

Photochemical Behaviour of 9-(2-Anilinoethyl)- and 9-(3-Anilinopropyl)-anthracenes in Various Solvents

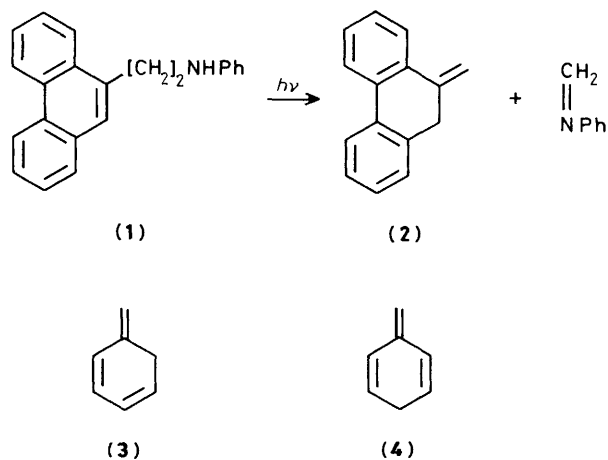
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Photochemical reactions of the title compounds and related aniline derivatives have been studied in various solvents. Products isolated from an irradiated mixture of 9-(2-anilinoethyl)anthracene (**5**) were: 9-methylene-9,10-dihydroanthracene (**6**), *N*-phenyl-9,10-dihydro-9,10-ethanoiminoanthracene (**7**), and 9,10-dihydro-9,10-(*o*-benzenoiminoethano)anthracene (**8**). The yield of the main product (**8**) decreased on changing the solvent from benzene to a polar solvent such as acetonitrile or a benzene-methanol mixture. The yield of compound (**6**) increased on adding a small quantity of protic solvent such as methanol in benzene. Polar and protic solvents seemed to have no particular influence on the yield of product (**7**). Similarly, 9-(3-anilinopropyl)anthracene (**11**) gave, on irradiation in benzene, three isomers of the starting amine (**11**): *N*-phenyl-9,10-dihydro-9,10-iminopropanoanthracene (**12**), 9,10-dihydro-9,10-(*o*-benzenoiminopropano)anthracene (**13**), and 1'-phenylspiro[9,10-dihydroanthracene-9,2'-pyrrolidine] (**14**). The yields decreased on adding methanol in solvent. Biradical intermediates were presumed for the reactions of both anthracene derivatives.

The reactions of amines with excited aromatic hydrocarbons have attracted considerable attention in recent years, mainly in connection with electron-transfer reactions and/or exciplex formation.¹ The intramolecular reactions of amines have also been studied² in order to elucidate the photophysical processes involved.

Our interest in this area has arisen from the photochemical cyclisation of hydrocarbons having an anilinoalkyl group. Previously, we reported the formation of 9-methylene-9,10-dihydrophenanthrene (**2**) isolated as the main product on photolysis of 9-(2-anilinoethyl)phenanthrene (**1**) in benzene.³



This product is a benzologue of methylenecyclohexa-1,3-diene (**3**),⁴ a non-aromatic isomer of toluene, and this photolytic method for the preparation of *exo*-methylene compounds has been extended in recent work⁵ to cover cyclic compounds such as 1-methylene-1,2-dihydronaphthalene. In the case of anthracene derivatives, however, the *exo*-methylene compound was a minor product, the main one being an intramolecular cyclisation compound; † in this case the *exo*-methylene compound is a benzologue of methylenecyclohexa-1,4-diene (**4**).⁴ Here we

report details of a study of the photoreaction products of the title and related compounds with the aim of obtaining a high yield of the *exo*-methylene compound.

Results and Discussion

Identification of Photoproducts.—Three products, (**A**), (**B**), and (**C**), as well as unchanged amine, were isolated from the photoreaction mixture obtained upon irradiation of 9-(2-anilinoethyl)anthracene (**5**). Their mass spectra suggested that products (**B**) and (**C**) were isomers of starting amine (**5**) and that compound (**A**) was a photolytic product.

Photoproduct (A). The mass spectrum of product (**A**) showed a similar pattern to that of 9-methylantracene suggesting the *exo*-methylene structure (**6**). Treatment of product (**A**) with trifluoroacetic acid gave 9-methylantracene which was identified by spectroscopic methods. The ¹H n.m.r. spectrum of product (**A**) showed aromatic proton signals (δ_{H} 7.26–7.76) and two singlet signals at δ_{H} 5.67 and 4.05 which may be assigned to the *exo*-methylene protons and the methylene protons of the dihydroanthracene ring,⁶ respectively. Moreover, the relative intensity of the signal at δ_{H} 4.05 of the product (**A**), isolated from the irradiated mixture of amine (**5**) in D₂O-saturated benzene, was reduced to about half that of the signal at δ 5.67. This means that a deuterium atom was incorporated in the molecule of the photoproduct (**A**) upon irradiation. That this deuterium atom was bonded to the carbon atom at the 10-position of the anthracene ring was confirmed as follows. Irradiation of the amine (**5**) in D₂O-saturated benzene, followed by treatment of the purified photoproduct (**A**) with trifluoroacetic acid, resulted in a reduction of the relative intensity of the signal at *ca.* δ 8.2 for the sample of 9-methylantracene obtained. These observations confirmed the structure (**6**) assigned to photoproduct (**A**). In contrast to the *exo*-methylene compound (**2**),³ which was accompanied by its more stable aromatic isomer, 9-methylantracene was not detected with the *exo*-methylene compound (**6**) in the mixture arising from irradiation of the amine (**5**).

Photoproduct (B). The mass spectrum of this compound (strong signals at *m/z* 297, 192, 178, and 106) showed a similar pattern to that of the starting amine (**5**) which has three signals at *m/z* 297 (*M*⁺), 192 (*M* – PhN=CH₂), and 106 (CH₂=N⁺HPh).

† See ref 5b, p. 669.

The signal at m/z 178 suggested the presence of a dihydroanthracene ring. The ^1H n.m.r. spectrum suggested that the photoproduct (**B**) had the bridged structure shown in (7). Thus, signals at δ_{H} 5.55 may be assigned to the proton at the 10-position of the 9,10-dihydroanthracene system under the influence of the adjacent nitrogen atom. A further signal, corresponding to the 9-position of dihydroanthracene, was observed as a triplet at δ_{H} 4.07. The triplet at δ_{H} 3.13 and the multiplet at 2.07–2.13 were assigned to the protons of the CH_2N and $\text{C}_{\text{anth}}\text{CH}_2\text{CN}$ groups respectively. The bridged structure (7) reasonably explains the presence of the m/z 106 signal in the mass spectrum: the fragmentation would begin with the scission of the N– C_{anth} bond to form the starting amine followed by the scission of the CH_2 – CH_2 bond.

Photoproduct (C). This was the major product formed on irradiation in benzene. Product (C) showed a simple mass spectrum with three strong signals at m/z 297 (M^+), 282 ($M - 15$), and 269 ($M - 28$). These data suggested that the product (C) contained one CH_2CH_2 (m/z 28) group. The ^1H n.m.r. spectrum showed two broad singlets at δ_{H} 2.48 and 1.93 in addition to the sharp signals at 5.36 (singlet) and 4.39 (triplet). The sharp signals could be assigned to the dihydroanthracene 9-H and 10-H and the broad ones to CH_2CH_2 . Irradiation of the amine (5) in D_2O -saturated benzene gave the mono-deuterated product (C) which, since it showed practically no detectable n.m.r. signal at δ 4.39, indicated deuterium incorporation at C-10. When the temperature was increased (from 22 °C to 67 °C in $[\text{D}_6]$ -benzene) the broad signals sharpened. These results suggest structure (8) for the photoproduct (C), with broadening of the ^1H signals induced by flipping or inversion (see Figure). The NH signal overlapped

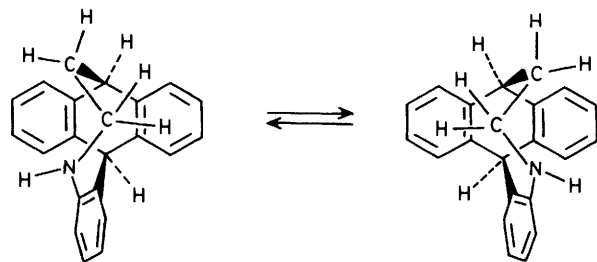
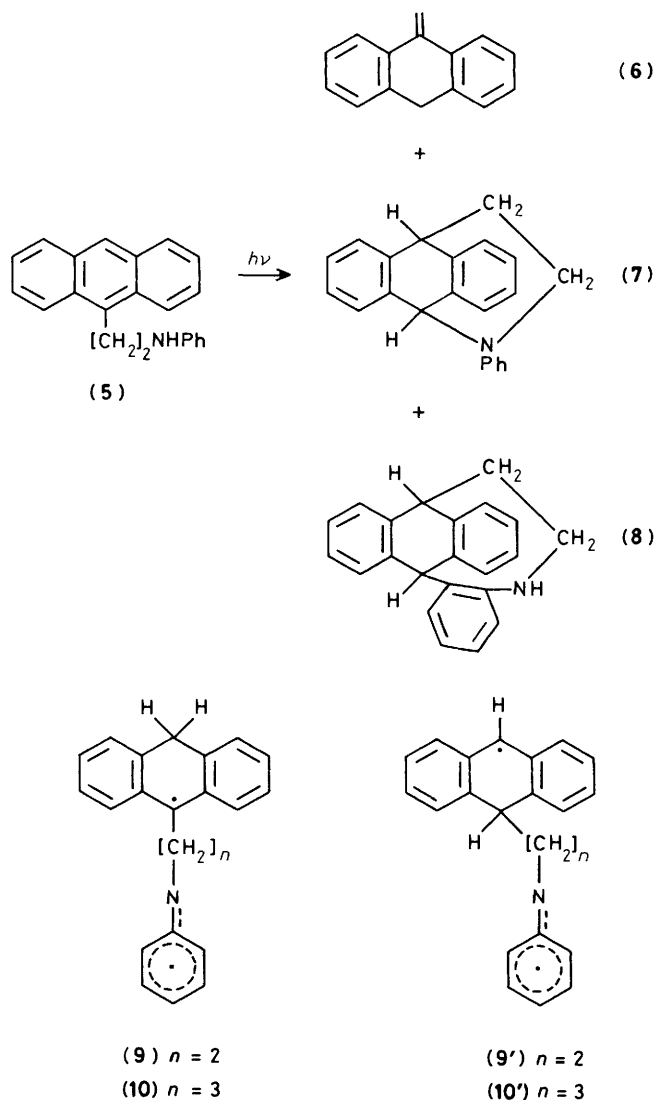


Figure. An example of flipping of (8)

with the broad signals at δ 2.48 and 1.93, as demonstrated by a reduction of intensity on adding D_2O to the sample solution. I.r. absorption of product (C) at $3\ 370\ \text{cm}^{-1}$ also demonstrated the presence of an NH group.

According to Yang,⁷ the photoreaction of anthracene with dimethylaniline in benzene proceeds *via* an exciplex to form a radical pair. Although the present reaction is intramolecular, a similar radical mechanism seems to be applicable. Thus formation of photoproducts can be explained in terms of (i) formation of the 1,4-biradical (9), and either (ii) scission of the C(2)–C(3) of the latter to give compound (6) or (iii) intramolecular coupling of the biradical (9') to give compounds (7) and (8). Irradiation of the photoproduct (7) converted it irreversibly into the product (8).^{*5b}

Irradiation of 9-(3-anilinopropyl)anthracene (11) in benzene gave three photoproducts (D), (E), and (F). Purification of product (E) was difficult because it changed readily in air to a dark brown compound. Irradiation of the photoproduct (D) in

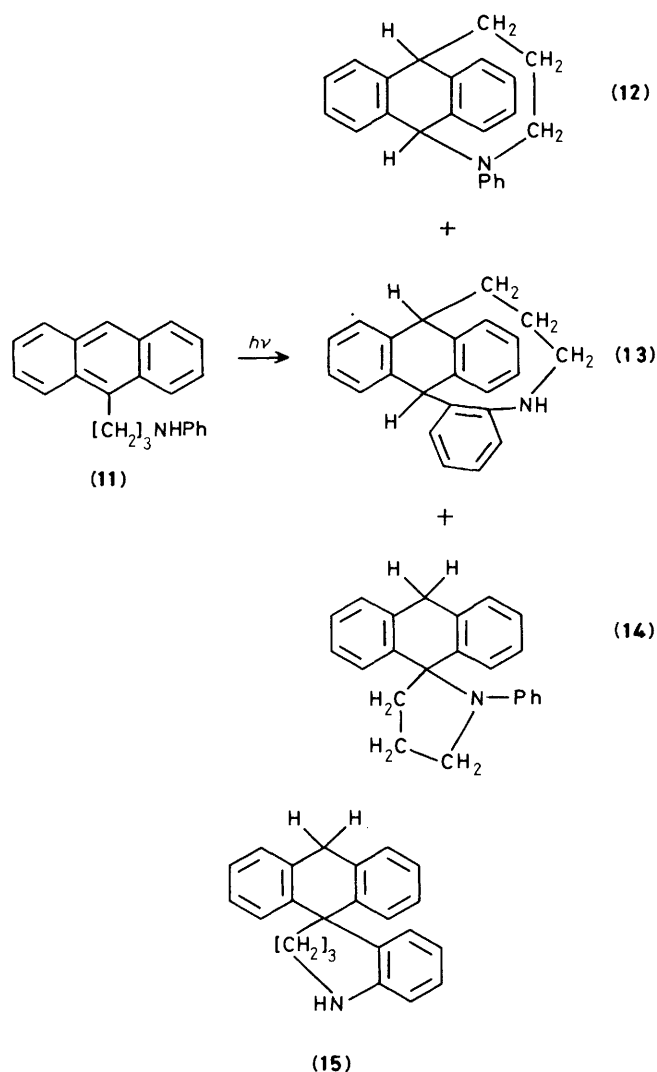


benzene gave many products, including compound (E) (17%). On the basis of spectroscopic results (^1H n.m.r., i.r., and m.s.) we propose structures (12), (13), and (14) for the photoproducts (D), (E), and (F) respectively. Similar considerations apply to the compounds (6), (7), and (8). Each of the isolated products showed a molecular ion peak at m/z 311 and their ^1H n.m.r. spectra were consistent with the assigned dihydroanthracene structures (12), (13), and (14). I.r. absorption consonant with the presence of NH was observed for the photoproduct (E) supporting the assignment of structure (13) to it.

Application of the above mechanism to the reaction of the amine (11), would suggest formation of the photoproducts (12–15) *via* intramolecular coupling of the biradicals (10) and (10'). In fact, although compounds (12), (13), and (14) were isolated, compound (15) was not. Among the photoproducts, the ^1H n.m.r. spectrum of the spiro compound (14) at 22 °C showed two broad signals at *ca.* δ_{H} 6.1 and 6.9, assignable to the protons of the anilino group (*o*- and *m*-position to amino group); these signals sharpened at 50 °C. These phenomena are explicable in terms of rotation of the phenyl group around the C(Ph)–N bond.

Photoreactions in Various Solvents.—In order to optimize the yield of the *exo*-methylene compound (6), the influence of various solvents on the reaction was examined; the results are

* Some photorearrangement reactions of this type were reported for aniline derivatives having a benzyl-type substituent; Y. Ogata and K. Takagi, *J. Org. Chem.*, 1970, **35**, 1642; *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2186.



summarised in the table. In the photoreaction of the amine (5), polar solvent increased the recovery of starting amine, reduced the yield of the product (8), and left the yields of the products (6) and (7) unchanged. Protic solvent (polar solvent) also reduced the yield of product (8) but increased that of the product (6). Although the maximum yield of compound (6) was obtained in methanol-benzene (1:19) addition of further methanol reduced it. As shown in the table, photoreaction of the amine (11) was also decreased by polar solvent. This unusual solvent effect did not affect the yields of phenanthrene derivatives in similar photochemical reactions.³ Thus, the reaction of 9-(2-anilinoethyl)phenanthrene (1) gave predominantly the *exo*-methylene compound (2) in 58% yield in benzene and 59% in benzene-methanol (3:1) (including the yield of the stable isomer, 9-methylphenanthrene). Similarly, 9-(3-anilinopropyl)phenanthrene gave 1'-phenylspiro[9,10-dihydrophenanthrene-9,2'-pyrrolidine] (16) in 93% yield in benzene, 95% in acetonitrile,

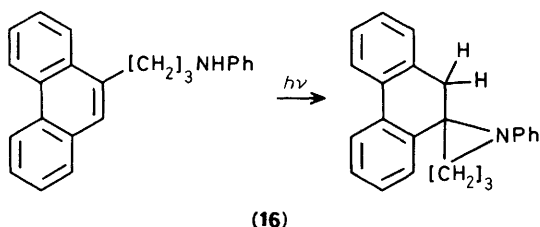


Table. Yields of photoproducts in various solvents

Solvent	Yield (%)						Recovery (%)
	(6)	(7)	(8)	(12)	(13)	(14)	
Benzene ^a	3	4	58	—	—	—	10
Dichloromethane ^a	1	5	1	—	—	—	93
Acetonitrile ^b	1	6	2	—	—	—	88
Benzene (95%)—methanol (5%) ^b	14	4	31	—	—	—	27
Benzene (90%)—t-butyl alcohol (10%)	11	2	73	—	—	—	0
Benzene (99%)—acetic acid (1%) ^a	16	3	50	—	—	—	17
Benzene ^a	—	—	—	25	4	4	36
Benzene (90%)—methanol (10%) ^a	—	—	—	18	1	4	52

^a 30 min Irradiation. ^b 90 min Irradiation.

94% in benzene-methanol (3:1), and 91% in benzene-methanol (1:1). This contrast between anthracene and phenanthrene derivatives for various solvents seems to arise as a result of a difference in the distance between the two reaction centres (presumably radicals).

Since no systematic investigation into the mechanism of the present intramolecular photoreaction has been attempted, the observations made are interpreted only in terms of the biradical intermediates, (9), (9'), (10), and (10'). This interpretation is similar to the mechanism proposed by Bryce-Smith *et al.*⁸ for the intermolecular reaction of benzene with amines: biradicals were formed *via* exciplex and/or *via* radical-anion and -cation pairs, according to the polarity of the solvent. In non-polar solvents, a cage reaction is presumed to take place, proton transfer then occurring from the proton donor which exists in the cage or/and outside the cage.* In polar solvents, a radical-ion pair formed by intramolecular electron-transfer may diffuse to the outside of the cage and be sufficiently stabilised to change into an intramolecular solvent-separated type ion-pair; this is then followed by back electron-transfer against the product formation.

In the case of phenanthrene derivatives, both reaction centres are near at hand. The reaction would take place before back electron-transfer.

Experimental

M.p.s were determined with a Yanaco micromelting point apparatus (MP-500) and are uncorrected. Mass spectra were obtained on a Shimadzu-LKB 9000 gas chromatograph-mass spectrometer. N.m.r. spectra were recorded on a Hitachi R-24A spectrometer (60 MHz) and/or JNM-GX270 (270 MHz) spectrometer using tetramethylsilane as internal standard. I.r. spectra were obtained on a Hitachi 215 infrared spectrophotometer.

Materials.—9-(2-Anilinoethyl)anthracene (5). 9-Anthrylacetic acid [prepared by hydrolysis of 9-anthrylacetonitrile (m.p. 162.5–164 °C, lit.,¹⁰ 163.5–164.5 °C)] was converted into the corresponding anilide *via* the acid chloride, m.p. 257–261 °C; ν_{max} (KBr) 1 660 (CO) and 3 300 cm^{-1} (NH). To a solution of this anilide (2.5 g, 8.22 mmol) in tetrahydrofuran (500 ml) was

* As well as the protic solvent, the starting amine itself should be a proton donor. As shown in the reaction of anthracene with dimethylaniline by N. C. Yang,⁹ a trace of water (solvent contaminant) may function as a mediator in the present reaction.

added lithium aluminium hydride (2.5 g, 65.9 mmol) in small portions at 50 °C, and the mixture was refluxed for 4 h; it was then cooled, treated with aqueous ammonium chloride, and extracted with ether. The extract was dried (Na₂SO₄) and evaporated and the residue was chromatographed on silica gel with benzene to give (5) (0.91 g, 37%), m.p. 104–105 °C (hexane) (Found: C, 88.5; H, 6.4; N, 4.75. C₂₂H₁₉N requires C, 88.85; H, 6.4; N, 4.7%; v_{max}(KBr) 3 400 cm⁻¹ (NH); δ_H(270 MHz, CDCl₃) 3.59–3.65 and 3.93–3.98 (4 H, m, CH₂CH₂), and 6.64–8.40 (14 H, m, ArH); m/z 297 (M⁺, 8%), 192 (45), and 106 (100). The same amine (5) was obtained from 9-anthrylethanol (m.p. 103.5–105 °C, lit.,¹¹ 106.5–107.5 °C) via the corresponding bromide.

9-(3-Anilinopropyl)anthracene (11). 3-(9-Anthryl)propanol (m.p. 93.5–94 °C, lit.,¹⁰ 97.5–98.5 °C) was converted into the amine (11) by a standard method via the corresponding bromide: a mixture of the propanol (1.85 g, 6.35 mmol), phosphorus tribromide (1 ml, 2.56 mmol), and benzene (75 ml) was heated at 50 °C for 2.5 h. After being cooled, the mixture was treated with aqueous sodium hydrogen carbonate and extracted with ether. The extract was dried (Na₂SO₄) and evaporated and the residue was chromatographed on silica gel to give a yellow solid, m.p. 83–84 °C (0.94 g, 63%); δ_H(60 MHz, CDCl₃) 2.0–2.6 (2 H, m, CH₂), 3.4–3.9 (4 H, m, ArCH₂ and BrCH₂), and 7.1–8.4 (9 H, m, ArH); m/z 300 (31%), 298 (M⁺, 31%), and 192 (100). A mixture of this bromide (1.05 g, 3.5 mmol), aniline (10 ml, 109 mmol), and potassium carbonate (2 g) was stirred at room temperature under nitrogen for 12 h. It was then washed with water and extracted with benzene. The solvent and remaining aniline were removed by evaporation under reduced pressure. The residue was chromatographed on silica gel with hexane–benzene (1:1) to give a pale yellow solid (11), (0.65 g, 60%), m.p. 86.5–88 °C (hexane) (Found: C, 88.8; H, 6.8; N, 4.5. C₂₃H₂₁N requires C, 88.7; H, 6.8; N, 4.5%; v_{max}(KBr) 3 390 cm⁻¹ (NH); δ_H(270 MHz, CDCl₃) 2.09–2.20 (2 H, m, CH₂CNPh), 3.34 (2 H, t, J 6.7 Hz, CH₂), 3.73 (2 H, t, J 7.9 Hz, CH₂), and 6.61–8.35 (14 H, m, ArH); m/z 311 (M⁺, 25%), 217 (9), 203 (16), 191 (22), 178 (26), 132 (100), and 106 (37).

Photoreactions: Preparative Irradiation.—A solution of the sample compound (1.6 × 10⁻² mol/l) in a Pyrex tube was degassed 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 solvent was removed under reduced pressure and the residue was chromatographed on silica gel.

Photoreaction of (5). After irradiation for 1.5 h (95 mg in 20 ml of benzene), the solvent was evaporated under reduced pressure. Chromatography of the residue with benzene–hexane (1:2) gave 9-methylene-9,10-dihydroanthracene (6) (trace), m.p. 72–73 °C (lit.,⁶ 74–75 °C); δ_H(270 MHz, CDCl₃) 4.05 (2 H, s, CH₂), 5.67 (2 H, s, =CH₂), and 7.26–7.76 (8 H, m, ArH); δ_C(CDCl₃) 35.3, 109.4, 124.3, 124.9, 126.6, 127.6, 127.7, 134.5, and 135.5; m/z 192 (M⁺, 100%).

The second fraction yielded N-phenyl-9,10-dihydro-9,10-ethanoiminoanthracene (7) (8 mg, 8%), as a colourless oil (Found: C, 88.7; H, 6.3; N, 4.2. C₂₂H₁₉N requires C, 88.85; H, 6.4; N, 4.7%; δ_H(270 MHz, CDCl₃) 2.07–2.13 (2 H, m, CH₂CN), 3.13 (2 H, t, J 6.1 Hz, CH₂N), 4.07 (1 H, t, J 4.3 Hz, CH), 5.55 (1 H, s, CH), and 6.73–7.37 (13 H, m, ArH); δ_C(CDCl₃) 32.8, 44.0, 45.5, 66.0, 116.1, 118.4, 125.6, 126.3, 126.7, 128.3, 129.0, 139.1, 144.5, and 150.9; m/z 297 (M⁺, 13%), 192 (33), 178 (18), and 106 (100).

The third fraction contained a trace amount of starting amine (5). The fourth fraction gave 9,10-dihydro-9,10-(o-benzoiminoethano)anthracene (8) (56 mg, 59%), m.p. 155.5–157 °C (Found: C, 88.9; H, 6.6; N, 4.7. C₂₂H₁₉N requires C, 88.85; H,

6.4; N, 4.7%; v_{max}(KBr) 3 370 cm⁻¹ (NH); δ_H(270 MHz, CDCl₃) 1.7–2.1 (2 H, brs, CH₂CN), 2.3–2.8 (2 H, brs, CH₂N), 4.40 (1 H, t, J 2.4 Hz, CH), 5.37 (1 H, s, CH), and 6.51–7.69 (12 H, m, ArH); δ_C(CDCl₃; 60 °C) 40.5, 45.4, 47.8, 52.8, 123.0, 125.0, 127.2, 127.8, 128.1, 128.7, 129.5, 134.0, 139.8, 140.3, 141.1, and 151.0; m/z 297 (M⁺, 100%), 282 (30), 269 (55), and 178 (17).

Photoreaction of (11). A solution of amine (106 mg, 0.34 mmol) in benzene (20 ml) was irradiated for 2 h. The first chromatographic fraction eluted with benzene–hexane (1:2) gave 1'-phenylspiro[9,10-dihydroanthracene-9,2'-pyrrolidine] (14) (6 mg, 6%), m.p. 191–193 °C (from EtOH) (Found: C, 88.6; H, 6.75; N, 4.45. C₂₃H₂₁N requires C, 88.7; H, 6.8; N, 4.5%; δ_H(270 MHz, CDCl₃) 2.03–2.11 (2 H, m, CH₂), 2.15–2.20 (2 H, m, CH₂), 3.99 (2 H, t, J 6.5 Hz, CH₂N), 4.05 and 4.13 (2 H, ABq, J 18.9 Hz, CH₂), and 6.13–7.36 (13 H, m, ArH); δ_C(CDCl₃) 22.0, 35.5, 44.0, 51.2, 68.6, 114.8, 115.4, 125.6, 126.47, 126.52, 128.1, 134.0, 141.4, and 144.8; m/z 311 (M⁺, 35%), 191 (9), 178 (11), 132 (19), and 106 (100).

The second fraction gave N-phenyl-9,10-dihydro-9,10-imino-propanoanthracene (12) (39 mg, 37%), m.p. 121–122 °C (from EtOH) (Found: C, 88.95; H, 6.8; N, 4.55. C₂₃H₂₁N requires C, 88.7; H, 6.8; N, 4.5%; δ_H(270 MHz, CDCl₃) 1.41–1.43 (2 H, m, CH₂CN), 2.08–2.14 (2 H, m, CH₂CCN), 2.86 (2 H, t, J 4.9 Hz, CH₂N), 4.23 (1 H, t, J 4.3 Hz, CH), 6.01 (1 H, s, CH), and 6.81–7.36 (13 H, m, ArH); δ_C(CDCl₃) 24.7, 39.6, 45.4, 45.5, 63.6, 118.6, 119.1, 126.4, 126.9, 127.7, 128.3, 129.0, 136.9, 142.7, and 151.1; m/z 311 (M⁺, 17%), 217 (7), 203 (8), 191 (12), 178 (47), and 132 (100).

The third fraction contained the starting amine (11) (31 mg, 29%).

Successive elution with ether gave a mixture of the other photoproducts. Separation by preparative t.l.c. with benzene–ether (5:1) gave only one product (R_F 0.6), 9,10-dihydro-9,10-(o-benzoimino)propanoanthracene (13) (6 mg, 6%), m.p. 141–143 °C; v_{max}(KBr) 3 400 cm⁻¹ (NH); δ_H(270 MHz, CDCl₃) 1.09–1.17 (2 H, m, CCH₂CN), 2.37–2.43 (2 H, m, CH₂CCN), 2.88 (2 H, t, J 5.2 Hz, CH₂N), 4.56 (1 H, t, J 4.6 Hz, CH), 5.41 (1 H, s, CH), and 6.71–7.59 (12 H, m, ArH); δ_C(CDCl₃) 25.5, 40.2, 43.6, 50.2, 52.2, 121.2, 124.8, 127.0, 127.2, 128.1, 128.3, 128.9, 131.1, 135.6, 138.36, 138.44, and 148.1; m/z 311 (M⁺, 100%), 283 (85), 282 (60), 267 (19), 252 (15), 178, (42), and 132 (52).

Yield estimation.—The yields of the photoreaction products and recovery of the starting amines were estimated by the following procedure. After irradiation, the solvent was evaporated to dryness and the residue was weighed and its ¹H n.m.r. spectrum recorded. The relative intensities of the signals arising from the starting amines [at δ_H 3.59–3.65 for amine (5) and 3.34 for amine (11)] and the products [at δ_H 5.67 for compound (6), 5.55 for compound (7), 5.37 for compound (8), 6.01 for compound (12), 5.41 for compound (13), and 6.42–6.52 for compound (14)] were measured. The solvent from the n.m.r. sample was subsequently evaporated and the residue was chromatographed on silica gel. The quantity of starting material isolated [or compound (8) in the case of low yield] was used to calculate the yield of other products.

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