

# Photolytic decomposition of some polycyclic $\alpha$ -diazoketones: generation and reactivity of 1,2-oxocarbenes in benzene with and without *tert*-butylamine

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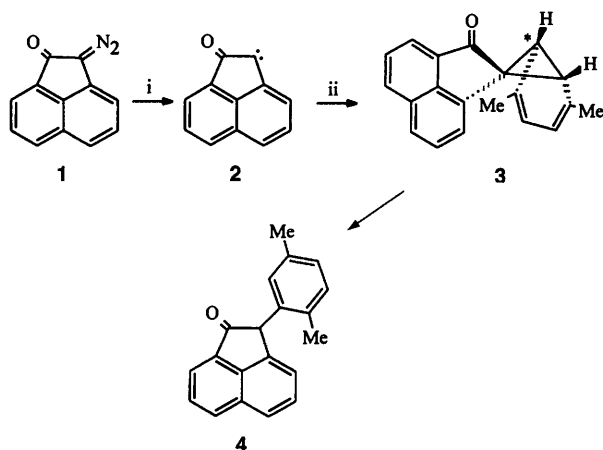
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Irradiation in benzene of the two isomeric 2,3-diazofluoranthrenones **11** and **14** results in the formation of only products due to the formal insertion of the intermediate oxocarbenes into the C–H bonds of the solvent, unless the reactions are carried out in the presence of *tert*-butylamine, whereupon products of an apparent [3 + 2]-cycloaddition of the oxocarbene to the solvent are also obtained, *viz.* dihydrofurans **13** and **16**, respectively. Wolff rearrangement of the generated oxocarbenes to give products derived from direct trapping of the ketene intermediates with *tert*-butylamine are not observed. The formal insertion product, 2-phenylfluoroanthren-3-ol **12** (from **11**) undergoes partial oxidation during chromatographic purification on silica to generate a persistent free radical species **17** which has been detected and characterised by EPR spectroscopy. A reinvestigation of the photolytic decomposition of the related polycyclic  $\alpha$ -diazoketone **5** under the same conditions has established that a more likely structure for the isolated dihydrofuran is **8**, and not the reported isomeric dihydrofuran **20**, which is formed from **8** by hydrogen migration during isolation by repeated thick-layer chromatography.

We reported some time ago<sup>1</sup> that photolysis of 2-diazoacacenaphthen-1-one **1** gives rise to an oxocarbene **2**, which can be trapped by aromatic receptors, *e.g.* *p*-xylene, to afford spiro[acenaphthen-1,7'-*cis*-norcaradiene-2',4'-diene]-2-one **3** (Scheme 1).



**Scheme 1** Reagents and conditions: i, photolysis, *p*-xylene; ii, reflux, toluene, 18 h or catalytic amount of either AgClO<sub>4</sub> or *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H

The strain inherent in this system prompted isomerisation to 2-arylacacenaphthen-1-one **4** when subjected to either heating in boiling toluene (18 h) or acid-catalysis with toluene-*p*-sulfonic acid. Significantly, aromatisation also occurred very rapidly with the production of a transient red colour under the influence of silver perchlorate (4%), thus providing the first extension of the silver-ion-catalysed cleavage of strained rings to the norcaradiene system.

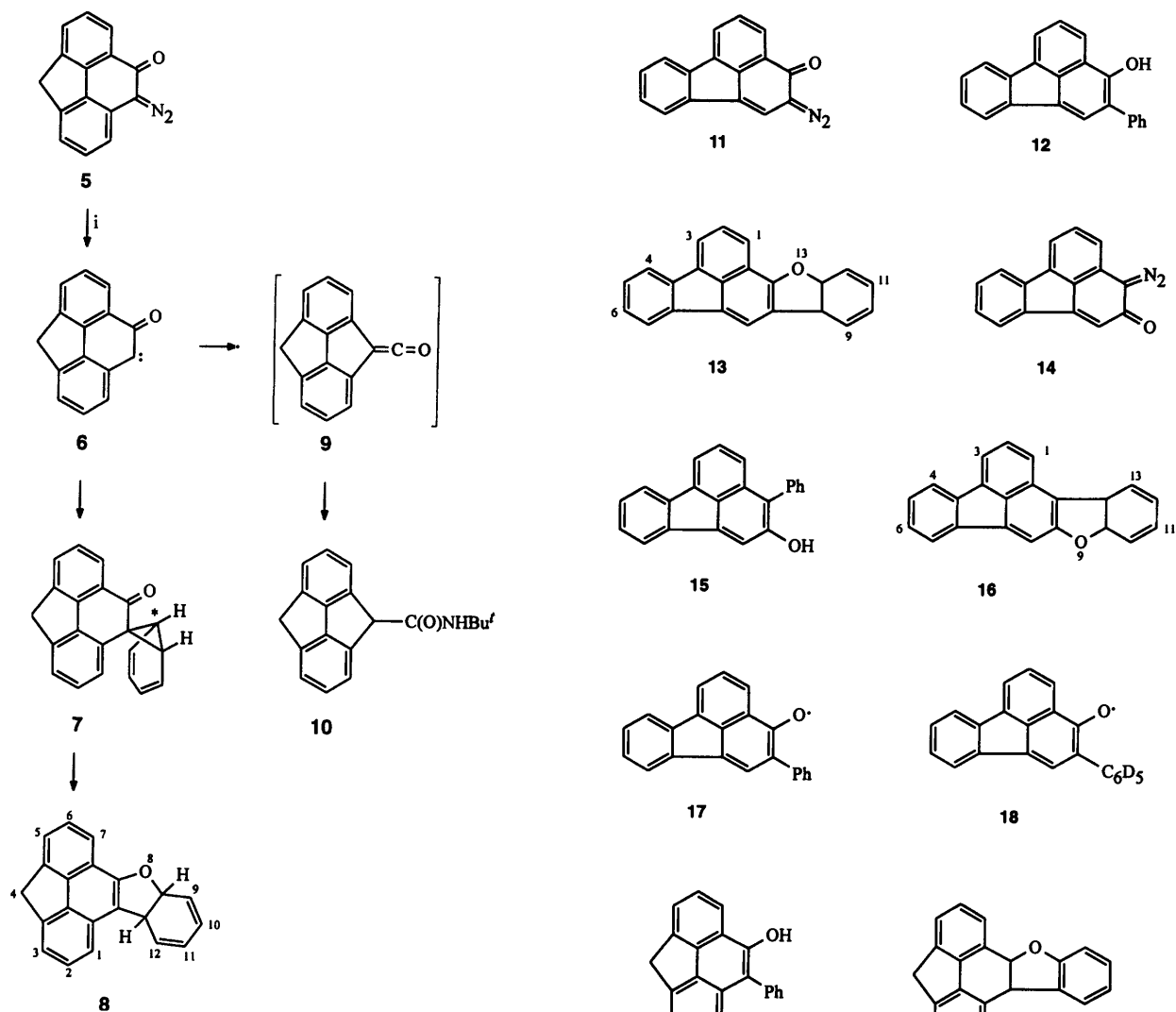
We viewed the formation of the norcaradiene **3** from the

oxocarbene **2** as a function of the inability of the latter to undergo a Wolff rearrangement,<sup>2</sup> but it was of interest not only for its rarity,<sup>3</sup> but also in comparison with the behaviour of oxocarbene **6**, which is generated by photolytic decomposition of 9-diazo-8,9-dihydro-4*H*-cyclopenta[*d,e,f*]phenanthren-8-one **5**<sup>4</sup> in benzene. Oxocarbene **6** is also reluctant to undergo a Wolff reaction, as evidenced by obtention of *ca.* 2% yield of carboxamide **10** from a trapping reaction of ketene intermediate **9** with *tert*-butylamine, but in sharp contrast to **2**, its trapping to afford the corresponding norcaradiene **7** was not detected, and the major compound isolated was purported to be the dihydrofuran **8**, which is the product of formal [3 + 2]-cycloaddition of the oxocarbene **6** to the solvent (Scheme 2). We ascribed this difference in behaviour to the greater accessibility of the ketone group with respect to the bridgehead carbon atom [marked with an asterisk (\*) in **7** compared with **3**].

In the present work, we have investigated the photolytic decomposition of the two isomeric diazofluoranthrenones **11** and **14** in benzene and have found only the products of formal insertion of the intermediate oxocarbene into the C–H bond of benzene, unless the reactions are carried out in the presence of *tert*-butylamine, whereupon the products of apparent [3 + 2]-cycloaddition of the oxocarbene to the solvent are also obtained. Wolff rearrangement of the generated oxocarbenes to give products derived by direct trapping of ketene intermediates with *tert*-butylamine is not observed.

## Results and discussion

Fluoranthene-2,3-quinone, prepared according to the method of Periasamy and Bhatt,<sup>5</sup> was reacted with *p*-toluenesulfonylhydrazide to give a yellow crystalline material from which the light-sensitive diazoketones **11** and **14** could be isolated in 39 and 20% yield, respectively, by column



**Scheme 2** Reagents and conditions: i, photolysis, benzene-Bu<sup>t</sup>NH<sub>2</sub> (ca. 30:1 v/v)

chromatography. The structural assignments are based largely on spectroscopic evidence, but are also consistent with what might be expected on the basis of prevailing attack by the hydrazide at the least sterically crowded carbonyl group of the quinone, and the spectral characteristics of the products obtained from the following chemical transformations.

On irradiation in benzene, 3-diazo-2-fluoranthene-1-one **14** gave as the only isolable product 3-phenylfluoranthene-2-ol **15** in 38% yield. In the case of the isomeric 2-diazo-3-phenylfluoranthene-1-one **11**, photolysis under similar conditions, followed by rapid chromatography over silica, afforded a 74% yield of 2-phenylfluoranthene-3-ol **12** as a fluorescent green crystalline solid which melted sharply at 140.5–141.5 °C. The <sup>1</sup>H NMR spectrum of this compound, unlike that of its isomer **15**, was extremely broad at room temperature, and although the spectrum sharpened considerably at lower temperatures, or upon addition of D<sub>2</sub>O, only progressive broadening occurred at temperatures up to 160 °C. EPR investigations indicated that this behaviour was associated with the presence in solution of a small amount of persistent radical species (*t*<sub>1/2</sub> > 2 days at room temperature) believed to be aryloxy radical **17**. The EPR spectrum [Fig. 1(a)] consisted of a series of overlapping multiplets giving overall at least 28 lines (*a*<sub>H</sub> = 0.06 mT). The wealth of fine structure is consistent with extensive delocalisation of the unpaired electron throughout the multi-ring system. The concentration of the radical was temperature dependent. On cooling to -50 °C the signal became almost undetectable, but returned to its full magnitude on re-warming to room

temperature. The amount at room temperature was estimated to be ca. 0.6% of the solute by comparison with standard solutions of 2,2-diphenyl-1-picrylhydrazyl. These results are in accord with the sharpening of the <sup>1</sup>H NMR spectrum at low temperature and implies that the radical exists in equilibrium with one or more dimers, whose formation is favoured at low temperature.

Radical **17** is believed to result from aerial oxidation of 2-phenylfluoranthene-3-ol **12** at the surface of the silica during chromatographic purification. To test this hypothesis a solution of compound **12** in toluene was saturated with oxygen and subsequently treated with silica. Only traces of the signal were detected initially, but addition of the silica generated an intense signal identical to that described above. No signal was detected on photolysis of **11** in de-gassed benzene.

Further evidence for the assignment of the spectrum to radical **17** was provided by a repeat experiment in which diazo compound **11** was photolysed in hexadeuteriobenzene. The

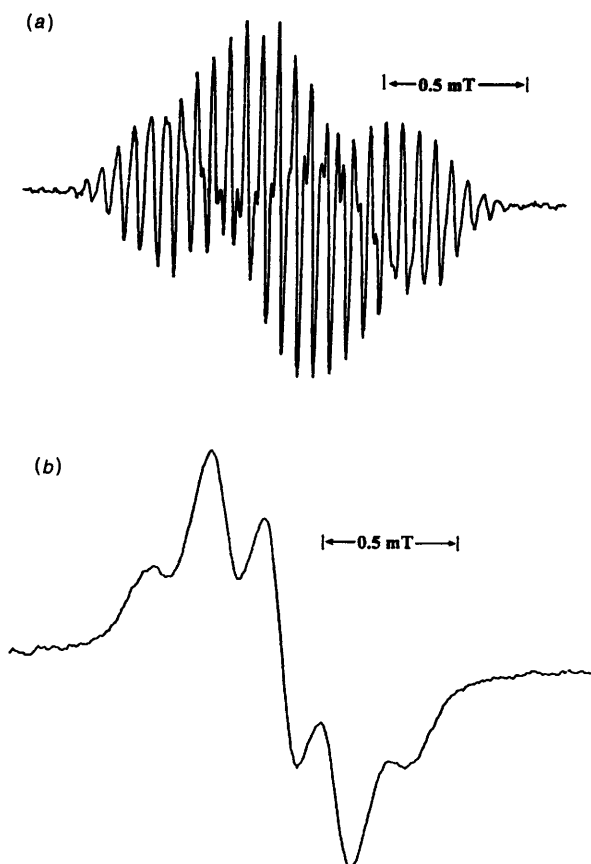


Fig. 1 EPR spectra of (a) radical 17 and (b) the deuterated analogue 18

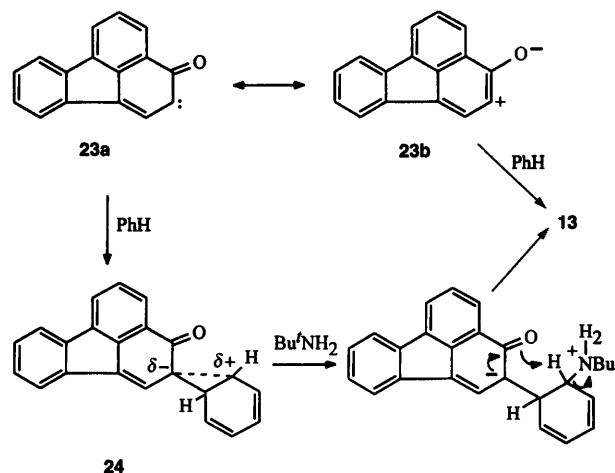
resulting signal [Fig. 1(b)] is assigned to radical 18 and shows loss of fine structure resulting from replacement of 2-phenyl ring protons by deuteriums.

Photolysis of the isomeric diazoketones 11 and 14 in benzene containing 6% *v/v* *tert*-butylamine led to the concomitant formation of minor amounts of the dihydrofurans 13 (3%) and 16 (12%), respectively. The structure of these compounds rests on their spectral properties, but further evidence is provided by  $^1\text{H}$  NMR spectral comparison with the aforementioned dihydrofuran 8 obtained by irradiation of 9-diazo-8,9-dihydro-4*H*-cyclopenta[*d,e,f*]phenanthren-8-one 5 under similar conditions. In particular, the striking similarities in the position of the resonances due to H-13a ( $\delta$  4.69) of 14 and H-12a ( $\delta$  4.67) of 8 may be cited as evidence in favour of the foregoing assignments to the structures of the diazoketones 11 and 14.

Note that in contrast to Trost and Kinson,<sup>4</sup> we have found that irradiation of 9-diazo-8,9-dihydro-4*H*-cyclopenta[*d,e,f*]phenanthren-8-one 5 in benzene proceeds in a manner analogous to the photolyses of diazoketones 11 and 14 described above, *i.e.* the sole isolable product is 9-phenyl-4*H*-cyclopenta[*d,e,f*]phenanthren-8-ol 19, the product of formal insertion into benzene, unless *tert*-butylamine (1.1% *v/v*) is present in which case 8 can also be isolated together with small amounts of the trapped product 10 arising from Wolff rearrangement of oxocarbene 6. While our assignment of 8 is consistent with its  $^1\text{H}$  NMR spectrum, the latter is not wholly identical to that reported previously by Trost and Kinson.<sup>4</sup> Comparison of both data suggests that a more likely structure for their compound is the isomeric dihydrofuran 20 which is formed from 8 by hydrogen migration (1,3-shifts) during isolation by repeated thick-layer chromatography. Most significant is the chemical shift difference for the methylene protons at C-4. The chemical shift for the methylene protons in 20 come at lower chemical shift ( $\delta$  3.50 *vs.* 4.28 for 8) in keeping with the change in hybridization of the 7b and 12b carbon atoms. The observed  $\delta$  values compare favourably with values of 3.72<sup>6</sup> and

4.13<sup>7</sup> for the corresponding methylene protons in 21 and 22, respectively. Additional evidence that our assignment was correct came from the observed rearrangement of 8 to 19 in the presence of acid.

The formation of the dihydrofurans, *e.g.* 13, may be rationalised by direct cycloaddition of the dipolar form 23b of the intermediate oxocarbene 23a to the solvent, but the role of *tert*-butylamine in this mechanism is obscure. It remains possible that the reaction proceeds *via* the intermediacy of a zwitterionic species 24<sup>8</sup> and that cyclisation to dihydrofuran 13 is aided by *tert*-butylamine as shown in Scheme 3. The question of the



Scheme 3

mechanism of formation of the dihydrofuran 8 remains an interesting problem. It is still possible that it arises *via* the intermediacy of norcaradiene species 7, since the formal insertion product 19 could arise *via* the same intermediate. However, 19 could also arise by rearrangement of the dihydrofuran, as demonstrated by its acid-catalysed rearrangement to 19 (*vide supra*), so that isolation of these two species does not by itself imply a common intermediate norcaradiene, and a dipolar cycloaddition mechanism could still hold.

## Experimental

Melting points are uncorrected.  $^1\text{H}$  NMR spectra were recorded on a Bruker WP-200 spectrometer for solutions in  $\text{CDCl}_3$ , unless stated otherwise, with chemical shifts quoted relative to  $\text{Me}_4\text{Si}$  as internal standard, and coupling constants, *J* values, in Hz; c refers to complex multiplet. IR spectra were recorded for Nujol mulls. Mass spectra were recorded on an AEI MS 902 mass spectrometer at 70 eV.

Photolyses were carried out using a water-cooled, 100 W medium-pressure mercury vapour lamp (Applied Photophysics) through a Pyrex filter. The reactions were carried out under an atmosphere of dry nitrogen, unless otherwise stated, the reaction mixture being stirred continuously. The course of the reactions was monitored by thick-layer chromatography (tlc) and the visible evolution of nitrogen gas.

The EPR instrumentation and methods were as previously described.<sup>9</sup>

### Preparation of 2- and 3-diazofluoranthrenones

Fluoranthene-2,3-quinone and *p*-toluenesulfonylhydrazide were reacted according to the method of Reid and Dietrich.<sup>10</sup> The quinone (1.12 g, 4.59 mmol) and the hydrazide (0.88 g, 4.91 mmol) were suspended in methanol (20 ml) and the mixture heated under reflux, under an atmosphere of dry  $\text{N}_2$ , for 20 min with occasional swirling. The mixture was cooled, and the solvent removed on a rotary evaporator. The residue was taken up in  $\text{CH}_2\text{Cl}_2$  (20 ml) and applied to the top of an alumina column which was wrapped in aluminium foil to exclude light. Elution

with  $\text{CH}_2\text{Cl}_2$ -petrol (50:50) gave 2-diazo-fluoranthren-3(2H)-one **11** (455 mg, 39%), mp 171–176 °C (decomp.) (lit.,<sup>7</sup> 165 °C);  $\nu_{\text{max}}/\text{cm}^{-1}$  2125 (C=N<sub>2</sub>) and 1630 (C=O);  $\delta_{\text{H}}$  8.10–7.28 (c) (Found:  $M^+$ , 244.0643,  $\text{C}_{16}\text{H}_8\text{N}_2\text{O}$  requires  $M$ , 244.0637). Elution with  $\text{CH}_2\text{Cl}_2$  gave 3-diazo-fluoranthren-2(3H)-one **14** (236 mg, 20%), mp 153–155.5 °C (decomp.);  $\nu_{\text{max}}$  2090 (C=N<sub>2</sub>) and 1630  $\text{cm}^{-1}$  (C=O);  $\delta$  7.75–6.99 (c) (Found:  $M^+$ , 244.0644.  $\text{C}_{16}\text{H}_8\text{N}_2\text{O}$  requires  $M$ , 244.0637).

#### Photolysis of 3-diazo-fluoranthren-2(3H)-one in benzene

3-Diazo-fluoranthren-2(3H)-one **14** (437 mg, 1.79 mmol) was dissolved in benzene (80 ml) and photolysed for 3 h. The solvent was removed on a rotary evaporator and the dark red oil obtained adsorbed onto silica and chromatographed under low pressure. Elution with petrol- $\text{CH}_2\text{Cl}_2$  (60:40) gave a red oil (67 mg) which tlc indicated to be composed of a mixture of at least five components. This was not examined further. Further elution gave a reddish brown oil, which yielded cream-coloured crystals on trituration with petrol, 3-phenylfluoranthren-2-ol **15** (200 mg, 38%), mp 110–111 °C (from petrol-acetone) (Found: C, 89.9; H, 4.8. Calc. for  $\text{C}_{22}\text{H}_{14}\text{O}$ : C, 89.75; H, 4.8%),  $\nu_{\text{max}}/\text{cm}^{-1}$  3490 (OH), 1605, 1170, 1147, 777, 756 and 706;  $\delta_{\text{H}}$  7.86–7.65 (4 H, c, H-1 and H-4–H-6), 7.53–7.27 (9 H, c, phenyl protons and H-7–H-10), and 5.42 (1 H, br, s, exchanges on shaking with  $\text{D}_2\text{O}$ , OH).

#### Photolysis of 3-diazo-fluoranthren-2(3H)-one in benzene-*tert*-butylamine

3-Diazo-fluoranthren-2(3H)-one **14** (920 mg, 3.77 mmol) was dissolved in benzene (75 ml) and *tert*-butylamine (5 ml) and the solution subjected to photolysis for 5.5 h. Removal of the solvent gave a dark green tarry material which was adsorbed onto silica and chromatographed under low pressure. Elution with petrol- $\text{CH}_2\text{Cl}_2$  (80:20) gave a fluorescent green solid, 9a,13a-dihydrobenzo[*b*]fluorantheno[3,2-*d*]furan **16** (132 mg, 12%), mp 162.5–164 °C (from toluene) (Found: C, 89.6; H, 4.8. Calc. for  $\text{C}_{22}\text{H}_{14}\text{O}$ : C, 89.75; H, 4.8%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1225, 1180, 1170, 907, 814, 770, 747 and 690;  $\delta_{\text{H}}$  7.86–7.54 (5 H, c, aromatic), 7.51 (1 H, s, H-8), 7.40–7.22 (2 H, c, aromatic), 6.32–5.86 (4 H, c, H-10–H-13), 5.60 (1 H, d of d, *J* 12, 4, H-9a) and 4.69 (1 H, c d, *J* 12, H-13a). Increasing the polarity of the solvent (petrol- $\text{CH}_2\text{Cl}_2$ , 60:40) gave 73 mg of a red oil which tlc indicated was similar to the multi-component mixture described above. Further elution gave 3-phenylfluoranthren-2-ol **15**, identical to that described above (257 mg, 23%). Back-flushing the column with ethyl acetate gave 624 mg of black tar.

#### Photolysis of 2-diazo-fluoranthren-3(2H)-one in benzene

2-Diazo-fluoranthren-3(2H)-one **11** (471 mg, 1.93 mmol) was dissolved in benzene (90 ml) and subjected to photolysis for 1 h. Removal of the solvent gave a dark brown oil which was adsorbed onto silica and chromatographed under low pressure. Elution with petrol- $\text{CH}_2\text{Cl}_2$  (80:20) gave a green solid, solutions of which exhibited green fluorescence, 2-phenylfluoranthren-3-ol **12** (419 mg, 74%), mp 140.5–141.5 °C (from ethanol) (Found: C, 89.7; H, 4.65. Calc. for  $\text{C}_{22}\text{H}_{14}\text{O}$ : C, 89.75; H, 4.8%),  $\nu_{\text{max}}/\text{cm}^{-1}$  3500 and 3400 (OH), 780, 760 and 705;  $\delta_{\text{H}}$  8.15–7.18 (13 H, br, c, aromatic) and 5.92 (1 H, s, exchanges on shaking with  $\text{D}_2\text{O}$ , OH). Spectrum sharpened considerably on cooling to –40 °C, or on shaking with  $\text{D}_2\text{O}$ .  $\delta_{\text{H}}$ ( $[\text{D}_6]\text{DMSO}$ ) 8.34 (1 H, d, *J* 8.5, H-4), 8.02–7.84 (4 H, c, aromatic), 7.68–7.20 (8 H, c, aromatic) and 3.6 (1 H, br, s, OH). The spectrum became progressively broader on heating to 160 °C and sharpened on cooling again. EPR spectroscopy (*vide infra*) indicated that the broadening of the  $^1\text{H}$  NMR spectrum was due to the presence of a small concentration of a long-lived free radical species **17**.

#### Photolysis of 2-diazo-fluoranthren-3(2H)-one in benzene-*tert*-butylamine

2-Diazo-fluoranthren-3(2H)-one **11** (666 mg, 2.73 mmol) was

dissolved in benzene (75 ml) and *tert*-butylamine (5 ml), and the mixture subjected to photolysis for 4.5 h. Removal of the solvent gave a dark brown tar which was adsorbed onto silica and chromatographed under low pressure. Elution with petrol- $\text{CH}_2\text{Cl}_2$  (95:5) gave a yellow solid, 8b,12a-dihydrobenzo[*b*]fluorantheno[2,3-*d*]furan **13** (20 mg, 2.5%), mp 79–83 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  2950, 2920, 2845, 1445, 1260, 1185, 1105 and 1015;  $\delta_{\text{H}}$  7.96–7.22 (8 H, c, aromatic), 6.16–5.94 (4 H, c, H-9–H-12), 5.72 (1 H, d of d, *J* 12, 3, H-12a) and 4.44 (1 H, d, *J* 12, H-8b) [Found:  $M^+$ , 294.1032(26); ( $M^+$ -2), 292.0876 (100).  $\text{C}_{22}\text{H}_{14}\text{O}$  requires  $M$ , 294.1045; ( $M$ -2) ( $\text{C}_{22}\text{H}_{12}\text{O}$ ), 292.0888]. Suitable analytical data could not be obtained from this compound because of the small amount of material available. Increasing the polarity of the solvent to petrol- $\text{CH}_2\text{Cl}_2$  (80:20) gave 2-phenylfluoranthren-3-ol **12** identical with that obtained previously (426 mg, 53%). Back-flushing the column with ethyl acetate gave a black tar (327 mg).

#### Photolysis of 9-diazo-8,9-dihydro-4H-cyclopenta[*d,e,f*]-phenanthren-8-one in benzene

9-Diazo-8,9-dihydro-4H-cyclopenta[*d,e,f*]phenanthren-8-one **5**<sup>4</sup> (1.04 g, 4.48 mmol) was dissolved in benzene (190 ml) and the solution subjected to photolysis for 2.5 h. The solvent was removed and the residue adsorbed onto silica and chromatographed under low pressure. Elution with petrol-ether (90:10) gave a pale purple solid, 9-phenyl-4H-cyclopenta[*d,e,f*]phenanthren-8-ol **19** (740 mg, 58.5%), mp 108–109 °C (from ethanol) (Found: C, 89.1; H, 5.1;  $M^+$ , 282.1032.  $\text{C}_{21}\text{H}_{14}\text{O}$  requires C, 89.35; H, 5.0%;  $M^+$ , 282.1045);  $\nu_{\text{max}}/\text{cm}^{-1}$  3490 and 3440 (OH), 1640, 1600, 1435, 1105, 1020, 773 and 702;  $\delta_{\text{H}}$  7.97 (1 H, m, H-7), 7.59–7.19 (10 H, c, aromatic), 5.76 (1 H, br, s, exchanges on shaking with  $\text{D}_2\text{O}$ , OH) and 4.09 (2 H, br, s,  $\text{CH}_2$ );  $\delta_{\text{H}}$ ( $[\text{D}_6]\text{acetone}$ ) 8.09 (1 H, m, H-7), 7.90 (1 H, br, s, exchanges on shaking with  $\text{D}_2\text{O}$ , OH), 7.63–7.22 (10 H, c, aromatic) and 4.21 (2 H, br, s,  $\text{CH}_2$ ).

#### Photolysis of 9-diazo-8,9-dihydro-4H-cyclopenta[*d,e,f*]phenanthren-8-one in benzene-*tert*-butylamine

9-Diazo-8,9-dihydro-4H-cyclopenta[*d,e,f*]phenanthren-8-one **5** (973 mg, 4.19 mmol) was dissolved in benzene (90 ml), *tert*-butylamine (1 ml) was added, and the resulting solution photolysed for 2 h. The solvent was removed and the residue obtained adsorbed onto silica and chromatographed under low pressure. Elution with petrol gave a colourless solid, 8a,12a-dihydro-4H-benzo[*b*]cyclopenta[4,4a,4b,5]phenanthro[9,10-*d*]furan **8** (120 mg, 10%), mp 112–113 °C (from petrol-benzene);  $\nu_{\text{max}}/\text{cm}^{-1}$  1160, 1155, 822, 802, 769, 720 and 698;  $\delta_{\text{H}}$  7.88–7.26 (6 H, c, aromatic), 6.33–6.08 (3 H, c, H-9–H-11), 5.93 (1 H, m, H-12), 5.70 (1 H, d of d, *J* 12, 4, H-8a), 4.67 (1 H, c d, *J* 12, H-12a) and 4.28 (2 H, br, s,  $\text{CH}_2$ ) (Found:  $M^+$ , 282.1051.  $\text{C}_{21}\text{H}_{14}\text{O}$  requires  $M^+$ , 282.1045). Satisfactory analytical data were not obtained for this compound because of the limited amount of pure material available after repeated recrystallisation. Elution with petrol-ether (90:10) gave 9-phenyl-4H-cyclopenta[*d,e,f*]phenanthren-8-ol **19** identical with that previously obtained (608 mg, 51%). Further elution gave a red oil (48 mg) which according to tlc contained at least five components and was not examined further. Increasing the polarity of the eluting solvent to petrol-ether (70:30) gave, as a red solid, *N-tert*-butyl-4,8-dihydrocyclopenta[*d,e,f*]fluorene-4-carboxamide **10** (33 mg, 3%), mp 124–127 °C (lit.<sup>4</sup> not reported);  $\nu_{\text{max}}/\text{cm}^{-1}$  3250 (NH) and 1640 (C=O);  $\delta_{\text{H}}$ (60 MHz) 8.0–7.0 (6 H, c, aromatic), 5.22 (1 H, br, s,  $\text{H}_a$ ), 4.25 (2, br, s,  $\text{CH}_2$ ), 3.99 (1 H, br, s, NH) and 1.27 (9 H, s, Bu');  $M^+$  277.

#### Acid-catalysed rearrangement of 8a,12a-dihydro-4H-benzo[*b*]cyclopenta[4,4a,4b,5]phenanthro[9,10-*d*]furan **8**

A sample of the dihydrofuran was dissolved in  $\text{CDCl}_3$  in an NMR tube and a single crystal of *p*-toluenesulfonic acid was added. After 75 min, the signals due to the protons of the di-

hydrofuran ring system had disappeared, and the spectrum indicated that a clean rearrangement to 9-phenyl-4*H*-cyclopental[*d,e,f*]phenanthren-8-ol **19** had occurred.

#### EPR spectroscopy studies

(a) EPR spectrum of radical **17** derived from 2-phenylfluoranthren-3-ol. A solution of 2-phenylfluoranthren-3-ol **12** in toluene (0.05 M) was prepared and a portion of the solution transferred to an EPR tube, degassed and the EPR spectrum observed at ambient temperature [Fig. 1(a)]. A strong signal was obtained which, when resolved, was found to be rather complex, consisting of a symmetrical multiplet centred on  $g = 2.0072 \pm 0.0002$ . The smallest observed splitting was 0.58 ( $\pm 0.02$ ) mT and the total width of the spectrum was 15.5 ( $\pm 0.1$ ) mT (total number of lines >28). By comparison of the intensity of the signal with those of signals obtained from solutions of diphenylpicrylhydrazyl (DPPH) of known concentrations, it was possible to estimate that at room temperature the radical species present constituted between 0.4 and 0.8% of the solute. The concentration of the radical was also shown to be temperature dependent, the intensity of the signal decreasing considerably on cooling to  $-50^\circ\text{C}$  and returning to its original level on returning to room temperature.

(b) EPR spectrum of radical **18** derived from 2-phenyl- $[\text{}^2\text{H}_3]$ fluoranthren-3-ol. 2-Diazofluoranthren-3(2*H*)-one **11** (60 mg, 0.25 mmol) was dissolved in  $[\text{}^2\text{H}_6]$ benzene (2 ml), which had been dried over a molecular sieve, and the solution placed in an NMR tube. The tube was attached to the cooling jacket of a photochemical reactor and the solution photolysed for 3 h, after which time the NMR spectrum indicated that 2-phenyl $[\text{}^2\text{H}_3]$ fluoranthren-3-ol had been produced. The solution was chromatographed over silica and eluted with petrol- $\text{CH}_2\text{Cl}_2$  (50:50) to give a red oil. A repeat examination by  $^1\text{H}$  NMR spectroscopy showed that exchange of the *O*-deuterium for hydrogen had occurred to give 2-phenyl $[\text{}^2\text{H}_3]$ fluoranthren-3-ol (48 mg, 65%) [ $\delta_{\text{H}}$  8.4-7.0 (H, br c, aromatic) and 5.04 (1 H, br s, OH)] and that the spectrum sharpened considerably on cool-

ing to  $-60^\circ\text{C}$ . A solution of this material in toluene (0.1 M) was prepared and a portion transferred to an EPR tube, degassed and its spectrum recorded. A strong symmetrical signal, consisting of five broad lines with the same centre as the EPR spectrum already described, was obtained [Fig. 1(b)].

#### Acknowledgements

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