 g, 51%) of the Diels–Alder adduct, m.p. 137.3—141.5 °C. 5-Methylhexa-1,3-diene was prepared by the reaction of isobutylmagnesium bromide with acrolein followed by dehydration with potassium hydrogensulphate.[15]

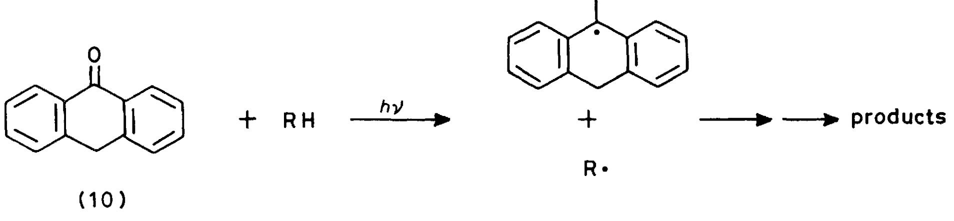
For the dehydrogenation of the Diels–Alder adduct, adduct (12.2 g, 47.8 mol) was dissolved in 5% ethanolic potassium hydroxide solution (180 ml) and a current of oxygen was slowly bubbled through the solution for 3 h. The yellow quinone that had separated was then filtered and washed, first with water (50 ml), then with ethanol (25 ml), and finally with ether (10 ml). Recrystallization from ethanol gave (11) (8.6 g, 72%),



Scheme 3. *Reagents:* i, 5-methylhexa-1,3-diene, EtOH; ii, KOH–O_2, EtOH; iii, $SnCl_2$–HCl, AcOH; iv, H_2SO_4, 95 °C; v, 2-isopropylphenylmagnesium bromide, THF–C_6H_6



(1)



(2)

m.p. 97.9—99.8 °C; $\nu_{max.}$ (Nujol) 1 681sh and 1 674 (C=O), 1 585, 1 302, 1 267, and 980 cm^{-1}; $\delta(CDCl_3)$ 1.33 [6 H, d, *J* 6.8 Hz, $CH(CH_3)_2$], 4.42 [1 H, sept, *J* 6.8 Hz, $CH(CH_3)_2$], and 7.53—8.23 (7 H, m, ArH) (Found: C, 81.65; H, 5.55. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.65%).

B. To a well stirred solution of phthalic anhydride (21.3 g, 0.144 mol) in anhydrous benzene (320 ml) and dry ether (110 ml) was added slowly 2-isopropylphenylmagnesium bromide, prepared from 2-isopropylbromobenzene (19.5 g, 98 mol),[16] magnesium turnings (2.3 g, 93 mmol), and a small crystal of iodine in absolute ether (80 ml). A pale yellow solid formed immediately. The mixture was refluxed with stirring for 12 h. The resultant solution was poured into ice–hydrochloric acid and extracted with ether. The organic layer was evaporated, and the resulting solid was dissolved in dilute sodium hydroxide solution, filtered, and then reprecipitated with dilute hydrochloric acid. The resulting solid, 2-(2-isopropylbenzoyl)-benzoic acid (12), was recrystallized from benzene containing ligroin to afford crystals (5.0 g, 20%), m.p. 144.6—145.8 °C; $\nu_{max.}$ (Nujol) 3 300—2 500br and 1 681 (CO_2H), 1 670 (ketone C=O), 1 300, 928, and 788 cm^{-1}; $\delta(CDCl_3)$ 1.25 [6 H, d, *J* 6.8 Hz, $CH(CH_3)_2$], 3.73 [1 H, sept, *J* 6.8 Hz, $CH(CH_3)_2$], 7.00—7.95 (8 H, m, aromatic), and 10.79br (1 H, s, CO_2H) (Found: C, 75.9; H, 5.95. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%).

Compound (12) (3.5 g, 13 mmol) was dissolved in concentrated sulphuric acid (35 ml) at room temperature. The solution was heated at 95 °C for 3 h. The resulting deep red solution was poured into ice–water (500 ml) and extracted with benzene (600 ml). The benzene solution was washed with sodium hydrogencarbonate solution (200 ml), then with water, and dried ($MgSO_4$). The solution was evaporated to dryness to give a green solid (2.1 g). Separation by column chromatography on silica gel (Wakogel C-200, 100 g; solvent, benzene), followed by recrystallization from ethanol, afforded (11) (980 mg, 31%) as yellow needles. This material (m.p. 86.5—88.7 °C) was still contaminated with a small amount of impurity.

Preparation of 1- *and* 4-*Isopropylanthrones* (8) *and* (9).—To a mixture consisting of (11) (1.2 g, 4.8 mmol) and acetic acid (8 ml) was added a solution made by warming a mixture of tin(II) chloride dihydrate (2.6 g, 11.5 mmol) with concentrated hydrochloric acid (2.6 ml). The mixture was refluxed

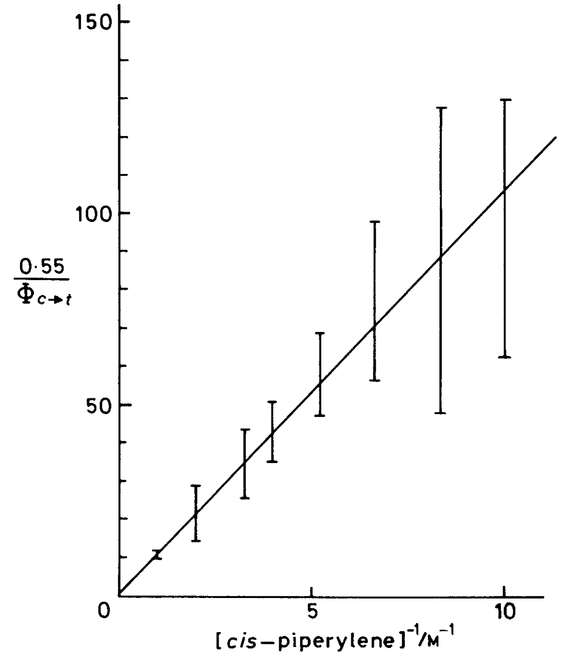


Figure 1. Quantum yield ($\Phi_{c \to t}$) for sensitized *cis–trans* isomerization of *cis*-piperylene by 1-isopropylanthrone (8) as photosensitizer, as a function of *cis*-piperylene concentration. Conditions: degassed benzene solution [0.05M in (8), 0.1—1M in *cis*-piperylene] irradiated at 313 nm

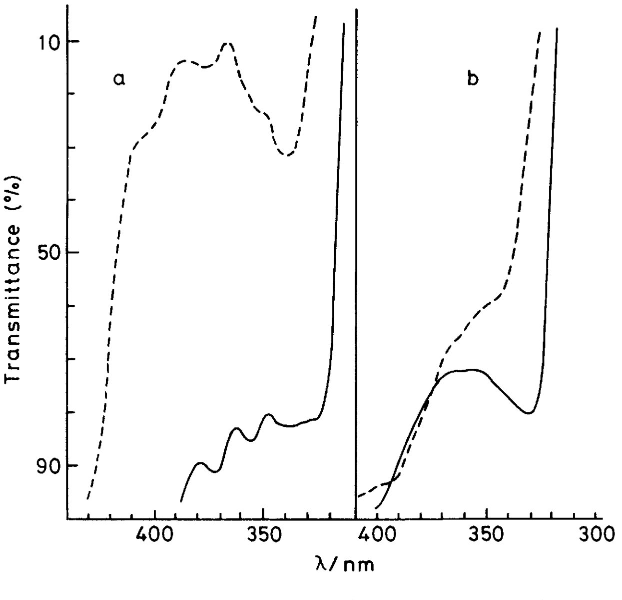


Figure 2. Absorption spectra of a, (9) and b, (8) in cyclohexane (solid line) and in ethanol (dotted line): [(8)] 7.62 × 10^{-4}M (C_6H_{12}), 9.73 × 10^{-4}M (EtOH); [(9)] 1.18 × 10^{-3}M (C_6H_{12}), 9.73 × 10^{-4}M (EtOH). ε_{360} 190 for (8) in C_6H_{12}. ε_{380} 35, ε_{363} 68, and ε_{348} 75 for (9) in C_6H_{12}

for 1.5 h. The solution was diluted with water (*ca.* 5 ml) and extracted with ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated to give a mixture of (8) and (9). This was separated by column chromatography (Wakogel C-200, 200 g; solvent, light petroleum–benzene), followed by recrystallization from ethanol, to afford (8) (190 mg, 17%) and (9) (140 mg, 12%).

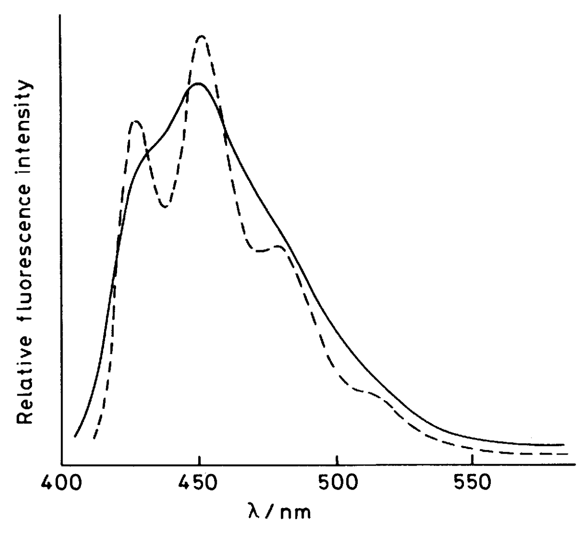


Figure 3. Fluorescence spectra of 4-isopropylanthrone (8) in ethanol (1 × 10^{-3}M) at room temperature (solid line) and at 77 K (dotted line): 400 nm excitation

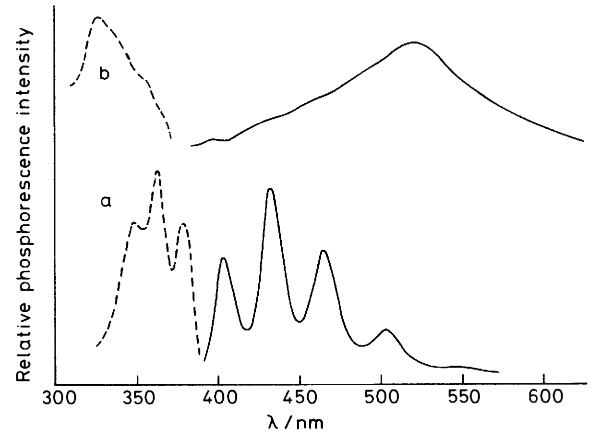


Figure 4. Phosphorescence (solid line) and phosphorescence excitation (dotted line) spectra of a, (9) and b, (8) in methylcyclohexane (7 × 10^{-4}M) at 77 K: (8), 340 nm excitation; (9), 360 nm excitation

Compound (8) gave crystals, m.p. 60.5—61.7 °C; $\nu_{max.}$ (Nujol) 1 660sh and 1 640 (C=O), 1 589, 1 320, 1 284, 1 166, 924, 750, and 720 cm^{-1}; δ($CDCl_3$) 1.32 [6 H, d, *J* 6.6 Hz, $CH(CH_3)_2$], 4.23 (2 H, s, CH_2), 4.44 [1 H, sept, *J* 6.6 Hz, $CH(CH_3)_2$], 7.12—7.58 (6 H, m, ArH), and 7.89—8.23 (1 H, m, ArH) (Found: C, 86.3; H, 6.75. $C_{17}H_{16}O$ requires C, 86.4; H, 6.85%).

Compound (9) formed pale yellow crystals, m.p. 95.0—97.0 °C; $\nu_{max.}$ (Nujol) 1 651 (C=O), 1 589, 1 301, 1 140, 1 085, 815, 740, and 719 cm^{-1}; δ($CDCl_3$) 1.32 [6 H, d, *J* 6.6 Hz, $CH(CH_3)_2$], 3.32 [1 H, sept, *J* 6.6 Hz, $CH(CH_3)_2$], 4.26 (2 H, s, CH_2), 7.15—7.63 (5 H, m, ArH), and 7.89—8.34 (2 H, m, ArH) (Found: C, 86.4; H, 7.1%).

Photolyses.—A solution of the anthrone (8) (201 mg, 0.848 mmol, 5.7 × 10^{-2}M) in benzene (15 ml) was placed in a Pyrex tube and was irradiated externally with a 400 W high-pressure mercury lamp for 10.5 h while bubbling through nitrogen. N.m.r. and t.l.c. monitoring of the reaction revealed no appreciable sign of product formation.

Similarly a methanol solution of (8) was irradiated for 7 h. N.m.r. analysis of the mixture indicated >90% recovery of (8).

Similarly a methanol solution of (9) was irradiated for 7 h. N.m.r. analysis of the mixture indicated *ca.* 20% recovery of (9). Characterization of photoproducts (two main spots on t.l.c.) was not attempted.

Photosensitized cis-trans *Isomerization of* cis-*Piperylene by* (8).—This was carried out as described previously.[3d] A main source of the error (Figure 1) arises from g.l.c. analysis. A Shimadzu GC-3BT chromatograph equipped with a thermal conductivity detector and a 6 m column containing 30% 1,2,3-tris-(2-cyanoethoxy)propane was used for *trans*-piperylene analyses. Benzophenone-sensitized *cis–trans* isomerization of *cis*-piperylene[7] was used for actinometry.

Spectra.—U.v. and emission spectra of (8) and (9) were measured on the day following preparation of sample solutions.

Acknowledgements

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