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Photolysis of Some Cyclopentadioxinones ¹

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The photolysis of four cyclopentadioxinones is reported. The products from the reactions are cyclopentaphenanthrenones formed by a novel stilbene-type cyclisation under non-oxidative conditions utilising a leaving group in the aromatisation step.

THE interest in the photochemical cyclisation of stilbene derivatives was stimulated by the observations of Parker and Spoerri² who isolated phenanthrene from the photolysis of the parent stilbene, in a re-investigation of an earlier study.³ More recently reviews on this subject have been published.^{4,5} Most pertinent to the work reported here is the photochemistry of tetraphenylcyclopentadienone⁶ where cyclisation to the phenanthrene skeleton took place under non-oxidative conditions. We now report the study of the photolysis of cyclopentadioxinones under non-oxidative conditions.

DISCUSSION

Most of the dioxinones (1a-f) examined exhibited ⁷ a u.v. absorption at ca. 300 nm in methanol and thus a medium-pressure mercury-arc lamp was utilised in conjunction with a Pyrex filter. Propan-2-ol was selected as the solvent for most of the reactions. The photolysis of the cyclopentadioxinone (1a) was readily followed visually by the almost instant deepening of colour in the solvent closest to the arc lamp. Eventually a deep red flocculent precipitate developed which was filtered off. Identification of this product was simple although its relative insolubility in the usual solvents prevented a reasonable study of its n.m.r. spectrum. However, the i.r. spectrum showed a carbonyl absorption at 1705 cm⁻¹, which, by comparison with values for the starting material (1715 cm⁻¹) and tetraphenylcyclopentadienone (1708 cm⁻¹) suggested that the environment of the carbonyl group had altered from that in cyclopentenone (1a) to one similar to but not identical with that in tetraphenylcyclopentadienone. Further examination of the i.r. spectrum of the product showed the absence of dioxin C-O-C absorptions and also an additional complexity of the aryl C-H region. On the basis of this evidence the adduct was tentatively assigned the phenanthrene structure (2a). This compound had previously been prepared by Moritani et al.6 from dehydration of the alcohol (3) with hydrogen sulphate. However, although the carbonyl absorption reported by them was in reasonable agreement with our value, the m.p. of the compounds differed by 10°. Thus, to prove further our structural assignments the remaining enone double bond of compound (2a) was epoxidised by sodium hydroxide-hydrogen peroxide to afford a yellow crystalline epoxide (4). This epoxide exhibited thermochromic properties, becoming red at its m.p. and returning to its original yellow colour when cooled. Although no

¹ Preliminary communication; W. M. Horspool, Chem. Comm., 1969, 467.

 ² C. O. Parker and P. E. Spoerri, Nature, 1950, 166, 603.
 ³ A. Smakula, Z. phys. Chem. (Leipzig), 1934, 1325, 90;
 G. N. Lewis, T. T. Magel, and D. Lipkin, J. Amer. Chem. Soc., 1940, 62, 2973.

⁴ F. R. Stermitz, Org. Photochem., 1967, 1, 247.

⁵ E. V. Blackburn and C. J. Timmons, Quart. Rev., 1969, 23,

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6</sup> I. Moritani and N. Toshima, *Tetrahedron Letters*, 1967, 367, 467; I. Moritani, N. Toshima, S. Nakagawa, and M. Yakushÿi, Bull. Chem. Soc. Japan, 1967, 40, 2129; N. Toshima and I. Moritani, *ibid.*, p. 1495.
⁷ See preceding paper for syntheses of dioxinones.

spectroscopic evidence was obtained for the identity of the red compound produced on melting it seems likely that at the m.p. the epoxide (4) is in equilibrium with its



valence tautomer (5). Such behaviour has been recognised and extensively examined for the structurally similar 2,3-diphenylindenone epoxide.⁸



All the evidence thus obtained confirmed the assignment of the product from the photolysis as the cyclopentaphenanthrenone (2a) regardless of the discrepancies between the results reported here and those obtained by others.6

It was apparent that the photolysis had effected a cyclodehydrogenation with an elimination under nonoxidative conditions. Non-oxidative conditions for phenanthrene formation had previously been reported not only by the Japanese group⁶ but also in earlier studies by Brockmann and Mühlmann.⁹ However, these reactions apparently utilised the excited keto-groups as

⁸ E. F. Ullman and J. E. Milks, J. Amer. Chem. Soc., 1964,

86, 3814.
⁹ H. Brockmann and R. Mühlmann, Chem. Ber., 1949, 82,

hydrogen scavengers. Thus in Brockmann's work 9 the helianthrone (6) was converted into a 1:1 mixture of *meso*-dianthrone (7) and diol (8).



The work of Moritani et al.⁶ is not quite so clear cut but the products from the photolysis of tetraphenylcyclopentadiene in propan-2-ol do contain reduced and deoxygenated products [(9) and (10) respectively] suggesting some involvement of the enone system as a hydrogen scavenger. The reaction reported here is much cleaner producing only one product in addition to tetrachlorocatechol and unchanged starting material with no evidence for reduction of the carbonyl function of the



product (2a). It is tempting to propose some involvement of the enone chromophore in our photolyses but the adducts all showed intense absorptions ($\varepsilon = 10,000$) at ca. 300 nm and although the absorptions were broadened when the solvent changed from cyclohexane to methanol no hypso- or batho-chromic shifts were observed. In the absence of either of these effects it is impossible to assign either $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ absorptions for the initial electronic excitations.¹⁰ Added to this is the recent report that the photo-cyclisation of hetero-stilbene analogues is prohibited if there is a low-lying $n \rightarrow \pi^*$ state.¹¹ Also, the presence of acetyl functions, although aiding intersystem crossing in stilbenes, prevents stilbenes from cyclising.¹² Thus the nature of the excited state in our reactions cannot be identified.

N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, 1967; J. W. Sidman, *Chem. Rev.*, 1958, 58, 689.
 E. V. Blackburn and C. J. Timmons, *J. Chem. Soc.* (C),

1970, 172.

¹² M. Kasha, Discuss. Faraday Soc., 1950, 9, 14.

However, it is possible to infer some information on a possible reaction mechanism from the present experiments. Two mechanistic routes were considered, the first of which is shown in Scheme 1. Thus the reaction



could involve elimination of tetrachloro-1,2-benzoquinone to produce an excited tetracyclone which might cyclise to the dihydrophenanthrene (A). Oxidation of this could be effected by use of the quinone. There is a precedent for such a reversal of quinone addition in the photolysis of the dioxole (11) to produce a carbene.¹³ It was thought that tetrachloro-1,2-benzoquinone could therefore behave as an oxidant in place of air or iodine 4,5



for photo-produced dihydrophenanthrenes, and from the photolysis of a mixture of tetraphenylcyclopentadienone and tetrachloro-1,2-benzoquinone in propan-2-ol a low yield of adduct (2a) was obtained. However, this experiment did not eliminate the possibility of a fast thermal addition of the quinone to the tetracyclone to form adduct (1a) which is subsequently photolysed. This first mechanism was eventually eliminated by showing that it was essential to have a stilbene portion in the adducts for the photo-reaction to take place. Thus the indenone adduct (12) failed to form the expected indenophenanthrenone (13). The photolysis of the indenone adduct (12) was wavelength dependent. Irradiation through Pyrex afforded only 2,3-diphenylindenone by a slow retro-Diels-Alder reaction whereas with a quartz filter some cyclisation took place giving a deoxygenated product indeno[1,2-l] phenanthrene. The indenophenanthrene (13) could be formed in low yield by direct photolysis of 2,3-diphenylindenone under nitrogen.



The favoured route to product formation is shown in Scheme 2. Cyclisation of the aryl groups on C-2 and C-3 of the adduct affords the dihydrophenanthrene (B) which can eliminate tetrachlorocatechol by a thermal process. The involvement of the aryl groups on the enone double bond was verified by the efficient formation of the cyclopentaphenanthrenone (2b) by photolysis of adduct (1b) in alcohol. The mechanism depicted in Scheme 2 should also show some solvent dependency. Thus in hydroxylic solvents, where proton removal and solvation of the catecholate anion are possible, the reaction is efficient while in cyclohexane no reaction could be detected. The possibility that the cyclohexane reaction proceeded to the dihydrophenanthrene stage was considered but attempts to test this have so far failed.

Finally, the scope of the reaction was investigated by the introduction of deactivating and activating substituent into the aryl groups on C-3 and C-4. Neither of the substituents, chloro or methoxy, appeared to have a large effect on the reaction and both adducts (1c and d) were readily converted into the corresponding cyclopentaphenanthrenones (2c and d). Tetrabromo-1,2benzoquinone was also used as the leaving group and the adducts (1e and f) were transformed inefficiently into cyclopentaphenanthrenones (2a and b) respectively.

EXPERIMENTAL

Photolyses were carried out for solutions in propan-2-ol under nitrogen in a photochemical reactor with a Pyrex or quartz immersion well and a 450 W medium-pressure mercury-arc lamp. N.m.r. spectra were recorded on a Perkin-Elmer R10 60 MHz spectrometer for solutions in deuteriochloroform with tetramethylsilane as internal standard. U.v. spectra were recorded on a Unicam SP 800 spectrophotometer.

¹³ R. M. G. Nair, E. Meyer, and G. W. Griffin, Angew. Chem., 1968, 7, 402.

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Photolysis of Adduct (1a).—A solution of the adduct (1a) ν_{\max} 1715 cm⁻¹, λ_{\max} (MeOH) 309 nm; log ε 4·04) (1·0 g) in hot propan-2-ol (450 ml) was purged with nitrogen in the photochemical reactor for 0·5 h. After irradiation for 7 h a flocculent precipitate had appeared which was filtered off and crystallised from benzene–light petroleum as maroon needles of cyclopenta[1]phenanthren-1-one (2a) (0·3 g, 50%), m.p. 284—286° (lit.,⁶ 276°), ν_{\max} (Nujol) 1705 cm⁻¹, τ (satd. soln. in CDCl₃; 100°; spectrum is the result of 21 scans on a C.A.T.) 0·88 (1H, m), 1·39 (2H, m), and 2·35—2·90 (15H, m) (Found: M^+ 382·1363. C₂₉H₁₈O requires M 382·1358).

Photolysis of Tetraphenylcyclopentadienone and Tetrachloro-1,2-benzoquinone in Propan-2-ol.—Tetraphenylcyclopentadienone (1.97 g) and tetrachloro-1,2-benzoquinone (1.23 g) were dissolved in propan-2-ol (470 ml) and irradiated for 10 h under nitrogen. The propanol-insoluble material was removed and crystallised from benzene-light petroleum to give cyclopenta[l]phenanthren-1-one (2a) (0.14 g, 18%).

Epoxidation of Cyclopenta[1]phenanthren-1-one (2a).—A solution of the ketone (2a) (0.1 g) in a mixture of benzene (40 ml), ethanol (100 ml), and 1,2-dimethoxyethane (60 ml) was refluxed and a solution of hydrogen peroxide (10 ml; 30%) and sodium hydroxide (0.5 g) in water (10 ml) was added in two portions. After the first addition the solution was refluxed for 3 h by which time the colour of the ketone faded somewhat. Addition of the second aliquot portion and a further 3 h under reflux discharged the colour completely. The mixture was cooled and poured into water and the organic layer was separated. Evaporation of this layer gave a yellow solid which was recrystallised from cyclohexane-light petroleum to give 2,3-dihydro-2,3-diphenyl-2,3-epoxycyclopenta[l]phenanthren-1-one (0.06 g), m.p. 171–174° (red at m.p.), $\nu_{\rm max.}$ (Nujol) 1710 cm⁻¹ (Found : M^+ 398·1312. $C_{29}H_{18}O_2$ requires M 398·1307).

Photolysis of Adduct (12).—(a) Pyrex filter. A solution of the adduct (12) $[v_{max}$ (Nujol) 1735 cm⁻¹] (1·1 g) in propan-2-ol (500 ml) was flushed with nitrogen and irradiated for 10 h. The solution turned orange. Chromatographic work up of the residue gave only the unchanged adduct and 2,3-diphenylindenone (0·06 g).

(b) Quartz filter. A solution of the adduct (12) (1.0 g) in propan-2-ol (500 ml) was irradiated under nitrogen for 3 h. Solvent was removed and the tarry residue was chromatographed on alumina. Light petroleum-ether (18:7) eluted a crystalline material which was recrystallised from hexane as needles identified as indeno[1,2-*l*]phenanthrene (50 mg), m.p. 159–161° (lit.,¹⁴ 158°), ν_{max} (Nujol) 778, 760, 755, and 726 cm⁻¹, τ 1.36 (2H, m), 1.78 (1H, m), 2.0–2.9 (9H, m), and 5.96 (2H, s).

Photolysis of 2,3-Diphenylindenone.—A solution of 2,3diphenylindenone (2.0 g) in propan-2-ol (500 ml) was irradiated under nitrogen for 5 h through a quartz filter. Chromatography of the solid residue which was mainly 2,3diphenylindenone gave on elution with benzene indeno-[1,2-*I*]phenanthren-13-one (50 mg), m.p. 185—187° (lit.,¹⁵ 185—187°), v_{max} (Nujol) 1700 cm⁻¹.

Photolysis of Adduct (1b).—(a) In propan-2-ol. A solution of the adduct (1b) [ν_{max} . (Nujol) 1720 cm⁻¹, λ_{max} . (MeOH) 309 nm, log ε 4.06] (0.5 g) in propan-2-ol (450 ml) was flushed with nitrogen and irradiated for 5 h. Solvent was removed under reduced pressure and the red residue was chromatographed on alumina. Benzene eluted a red band. Crystallisation of this material from benzene–light petroleum gave 2-methyl-3-phenylcyclopenta[1]phenanthren-1-one as fine

brown needles (0·14 g, 49%), m.p. 166—168°, $v_{\rm max}$ (Nujol) 1690 cm⁻¹, $\lambda_{\rm max}$ (MeOH) 246 nm (log ε 4·61), 258sh (4·48), 270 (4·12), 310 (3·98), 320 (3·91), 412 (3·08), and 485 (2·90), τ 0·98 (1H, m), 1·20 (3H, m), 3·35—3·80 (10H, m), and 8·22 (3H, s) (Found: M^+ 320·1201. C₂₄H₁₆O requires M320·1201).

(b) In ethanol. The adduct (1.5 g) was dissolved in benzene (50 ml; anhydrous) and ethanol (400 ml) was added. The solution was flushed with nitrogen and irradiated for 10 h; it became ruby red. Removal of solvent and chromatography on alumina gave 2-methyl-3-phenylcyclopenta[I]phenanthren-1-one.

(c) In cyclohexane. The adduct (1.0 g) was irradiated in cyclohexane (650 ml) under nitrogen for 8 h. No colour change was detected. The u.v. spectrum of the solution showed an absorption at 275 nm but work up gave no isolable products.

(d) In cyclohexane. The adduct (1.0 g) was irradiated in cyclohexane (650 ml) under nitrogen for 8 h. The mixture was concentrated to 30 ml under nitrogen. This solution (15 ml) was diluted with methanol (650 ml) and irradiated for 1.5 h but no coloured product was detected. The other half of the solution (15 ml) was diluted with methanol (250 ml) and heated at reflux for 1.5 h. No coloured product was detected.

Photolysis of Adduct (lc).—A solution of the adduct (lc) $[\nu_{\rm max.}~({\rm Nujol})~1709~{\rm cm^{-1}},~\lambda_{\rm max.}~({\rm MeOH})~348~{\rm nm},~{\rm log}~\epsilon~4\cdot08]~(0\cdot5~{\rm g})$ in propan-2-ol (350 ml) was irradiated for 2 h. When the lamp was switched on the solution darkened instantly at the interface between the Pyrex well and the solution. At the end of the irradiation the solution was deep maroon. Solvent was removed under reduced pressure and the residue was chromatographed on alumina. Benzene-ether (1:1) eluted a maroon band. The solid obtained was recrystallised from benzene-light petroleum to afford dark maroon crystals of 3-p-anisyl-6-methoxy-2phenylcyclopenta[1]phenanthren-1-one (62%), m.p. 213-215°, ν_{max} (Nujol) 1700 cm⁻¹, λ_{max} (MeOH) 255 (log ε 5·15), 285sh (4.75), 322 (4.52), 335 (4.47), 420sh (3.44), and 510 (2.91) nm, τ 0.95 (1H, m), 1.50 (2H, m), 2.02 (1H, d), 2·35-3·15 (12H, m), 6·05 (3H, s), and 6·13 (3H, s) (Found: C, 84.2; H, 5.0. C₃₁H₂₂O₃ requires C, 84.0; H, 4.8%).

Photolysis of Adduct (1d) .- A suspension of the adduct (1d) $[\nu_{max}$ (Nujol) 1720 cm⁻¹, λ_{max} (MeOH) 255 and 300sh nm] (1.0 g) in propan-2-ol (700 ml) was irradiated for 11 h. Most of the adduct had then reacted but some (0.15 g) was filtered off. The ruby-red solution was evaporated to dryness under reduced pressure. The residue was dissolved in benzene-light petroleum (1:1) and chromatographed on alumina. Benzene-light petroleum (1:1) eluted a purple band which gave a dark solid (0.20 g) on removal of solvent. This was crystallised from benzene-light petroleum to give purple needles of 6-chloro-3-p-chlorophenyl-2-phenylcyclopenta[l]phenanthren-1-one (53%), m.p. 223–225°, ν_{max} (Nujol) 1709 cm⁻¹, λ_{max} (MeOH) 265 (log ε 5.04), 285sh (4.71), 325sh (4.42), 420 (3.03), and 500 (2.89) nm, τ (CDCl₃; satd. soln.; 100°; 12 scans on C.A.T.) 0.92 (1H, m), 1.39 (1H, m), 1.59 (1H, m), and 2.21-2.83 (13H, m) (Found: C, 77.4; H, 3.6; Cl, 15.7. C₂₉H₁₆Cl₂O requires C, 77.2; H, 3.6; Cl, 15.7%).

Photolysis of Adduct (1e).—The adduct (1e) (0.3 g) was issolved in hot benzene (10 ml) and diluted with propan-2-ol

¹⁴ M. Vaillant, Compt. rend., 1952, 234, 534.

¹⁵ P. M. G. Bavin, Canad. J. Chem., 1959, 37, 2023.

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(300 ml). Irradiation ($\lambda >$ 300 nm) of this solution for 4 h gave after work-up and chromatography 2,3-diphenyl-cyclopenta[l]phenanthren-1-one (13%).

Photolysis of Adduct (1f).—The adduct (1f) (0.5 g) was dissolved in propan-2-ol (350 ml) and irradiated for 8 h. Work-up and chromatography gave 2-methyl-3-phenyl-cyclopenta[I]phenanthren-1-one (13%).

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