Tetrahedron Vol. 42, No. 14, pp. 3943 to 3956, 1986 Printed in Great Britain.

# PREPARATION AND PYROLYSIS OF SUBSTITUTED ETHAMOANTHRACENES - A GENERAL SYNTHESIS OF 2,3-DISUBSTITUTED ANTHRACENES

Jack E. Baldwin<sup>\*</sup>, Alistair G. Swanson, and (in part) Jin Kun Cha and John A. Murphy

The Dyson Perrins Laboratory, Oxford University, South Parks Road, Oxford, OX1 3QY, U.K.

## (Received in UK 11 April 1986)

Abstract: 9,10-Ethano-9,10-dihydroanthracene has been functionalised regioselectively to give a range of 2-substituted and 2,3-disubstituted derivatives. Flash vacuum pyrolysis of these compounds has provided the first general synthesis of 2,3-disubstituted anthracenes. The observed regioselectivity is in accord with the Finnegan-Streitwieser model of the electronic influence of a strained ring fused to an aromatic ring.

## INTRODUCTION

In the course of work on the synthesis of derivatives of triptycene, we required a general method for the preparation of 2,3-disubstituted anthracenes (1).



Since electrophilic substitution of anthracene occurs almost exclusively at the 9 and 10 positions and the 8 positions (2, 3, 6 and 7) tend to be the least reactive, there have been few reports of anthracenes with this substitution pattern. Those which have been prepared have generally been made by reduction of the corresponding quinones<sup>1</sup> although these are often themselves difficult to prepare and the reductions frequently do not proceed cleanly or in high yield. The use of anthraquinone derivatives in the synthesis of substituted anthracenes is further limited both by their susceptibility to reaction at the carbonyl groups and by their often very poor solubility.

It has been known since 1946 that the Diels-Alder reaction of anthracene and ethylene to form 9,10-ethano-9,10-dihydroanthracene (EDA, 2) could be reversed by pyrolysis to regenerate anthracene.<sup>2</sup> Since then this method has been extended to the preparation of other olefins, including cumulenes, from appropriately 11- and 11,12-functionalised EDAderivatives.<sup>3</sup> The only reported extension to the preparation of substituted anthracenes, however, was when Tanida showed that 2 could be nitrated to give mainly 2-nitro-EDA (3) which furnished 2-nitroanthracene (4) on pyrolysis.





We wish to report the conversion of 3 into a range of 2-substituted and 2,3-disubstituted derivatives and that flash vacuum pyrolysis of these provides an efficient general synthesis of the corresponding substituted anthracenes.

## RESULTS AND DISCUSSION

# (1) Preparation of substituted EDA derivatives.

Reduction of 2-nitro-EDA with hydrogen and a palladium catalyst, or more conveniently with hydrazine and palladium, gave 2-amino-EDA (5) in essentially quantitative yield.



Further functionalisation of amine 5 [or its acetamide (6)] gave a wide range of 2,3-disubstituted EDA derivatives (7 - 13) as shown in Scheme 1. Bromination and nitration of 6 and iodination of 5 gave only the desired 2,3-disubstituted products (7, 8 and 10). None of the unwanted 1,2-disubstituted products could be isolated from any of these reactions.

In principle, either steric hindrance of the 1-position by the ethanobridge or an electronic effect resulting from strain in the fused rings could have been primarily responsible for this regioselectivity. To distinguish between these possibilities we have compared the regioselectivity of both electrophilic substitution and lithiation of 2-pivalamido-EDA (14) with the same reactions of the corresponding 3,4-dimethylaniline derivative (15) for which steric effects should dominate.







Scheme 1. Reagents: i. Ac<sub>2</sub>O / pyridine; ii. Br<sub>2</sub> / AcOH; iii. HNO<sub>3</sub> / Ac<sub>2</sub>O;
 iv. NaOH; v. I<sub>2</sub> / K<sub>2</sub>CO<sub>3</sub>; vi. NO<sup>+</sup>HSO<sub>4</sub><sup>-</sup>, KI; vii. CO / PdCl<sub>2</sub> / Et<sub>3</sub>N / MeOH.

Bromination of 14 gave 3-bromo-2-pivalamido-EDA (16) in 99% yield while under the same conditions 15 gave a 7.9:1 mixture (by n.m.r.) of the 6-bromo and 2-bromo products (17 and 18) in 98% yield.



Gschwend has shown that N-aryl pivalamides can be ortho-metallated by strong bases such as butyl lithium.<sup>5</sup>



Both 14 and 15 were reacted with excess n-butyl lithium in TMEDA/hexane and the resulting anions were quenched with  $D_2O$ . The aromatic proton resonances in the n.m.r. spectra of the amides, however, were not sufficiently well separated to permit accurate measurement of the levels of deuteration at the different sites.

This problem was overcome by the reduction of the amides with lithium aluminium hydride to the corresponding <u>neo</u>-pentyl amines (19 and 20) which gave easily analysed n.m.r. spectra.



When the products from the lithiation/deuteration of the amides 14 and 15 were reduced in this way it was found that the EDA derivative 14 gave 19 containing 0.85 atoms of deuterium per molecule distributed between the 1and 3-positions in a 3.25:1 ratio. In contrast the xylene derivative 15 gave 20 containing 1.0 atoms of deuterium per molecule. Of this, 28% was incorporated in the benzylic methyl groups and the remainder was distributed between the 2- and 6-positions in a 1:7.1 ratio.



Starting amide

14	3.25	1
15	1	7.1

Hence there is a clear difference between 14 and 15 in the way they react with butyl lithium while they both react with bromine preferentially at the site remote from the alkyl substituents. These results are consistent with the existence of an electronic factor influencing the behaviour of the EDA derivatives.

A tendency for benzocycloalkenes with strained rings to react with electrophiles mainly  $\beta$  to the ring junction was first reported by Mills and Nixon over 50 years ago.<sup>6</sup> More recently Finnegan and Streitwieser have shown that the hydrogens  $\alpha$  to the ring junction in such compounds show enhanced acidity. They have rationalised these observations on the basis that the carbons at the ring junction rehybridise to accommodate the small

3946

bond angles of the strained ring (Figure 1).7,8 These hybridisation changes and the resultant increase in the electronegativity of the carbons a to the ring junction can then be used to explain the observed reactivity.



**Q** Increased s character. Decreased s character.

Figure 1: The effect of a small fused ring on the hybridisation of the carbon atoms of benzene.

Hence it appears that an electronic effect arising from the strain introduced by the ethano-bridged ring is responsible for the observed regioselectivity in the reaction of EDA derivatives.

#### Pyrolysis of the EDA derivatives; formation of substituted (2) anthracenes

Our initial attempts to remove the ethano-bridge by pyrolysis in solution at up to 340<sup>0</sup>C were unsuccessful and passing a benzene solution of the compound through a heated guartz tube in an atmosphere of nitrogen gave some conversion only for 2-nitro-EDA (3) either no reaction or carbonisation (depending on tube temperature) being observed in the other cases. In contrast, flash vacuum pyrolysis (FVP) of the EDA derivatives gave the desired anthracenes in good to excellent yield (Table 1).



Entry	Starting	X	Y	Pressure	Product	Yield	Unreacted
	material			(man Higi)		$(8)^{(1)}$	s.m. (%) <sup>(2)</sup>
1	3	NO2	Ħ	1x10 <sup>-2</sup>	4	70.5	24
2	3	NO2	Ħ	1x10 <sup>-4</sup>	4	70.0	26
3	6	NHAC	Ħ	1x10 <sup>-4</sup>	21	86.5	6
4	9	NH2	NO2	1x10 <sup>-4</sup>	22	75.3	12.5
5	11	ī	ī	2x10 <sup>-3</sup>	23	67.8	30.3
6	12	NHAC	I	$1 \times 10^{-4}$	24	91.2	0
7	13	NHAC	CO <sub>2</sub> Me	4x10 <sup>-3</sup>	25	94.2	0

650°C, -C<sub>2</sub>H<sub>4</sub>

## Table 1 Results of FVP experiments

(1) Isolated yield. (2) From n.m.r. of crude product.

The FVP apparatus used was similar to that described by Campbell.<sup>9</sup> It was found that optimum conversion to the anthracenes was obtained with a tube temperature of 650°C or slightly higher at pressures of  $10^{-2}$ -10<sup>-4</sup> mm Hg. The EDA derivatives could be sublimed easily into the pyrolysis tube at these pressures. The yield of the pyrolyses did not vary significantly with either the amount of starting material (up to 400 mg per run) or the sublimation rate (5 minutes to 1 hour for 100 mg). None of the functional groups examined has proved incompatible with the reaction conditions and the high selectivity of the method was clearly demonstrated by the pyrolysis of 2,3-diiodo-EDA (11) (entry 5 in Table 1). No iodine was produced and no carbonisation was observed, the only reaction product being 2,3-diiodoanthracene (23) arising from loss of ethylene.

## CONCLUSION

We have shown that electrophilic substitution of 2-amino-9,10-ethano-9,10-dihydroanthracene and its N-acylated derivatives gives exclusively 2,3-disubstituted products and that these compounds can be cleanly converted to the corresponding anthracenes by flash vacuum pyrolysis.

### EXPERIMENTAL

Melting points were determined using a Büchi 510 capillary apparatus and are uncorrected. Ultraviolet and visible spectra were recorded on a Perkin-Elmer 555 spectrophotometer. Absorption maxima are reported in nanometers with the logarithm of the extinction coefficient in parentheses. Infrared spectra were recorded on a Perkin-Elmer 681 spectrophotometer. Absorption maxima are reported in wavenumbers and the following abbreviations are used: s strong, m moderate, w weak, br broad. <sup>1</sup>H and  $^{13}$ C n.m.r. spectra were recorded at 300 and 75.4 MHz respectively on a Brüker WH300 spectrometer. Chemical shifts are quoted in parts per million downfield from TMS. Residual solvent resonance was used as internal reference. The following abbreviations are used: s singlet, d doublet, t triplet, m multiplet, br broad. Quote marks ' ' signify an apparent multiplicity. Electron impact mass spectra were obtained on a VG Micromass 16F spectrometer and in-beam electron impact and high resolution mass spectra were obtained on a VG Micromass ZAB-1F spectrometer. Microanalyses were carried out by Dr. F.B. Strauss of the Dyson Perrins Laboratory. Chromatography refers to column chromatography using the 'Flash' method of Still.<sup>11</sup> Solvents were distilled before use and, unless stated otherwise, all reactions were carried out under an atmosphere of argon.

### 9,10-Sthano-9,10-dihydro-2-mitroanthracene, 3

Fuming 95% nitric acid (4.42 ml, 100 mmol) was added dropwise to acetic anhydride (15 ml) at 0°C and the resulting solution was added with stirring to a solution of 9,10ethano-9,10-dihydroanthracene<sup>2</sup> (20.00 g, 97.1 mmol) in acetic anhydride (150 ml) and nitromethane (200 ml) at 0°C. The resulting solution was kept at 0°C for 24 hours and poured into water (2000 ml). After stirring for 3 hours the solid was collected by filtration and dissolved in dichloromethane (200 ml). The solution was then dried over magnesium sulphate, filtered and evaporated to give a yellow solid (21.5 g). Crystallisation from xylene gave 3 as a pale yellow solid (19.52 g, 73.1 mmol, 75.3\$), m.p. 164- $5^{\circ}$ C (lit.<sup>4</sup> 164- $5^{\circ}$ C);  $v_{max}$  (CHCl<sub>3</sub>) 3050m, 2980m, 1540s, 1480m, 1360s, 950m cm<sup>-1</sup>;

3948

 $\delta_{H}(CDC1_{3})$  8.14(1H, d, J = 2 Hz), 8.03(1H, dd, J = 2 Hz, 8 Hz), 7.41(1H, d, J = 8 Hz), 7.32(2H, m), 7.17(2H, m), 4.48(2H, 's'), 1.78(4H, m); m/z(EI) 251(M<sup>+</sup>, 9), 224(17), 223(M-C<sub>2</sub>H<sub>H</sub>, 100), 177(53).

## 2-Amino-9,10-etheno-9,10-dihydroanthracene, 5

9,10-Ethano-9,10-dihydro-2-nitroanthracene (15.00 g, 59.7 mmol) was dissolved in ethanol (400 ml) and argon was bubbled through the solution for 10 minutes. 105 palladium on charcoal (1.0 g) was added and the suspension was brought to reflux. Hydrazine hydrate (6.0 ml, 6.18 g, 123 mmol) was added dropwise to the refluxing solution and heating under reflux was continued for 2 hours. The mixture was cooled, filtered and the solvent evaporated to give a white solid which was homogeneous by tlc, m.p. 139-40°. Crystallisation from ethanol/water gave 5 (13.06 g, 59.1 mmol, 99%) m.p. 140-40.5°C; Vmar. (CHC13) 3440w, 3380w, 3005m, 2955m, 1625m, 1495m, 1475m, 1295m, 1145m, 1135m, 1120m, 870m, 820m cm<sup>-1</sup>; \$4(CDCl<sub>2</sub>) 7.23(2H, m), 7.09(2H, m), 7.03(1H, d, J = 8 Hz), 6.67(1H, d, J = 2.2 Hz, 6.41(1H, dd, J = 2.2 Hz, 8 Hz), 4.22(1H, s), 4.20(1H, s), 3.0-4.0(2H, br, -NH\_2), 1.70(4H, m); 8c(CDCl<sub>2</sub>) 144.7(s, Cla), 144.4(s, C8a or C5a), 144.0(s, C2), 143.5(s, C5a or C8a), 133.8(s, C4a), 125.2 and 125.1(2 x d, C6, C7), 123.5(d, C4), 122.9 and 122.7(2 x d, C5, C8), 111.4(d, C3), 110.8(d, C1), 44.0 and 42.9(2 x d, C9, C10), 27.0 and 26.5(2 x t, C11, C12); m/z(EI) 221(M<sup>+</sup>, 14), 193(M-C<sub>2</sub>H<sub>2</sub>, 100), 165(30), 97(37); Found C 86.9, H 6.9, N 6.35. C<sub>16</sub>H<sub>15</sub>N requires C 86.85, H 6.8, N 6.35≸.

## 2-Acetylamino-9, 10-ethano-9, 10-dihydroanthracene, 6

Pyridine (8.07 ml, 7.91 g, 100 mmol) was added to a solution of 2-amino-9,10-ethano-9,10-dihydroanthracene (5.20 g, 25.53 mmol) in chloroform (150 ml) and acetic anhydride (3.62 ml, 3.91 g, 38.3 mmol) was added to the resulting solution. The mixture was stired for 3½ hours at room temperature, washed with water (2 x 200 ml), 2N hydrochloric acid (200 ml) and brine (200 ml), dried over magnesium sulphate and evaporated to give 6 as a white foam (6.13 g, 25.31 mmol, 99%), m.p.  $191-3^{\circ}$ C;  $v_{max.}$  (CHCl<sub>3</sub>) 3420w, 3020m, 2960m, 2880m, 1680s, 1520s, 1420m, 1140m, 940m, 840m cm<sup>-1</sup>;  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 7.57(1H, d, J = 1.7 Hz), 7.29(1H, br s, -NH-), 7.22(2H, m), 7.18(1H, d, J = 8.0 Hz), 7.10(2H, m), 7.05(1H, dd, J = 1.7 Hz, 8.0 Hz), 4.25(2H, m), 2.16(3H, s), 1.69(4H, 's');  $\delta_{\rm C}$ (DMSO-d<sup>6</sup>) 168.1(s, <u>C</u>=0), 143.9(s, C1a), 143.8 and 143.4 (2 x s, C5a and C8a), 138.5(s, C4a), 136.9(s, C2), 125.3 and 125.1(2 x d, C6 and C7), 123.1(2 x d, C5 and C8), 122.9(d, C4), 116.1(d, C3), 114.9(d, C1), 43.4(d), 42.5 (d), 26.5(t), 26.2(t), 23.8(q); m/z(EI) 263(M<sup>+</sup>, 11), 235(M-C<sub>2</sub>H<sub>4</sub>, 59), 193(100), 165(45), 145(22), 115(12), 85(58), 43(72); Found C 82.1, H 6.55, N 5.3. C<sub>18</sub>H<sub>17</sub>NO requires C 82.1, H 6.5, N 5.3%.

## 2-Acetylamino-3-bromo-9, 10-ethano-9, 10-dihydroanthracene, 7

To a solution of 2-acetylamino-9,10-ethano-9,10-dihydroanthracene (1.10 g, 4.18 mmol) in acetic acid (15 ml) at room temperature was added bromine (236 µl, 735 mg, 4.6 mmol). The mixture was stirred for 1 hour and then poured into a vigorously stirred solution of sodium thiosulphate (5 g) in water (60 ml). The resulting suspension was extracted into ether (3 x 20 ml) and the ether extracts were combined, washed with water (2 x 50 ml), and brine (25 ml), dried over sodium sulphate and evaporated to give 7 as a white solid (1.37 g, 4.01 mmol, 95.9\$), which was crystallised from ethanol/water, m.p.  $165^{\circ}C$ ;  $v_{max.}$  (CHCl<sub>3</sub>) 3420m, 3020m, 2960m, 1690s, 1580m, 1500s, 1410s, 1135m, 930m cm<sup>-1</sup>;  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.26(1H, s), 7.56(1H, br s,  $-N\underline{\rm H}$ -), 7.42(1H, s), 7.25(2H, m), 7.11(2H, m), 4.34(1H, s), 4.25(1H, s), 2.21(3H, s), 1.70(4H, 's'); m/z(EI) 343(15), 341(16), 315(28), 313(28), 273(34), 234(M-C<sub>2</sub>H<sub>4</sub>-Br, 100), 165(38), 43(35); Found C 63.0, H 4.6, Br 23.2, N 4.15. C<sub>18</sub>H<sub>16</sub>BrNO requires C 63.15, H 4.7, Br 23.35, N 4.1%.

## 2-Acetylamino-9,10-ethano-9,10-dihydro-3-nitroanthracene, 8

A solution of 2-acetylamino-9,10-ethano-9,10-dihydroanthracene (23.35 g, 88.78 mmol) in acetic anhydride (125 ml) was cooled to 0°C and a precooled solution of fuming nitric acid (4.32 ml, p 1.5, 95% HNO<sub>3</sub>, 97.66 mmol) in acetic anhydride (20 ml) was added. The mixture was kept at 0°C for 16 hours then poured into water (500 ml) and filtered. The solid was diasolved in  $CH_2Cl_2$  (100 ml), washed with saturated sodium carbonate solution until no more gas was evolved then with brine (2 x 100 ml), dried over magnesium sulphate and evaporated to give 8 as a pale yellow solid (25.80 g, 94%), m.p. 159-60°C;  $v_{max}$ . (CHCl<sub>3</sub>) 3360m, 2960m, 1710s, 1630m, 1587s, 1495s, 1475s, 1450s, 1330s, 1305m, 1260m, 1145m cm<sup>-1</sup>:  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 10.48(1H, br s, -N<u>H</u>-), 8.73(1H, s), 8.10(1H, s), 7.28(2H, m), 7.15(2H, m), 4.44(1H, s), 4.37(1H, s), 2.28(3H, s), 1.76(4H, m); m/z(EI) 308(M<sup>+</sup>, 30), 280(M-C\_2H\_4, 76), 238(100), 234(42), 165(55), 43(76). An analytical sample was prepared by chromatography on silica eluting 1:1 ethyl acetate:petrol, m.p. 160°C; Found C 70.0, H 5.3, N 8.9.  $C_{18}H_{16}N_2O_3$  requires C 70.1, H 5.25, N 9.1%.

## 2-Amino-9,10-ethano-9,10-dihydro-3-nitroanthracene, 9

A solution of 2-acetylamino-9,10-ethano-9,10-dihydro-3-nitroanthracene (3.227 g, 10.48 mmol) and sodium hydroxide (3.0 g, 75 mmol) in ethanol (20 ml) and water (8 ml) was heated under reflux for 1 hour, allowed to cool and extracted with carbon tetrachloride (2 x 50 ml). The organic layers were combined, washed with water (2 x 100 ml) and dried over sodium sulphate. Evaporation gave a deep yellow foam which was chromatographed on silica, eluting with 40% ethyl acetate in petrol to give an orange solid (2.337 g, 84%), m.p. 220-1°C. Crystallisation from toluene gave 9 m.p.  $222^{\circ}$ C;  $v_{max.}$  (CHCl<sub>3</sub>) 3520m, 3400m, 2960m, 1647m, 1590m, 1505ms, 1465m, 1425m, 1330ms, 1315ms, 1250ms, 1150m, 1140m cm<sup>-1</sup>;  $\hat{q}_{\rm H}$  (CDCl<sub>3</sub>) 7.95(1H, s), 7.25(2H, m), 7.15(2H, m), 6.69(1H, s), 6.08(2H, br s,  $-N\underline{H}_2$ ), 4.23(1H, s), 4.20(1H, s), 1.73(4H, 's');  $\delta_{\rm C}$ (CDCl<sub>3</sub>) 152.7(s), 143.9(s), 143.3(s), 141.4(s), 133.1(s), 129.7(s), 126.3(d), 126.0(d), 123.6(d), 123.3(d), 119.7(d), 113.1(d), 43.9(d), 42.6(d), 26.7(t), 26.1(t); m/z(EI) 266(M<sup>+</sup>, 20), 239(17), 238 (M-c\_2H\_4, 100), 192(26), 165(54); Found C 72.05, H 5.35, N 10.5. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires C 72.15, H 5.3, N 10.5%.

## 2-Amino-9,10-ethano-9,10-dihydro-3-iodoanthracene, 10

2-Amino-9,10-ethano-9,10-dihydroanthracene (2.252 g, 10.19 mmol), iodine (2.59 g, 10.19 mmol) and potassium carbonate (2.82 g, 20.4 mmol) were stirred together in a two phase system of ether (75 ml) and water (50 ml) for 16 hours at room temperature then heated under reflux for 30 minutes and cooled. The organic layer was separated, washed with aqueous sodium thiosulphate (2 x 100 ml), water (100 ml) and brine (2 x 50 ml), dried over sodium sulphate and evaporated to give a brown foam (2.871 g). Chromatography on silica eluting with chloroform gave 10 as an off-white foam (2.258 g, 63.4\$), m.p.  $147^{\circ}$ ;  $v_{max}$  (CHCl<sub>3</sub>) 3480w, 3385w, 3010m, 2960m, 2875m, 1620m, 1490m, 1468m, 1415m, 1340m, 1135m, 970m, 885m, 840m cm<sup>-1</sup>;  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 7.53(1H, s), 7.24(2H, m), 7.12(2H, m), 6.73(1H, s), 4.18(2H, 's'), 3.91(2H, br s,  $-NH_2$ ), 1.68(4H, 's'); m/z(EI) 347(M<sup>+</sup>, 28), 319(M-C<sub>2</sub>H<sub>4</sub>, 100), 165(42); Found M<sup>+</sup> 347.0169. C<sub>16</sub>H<sub>14</sub>NI requires 347.0170.

### 9,10-Ethano-9,10-dihydro-2,3-diiodoanthracene, 11

2-Amino-9,10-ethano-9,10-dihydro-3-iodoanthracene (2.078 g, 5.98 mmol) was dissolved in a mixture of acetic acid (14 ml) and propionic acid (6 ml) at  $0^{\circ}C$  with stirring. Nitrosyl-sulphuric acid (2.28 g, 17.97 mmol, 3 equiv) was added over 2 minutes and the resulting dark-brown solution was stirred for 20 minutes at 0°C before being poured into a solution of potassium iodide (32 g) in water (200 ml). The resulting suspension was stirred for 30 minutes at room temperature then for 10 minutes at 70°C. After cooling, aqueous sodium thiosulphate was added until the iodine colour was discharged. The solution was extracted with ether (2 x 75 ml) and the combined organic layers were washed with aqueous sodium thiosulphate (100 ml), 2N sodium hydroxide (3 x 200 ml), 2N hydrochloric acid (3 x 300 ml) and brine (2 x 200 ml), dried over magnesium sulphate and evaporated to give an orange foam (2.62 g). Chromatography on silica eluting with 10\$ dichloromethane in petrol gave 11 as a pinkish solid (2.06 g, 4.50 mmol, 75.3%), m.p. 183-5°C. Crystallisation from carbon tetrachloride gave a white solid m.p. 188-8.5°C which slowly turned pink on exposure to light; vmax.(CHC13) 3010m, 2960m, 2875m, 1485m, 1447m, 1363m, 1140m, 950m, 890m, 855 cm<sup>-1</sup>; δ<sub>H</sub>(CDCl<sub>3</sub>) 7.71(2H, s), 7.15(2H, m), 7.03(2H, m), 4.16(2H, s), 1.62(4H, 's'); m/z(EI) 458(M<sup>+</sup>, 23), 430(M-C<sub>2</sub>H<sub>4</sub>, 100), 176(C<sub>14</sub>H<sub>8</sub><sup>+</sup>, 88); Found C 42.05, H 2.85, I 55.0. C16H12I2 requires C 41.95, H 2.65, I 55.4%.

## 2-Acetylamino-9,10-ethano-9,10-dihydro-3-iodoanthracene, 12

Pyridine (5.0 ml, 4.89 g, 62.6 mmol) was added to a solution of 2-amino-9,10-ethano-9,10-dihydro-3-iodoanthracene (7.50 g, 21.61 mmol) in dichloromethane (100 ml) at 0°C and acetic anhydride (2.75 ml, 2.98 g, 29.2 mmol) was added to the resulting solution. The solution was stirred for 3 hours at room temperature and washed with 2N hydrochloric acid (3 x 150 ml), 2N sodium hydroxide (2 x 100 ml) and brine (100 ml), dried over magnesium sulphate and evaporated to give a pale brown foam (7.88 g) which was chromatographed on silica, eluting with ether, to give 12 as a pale beige solid (7.819 g, 20.10 mmol, 93.0%), m.p. 192-3°C;  $v_{max}$ .(nujol) 3240m, 1680s, 1610m, 1545m, 1375m, 1290m, 1040m, 780 cm<sup>-1</sup>;  $\delta_{\rm H}({\rm CDC1}_3)$  8.14(1H, s), 7.67(1H, s), 7.36(1H, br s,  $-{\rm NH}$ -), 7.25(2H, m), 7.10(2H, m), 4.36(1H, s), 4.24(1H, s), 2.24(3H, s), 1.71(4H, 's'); m/z(IBEI) 389(M<sup>+</sup>, 22), 361(M-C<sub>2</sub>H<sub>4</sub>, 39), 319(27), 291(20), 262(M-I, 26), 234 (M-C<sub>2</sub>H<sub>4</sub>-I, 100), 165(47), 43(25); a sample was sublimed at 140°C/1 x 10<sup>-4</sup> mm Hg; Found C 55.7, H 4.05, N 3.45. C<sub>18</sub>H<sub>16</sub>INO requires C 55.55, H 4.15, N 3.6%.

# Methyl 3-acetylamino-9,10-ethano-9,10-dihydroasthracene-2-carboxylate, 13

A solution of 2-acetylamino-9,10-ethano-9,10-dihydro-3-iodoanthracene (2.195 g, 5.64 mmol) and triethylamine (1.00 ml, 728 mg, 7.2 mmol) in methanol (75 ml) containing palladium(II) chloride (1.00 g, 5.64 mmol) in a 150 ml glass-lined steel autoclave was purged with carbon monoxide. The autoclave was then pressurised to 60 p.s.i.g. with carbon monoxide and the vessel was closed off. The mixture was heated to  $100^{\circ}$ C with magnetic stirring for 60 hours and allowed to cool. The autoclave was opened and the reaction mixture was filtered. The solid was washed with ether (25 ml) and the combined filtrate and washings were evaporated to give a beige foam which was chromatographed on silica, eluting with 10% ethyl actetate in dichloromethane, to give 13 as a white solid (1.806 g, 5.63 mmol, 99.8%), m.p.  $72^{\circ}$ C;  $v_{max}$ .(CHCl<sub>3</sub>) 3320m, 3265m, 3010m, 2980m, 1690s, 1680s, 1590s, 1510s, 1440ms, 1420ms, 1265s, 1135m, 1070m cm<sup>-1</sup>;  $\delta_{\rm H}(\rm CDCl_3)$  11.11(1H, br s,  $-N\underline{H}$ -), 8.70(1H, s), 7.91(1H, s), 7.26(2H, m), 7.12(2H, m), 4.41(1H, s), 4.30(1H, s), 3.91(3H, s), 2.23(3H, s), 1.73(4H, 's');  $m/z(\rm IBEI)$  321(M<sup>+</sup>, 22), 294(19), 293(M-C<sub>2</sub>H<sub>4</sub>, 100), 251(50), 219(21); Found M<sup>+</sup> 321.1365. C<sub>20</sub>H<sub>19</sub>NO<sub>3</sub> requires 321.1365.

# 2-(2,2-Dimethylpropanoylamino)-9,10-ethano-9,10-dihydroanthracene, 14

Triethylamine (631 µl, 458 mg, 4.525 mmol) was added to a stirred solution of 2-amino-9,10-ethano-9,10-dihydroanthracene (1.000 g, 4.525 mmol) in dry dichloromethane (15 ml) and 2,2-dimethylpropanoyl chloride (557 µl, 546 mg, 4.525 mmol) was added to the resulting solution. The stirred reaction mixture was monitored by the and reaction was complete in 45 minutes at room temperature. The solution was washed with water (2 x 25 ml), dried over potassium carbonate and evaporated to leave a white solid, (1.377 g, 99.8%), which was homogeneous by the. Crystallisation of a sample from ethanol/water gave 14 as tiny white crystals, m.p.  $167^{\circ}$ C;  $v_{max}$ .(CHCl<sub>3</sub>) 3460m, 3015m, 2960m, 2880m, 1680s, 1520s, 1495m, 1420m, 1170m, 1135m, 825m cm<sup>-1</sup>;  $\delta_{\rm H}(\rm CDCl_3)$  7.65(1H, d, J = 2 Hz), 7.25(4H, m), 7.10(3H, m), 4.30(2H, 's'), 1.80(4H, s), 1.30(9H, s); m/z(EI) 305(M<sup>+</sup>, 22), 278(22), 277(M-C<sub>2</sub>H<sub>4</sub>, 100), 193(46), 165(31), 57(C<sub>4</sub>H<sub>9</sub><sup>+</sup>, 84); Found C 82.2, H 7.45, N 4.65. C<sub>21</sub>H<sub>23</sub>NO requires C 82.55, H 7.6, N 4.6%.

### 3,4-Dimethyl-N-(2,2-dimethylpropanoyl)aniline, 15

Triethylamine (7.0 ml, 5.06 g, 50 mmol) was added to a solution of 3,4-dimethylaniline (5.0 g, 41.3 mmol) in ether (100 ml) and 2,2-dimethylpropanoyl chloride (6.16 ml, 6.03 g, 50 mmol) in ether (50 ml) was added to the resulting solution. The mixture was stirred for 1 hour at room temperature and the solvent was evaporated. The residue was dissolved in dichloromethane (100 ml) and the solution was washed with water (3 x 100 ml) and brine (100 ml) and dried over magnesium sulphate. The solvent was evaporated to give a cream solid. Crystallisation from ethanol/water gave 15 as white needles (6.28 g, 30.6 mmo, 74.1%), m.p.  $130^{\circ}$ C;  $\nu_{max.}$  (CHCl<sub>3</sub>) 3460m, 3000m, 2965m, 2880w, 1675s, 1600m, 1520s, 1410m, 665m cm<sup>-1</sup>;  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 7.37(1H, d, J = 2 Hz), 7.34 (1H, br s, -N<u>H</u>-), 7.22(1H, dd, J = 2 Hz, 8 Hz), 7.05(1H, d, J = 8 Hz), 2.25(3H, s), 2.23(3H, s), 1.32(9H, s); m/z(EI) 205(M<sup>+</sup>, 49), 121(60), 120(18), 57(100); Found C 75.65, H 9.35, N 7.0. C<sub>13</sub>H<sub>19</sub>NO requires C 76.05, H 9.35, N 6.8%.

## Bromination of 14 : 2-(2,2-dimethylpropanoylamino)-3-bromo-9,10-ethano-9,10-dihydroanthracene, 16

Bromine (0.4 ml, 1.0 M solution in acetic acid, 0.4 mmol) was added to a solution of 2-(2,2-dimethylpropancylamino)-9,10-ethano-9,10-dihydroanthracene (112 mg, 0.367 mmol) in acetic acid (4 ml) at room temperature. The resulting solution was stirred for 4 hours and was then poured into water (100 ml) containing sodium thiosulphate (2 g). The solution was extracted with ether (3 x 15 ml) and the combined organic layers were washed with brine (50 ml), dried over magnesium sulphate and evaporated to give an oil. Chromatography on silica, eluting with 20% ethyl acetate in petrol, gave 16 as a colourless oil (139.8 mg, 0.363 mmol, 99%);  $v_{max}$ . (CHCl<sub>3</sub>) 3420m, 2960m, 2880m, 1680s, 1580m, 1510s, 1480m, 1410ms om<sup>-1</sup>;  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 8.38(1H, s), 7.96(1H, br s, -NH-), 7.43 (1H, s), 7.25(2H, m), 7.10(2H, m), 4.35(1H, s), 4.27(1H, s), 1.73(4H, 's'), 1.37 (9H, s); m/z(IBEI) 385(15), 383(14), 357(18), 355(16), 304(34), 277(43), 276(M-Br-C\_2H\_4, 100), 273(24), 271(24), 245(15), 243(14), 165(22), 57(98); Found M<sup>+</sup> 383.0886. C<sub>21</sub>H<sub>22</sub><sup>79</sup>BrNO requires 383.0885.

# Bromination of 15 : 6 (and 2)-bromo-3,4-dimethyl-N-(2,2-dimethylpropanoyl)aniline, 17 and 18

Bromine (0.55 ml, 1.0 M solution in acetic acid, 0.55 mmol) was added to a solution of 3,4-dimethyl-N-(2,2-dimethylpropanoyl)aniline (103 mg, 0.50 mmol) in acetic acid (5 ml) at room temperature. The resulting solution was stirred for 4 hours and was then poured

into water (100 ml) containing sodium thiosulphate (2 g). The solution was extracted with ether (3 x 15 ml) and the combined organic layers were washed with brine (2 x 50 ml) and dried over magnesium sulphate. Evaporation of the solvent gave a light brown solid which was chromatographed on silica, eluting with 20% ethyl acetate in petrol, to give a 7.9:1 (by n.m.r.) mixture of 17 and 18 (139 mg, 0.49 mmol, 97.9%) which appeared as a single spot on tlc; for 17  $\delta_{\rm H}(\rm CDCl_3)$  8.17(1H, s), 7.87(1H, br s,  $-\rm NH-$ ), 7.27(1H, s), 2.23(3H, s), 2.18(3H, s), 1.37(9H, s); for 18  $\delta_{\rm H}(\rm CDCl_3)$  8.09 (1H, d, J = 8 Hz), 7.07(1H, d, J = 8 Hz), 2.38(3H, s), 2.30(3H, s), 1.37(9H, s); two crystallisations from ethanol gave 17, m.p. 113°C;  $\nu_{\rm max}(\rm CHCl_3)$  3420m, 2980m, 1685s, 1580m, 1520s, 1380m, 1170m, 910m cm<sup>-1</sup>; m/z(EI) 285(9), 283(9), 204(72), 201 (18), 199(20), 57(100); Found C 55.0, H 6.45, N 5.1. C<sub>13</sub>H<sub>18</sub>BrNO requires C 54.95, H 6.4, N 4.95%.

## 2-neo-pentylamino-9, 10-ethano-9, 10-dihydroanthracene, 19

Lithium aluminium hydride (151.8 mg, 4.0 mmol) was added in small portions to a stirred solution of 2-(2,2-dimethylpropanoylamino)-9,10-ethano-9,10-dihydroanthracene (305 mg, 1.00 mmol) in dry THF (5 ml) at room temperature. When the initial reaction had subsided the resulting suspension was heated under reflux for 4 hours and allowed to cool. Water (0.5 ml) and 2N sodium hydroxide (3.0 ml) were added carefully and the mixture was filtered. The THF was removed in vacuo and the aqueous residue was extracted with ether (3 x 15 ml). The combined organic layers were washed with water (15 ml) and extracted with 0.5N hydrochloric acid (3 x 20 ml). The acidic extracts were washed with ether (15 mal) and basified with 10N sodium hydroxide. The resulting mixture was extracted with ether (3 x 15 ml) and the combined organic layers were washed with brine (25 ml) and dried over sodium sulphate. Evaporation of the solvent gave an off-white solid which was chromatographed on silica, eluting with ether, to give 19 as a white solid (235.6 mg, 0.81 mmol, 81.0%), m.p. 215-20°C (dec.). Crystallisation from ethanol/water gave white needles, m.p. 220°C (dec.); v<sub>max.</sub>(CHCl<sub>3</sub>) 3450w, 3010m, 2980s, 2875m, 1620ms, 1500ms, 1475ms, 1135m, 820m cm<sup>-1</sup>;  $\delta_{H}$ (CDCl<sub>3</sub>) 7.27(2H, m), 7.08(3H, m), 6.63(1H, d, J = 2 Hz, H1), 6.37(1H, dd, J = 2 Hz, 8 Hz, H3), 4.22(2H, s), 3.5(1H, br, -NH-), 2.88(2H, s), 1.72(4H, m), 1.02(9H, s); m/z(EI) 291(M<sup>+</sup>, 21), 263 (M-C<sub>2</sub>H<sub>4</sub>, 42), 234(38), 206(M-C<sub>4</sub>H<sub>6</sub>-C<sub>2</sub>H<sub>4</sub>, 100); Found C 86.15, H 8.8, N 4.7. C21H25N requires C 86.55, H 8.65, N 4.8%.

## 3,4-Dimethyl-N-Dec-pentylaniline, 20

Lithium aluminium hydride (151.8 mg, 4.0 mmol) was added in small portions to a stirred solution of 3,4-dimethyl-N-(2,2-dimethylpropanoyl)aniline (205 mg, 1.00 mmol) in dry THF (5 ml) at room temperature. When the initial reaction had subsided the resulting suspension was heated under reflux for 4 hours and allowed to cool. Water (0.5 ml) and 2N sodium hydroxide (3.0 ml) were added carefully and the mixture was filtered. The THF was removed in vacuo and the aqueous residue was extracted with ether (3 x 10 ml). The combined organic layers were washed with water (15 ml) and extracted with 2N hydrochloric acid (3 x 15 ml). The acidic extracts were washed with ether (10 ml) and basified with 10N sodium hydroxide. The resulting mixture was extracted with ether (3 x 10 ml) and the combined organic layers were washed with brine (20 ml) and dried over sodium sulphate. Evaporation of the solvent gave an oil which was chromatographed on silica, eluting with ether, to give 20 as a colourless oil (145.4 mg, 0.76 mmol, 76.1\$); v max.(liquid film) 3420m, 2950s, 2860ms, 1620s, 1515s, 1480ms, 1320ms, 1260ms, 800ms cm<sup>-1</sup>; <sup>6</sup><sub>H</sub>(CDCl<sub>3</sub>) 6.97(1H, d, J = 8 Hz, H5), 6.50(1H, d, J = 2 Hz, H2), 6.45(1H, dd, J = 2 Hz, 8 Hz, H6), 3.2(1H, br, -NH-), 2.92(2H, s, -CH<sub>2</sub>N-), 2.25(3H, s), 2.20(3H, s), 1.04(9H, s). A sample was dissolved in ether and a saturated solution of HCl in ether was added. The white precipitate was collected and crystallised from water to give 3,4-dimethyl-N-neopentylaniline hydrochloride as white needles, m.p. 205°C (dec.); Found C 68.65, H 9.45, N 6.35. C13H22NCl requires C 68.55, H 9.75, N 6.15%.

### Lithiation and deuteration of 2-pivalamido-KDA, 14

n-Butyl lithium (2.50 ml, 1.6M solution in hexane, 4.0 mmol) was added to a solution of 2-(2,2-dimethylpropanoylamino-9,10-ethano-9,10-dihydroanthracene (240 mg, 0.787 mmol) in TMEDA (2.0 ml) and the resulting solution was stirred at room temperature for 15 hours.  $D_{2}O(0.5 ml)$  was added, the mixture was stirred for 10 minutes and then 2N hydrochloric acid (25 ml) was added. The resulting suspension was extracted with ether (3 x 20 ml). The combined organic layers were washed with 2N hydrochloric acid (50 ml) and brine (100 ml) and dried over magnesium sulphate. Evaporation of the solvent gave a white solid Lithium aluminium hydride (135 mg, (233.7 mg) which was dissolved in dry THF (5 ml). 3.55 mmol) was added in small portions and the resulting suspension was heated under Water (0.5 ml) and 2N sodium hydroxide (3.0 ml) reflux for 4 hours and allowed to cool. were added carefully and the mixture was filtered. The THF was removed in vacuo and the aqueous residue was extracted with ether (3 x 15 ml). The combined organic layers were washed with water and extracted with 0.5N hydrochloric acid (3 x 20 ml). The acid extracts were washed with ether (15 ml) and basified with 10N sodium hydroxide. The resulting mixture was extracted with ether (3 x 15 ml) and the combined organic layers were washed with bring (25 ml) and dried over sodium sulphate. Evaporation of the solvent and chromatography of the resulting solid on silica, eluting with ether, gave deuterated 2-neo-pentylamino-9,10-ethano-9,10-dihydro-anthracene, 19, as a white solid (183.4 mg, 0.628 mmol, 79.8%), m.p. 215-8°C(dec.);  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 7.27(2H, m), 7.08(3H, m), 6.63(0.35H, 's'), 6.37(0.80H, 'd', J = 8 Hz), 4.22(2H, s), 3.5(1H, br, -NH-), 2.88(2H, s), 1.72(4H, m), 1.02(9H, s).

## Lithiation and deuteration of 3,4-dimethylpivalanilide, 15

n-Butyl lithium (2.73 ml, 1.6M solution in hexane, 4.36 mmol) was added to a solution of 3,4-dimethyl-N-(2,2-dimethylpropanoyl)aniline (179 mg, 0.873 mmol) in TMBDA (2.0 ml) and the resulting solution was stirred at room temperature for 15 hours. D<sub>2</sub>O (0.5 ml) was added, the mixture was stirred for 10 minutes and then 2N hydrochloric acid (25 ml) was added. The resulting suspension was extracted with ether (3 x 20 ml). The combined organic layers were washed with 2N hydrochloric acid (50 ml) and brine (100 ml) and dried over magnesium sulphate. Removal of the solvent gave a white solid (164.8 mg) which was dissolved in dry THF (5 ml). Lithium aluminium hydride (152 mg, 4.0 mmol) was added in small portions and the resulting suspension was heated under reflux for 4 hours and allowed to cool. Water (0.5 ml) and 2N sodium hydroxide (3.0 ml) were added carefully and the mixture was filtered. The THF was removed in vacuo and the aqueous residue was extracted with ether (3 x 20 ml). The combined organic layers were washed with water and extracted with 2N hydrochloric acid (3 x 15 ml). The acidic extracts were combined. washed with ether (10 ml) and basified with 10M sodium hydroxide. The resulting mixture was extracted with ether (3 x 10 ml) and the combined organic layers were washed with brine (20 ml) and dried over sodium sulphate. Evaporation of the solvent and chromatography of the resulting oil on silica, eluting with ether, gave deuterated 3,4-dimethyl-N-neo-pentylaniline, 20, as an oil (111.6 mg, 0.581 mmol, 66.6\$);  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 6.97(1H, m), 6.50(0.91H, 's'), 6.45(0.36H, dd, J = 2 Hz, 8 Hz), 3.2(1H, br, -NH-), 2.92(2H, s), 2.25(2.72H, s), 2.20 (3H, s), 1.04(9H, s).

### 2-Mitroanthracens, 4

9,10-Ethano-9,10-dihydro-2-nitroanthracene (154.2 mg, 0.614 mmol) was slowly sublimed at 0.01 mm Hg into the quartz tube of the FVP apparatus which was heated to  $650^{\circ}$ C. The product was obtained as a yellow solid (136.5 mg) which, by n.m.r. comprised 4 (76%) and unreacted starting material (24%). The recovery of material was 96.7%. Crystallisation of the product from ether/benzene/petrol at -78°C gave 4 (96.5 mg, 0.433 mmol, 70.5%), m.p. 174°C(1it.<sup>4</sup> 174-5°C;  $\lambda_{max.}$  (EtOH) 212(3.3), 235 (3.9), 261(3.5), 301(3.5), 308(3.5), 329(infl, 2.9), 345(2.9), 362(2.7), 411(2.8)nm;  $\nu_{max.}$  (CHCl<sub>3</sub>) 3020m, 1520s, 1345s, 1080m, 920m, 890m, 870m, 815w cm<sup>-1</sup>;  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.97(1H, s), 8.62(1H, s), 8.50(1H, s), 8.13(2H, m), 8.06(2H, m), 7.60 (2H, m); m/z(EI) 223(M<sup>+</sup>, 100), 177(87), 176(45), 165(26), 151(17), 150(11).

#### 2-Acetylaminoanthracene, 21

2-Acetylamino-9,10-ethano-9,10-dihydroanthracene (200 mg, 0.760 mmol) was sublimed over 10 minutes at 1 x 10<sup>-4</sup> mm Hg into the pyrolysis tube which was heated to  $650^{\circ}$ C. The product comprised 21 (94%) and unreacted starting material (6%) by n.m.r. and the recovery of material was 96%. Crystallisation from ethanol gave 21 (154.5 mg, 0.65 mmol, 86.5%), m.p. and mixed m.p. 244-4.5°C(11t.<sup>10</sup> 238°C);  $\lambda_{max.}$  (EtOH) 226(3.8), 238(3.8), 258(4.4), 268(4.4), 276(4.4), 324(2.9), 338(3.1), 354(3.2), 368(3.2), 388(3.1)nm;  $\nu_{max.}$  (KBr) 3280m, 3100w, 3060w, 1660s, 1570ms, 1550ms, 1385ms, 900ms, 740ms cm<sup>-1</sup>;  $\delta_{\rm H}$ (DMSO-d<sup>6</sup>) 10.20(1H, br s, -N<u>H</u>-), 8.50(1H, br 's'), 8.47(1H, s), 8.43(1H, s), 8.02(3H, m), 7.55(1H, dd, J = 2 Hz, 9 Hz), 7.46(2H, m), 2.14(3H, s).

## 2-Amino-3-mitroanthracene, 22

2-Amino-9,10-ethano-9,10-dihydro-3-nitroanthracene (157 mg, 0.59 mmol) was sublimed over 10 minutes at 1 x 10<sup>-4</sup> mm Hg into the pyrolysis tube which was heated to  $650^{\circ}$ C. The product comprised 22 (87.5%) and unreacted starting material (12.5%) and the recovery of material was 91.1%. Crystallisation from hot toluene gave 22 as a purple-black solid (105.6 mg, 0.444 mmol, 75.3%), m.p.  $257-8^{\circ}$ C;  $\lambda_{max.}$  (EtOH) 223(3.0), 240(infl, 3.2), 267(3.7), 292(3.3), 336(3.1), 381(2.7), 388(2.7)nm;  $\lambda_{max.}$  (DMF) 420-740(2.9 at 533nm, 1.7 at 700nm)nm;  $\nu_{max.}$  (Nujol) 3500m, 3400m, 1635ms, 1505ms, 1320ms, 1040m, 880m, 755m, 745m om<sup>-1</sup>;  $\delta_{\rm H}$  (DMF-d<sup>7</sup>) 9.05 (1H, s), 8.74(1H, s), 8.23(1H, s), 7.95(2H, m), 7.55(1H, s), 7.52(1H, 't'), 7.40(1H, 't'), 6.64(2H, br s,  $-NH_2$ ); m/z(IBEI) 238(M<sup>+</sup>, 96), 192(32), 165(100). A sample was sublimed at 135°C/1 x 10<sup>-4</sup> mm Hg, m.p. 258°C; Found C 70.8, H 4.55, N 11.95. C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> requires C 70.6, H 4.25, N 11.75%.

### 2,3-Diiodoanthracene, 23

9,10-Ethano-9,10-dihydro-2,3-diiodoanthracene (150 mg, 0.328 mmol) was sublimed over 5 minutes at 2 x 10<sup>-3</sup> mm Hg into the pyrolysis tube which was heated to 650°C. The product comprised 69.7% 23 and 30.3% unreacted starting material and the recovery of material was 98.3 mol %. Washing the crude product with carbon tetrachloride (10 x 1 ml) gave pure 23 as an off-white solid (95.5 mg, 0.222 mmol, 67.8%), m.p. 248.5-9°C;  $v_{max.}$ (KBr) 3040w, 3020w, 1600m, 940m, 900s, 750ms cm<sup>-1</sup>;  $\delta_{\rm H}$ (DMF-d<sup>7</sup>) 8.85(2H, s), 8.59(2H, s), 8.12(2H, m), 7.58(2H, m); m/z(IBEI) 431(16), 430(M<sup>+</sup>, 100), 176(C<sub>14</sub>H<sub>8</sub><sup>+</sup>, 80); Found C 39.1, H 2.1, I 58.9. C<sub>14</sub>H<sub>8</sub>I<sub>2</sub> requires C 39.1, H 1.9, I 59.0%.

### 2-Acetylamino-3-iodoanthracene, 24

2-Acetylamino-9,10-ethano-9,10-dibydro-3-iodomnthracene (194.5 mg, 0.500 mmol) was sublimed over 10 minutes at 1 x  $10^{-4}$  mm Hg into the pyrolysis tube which was heated to

650°C. The product consisted only of 24 (by n.m.r.) and the recovery of material was 98%. Sublimation at 150°C/1 x 10<sup>-4</sup> mm Hg gave 24 as a cream solid (164.6 mg, 0.456 mmol, 91.2%), m.p. 259-60°C;  $\lambda_{max.}$  (EtOH) 237(infl, 4.3), 266(4.9), 330(3.4), 346(3.6), 364(3.6), 383(3.5)nm;  $v_{max.}$  (KBr) 3260br, ms, 3050w, 1660s, 1615m, 1540s, 1420m, 1370m, 1290m, 1270m, 900s, 740s om<sup>-1</sup>;  $\delta_{\rm H}$ (DMSO-d<sup>6</sup>) 9.7(1H, br s, -N<u>H</u>-), 8.76 (1H, s), 8.55(1H, s), 8.53(1H, s), 8.12(1H, s), 8.05(2H, m), 7.55(2H, m), 2.13(3H, s); m/z(IBEI) 361(M<sup>+</sup>, 51), 319(46), 234(M-I, 100), 165(52); Found C 53.35, H 3.3, N 3.9.  $C_{16}H_{12}$ INO requires C 53.2, H 3.35, N 3.9%.

### Methyl 3-acetylaminoanthracene-2-carboxylate, 25

Methyl 3-acetylamino-9,10-ethano-9,10-dihydroanthracene-2-carboxylate (160.5 mg, 0.500 mmol) was sublimed over 5 minutes at 4 x  $10^{-3}$  mm Hg into the pyrolysis tube which was heated to  $650^{\circ}$ C. The product contained no unreacted starting material (by n.m.r.) and the recovery of material was 98.6%. Crystallisation from hot toluene gave 25 as thin yellow sheets (138.0 mg, 0.471 mmol, 94.2%), m.p.  $204^{\circ}$ C;  $\lambda_{max}$ .(EtOH) 209(4.0), 234(4.2), 260(4.6), 278(4.9), 328(3.6), 344(3.7), 362(3.2), 384(3.2), 412(3.3)nm;  $\nu_{max}$ .(Nujol) 3345m, 3280m, 1695-1670s, 1600m, 1500m, 1265s, 1130m, 905s, 730s cm<sup>-1</sup>;  $\xi_{\rm H}$ (DMSO-d<sup>6</sup>) 10.5(1H, s,  $-M_{\rm H}$ -), 8.80(1H, s), 8.75(1H, s), 8.71(1H, s), 8.54(1H, s), 8.09(2H, 'd', J = 9.5 Hz), 7.55(2H, m), 3.94(3H, s), 2.17(3H, s); m/z(EI) 293(M<sup>+</sup>, 76), 251(74), 219(54), 192(30), 191(26), 190(33), 165(39), 164(48), 163(30), 43(100); Found C 73.55, H 5.1, N 4.9. C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub> requires C 73.7, H 5.15, N 4.8%.

#### ACKNOWLEDGEMENT

One of us (A.G.S.) would like to thank the S.E.R.C. for financial support.

#### REFERENCES

- See for example H. E. Zimmerman and D. R. Amick, <u>J. Am. Chem. Soc.</u>, 1973, 95, 3977.
- 2. C. L. Thomas, U.S.P. 2406645/1946.
- 3. (a) J. L. Ripoll and A. Thuillier, <u>Tetrahedron</u>, 1977, 33, 1333.
  (b) M. Oda, N. Fukazawa and Y. Kitahara, <u>Tetrahedron Lett</u>., 1977, 3277.
- H. Tanida and H. Ishitobi, <u>Tetrahedron Lett</u>., 1964, 807.
   H. Tanida, Jap. P. 7455/1967.
- 5. H. W. Gschwend and W. Fuhrer, J Org Chem., 1979, 44, 1133.
- 6. W. H. Mills and I. G. Nixon, <u>J. Chem. Soc</u>., 1930, 2510.
- 7. R. A. Finnegan, J. Org. Chem., 1965, 30, 1333.
- A. Streitwieser Jr., G. R. Ziegler, P. C. Mowery, A. Lewis and R. G. Lawler, <u>J. Am. Chem. Soc</u>., 1968, 90, 1357.
- 9. J. J. A. Campbell, P. Halliwell and P. W. Manley, <u>Chem. Ind. (London)</u>, 1978, 842.
- 'Elsevier's Encyclopaedia of Organic Chemistry', Elsevier, Amsterdam, 1946, 13, 267.
- 11. W. C. Still, M. Kahn and A. Mitra, <u>J. Org. Chem</u>., 1978, 43, 2923.