

The $2\pi_s + 2\pi_s$ Photocycloadditions of Triplet Pyrene to Cyclohexa-1,3-diene

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exo-(8bSR,8cSR,12bRS,12aSR)-8b,8c,11,12,12a,12b-Hexahydrobenzocyclobuta[1,2-*e*]pyrene and *endo*-(8bSR,8cSR,12bRS,12aRS)-8b,8c,11,12,12a,12b-hexahydrobenzocyclobuta[1,2-*e*]pyrene have been isolated; this is the first example of a $2\pi_s + 2\pi_s$ photocycloaddition between cyclohexa-1,3-diene and 3 pyrene*.

In recent years, many theoretical and experimental investigations of the role of exciplexes as intermediates in the photocycloadditions of arenes to 1,3-dienes have been carried out.¹ Although there are several examples of reactions in which exciplexes have been suggested as intermediates,² there are no reports of $2\pi_s + 2\pi_s$ photocycloadditions of 1,3-dienes to pyrenes although the latter compounds have been extensively studied.^{3,4} We now report the isolation of *exo*-(8bSR,8cSR,12bRS,12aSR)-8b,8c,11,12,12a,12b-hexahydrobenzocyclobuta[1,2-*e*]pyrene (1) and *endo*-(8bSR,8cSR,12bRS,12aRS)-8b,8c,11,12,12a,12b-hexahydrobenzocyclobuta[1,2-*e*]pyrene (2) as $2\pi_s + 2\pi_s$ photoadducts from the photoreaction of pyrene and cyclohexa-1,3-diene (CHD).

Results and Discussion

A solution of pyrene and CHD in benzene was irradiated with an Ushio 100-W high-pressure mercury arc through a Pyrex filter for 37 h under nitrogen. After evaporation of the benzene, the residue was chromatographed on silica gel eluting with hexane to give compounds (1) and (2) in 12 and 31% yield, respectively. Because of their complex 1 H n.m.r. spectra, the structures of (1) and (2) were established by preparing the corresponding epoxides (8bSR,8cSR,9SR,10RS,12aRS,12bSR)-9,10-epoxy-11,12,12a,12b-hexahydrobenzocyclobuta[1,2-*c*]pyrene (3) and (8bSR,8cSR,9RS,10SR,12aRS,12bRS)-9,10-epoxy-8b,8c,11,12,12a,12b-hexahydrobenzocyclobuta[1,2-*e*]pyrene (4). Compounds (1) and (2) were treated with *m*-chloroperbenzoic acid (MCPBA) (1 equiv.) in CHCl_3 to give the epoxides (3) (54.4%) and (4) (50.3%), respectively. In the 1 H n.m.r. spectrum of (4), 11'-H (δ 0.36) lies over the transannular phenanthrene ring, and is shifted to higher field than that of (3) (δ 2.32) by the anisotropic effect of the phenanthrene ring current. The coupling constants ($J_{8c,8b}$, $J_{12a,12b}$, $J_{8b,12b}$, and $J_{12a,8c}$) are all 10.5 Hz which is reasonable for a structure with all the adjacent protons *cis* to each other on the cyclobutane ring. In contrast to compound (4), the corresponding coupling constants for (3) ($J_{8b,12b}$, $J_{12b,12a}$, $J_{8c,12a}$, and $J_{8b,8c}$) are 10, 7.5, and 2.5 Hz, respectively.† These coupling constants together with the results of a shift reagent experiment (details of which are available as a Supplementary Publication,‡ SUP No. 23843, 6 pp.) led to the assignment of the configuration of the cyclobutane ring shown in formula (3).

Treatment of compound (2) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in refluxing CHCl_3 gave 4-

† The assignments of the chemical shifts and coupling constants for (3) and (4) were confirmed by a computer simulation method (see Supplementary Publication).

‡ For details of the Supplementary Publications Scheme see Instructions for Authors (1984) in *J. Chem. Soc., Perkin Trans. I*, 1984, Issue 1.

Table 1. Quantum (Φ) and relative yields for the formation of compounds (1) and (2)

Concentration (M) of pyrene	Concentration (M) of CHD	Relative yield (%)		Φ
		(1)	(2)	
9.05×10^{-5}	1	<i>a</i>	<i>a</i>	1.69×10^{-3}
9.05×10^{-4}	1	27	73	1.48×10^{-2}
9.05×10^{-3}	1	22	78	2.52×10^{-2}

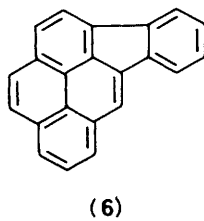
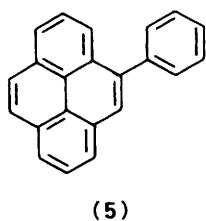
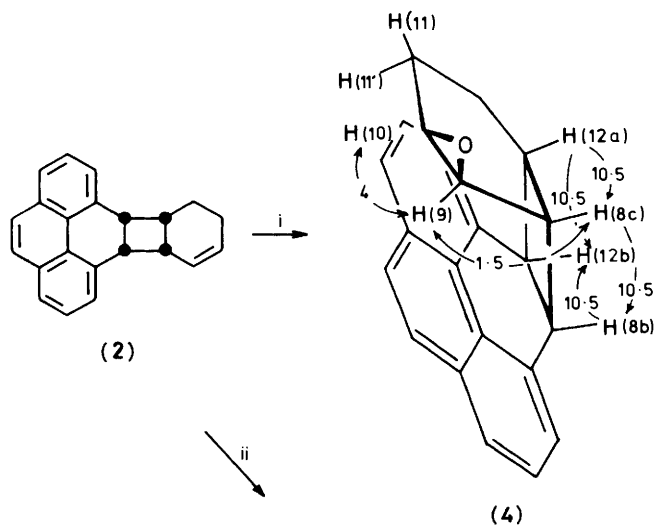
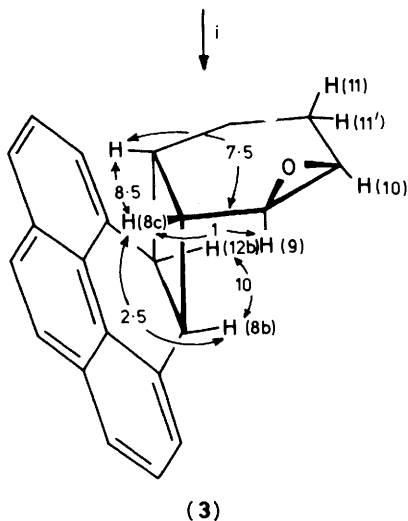
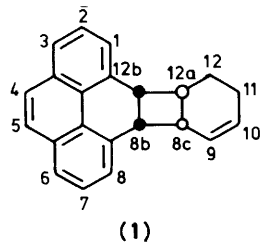
* Not measured.

phenylpyrene (5) and indeno[1,2,3-*cd*]pyrene (6); in their mass spectra both (1) (M^+ 282) and (2) (M^+ 282) show the loss of the fragment C_6H_8 (m/z 80) on electron impact (70 eV), to give pyrene (base peak, m/z 202), and their electronic spectra show the presence of a phenanthrene moiety. Thus, the structures (1)§ and (2) were assigned on the basis of their spectral properties as well as comparison of their 1 H n.m.r. spectra with those of the corresponding epoxides (3) and (4), and the above chemical reactions.

An interesting question is how these $2\pi_s + 2\pi_s$ adducts are formed in the photoreaction. The quantum yields for the formation of compounds (1) and (2) in benzene, using deoxygenated (argon) samples and a conventional merry-go-round apparatus, with light of wavelength 313 nm, at $25 \pm 1^\circ\text{C}$, are summarized in Table 1. As the concentration of pyrene is increased, there is a slight increase in the quantum yield for the formation of the photoproducts, and also an increase in the concentration of the pyrene excimer.⁴ We investigated the possibility that the excimer of pyrene reacts with CHD efficiently at high concentrations of pyrene, but it was ruled out by the fact that the fluorescence lifetimes from the monomer and the excimer were not affected by the presence of CHD (Table 2). There are three combinational processes ($S_1 \rightsquigarrow T_1$, $T_1 \rightsquigarrow S_0$, $T_1 \rightsquigarrow S_0 + h\nu$) that are influenced by spin-orbital coupling perturbation due to the external heavy atom effect (HAE); the presence of enhanced spin-orbital coupling should therefore give a shorter phosphorescence lifetime.⁵ The nature of the external HAE on pyrene is shown by the data in Table 3. It should be noted that the ratio of (2):(1) is approximately doubled in the presence of oxygen or in halogenated solvents; however, we can not explain this result.

The results indicate that the rate constants for the processes $T_1 \rightsquigarrow S_0$ and/or $T_1 \rightsquigarrow S_0 + h\nu$ are influenced by

§ The X-ray analysis of (1) carried out by Professor S. Kashino (Okayama University) supported our proposed structure and will be reported elsewhere.



Reagents: i, MCPBA; ii, DDQ

spin-orbital coupling, and the triplet state (T_1) of pyrene is quenched by the presence of oxygen. The results in Table 3 which show a positive HAE also indicate that the reactive state

Table 2. Lifetimes of pyrene fluorescence (τ_f) in benzene at 25 °C^a

Pyrene (M)	τ_f (380 nm)/ns Monomer	τ_f (475 nm)/ns Excimer
9.05×10^{-5}	162.0	
9.05×10^{-4}	74.5	80.8
9.05×10^{-4b}	74.3	79.9
9.05×10^{-3}	15.3	31.4
9.05×10^{-3b}	15.2	30.9
9.05×10^{-2}	2.7	27.8

^a Lifetimes were determined with a single photon counter. Each sample was deoxygenated using argon. ^b CHD (1M) present.

Table 3. The effects of heavy-atom solvents and oxygen on the quantum (Φ) and relative yields for the formation of compounds (1) and (2)^a

Solvent	Relative yield (%)		$\Phi (\times 10^{-2})$
	(1)	(2)	
Benzene	27	73	1.48
Benzene ^b	14	86	0.96
PrCl	11	89	0.70
PrBr	12	88	0.12
PrI			0.00

^a Concentration of pyrene = 9.05×10^{-4} M, concentration of CHD = 1M. ^b Saturated with oxygen.

of pyrene (which is involved in the cycloaddition) is the triplet state. We therefore assumed that the triplet state of pyrene is the reactive state for these unique $2\pi_s + 2\pi_s$ photocycloadditions.

Experimental

The i.r. spectra were measured in CHCl_3 and the ^1H n.m.r. (200 MHz) spectra were recorded in CDCl_3 with tetramethylsilane as the internal standard, unless otherwise stated. Mass spectra were obtained on a JEOL JMS-D 300 mass spectrometer. H.p.l.c. analyses were performed on a HITACHI-655 high pressure liquid chromatograph (ZORBZX ODS; 4.6 mm, 15 cm). The lifetimes of the pyrene fluorescence were determined using a single photon counter (ORTEC).

exo-(8bSR,8cSR,12bRS,12aSR)-8b,8c,11,12,12a,12b-Hexahydrobenzocyclobuta[1,2-*e*]pyrene (1) and *endo*-(8bSR,8cSR,12bRS,12aRS)-8b,8c,11,12,12a,12b-Hexahydrobenzocyclobuta[1,2-*e*]pyrene (2).—A solution of pyrene (1.0 g, 4.9 mmol) and cyclohexa-1,3-diene (5.9 g, 74 mmol) in benzene (110 ml) was irradiated with an Ushio 100-W high-pressure mercury arc through a Pyrex filter for 37 h under nitrogen. The benzene was evaporated off under reduced pressure and the residue was chromatographed on silica gel eluting with hexane. Pyrene (0.7 g) was recovered, and products (1) (49 mg, 12%) and (2) (130 mg, 31%) were separated. *Compound* (1) had m.p. 132–133 °C (EtOH); ν_{max} . 3 040, 3 000, 2 920, and 2 840 cm^{-1} ; δ 1.58 (1 H, m), 1.80 (1 H, m), 2.16 (1 H, m), 2.38 (1 H, m), 2.84 (1 H, m), 3.00 (1 H, m), 3.38 (2 H, m), 5.97 (1 H, m), 6.12 (1 H, m), 7.27 (1 H, d), 7.43 (1 H, d), 7.53 (2 H, t), and 7.76 (4 H, m); λ_{max} (EtOH) 347 (log ϵ 2.55), 338 (2.74), 323 (2.68), 303 (3.84), 274 (4.32), 263sh, 230 (4.52), and 195 nm (4.32) (Found: C, 93.8; H, 6.2. $\text{C}_{22}\text{H}_{18}$ requires C, 93.57; H, 6.43%). *Compound* (2) was obtained as an oil, b.p. 160–165 °C at 0.4 Pa; ν_{max} . 3 010, 3 040, 2 910, and 2 830 cm^{-1} ; δ 1.08–1.04 (3 H, m), 1.53 (1 H, m), 3.14 (1 H, m), 3.58 (1 H, m), 4.43 (2 H, m), 5.48 (2 H, m), 7.26 (1 H, d), 7.34 (1 H, d), 7.51 (2 H, t), and 7.71 (4 H, m); λ_{max} (EtOH) 343 (log ϵ 2.98), 329 (2.94), 302 (4.00), 272 (4.48), 261sh, 224 (4.66), and 196 nm

(4.34) (Found: C, 93.8; H, 6.1. $C_{22}H_{18}$ requires C, 93.57; H, 6.43%).

exo-(8bSR,8cSR,9SR,10RS,12aRS,12bSR)-9,10-Epoxy-8b,8c,11,12,12a,12b-hexahydrobenzocyclobuta[1,2-c]pyrene (3) and (8bSR,8cSR,9RS,10SR,12aRS,12bRS)-9,10-Epoxy-8b,8c,11,12,12a,12b-hexahydrobenzocyclobuta[1,2-e]pyrene (4).—Compound (1) was treated with *m*-chloroperbenzoic acid (35 mg, 0.2 mmol) in $CHCl_3$ (5 ml) at room temperature to give the epoxide (3) (9.5 mg, 54.4%). The analogous reaction of compound (2) was carried out as described for the preparation of (3) from (1), and the epoxide (4) was obtained in 50.3% yield. The epoxide (3) had m.p. 160.5–161.5 °C (EtOH), ν_{max} (Nujol) 3 050, 955, and 825 cm^{-1} ; δ 1.56 (2 H, m, $J_{12,12}$, 14.5 Hz), 2.32 (2 H, m, $J_{11,11}$, 14.5 Hz), 2.62 (1 H, hept., $J_{12a,8c}$ 8.5 Hz, $J_{12a,12b}$ 7.5 Hz), 3.04 (1 H, br d, $J_{8c,12a}$ 8.5 Hz, $J_{8c,8b}$ 2.5 Hz, $J_{8c,9}$ 1 Hz), 3.52 (2 H, br s, $J_{8c,9}$ 1 Hz, $J_{10,11}$, $J_{10,11}$, 1 Hz), 3.93 (1 H, dd, $J_{8b,12b}$ 10 Hz, $J_{8b,8c}$ 2.5 Hz), 4.02 (1 H, dd, $J_{12b,8b}$ 10 Hz, $J_{12b,12a}$ 7.5 Hz), 7.23 (1 H, dd, J 8 Hz, J 1.25 Hz), 7.48 (1 H, dd, J 8 Hz, J 1.25 Hz), 7.52 (1 H, t, J 8 Hz), 7.62 (1 H, t, J 8 Hz), 7.77 (2 H, td, J 8 Hz, J 1.25 Hz), and 7.76 (2 H, br s) (Found: C, 88.3; H, 6.05. $C_{22}H_{18}O$ requires C, 88.56; H, 6.08%). The epoxide (4) had m.p. 116–117 °C (EtOH); ν_{max} (Nujol) 3 050, 960, and 830 cm^{-1} ; δ 0.36 (1 H, m), 1.34 (2 H, m), 1.61 (1 H, m), 2.34 (1 H, br s, $J_{10,9}$ 4 Hz, $J_{10,11}$ 3 Hz, $J_{10,11}$ 2 Hz), 2.52 (1 H, dd, $J_{9,8c}$ 1.5 Hz, $J_{9,10}$ 4 Hz), 3.18 (1 H, m, $J_{12a,12b}$ 10.5 Hz, $J_{12a,8c}$ 10.5 Hz), 3.44 (1 H, t, $J_{8c,8b}$ 10.5 Hz, $J_{8c,12a}$ 10.5 Hz, $J_{8c,9}$ 1.5 Hz, $J_{8c,10}$ 1.5 Hz), 4.39 (1 H, t, $J_{12b,8b}$ 10.5 Hz, $J_{12b,12a}$ 10.5 Hz), 4.66 (1 H, t, $J_{8b,12b}$ 10.5 Hz, $J_{8b,8c}$ 10.5 Hz), 7.28 (1 H, dt, J 8 Hz, J 1.25 Hz), 7.36 (1 H, dt, J 8 Hz, J 1.25 Hz), 7.54 (1 H, t, J 8 Hz), 7.56 (1 H, J 8 Hz), 7.74 (1 H, dd, J 8 Hz, J 1.25 Hz), 7.75 (2 H, br s), and 7.76 (1 H, dd, J 8 Hz, J 1.25 Hz) (Found: C, 88.8; H, 5.8. $C_{22}H_{18}O$ requires C, 88.56; H, 6.08%).

Reaction of Compound (2) with DDQ.—Treatment of compound (2) (155 mg, 0.55 mmol) with DDQ (749 mg, 3.2 mmol) in refluxing $CHCl_3$ (10 ml) gave 4-phenylpyrene (5) (15 mg) and indeno[1,2,3-*cd*]pyrene (6) (6.1 mg) in 10 and 4% yield, respectively. Compound (5) had m.p. 129–130 °C (EtOH) (lit.,^{6a} 132–134 °C); λ_{max} (EtOH) 340 (log ϵ 4.45), 325 (4.28), 311 (3.88), 277 (4.54), 267 (4.26), 242 (4.69), and 234 nm (4.48). These data are consistent with those obtained by Lang.^{6a} Compound (6) had m.p. 163–164 °C (benzene) (lit.,^{6b} 163–164 °C); λ_{max} (cyclohexane) 359 (log ϵ 3.92), 316 (4.15), 303 (4.22), 291 (4.11), 276 (4.06), 268 (4.05), 251 (4.49), 243 (4.34), and 211 nm (4.23). These data are also consistent with those obtained by Lang.^{6b}

Quantum Yield Determination for the Formation of Compounds (1) and (2), and Measurement of the Lifetime of the Pyrene Fluorescence.—Ten solutions (4 ml) containing pyrene and CHD in spectrograde dry benzene (Tables 1 and 3) and heavy-atom solvents were prepared as shown in Table 2. These were degassed using a vacuum line (8×10^{-2} Pa) by three freeze-thaw cycles. Irradiation at 3 130 Å was carried out with a Toshiba 450-W mercury lamp through a filter system [Pyrex, $NiSO_4$ (1 kg), H_2O (1 l), 0.5-cm path length, Toshiba UV-25] at 25 °C. The yields of the products (1) and (2) were determined by h.p.l.c. eluting with MeOH. Benzophenone-benzhydrol actinometry was used for the quantum yield determinations.⁷ The lifetimes of the pyrene fluorescence (τ_f , Table 2) were determined in benzene at 25 °C with a single photon counter. Each sample was deoxygenated using argon.

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References

- N. C. Yang, J. Masnovi, and W-L. Chiang, *J. Am. Chem. Soc.*, 1979, **101**, 6465; J. Saltiel, D. E. Townsend, L. L. Metts, M. Wrighton, W. Mueller, and R. C. Rosanske, *J. Chem. Soc., Chem. Commun.*, 1978, 588; G. Kaupp, *Angew. Chem. Int. Ed. Engl.*, 1972, **11**, 718; N. C. Yang, and J. Libman, *J. Am. Chem. Soc.*, 1972, **94**, 1405.
- M. Kimura, S. Sagara, and S. Morosawa, *J. Org. Chem.*, 1982, **47**, 4344; N. C. Yang, H. Shou, T. Wang, and J. Masnovi, *J. Am. Chem. Soc.*, 1980, **102**, 6654.
- Y. Taniguchi, Y. Nishina, and N. Mataga, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 764.
- N. J. Turro, 'Modern Molecular Photochemistry,' The Benjamin/Cummings Publishing Co. Inc., 1978, p. 141; J. A. Barltrop and J. D. Coyle, 'Excited States in Organic Chemistry,' John Wiley and Sons, 1975; C. A. Parker and C. H. Hatchard, *Trans. Faraday Soc.*, 1963, **59**, 284.
- N. J. Turro, 'Molecular Photochemistry,' W. A. Benjamin Inc., 1965, p. 57.
- (a) K. F. Lang, *Liebigs Ann. Chem.*, 1937, **531**, 112; *Chem. Commun.*, 1966, 345; (b) K. F. Lang and H. Buffleb, *Chem. Ber.*, 1957, **90**, 2894.
- S. L. Murov, 'Handbook of Photochemistry,' Marcel Dekker Inc., New York, 1973.

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