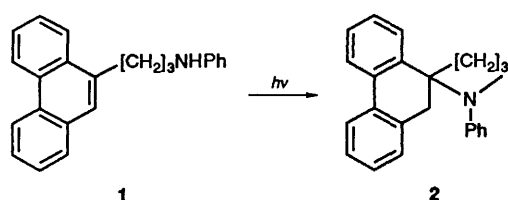


Photochemical Reactions of 9-(ω -Anilinoalkyl)-10-bromophenanthrenes

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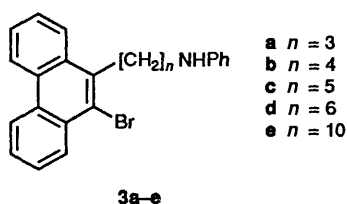
Irradiation of the title compounds $\text{Ar}(\text{CH}_2)_n\text{NHPH}$ ($\text{Ar} = 10\text{-bromo-9-phenanthryl}$, $n = 3, 4, 5, 6, 10$) gave debrominated aniline derivatives in all cases. For $n = 3$ and 4, the cyclic compounds **4a,b** were isolated in moderate yields. A photo-induced electron-transfer mechanism is proposed.

We reported earlier that irradiation of 9-(3-anilino-propyl)-phenanthrene **1** in benzene affords the spiro compound **2** by an intramolecular addition of the N-H function to the phenanthrene ring (Scheme 1),¹ a reaction for which we



Scheme 1

proposed a mechanistic pathway proceeding *via* an exciplex intermediate formed by interaction between the excited phenanthrene moiety and the anilino group; the interaction between the two chromophores serves to bring them into favourable positions for cyclisation. We have attempted to form nitrogen heterocycles in this way and here we describe the photochemical reaction of 9-(ω -anilinoalkyl)-10-bromophenanthrenes **3a-e**, in which the anilino group may undergo intramolecular cyclisation to the 10-position of the phenanthrene ring.²



3a-e

Results and Discussion

9-(ω -Anilinoalkyl)-10-bromophenanthrenes **3a-e**.—9-(ω -bromoalkyl)phenanthrenes ($n = 3, 4, 5, 6, 10$), prepared from dibromoalkanes and phenanthryllithium,* when treated with bromine gave 10-bromo-9-(ω -bromoalkyl)phenanthrenes which were converted into the title anilinoalkyl derivatives **3a-e** by reaction with aniline in the presence of potassium carbonate. The position of bromination of the phenanthrene ring was determined by ¹H NMR spectroscopy: *i.e.* disappearance of 10-H (s); downfield shift of 1-H to δ_{H} 8.4–8.5 by bromination at the *peri*-position; and similarity of the aromatic signal patterns to those of 9-bromo-10-methylphenanthrene.^{†,3}

* This procedure is applicable to the preparations of $\text{Ar}-(\text{CH}_2)_n-\text{Br}$ ($\text{Ar} = 9\text{-phenanthryl}$, $n = 3\text{--}10$ and 12; $\text{Ar} = 9\text{-anthryl}$, $n = 6$; $\text{Ar} = 1\text{-naphthyl}$, $n = 6$; $\text{Ar} = 2\text{-benzo}[b]\text{thienyl}$ and 2-naphthyl , $n = 7$).
[†] δ_{H} 7.55–7.66 (4 H, m, ArH), 8.05–8.08 (1 H, m, ArH), 8.42–8.45 (1 H, m, ArH), 8.58–8.65 (2 H, m, ArH) and 2.91 (3 H, s, Me).

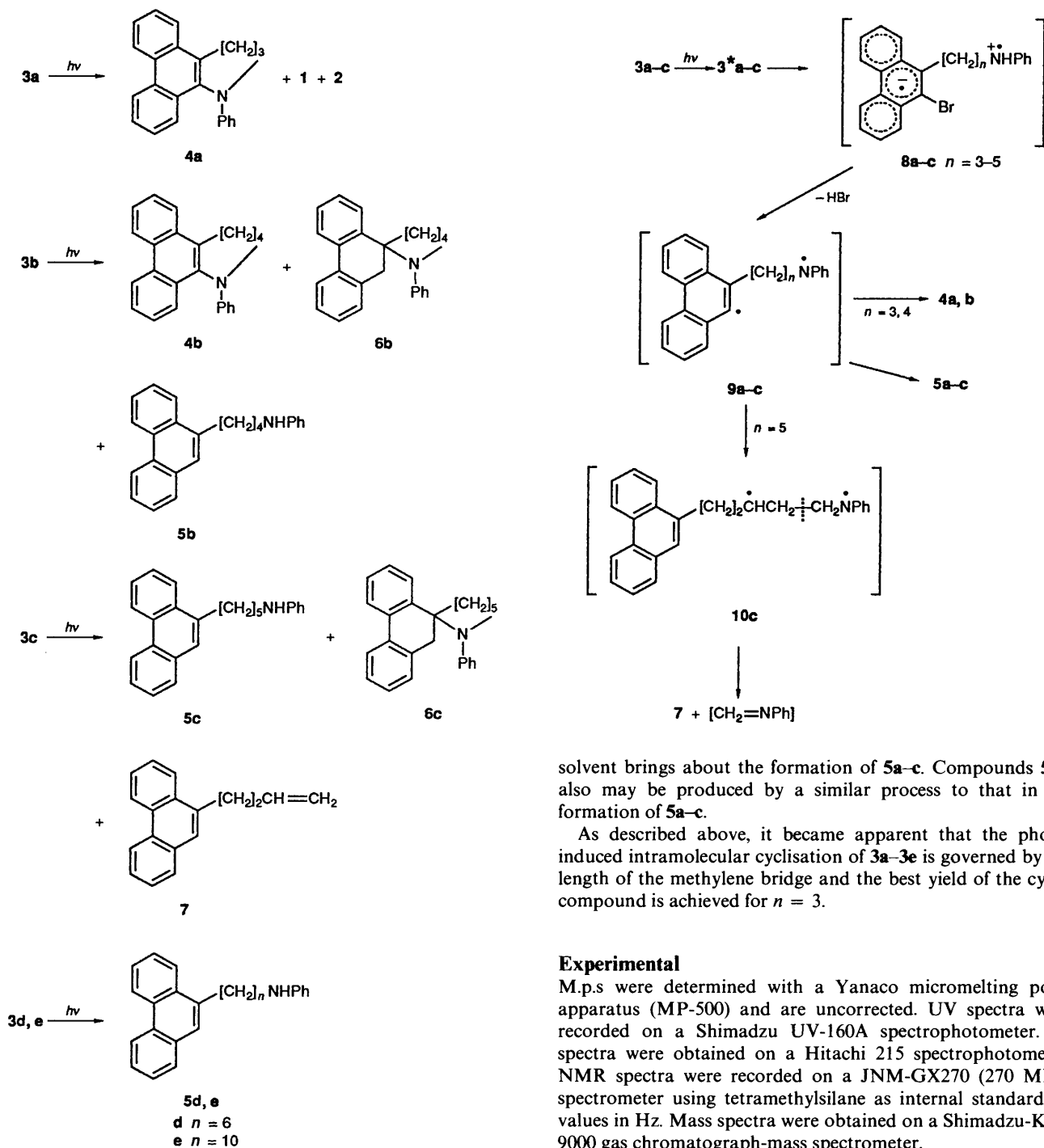
Photoreaction.—A de-gassed solution of each of compounds **3a-e**, in a sealed Pyrex tube, was irradiated at a distance of 5 cm from a 300 W high-pressure mercury lamp. Hydrogen bromide generated in the photoreaction was captured by diethyl- or triethyl-amine added to the solution. The reaction products were separated by column chromatography. Although five or more products were detected by TLC, those identified were the debrominated compounds **1** and **5b-e**, spiro compounds **2**, **6b, c**, and the expected cyclic compounds **4a,b** (Scheme 2). The structures of compounds **1**, **5b-e**, **2** and **6b** were determined by spectral comparison with those of the corresponding authentic specimens.¹

The structure of compound **6c** was determined by comparison of its NMR spectrum with that of the authentic compound (prepared by the photoreaction of amine **5c**); its ¹H NMR spectrum was similar to those of **2** and **6b**. In particular, the 4- and 5-H signals of the phenanthrene ring at δ *ca.* 8.7 were not observed, indicating formation of the 9,10-dihydrophenanthrene. Moreover, the AB quartet signals (probably 10-H of the 9,10-dihydrophenanthrene moiety) were observed at δ 2.72 and 4.10. Compound **6c** was easily converted into the aniline derivative **5c** by treatment with acid, this being characteristic of the spiro compounds **2** and **6b**.

The structures of **4a,b** were determined from spectral data (see Experimental section); the signals at δ_{H} 8.62–8.70 (mult) indicated the presence of a phenanthrene ring. The spectrum of **4b** showed δ_{H} *ca.* 6.6 and 7.1 (br \times 2, ArH) at room temperature; these sharpened at 50 °C. In contrast the signals of the aliphatic protons (8 \times mult at 27 °C) were broad at 50 °C, suggesting a restricted flipping motion of the tetrahydroazepine ring.

The structure of 4-(9-phenanthryl)but-1-ene **7** was determined by comparing its spectral characteristics with those of an authentic specimen.⁴

Yields for the isolated photoproducts and the recovery of unchanged materials are shown in Table 1. A solution of each of compounds **3a-e** in refluxing toluene (0.016 mol dm⁻³) was unchanged after 24 h, an indication that the products in Table 1 are formed only by the photoreaction. The expected cyclic compounds were obtained only in the photoreactions of **3a** and **3b** (Scheme 2). Diethyl- and triethyl-amine were effective in raising the yields of **4a,b** by capturing HBr generated in the reactions; in their absence HBr must be captured by the starting material. Use of tetrahydrofuran (THF) as solvent increased yields of the debrominated compounds and decreased recovery of the starting materials, non-isolable compounds being formed. In the case of **3c**, the phenanthrylbutene **7** was produced (2–6%) together with **5c** and **6c** (Scheme 2). The photoreaction of **3e** ($n = 10$) (Scheme 2) resulted in a decreased yield of the debrominated compound **5e**, although non-isolable compounds were produced. The spiro compounds, obtained from **3a-c** in low yields, may be formed by photocyclisation of the debrominated compounds **1** and **5b,c**.¹



Scheme 2

The photo-debromination⁵ suggests that the reaction proceeds by photoinduced electron-transfer from the anilino group to the phenanthrene moiety. A possible pathway for the formation of the intended cyclic compounds **4a,b** and the butene derivative **7** is proposed in Scheme 3. The excitation of **3a-c** is considered to bring about an intramolecular electron-transfer from the anilino group to the excited phenanthrene moiety to form **8a-c**. The heterolytic cleavage of the C-Br bond of **8a-c**, accompanied by deprotonation with base, gives compounds **9a-c**. For $n = 3$ and 4, the radical coupling of **9a,b** gives **4a,b** and for $n = 5$, the intramolecular abstraction of hydrogen from the methylene chain of **9c** to form **10c**, followed by the β -fission of the 1,4-biradical, gives **7**. The abstraction of hydrogen by **9a-c** from the methylene group of other molecules or THF as a

solvent brings about the formation of **5a-c**. Compounds **5d,e** also may be produced by a similar process to that in the formation of **5a-c**.

As described above, it became apparent that the photo-induced intramolecular cyclisation of **3a-3e** is governed by the length of the methylene bridge and the best yield of the cyclic compound is achieved for $n = 3$.

Experimental

M.p.s were determined with a Yanaco micromelting point apparatus (MP-500) and are uncorrected. UV spectra were recorded on a Shimadzu UV-160A spectrophotometer. IR spectra were obtained on a Hitachi 215 spectrophotometer. NMR spectra were recorded on a JNM-GX270 (270 MHz) spectrometer using tetramethylsilane as internal standard; J -values in Hz. Mass spectra were obtained on a Shimadzu-KLB 9000 gas chromatograph-mass spectrometer.

ω -(9-Phenanthryl)alkyl Bromides.—These were prepared according to the method described in an earlier paper.¹ Yields, m.p.s, and analytical data are shown in Table 2.

Bromination of ω -(9-Phenanthryl)alkyl Bromides.—To a solution of the bromide in carbon tetrachloride was added dropwise a solution of bromine in the same solvent at room temperature. After the mixture had been stirred for 2 h, the solvent was removed by distillation under reduced pressure and the residue was chromatographed to give the 10-bromophenanthrene. The structures were confirmed by ¹H NMR spectroscopy.

9-(ω -Anilinoalkyl)-10-bromophenanthrenes 3a-e.—A general procedure is given for the preparation of the phenanthrene **3c** and yields, m.p.s, and analytical data are shown in Table 3.

Table 1 Photochemical reactions of 3a-e^a

Compound	Additive	Solvent	Product (yield) ^b (%)	Recovered 3 (%)
3a	None	PhH	4a (17), 1 (10), 2 (2)	54
	Et ₂ NH	PhH	4a (39), 1 (11), 2 (trace)	28
	Et ₃ N	PhH	4a (29), 1 (10), 2 (trace)	22
	Et ₂ NH	THF	4a (11), 1 (15), 2 (9)	12
3b	None	PhH	4b (10), 5b (9), 6b (trace)	59
	Et ₂ NH	PhH	4b (12), 5b (4), 6b (5)	27
	Et ₂ NH	THF	4b (11), 5b (17), 6b (8)	17
3c	Et ₂ NH	PhH	7 (5), 5c (12), 6c (trace)	34
	Et ₃ N	PhH	7 (2), 5c (6), 6c (0)	37
	Et ₂ NH	THF	7 (6), 5c (15), 6c (3)	8
3d	None	PhH	5d (10)	43
	Et ₂ NH	PhH	5d (14)	35
3e	None	PhH	5e (8)	56
	Et ₂ NH	PhH	5e (3)	59

^a Irradiation for 5 h in a sealed tube; molar ratio additive: 3 = 3:1. ^b Isolated.

Table 2 Data for 9-C₁₄H₉-(CH₂)_n-Br

Formula	M.p. (°C)	Yield ^a (%)	Found (required) (%)		δ_{H}	
			C	H	(CH ₂) _n	ArH
C ₁₇ H ₁₅ Br	60–62	21	67.95 (68.2)	4.9 (5.05)	2.32–3.54	7.55–8.77
C ₁₈ H ₁₇ Br	114.5–116.5	42	69.1 (69.0)	5.6 (5.5)	1.95–3.51	7.54–8.77
C ₁₉ H ₁₉ Br	72–74.5	76	69.6 (69.7)	5.9 (5.85)	1.60–3.45	7.54–8.76
C ₂₀ H ₂₁ Br	88.5–90	82	70.1 (70.4)	6.2 (6.2)	1.47–3.44	7.56–8.76
C ₂₄ H ₂₉ Br	79–80.5	57	72.6 (72.5)	7.5 (7.4)	1.26–3.42	7.54–8.75

^a Based on 9-bromophenanthrene.

Table 3 Data for phenanthrenes 3a–e

Compound (formula)	Yield ^a (%)	M.p. (°C)	Found (required) (%)		
			C	H	N
3a (C ₂₃ H ₂₀ NBr)	50	131.5–133.5	70.5 (70.78)	5.4 (5.16)	3.55 (3.59)
3b (C ₂₄ H ₂₂ NBr)	73	96–97.5	71.35 (71.29)	5.5 (5.48)	3.6 (3.46)
3c (C ₂₅ H ₂₄ NBr)	54	88–91	71.9 (71.77)	5.7 (5.78)	3.6 (3.35)
3d (C ₂₆ H ₂₆ NBr)	59	110.5–112	72.2 (72.22)	6.0 (6.06)	3.0 (3.24)
3e (C ₃₀ H ₃₄ NBr)	61	64–66	73.55 (73.76)	7.1 (7.02)	2.9 (2.87)

^a Based on the corresponding 9-(ω -bromoalkyl)phenanthrene.

A mixture of aniline (28 cm³, 0.3 mol), potassium carbonate (1.7 g, 12.4 mmol), and 10-bromo-9-(5-bromopentyl)phenanthrene [prepared by the reaction of 9-(5-bromopentyl)phenanthrene (4.35 g, 13.3 mmol) and bromine (0.75 cm³, 14.6 mmol) in tetrachloromethane (60 cm³)] was stirred for 30 h under argon at room temperature. The reaction mixture was washed with a mixture of benzene* and water, and the benzene layer was separated, dried (Na₂SO₄), and distilled under reduced pressure almost to dryness. Chromatography of the residue gave 9-(5-anilinopentyl)-10-bromophenanthrene 3c; λ_{max} (hexane)/nm 257 (log ϵ 4.78), 291 (4.14) and 303 (4.16); ν_{max} /cm⁻¹ 3400 (NH); δ_{H} (CDCl₃) 1.65–1.85 (6 H, m, CH₂), 3.15–5.20 (2 H, t, CH₂), 3.42–3.48 (2 H, t, CH₂), 3.64 (1 H, br s, NH), 6.59–6.72 (3 H, m, ArH), 7.14–7.22 (2 H, m, ArH), 7.62–7.72 (4 H, m, ArH), 8.10–8.14 (1 H, m, ArH), 8.48–8.51 (1 H, m, ArH) and 8.66–8.75 (2 H, m, ArH).

9-(3-Anilinopropyl)-10-bromophenanthrene 3a. λ_{max} (cyclohexane)/nm 258 (log ϵ 4.78), 292 (4.16) and 304 (4.15); ν_{max} (KBr)/cm⁻¹ 3380 (NH); δ_{H} (CDCl₃) 2.04–2.15 (2 H, m,

CH₂), 3.35–3.40 (2 H, t, CH₂), 3.53–3.59 (2 H, m, CH₂), 3.79 (1 H, br s, NH), 6.65–6.74 (3 H, m, ArH), 7.16–7.23 (2 H, m, ArH), 7.57–7.71 (4 H, m, ArH), 8.08–8.11 (1 H, m, ArH), 8.47–8.51 (1 H, m, ArH) and 8.66–8.74 (2 H, m, ArH).

9-(4-Anilinobutyl)-10-bromophenanthrene 3b. λ_{max} (cyclohexane)/nm 258 (log ϵ 4.83), 292 (4.21) and 304 (4.21); ν_{max} (KBr)/cm⁻¹ 3375 (NH); δ_{H} (CDCl₃) 1.85–1.93 (4 H, m, CH₂CH₂), 3.22–3.27 (2 H, t, CH₂), 3.45–3.51 (2 H, m, CH₂), 3.65 (1 H, br s, NH), 6.61–6.73 (3 H, m, ArH), 7.15–7.21 (2 H, m, ArH), 7.60–7.71 (4 H, m, ArH), 8.09–8.13 (1 H, m, ArH), 8.47–8.51 (1 H, m, ArH) and 8.65–8.74 (2 H, m, ArH).

9-(6-Anilinohexyl)-10-bromophenanthrene 3d. λ_{max} (hexanes)/nm 225 (log ϵ 4.45), 257 (4.78), 291 (4.14) and 303 (4.16); ν_{max} (KBr)/cm⁻¹ 3350 (NH); δ_{H} (CDCl₃) 1.4–1.83 (8 H, m, CH₂), 3.11–3.16 (2 H, t, CH₂), 3.40–3.46 (2 H, t, CH₂), 3.61 (1 H, br s, NH), 6.58–6.71 (3 H, m, ArH), 7.13–7.21 (2 H, m, ArH), 7.61–7.71 (4 H, m, ArH), 8.08–8.13 (1 H, m, ArH), 8.46–8.52 (1 H, m, ArH) and 8.64–8.74 (2 H, m, ArH).

9-(10-Anilinodecyl)-10-bromophenanthrene 3e. λ_{max} (hexanes)/nm 226 (log ϵ 5.46), 257 (5.78), 292 (4.14) and 303 (4.16); ν_{max} (KBr)/cm⁻¹ 3390 (NH); δ_{H} (CDCl₃) 1.34–1.80 (16 H, m, CH₂), 3.07–3.13 (2 H, t, CH₂), 3.38–3.44 (2 H, m, CH₂), 3.59 (1 H, br s, NH), 6.58–6.71 (3 H, m, ArH), 7.13–7.20 (2 H, m, ArH),

* **WARNING:** Benzene is hazardous to health, although it is a good solvent for the aniline derivatives.

7.61–7.71 (4 H, m, ArH), 8.11–8.14 (1 H, m, ArH), 8.46–8.51 (1 H, m, ArH) and 8.64–8.74 (2 H, m, ArH).

Photoreactions.—**Preparative irradiation.** Argon was bubbled through a solution of the sample compound (1.6×10^{-2} mol dm^{-3}) and diethylamine in benzene in a Pyrex vessel for 30 min after which the solution was irradiated with a 300 W high-pressure mercury lamp with continued passage of argon. After irradiation, the mixture was filtered to remove diethylammonium bromide and the filtrate evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene–hexane (1:1, v/v).

Photoreaction of 3a. After irradiation for 1.5 h **3a** (312 mg) and diethylamine (70 mg) in benzene (50 cm^3), the mixture was filtered (ca. 80 mg, 65% of diethylammonium bromide, identified from its IR spectrum, was obtained) and the filtrate evaporated under reduced pressure. Chromatography of the residue gave a mixture of 1,2,3,4-tetrahydro-1-phenyldibenzo[*f,h*]quinoline **4a** and 1'-phenylspiro[9,10-dihydrophenanthrene-9,2'-pyrrolidine]**2** (125 mg) [6:1 molar ratio, estimated by NMR, *i.e.* yields **4a** (43%) and **2** (8%)]. The pure quinoline derivative **4a** was obtained by the slow addition of hexane to a benzene solution of the mixture; m.p. 202–204 °C (Found: C, 89.2; H, 6.0; N, 4.5. $\text{C}_{23}\text{H}_{19}\text{N}$ requires C, 89.28; H, 6.19; N, 4.53%); λ_{max} (hexane)/nm 245infl, 254 (log ϵ 4.69), 265sh, 280sh and 323 (4.05); δ_{H} (CDCl_3) 1.98–2.07 (2 H, m, CH_2), 3.91–3.25 (2 H, t, CH_2), 3.89–3.94 (2 H, m, CH_2), 6.87–6.92 (3 H, m, ArH), 7.13–7.19 (2 H, m, ArH), 7.29–7.36 (1 H, m, ArH), 7.46–7.66 (3 H, m, ArH), 7.80–7.83 (1 H, m, ArH), 8.00–8.03 (1 H, m, ArH) and 8.62–8.70 (2 H, m, ArH).

The second fraction yielded starting amine **3a** (108 mg, 35% recovery) and the third a mixture of unidentified compounds.

Photoreaction of 3b. A solution of amine [**3b** (609 mg) and diethylamine (141 mg) in benzene (100 cm^3)] was irradiated for 1.5 h and then diethylammonium bromide (ca. 100 mg, 43%) was removed.

The first chromatographic fraction gave 2,3,4,5-tetrahydro-1-phenyl-1*H*-phenanthro[9,10-*b*]azepine **4b** (91 mg, 19%), m.p. 215–217 °C (from hexane–benzene) (Found: C, 88.9; H, 6.5; N, 4.2. $\text{C}_{24}\text{H}_{21}\text{N}$ requires C, 89.13; H, 6.54; N, 4.33%); λ_{max} (hexane)/nm 250infl, 257 (log ϵ 4.81), 268sh, 278 (4.11), 290 (4.07), 302 (4.09) and 335 (3.45); δ_{H} (CDCl_3) 1.47–1.73 (2 H, m, CH_2), 2.04–2.31 (2 H, m, CH_2), 2.77–2.87 (1 H, m, CH_2), 3.24–3.50 (2 H, m, CH_2), 4.31–4.39 (1 H, m, CH_2), 6.2–7.3 (5 H, m, ArH), 7.44–7.71 (4 H, m, ArH), 7.87–7.90 (1 H, m, ArH), 8.19–8.22 (1 H, m, ArH) and 8.71–8.81 (2 H, m, ArH).

The second fraction gave 1'-phenylspiro[9,10-dihydrophenanthrene-9,2'-piperidine] **6b** (53 mg, 11%). The third fraction contained the starting amine **3b** (346 mg, 57%), and successive elution with benzene–methanol gave a mixture of the other unidentified products.

Irradiation in a sealed tube (Table 1). A solution of the sample compound (1.6×10^{-2} mol dm^{-3}) in a Pyrex tube was de-gassed by three freeze–pump–thaw cycles under argon, and the tube was sealed under reduced pressure. The solution was irradiated externally with a 300 W high-pressure mercury lamp using a merry-go-round apparatus (Eikosha PIH-300). After irradiation, the same procedure as the case of preparative irradiation was carried out.

Photoreactions of 3a and 3b. Debrominated amine **5a** (or **5b**) was obtained from the eluent after the fraction containing the unchanged amine. In the preparative irradiation described above, **5a** and **5b** were converted into the corresponding spiro compounds owing to the intense light.

Photoreaction of 3c. After irradiation [**3c** (140 mg) and diethylamine (72 mg) in benzene (20 cm^3)], the solvent was evaporated under reduced pressure.

The first chromatographic fraction eluted with benzene–hexane (1:1) gave 4-(9-phenanthryl)but-1-ene **7** (4 mg, 5%); δ_{H} (CDCl_3) 2.55–2.63 (2 H, m, CH_2), 3.19–3.25 (2 H, m, CH_2), 5.02–5.18 (2 H, m, $=\text{CH}_2$), 5.92–6.07 (1 H, m, $=\text{CH}$), 7.54–7.69 (5 H, m, ArH), 7.81–7.85 (1 H, m, ArH), 8.08–8.13 (1 H, m, ArH) and 8.65–8.76 (2 H, m, ArH).

The second fraction contained 1'-phenylspiro[9,10-dihydrophenanthrene-9,2'-azepane] **6c** (trace, detected by NMR spectrum).

The third fraction gave unchanged amine **3c** (48 mg, 34%) and the fourth yielded compound **5c** (13 mg, 12%).

Photoreaction of 3d. After irradiation [**3d** (134 mg) in benzene (20 cm^3)], the solvent was removed under reduced pressure. The first chromatographic fraction eluted with benzene–hexane (1:1) gave unchanged amine **3d** (57 mg, 43%). The second eluent contained compound **5d** (11 mg, 10%).

Photoreaction of 3e. By the same procedure as for **3d**, unchanged amine (83 mg, 56%) and compound **5e** (10 mg, 8%) were obtained from the starting amine **3e** (148 mg).

Authentic Compounds

Spiro Compound 6c.—**Irradiation of 9-(5-anilinopentyl)phenanthrene 5c.** The photoreaction was carried out in a sealed tube as described above. Compound **6c** was obtained from the first chromatographic fraction with benzene–hexane (1:1) (15% yield), m.p. 152–156 °C (hexane) (Found: C, 88.2; H, 7.4; N, 4.3. $\text{C}_{25}\text{H}_{25}\text{N}$ requires C, 88.45; H, 7.42; N, 4.12%); λ_{max} (hexane)/nm 211 (log ϵ 4.72), 260 (4.47) and 300sh; δ_{H} (270 MHz; CDCl_3) 1.54–1.70 (4 H, m, CH_2), 1.80–2.02 (4 H, m, CH_2), 2.72 (1 H, ABq, *J* 16.5, CH), 3.76–3.97 (2 H, m, CH_2), 4.10 (1 H, ABq, *J* 16.5, CH), 6.58–6.69 (3 H, m, ArH), 6.96–7.03 (2 H, m, ArH), 7.12–7.32 (6 H, m, ArH) and 7.77–7.87 (2 H, m, ArH); *m/z* 339 (M^+). The second chromatographic fraction gave the unchanged amine (23%).

4-(9-Phenanthryl)but-1-ene 7.—To a solution of potassium *tert*-butoxide (210 mg, 1.9 mmol) in dimethyl sulfoxide (DMSO) (2 cm^3) was added dropwise a solution of 4-(9-phenanthryl)butyl bromide (380 mg, 1.2 mmol) in DMSO (4 cm^3) with stirring; after 5 min, the reaction mixture was poured into ice-water (60 cm^3), and then extracted with benzene. The benzene solution was dried (Na_2SO_4) and evaporated to dryness. Purification by chromatography yielded the title butene **7** (148 mg, 53%), m.p. 46.5–47.5 °C (from methanol) (Found: C, 93.1; H, 6.95. $\text{C}_{18}\text{H}_{16}$ requires C, 93.06; H, 6.94%); λ_{max} (hexane)/nm 253 (log ϵ 4.76), 276 (4.14), 286 (4.02) and 297 (4.07).

9-(ω -Anilinoalkyl)phenanthrenes 5a–e.—These aniline derivatives were prepared as for the amines **3a–e**. Amines **5a** and **5b** were prepared by the method described in ref. 1.

9-(5-Anilinopentyl)phenanthrene 5c. M.p. 103.5–105.5 °C (from hexane) (lit.,¹ 101.5–103 °C).

9-(6-Anilinohexyl)phenanthrene 5d. Obtained from the corresponding bromide (92%), m.p. 74.5–76.5 °C (hexane) (Found: C, 88.5; H, 7.9; N, 3.8. $\text{C}_{26}\text{H}_{27}\text{N}$ requires C, 88.34; H, 7.70; N, 3.96%); ν_{max} (KBr)/ cm^{-1} 3375 (NH); λ_{max} (hexane)/nm 253 (log ϵ 4.81) and 298 (4.12); δ_{H} (CDCl_3) 1.43–1.67 (6 H, m, CH_2), 1.79–1.87 (2 H, m, CH_2), 3.09–3.15 (4 H, m, CH_2), 3.59 (1 H, br s, NH), 6.57–6.71 (3 H, m, ArH), 7.13–7.20 (2 H, m, ArH), 7.54–7.68 (5 H, m, ArH), 7.80–7.84 (1 H, m, ArH), 8.08–8.12 (1 H, m, ArH) and 8.64–8.76 (2 H, m, ArH); *m/z* 353 (M^+).

9-(10-Anilinodecyl)phenanthrene 5e. Yield 73%, m.p. 67–71 °C (from hexane–benzene) (Found: C, 88.0; H, 9.1; N, 3.4. $\text{C}_{30}\text{H}_{35}\text{N}$ requires C, 87.97; H, 8.61; N, 3.42%); λ_{max} (hexane)/nm 252 (log

ϵ 4.78) and 298 (4.19); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3400 (NH); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.21–1.87 (16 H, m, CH₂), 3.06–3.13 (4 H, m, CH₂), 3.5 (1 H, br s, NH), 6.58–6.71 (3 H, m, ArH), 7.13–7.23 (2 H, m, ArH), 7.53–7.66 (5 H, m, ArH), 7.80–7.84 (1 H, m, ArH), 8.08–8.12 (1 H, m, ArH) and 8.63–8.75 (2 H, m, ArH).

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