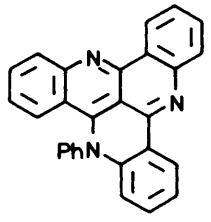
Cyclic Amidines. Part 26.[1] The Reported Syntheses of 7-Anilino-6-aryl-5,12-diazabenz[*a*]anthracenes are Reinvestigated and their Correct Structures Identified

Christopher Upton
School of Pharmacy and Pharmacology, University of Bath, Bath BA2 7AY

The reaction between aryl methyl ketones and triphenylguanidine reported to yield 7-anilino-6-aryl-5,12-diazabenz[*a*]anthracenes is reviewed. With anomalies in the reported data for some intermediates in this reaction, we propose and synthesise possible alternative structures for the title compounds and conclude that the reaction produces 6-anilino-7-aryl-5,12-diazabenz[*a*]anthracenes.

In an earlier paper[2] the preparation of 5-phenyl-5,10,15-triaza-5-*H*-tribenzo[*a*,*e*,*i*]phenalene[3] (**2**) by treatment of 7-chloro-6-(2-chlorophenyl)-5,12-diazabenz[*a*]anthracene (**1**) with aniline was described. The same triazaphenalene had previously been

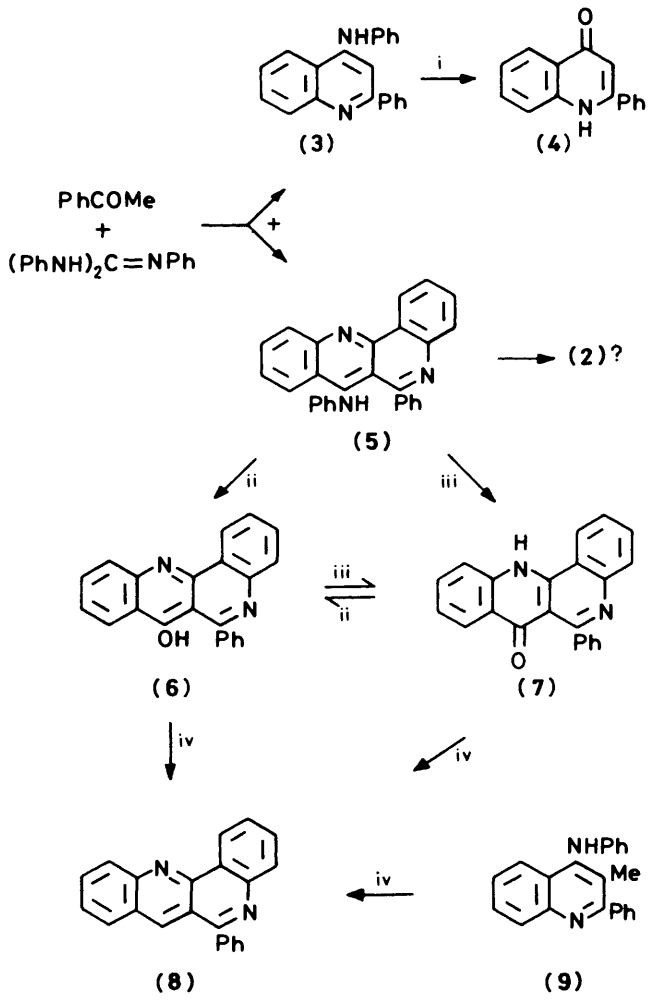
(**1**)



(**2**)

reported by Moszew[4] by oxidation of alleged 7-anilino-6-phenyl-5,12-diazabenz[*a*]anthracene (**5**). However the compound (**2**) prepared by the unequivocal method of Partridge[2] melted at 317 °C whereas Moszew reported a melting point of 245 °C and, more importantly, antitumour properties.[5] In the light of this atypical activity in a series of compounds noted for their frequent and often intense mutagenic and carcinogenic properties[6] it was decided to re-investigate the reaction and establish the structure of Moszew's product.

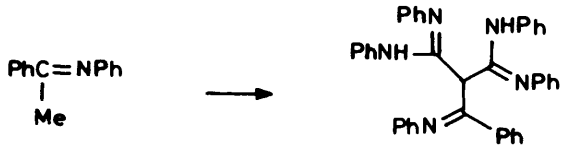
In a typical reaction[7] between acetophenone and diphenylthiourea Moszew identified the major product as 4-anilino-2-phenylquinoline (**3**) by its hydrolysis to the known quinolinone (**4**), reported a minor product, and assuming it to be derived from the anilinoquinoline (**3**), formulated it as the benzanthracene (**5**). In further work[8] diphenylthiourea was replaced by triphenylguanidine to afford higher yields of (**5**). The structure of compound (**5**) (summarised in the Scheme) was established by its hydrolysis in alkali at 200 °C under pressure, to benzanthracen-7-ol (**6**) or in acid to the tautomer (**7**), followed by a zinc dust distillation of either (**6**) or (**7**) to 6-phenyl-5,12-diazabenz[*a*]anthracene (**8**). The structure of this deoxygenated product (**8**) was confirmed by a zinc dust distillation of authentic 4-anilino-3-methyl-2-phenylquinoline (**9**) to give the same product (**8**). The synthetic work outlined in the Scheme was repeated to obtain samples of compounds (**5**)—(**8**) and, to ensure that no rearrangements had occurred during the severe hydrolysis of (**5**), compound (**7**) was converted to the chloro intermediate which reacted with aniline to regenerate the anilinoanthracene (**5**) in high yield [the tautomer (**6**) would not so behave]. Hydrogenolysis of this chloro compound was easily achieved in high yield but was dissimilar from compound (**8**). An authentic sample[2] of 6-(2-chlorophenyl)-5,12-diazabenz[*a*]-anthracen-7-ol (**10**) was converted to the anilino derivative (**14**)



Scheme. *Reagents:* i, H^+–H_2O; ii, KOH, 200 °C; iii, H^+, 200 °C; iv, Zn–H_2

and it was seen that compounds (**11**), (**13**), and (**14**) were different from (**6**) or (**7**), (**8**), and (**5**), respectively showing that the compounds described by the Scheme were not 6-phenyl-5,12-diazabenz[*a*]anthracenes.

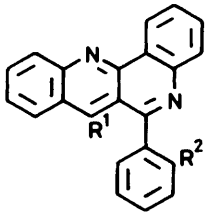
It is difficult to deduce alternative structures for (**5**) if it does arise from the preformed quinoline (**3**) without rearrangement. However if acetophenone or its anil (**15**) were to react with two



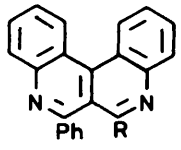
(15) (16)

molecules of diphenylcarbodi-imide prior to cyclisation, the diamidino intermediate (**16**) could eliminate aniline and cyclise in four possible ways to either 7-anilino-6-phenyl-5,12-diazabenz[*a*]anthracene (**14**) (shown not to occur), or 7-anilino-6-phenyl-5,8-diazabenzo[*c*]phenanthrene (**17**), or 11-anilino-12-phenyl-5,6-diazanaphthacene (**27**), or 6-anilino-7-phenyl-5,12-diazabenz[*a*]anthracene (**32**).

A double Friedlander condensation between ethyl benzoylacetate and 2,2′-diaminobenzophenone[9] gave 6-phenyl-5,8-diazabenzo[*c*]phenanthren-7-ol (**18**) which was converted *via* the phenanthrene (**19**) into the anilino compound (**17**). Hydrogenolysis of compound (**19**) gave the phenanthrene (**20**), and none of these compounds were similar to those shown in the Scheme and so excluded this series as benzo[*c*]phenanthrenes.



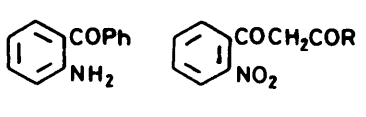
(**10**) R^1 = OH; R^2 = Cl
(**11**) R^1 = OH; R^2 = H
(**12**) R^1 = Cl; R^2 = H
(**13**) R^1 = R^2 = H
(**14**) R^1 = NHPh; R^2 = H



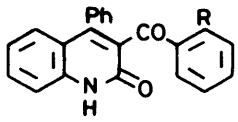
(**17**) R = NHPh
(**18**) R = OH
(**19**) R = Cl
(**20**) R = H

A Knorr condensation (after Hauser[10]) between 2-aminobenzophenone (**21**) and methyl 2-nitrobenzoylacetate (**22**) gave the expected 3-(2-nitrobenzoyl)-4-phenylquinolin-2-one (**24**) which was smoothly reduced in high yield with palladium to the 3-(2-aminobenzoyl)quinoline (**25**). This amine suffered cyclodehydration to 11-phenyl-5,6-diazanaphthacen-12-ol (**26**) at its melting point and was not identical to either compounds (**6**) or (**7**). It was not possible to synthesise the naphthacene (**27**) from (**26**) by the usual methods.

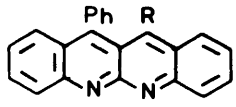
The final isomer required was the 7-phenylbenzanthracene (**32**) and this was less accessible. Attempts to persuade 2-aminobenzophenone (**21**) to react with methyl 2-nitrobenzoylacetate (**22**) or the less reactive anilide (**23**) in a Conrad-Limpach condensation to compound (**28**) or (**29**) failed: only starting material or the quinolinone (**24**) were isolable. Hydrolysis to the acid (**30**) and reduction should have given the tautomer of lactam (**31**). A similar condensation between 2-aminobenzophenone and 2-nitropropiophenone (using Fehnel's modification[11]) gave 3-methyl-2-(2-nitrophenyl)-4-phenylquinoline but this defied attempts to oxidise it to the required acid (**30**), even using conditions specifically designed for the oxidation of 3-methylquinolines.[12] Indane-1,3-dione and 2-aminobenzophenone reacted to form the azabenzofluoreneone (**35**) whose oxime (**36**) was expected, on Beckmann rearrangement, to give either (**31**) or 7-phenyl-6,12-diazabenz[*a*]-anthracen-5-ol but instead gave the dibenzacephenanthrylene (**37**), identical to an authentic sample.[9] Finally a modified Bernthsen reaction (after Buu Hoi[13]) between benzoic acid and



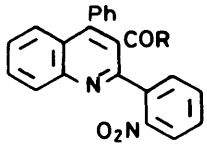
(**21**) (**22**) R = OMe (**23**) R = NHPh



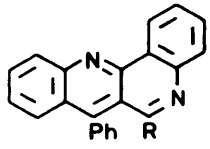
(**24**) R = NO_2 (**25**) R = NH_2



(**26**) R = OH
(**27**) R = NHPh



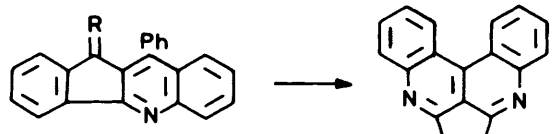
(**28**) R = OMe
(**29**) R = NHPh
(**30**) R = OH



(**31**) R = OH
(**32**) R = NHPh
(**33**) R = Cl
(**34**) R = H

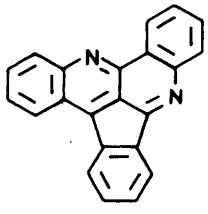
4-anilinoquinolin-2-one gave the required compound (**31**) in good yield. This was converted into compounds (**32**)—(**34**) which were identical with the corresponding compounds shown in the Scheme and confirmed that aryl methyl ketones and triphenylguanidine react to form 7-phenylbenz[*a*]anthracenes.

To confirm the structure of the series, 2-aminobenzophenone was condensed with 1,2,3,4-tetrahydroquinolin-4-one[14] to give, after chromatography, 7-phenyl-5,12-diazabenz[*a*]anthracene identical to (**34**) and to the hydrogenolysed chloro derivative of (**7**). The relationship of compound (**6**) to (**7**), regarded by Moszew as tautomeric, was shown to be due to (**6**) being a dihydro derivative of (**7**) (not unexpected with KOH in EtOH at 200 °C). Treatment of compound (**7**) with zinc in acetic acid



(**35**) R = O
(**36**) R = NOH

(**37**)



(**38**)

produced an almost quantitative yield of (**6**) which regenerated (**7**) in very high yield on oxidation (CrO_3–acetic acid). The ^1H n.m.r. spectrum of compound (**6**) showed three singlets (1 H) at δ 5.3 (C-H), 9.3, and 11.3. That at δ 11.3 exchanges immediately with D_2O (OH) while that at δ 9.3 does so much more slowly (NH) but rapidly in the presence of acid.

Moszew finally confirmed the structure of his compounds by a zinc dust distillation of (**6**), (**7**), and (**9**) to (**8**): it has already been shown that the chloro derivative from (**7**) does not produce compound (**8**) after hydrogenolysis, and that (**8**) is not the same as authentic 7-phenyl-5,12-diazabenz[*a*]anthracene (**34**). When the distillation of compounds (**6**) and (**7**) was repeated, the u.v. spectrum of the product was immediately recognised as that of 9,14-diazadibenz[*a,e*]aceanthrylene (**38**) obtained in an earlier piece of work,[1] and was confirmed by m.p., mixed m.p., i.r., and t.l.c. behaviour.

Experimental

M.p.s were determined on a Kofler hot bench except those designated uncorr. which are uncorrected and determined in a capillary tube. ^1H N.m.r. spectra were recorded on a Perkin-Elmer R12B instrument operating at 60 MHz (using tetramethylsilane as the internal standard). I.r. spectra were recorded on a Unicam S.P.200 using KBr discs.

7-Phenyl-5,8-diazabenzo[c]*phenanthren-6-ol* (**18**).—2,2-Diaminobenzophenone[9] (1.8 g, 95 mmol), ethyl benzoylacetate (2 ml), and acetic acid (10 drops) were heated at 160 °C for 20 min, stirred with methanol (5 ml) and the residue, on crystallisation from 2-ethoxyethanol gave the *phenanthrene* as pale yellow prisms (2.5 g, 91%), m.p. 378—380 °C (uncorr.) (Found: C, 82.1; H, 4.6; N, 8.2. $C_{22}H_{14}N_2O$ requires C, 82.0; H, 4.4; N, 8.6%).

6-Chloro-7-phenyl-5,8-diazabenzo[c]*phenanthrene* (**19**).—7-Phenyl-5,8-diazabenzo[*c*]phenanthren-6-ol (1.6 g, 5 mmol), thionyl chloride (20 ml), and dimethylformamide (2 ml) were refluxed together for 6 h. Unchanged thionyl chloride was removed and the residue was poured onto crushed ice (20 g) containing aqueous sodium hydroxide (10%; 10 ml). The resulting solidified oil was dissolved in toluene, poured through an alumina column and the initial toluene eluate evaporated to give, after crystallisation from benzene, *6-chloro-7-phenyl-5,8-diazabenzo*[c]*phenanthrene* (1.4 g, 84%), as colourless prisms, m.p. 197—198 °C (Found: C, 77.6; H, 3.9; N, 7.8. $C_{22}H_{13}ClN_2$ requires C, 77.5; H, 3.9; N, 8.1%).

6-Anilino-7-phenyl-5,8-diazabenzo[c]*phenanthrene* (**17**).—6-Chloro-7-phenyl-5,8-diazabenzo[*c*]phenanthrene (0.5 g, 1 mmol) and aniline (2 ml) were refluxed together for 2.5 h and cooled to give a yellow solid which was washed with water (10 ml). This solid (0.57 g) was extracted with boiling toluene (3 × 20 ml) and the concentrated extract chromatographed on alumina. The yellow toluene eluate possessing a greenish-yellow fluorescence was evaporated and the solid, on crystallisation from light petroleum (b.p. 80—100 °C), afforded the *phenanthrene* (0.3 g, 50%) as short yellow prisms, m.p. 190—191 °C (Found: C, 84.2; H, 5.0; N, 10.7. $C_{28}H_{19}N$ requires C, 84.6; H, 4.8; N, 10.6%).

6-Phenyl-5,8-diazabenzo[c]*phenanthrene* (**20**).—A solution of potassium hydroxide (0.02 g) in ethanol (4 ml) and toluene (1 ml), containing palladium catalyst (10% Pd-on-charcoal; 25 mg), was equilibrated with hydrogen in a microhydrogenator. 6-Chloro-7-phenyl-5,8-diazabenzo[*c*]phenanthrene (**19**) (15 mg) was introduced and hydrogen uptake allowed to proceed to completion. The suspension was filtered ('Supercel'), the solvent evaporated and the residual solid after crystallisation from light petroleum (b.p. 100—120 °C) gave *6-phenyl-5,8-diazabenzo*[c]*phenanthrene* (0.009 g, 69%), m.p. 191—192 °C, undepressed on admixture with an authentic sample.[1]

6-Phenyl-5,12-diazabenz[a]*anthracen-7-ol* (**11**).—The title compound was obtained (74% yield) from a palladium-catalysed hydrogenolysis of 6-(2-chlorophenyl)-5,12-diazabenz[a]anthracen-7-ol[2] as described for compound (**20**) above: it existed as a buff solid (DMF), m.p. above 430 °C (Found: C, 81.7; H, 4.3; N, 8.3. $C_{22}H_{14}N_2O$ requires C, 82.0; H, 4.4; N, 8.7%).

7-Chloro-6-phenyl-5,12-diazabenz[a]*anthracene* (**12**).—6-Phenyl-5,12-diazabenz[*a*]anthracen-7-ol (1.5 g, 5 mmol), thionyl chloride (20 ml) and dimethylformamide (2 ml) were refluxed together for 6 h and the remaining oil, after removal of the excess of thionyl chloride, was poured onto crushed ice (30 g) containing aqueous sodium carbonate (10%; 10 ml). The resulting solid on crystallisation from toluene gave the *chlorobenzanthracene* (1.12 g, 70%) as yellow prisms, m.p. 198—199 °C (Found: C, 77.2; H, 4.0; N, 8.4. $C_{22}H_{13}ClN_2$ requires C, 77.5; H, 3.9; N, 8.2%).

7-Anilino-6-phenyl-5,12-diazabenz[a]*anthracene* (**14**).—The foregoing chlorobenzanthracene (0.3 g, 1 mmol) and aniline (2 ml) were refluxed together for 3 h. After removal of unchanged aniline, the residue was basified with aqueous sodium hydroxide and extracted with toluene. The extract was chromatographed on alumina using toluene as the eluant and the yellow toluene eluate on evaporation produced a yellow material, *7-anilino-6-phenyl-5,12-diazabenz*[a]*anthracene* (0.18 g, 52%), which crystallised from benzene as yellow prisms, m.p. 228—230 °C (Found: C, 84.6; H, 4.8; N, 10.5. $C_{28}H_{19}N$ requires C, 84.6; H, 4.8; N, 10.6%).

3-(2-Nitrobenzoyl)-4-phenylquinolin-2-ol (**24**).—2-Aminobenzophenone (2.0 g, 0.01 mol), methyl 2-nitrobenzoylacetate (2.25 g), and acetic acid (10 drops) were heated together for 1 h at 160 °C and furnished, after crystallisation of the resulting glass from acetic acid, the *quinolin-2-ol* (3.2 g, 86%) as colourless prisms, m.p. 237—238 °C (Found: C, 71.1; H, 4.0; N, 7.3. $C_{22}H_{14}N_2O_4$ requires C, 71.4; H, 3.8; N, 7.6%); δ_H (60 MHz; Me_2SO) 3.28 (1 H, s, NH) and 7.0—7.8 (13 H, m, ArH).

3-(2-Aminobenzoyl)-4-phenylquinolin-2-one (**25**).—A solution of 3-(2-nitrobenzoyl)-4-phenylquinolin-2-ol (3.0 g, 8 mmol) in benzene (150 ml) was added to a hydrogen-equilibrated suspension of palladium catalyst (10% Pd-on-charcoal; 0.5 g) in ethanol (30 ml) and after the rapid uptake of the equivalent of 3.0 mol hydrogen the reaction was stopped, the suspension filtered and solvent removed. The residue gave a mass of small, colourless prisms of 3-(2-*aminobenzoyl*)-4-*phenylquinolin*-2-*one* (2.24 g, 82%) on crystallisation from acetic acid, m.p. 289—290 °C (decomp., uncorr.) (Found: C, 77.3; H, 4.8; N, 7.9. $C_{22}H_{16}N_2O_2$ requires C, 77.6; H, 4.7; N, 8.2%).

2-Phenyl-5,6-diazanaphthacen-11-ol (**26**).—A sample of the foregoing aminobenzoylquinolinone (0.1 g) was heated at 293 °C for 10 min and the yellow sublimate extracted into benzene and chromatographed on alumina. Elution with benzene furnished a yellow solution which on concentration deposited a mass of bright yellow prisms of *12-phenyl-5,6-diazanaphthacen-11-ol* (0.06 g, 63%) m.p. of which, after crystallisation from light petroleum (b.p. 100—120 °C), was 288—290 °C (decomp., uncorr.) (Found: C, 82.1; H, 4.4; N, 8.4. $C_{22}H_{14}N_2O$ requires C, 82.0; H, 4.4; N, 8.7%).

The following five compounds were prepared according to

the methods of Moszew[4,8] (as reference compounds) and possessing the alleged structures:

7-*Anilino*-6-*phenyl*-5,12-*diazabenz*[a]*anthracene* (**5**). This material existed as yellow-orange cubic crystals (from DMF), m.p. 245—247 °C (uncorr.). [lit.,[4] 245—246 °C (uncorr.)].

6-*Phenyl*-5,12-*diazabenz*[a]*anthracen*-7-*ol* (**7**). This material existed as bright yellow prisms (from DMF), m.p. 371—373 °C (lit.,[4] 370—373 °C).

The corresponding 7-chloro derivative was prepared from compound (**7**) as described for the preparation of 6-chloro-7-phenyl-5,12-diazabenz[*a*]anthracene (**33**). It existed as yellow prisms, after crystallisation from toluene, m.p. 235—236 °C (Found: C, 77.6; H, 4.2; N, 8.2. $C_{22}H_{13}ClN_2$ requires C, 77.5; H, 3.9; N, 8.2%).

7-*Anilino*-6-(4-*tolyl*)-5,12-*diazabenz*[a]*anthracene*. This existed as yellow prisms, m.p. 221—222 °C (lit.,[8] m.p. 222—223 °C) after crystallisation from dimethylformamide.

6-(4-*Tolyl*)-5,12-*diazabenz*[a]*anthracen*-7-*ol*. When prepared from the foregoing anilino compound this material formed yellow prisms (from DMF), m.p. 375—377 °C (lit.,[8] m.p. 375—377 °C).

4-*Anilinoquinolin*-2-*ol*. This was prepared by the method of Curd, Raisen, and Rose[15] and existed as pale violet prisms, m.p. 317—320 °C (lit.,[15] m.p. 319—321 °C).

7-*Phenyl*-5,12-*diazabenz*[a]*anthracen*-6-*ol* (**31**).—4-Anilinoquinolin-2-ol (1.0 g, 4 mmol), benzoic acid (0.9 g, 1 mmol) and freshly fused and powdered zinc chloride (1.1 g) were heated together at 285 °C for 3 h. The resultant dark glass was triturated with aqueous sodium hydroxide (10%; 20 ml) and the suspension was neutralised to give a yellow solid which was continuously extracted with boiling dimethylformamide. On cooling, the solution deposited 7-*phenyl*-5,12-*diazabenz*[a]-*anthracen*-6-*ol* (0.4 g, 30%) as bright yellow prisms, m.p. 370—373 °C (uncorr.) and the m.p. was not depressed on admixture with compound (**7**) (m.p. 370—373 °C) which was prepared by the method of Moszew[4] (Found: C, 82.3; H, 4.5; N, 8.4. $C_{22}H_{14}N_2O$ requires C, 82.0; H, 4.4; N, 8.7%).

7-(4-*Tolyl*)-5,12-*diazabenz*[a]*anthracen*-6-*ol*.—This was prepared in a similar way to the 7-phenyl compound (**31**) and existed as yellow prisms, m.p. 376—377 °C, again not depressed on admixture with the material (m.p. 375—377 °C), claimed as 6-(4-tolyl)-5,12-diazabenz[*a*]anthracen-7-ol prepared[8] from triphenylguanidine and 4-methylacetophenone (Found: C, 82.0; H, 4.5; N, 7.9. $C_{23}H_{16}N_2O$ requires C, 82.3; H, 4.8; N, 8.3%).

6-*Chloro*-7-*phenyl*-5,12-*diazabenz*[a]*anthracene* (**33**).—A solution of 7-phenyl-5,12-diazabenz[*a*]anthracen-6-ol (0.5 g, 2 mmol) in thionyl chloride (10 ml) and dimethylformamide (1 ml) was heated under reflux for 70 min after which time the solution was poured onto ice (60 g). The resulting solid was triturated with aqueous sodium hydroxide (10 ml; 10%) and crystallised from toluene to give 6-*chloro*-7-*phenyl*-5,12-*diazabenz*[a]*anthracene* (0.3 g, 63%) as yellow prisms, m.p. 234—236 °C, not depressed when mixed with a sample prepared from compound (**7**) (Found: C, 77.3; H, 3.6; N, 8.0. $C_{22}H_{13}ClN_2$ requires C, 77.5; H, 3.9; N, 8.2%).

6-*Chloro*-7-(4-*tolyl*)-5,12-*diazabenz*[a]*anthracene*.—This was prepared as for the 7-phenyl compound (**33**) above and existed as pale yellow prisms from toluene, m.p. 254—255 °C (Found: C, 77.9; H, 4.4; N, 7.7. $C_{23}H_{15}ClN_2$ requires C, 77.8; H, 4.2; N, 7.9%).

6-*Anilino*-7-*phenyl*-5,12-*diazabenz*[a]*anthracene* (**32**).—A solution of 6-chloro-7-phenyl-5,12-diazabenz[*a*]anthracene (0.1 g, 0.3 mmol) in aniline (5 ml) was refluxed for 50 min and poured, when cool, into ethanol (6 ml) to yield after crystallisation from toluene 6-*anilino*-7-*phenyl*-5,12-*diazabenz*-[a]*anthracene* (0.09 g, 78%), m.p. 244—246 °C undepressed on admixture with the anil (**5**), m.p. 244—246 °C prepared by the literature method[4] (Found: C, 84.3; H, 5.1; N, 10.4. $C_{28}H_{19}N_3$ requires C, 84.6; H, 4.8; N, 10.6%).

6-*Anilino*-7-(4-*tolyl*)5,12-*diazabenz*[a]*anthracene*.—This was prepared (71%) exactly as for the 7-phenyl derivative (**32**) above and existed as bright yellow prisms, m.p. 221—222 °C (uncorr.). The m.p. was not depressed when mixed with the material prepared by the literature method[8] and claimed as 7-anilino-6-(4-tolyl)-5,12-diazabenz[*a*]anthracene (Found: C, 84.6; H, 4.9; N, 9.8. $C_{29}H_{21}N_3$ requires C, 84.7; H, 5.1; N, 10.2%).

9,14-*Diazadibenzo*[a,e]*fluoranthene* (**38**).—A slow stream of hydrogen was passed over a mixture of 7-phenyl-5,12-diazabenz-[*a*]anthracen-6-ol (**31**) (0.1 g) and dried zinc dust packed between asbestos pads. The yellow distillate was dissolved in toluene and chromatographed on alumina, eluting the column with a solution of ether (10%) in toluene. The bright yellow eluate, on removal of the solvent and crystallisation of the residual solid from light petroleum (b.p. 100—120 °C) furnished 9,14-*dizabenzo*[a,e]*fluoranthene* (7 mg, 8%), m.p. and mixed m.p. 305—307 °C.

1,2,3,4-*Tetrahydroquinolin*-4-*one*.—This was prepared by the method of Clemo and Perkin.[14]

7-*Phenyl*-5,12-*diazabenz*[a]*anthracene* (**34**).—A solution of 2-aminobenzophenone (3 g, 15 mmol), 1,2,3,4-tetrahydroquinolin-4-one (2.2 g, 15 mmol) and sulphuric acid (0.25 ml) in acetic acid (30 ml), after being refluxed for 23 h, cooled, and poured into water (70 ml) containing ammonia (10%; 10 ml) gave an oily solid which was dissolved in acetone (40 ml). The stirred acetone solution was treated dropwise with a saturated solution of potassium permanganate in acetone until oxidation was complete and for 30 min more. The filtered solution was evaporated and furnished 7-*phenyl*-5,12-*diazabenz*[a]*anthracene* (3.6 g, 78%) after crystallisation from acetone, m.p. 201—202 °C as colourless prisms (Found: C, 86.5; H, 4.7; N, 8.7. $C_{22}H_{14}N_2$ requires C, 86.3; H, 4.6; N, 9.1%).

9,14-*Diazabenz*[a,e]*fluoranthene* (**38**).—This was prepared from the foregoing benzanthracene (**34**) (0.1 g) using the method previously described. It existed as bright yellow needles, m.p. 306—308 °C and was not depressed by admixture with an authentic sample.[1]

7,12-*Dihydro*-6-*phenyl*-5,12-*diazabenz*[a]*anthracene* *and* 6-*Phenyl*-5,12-*diazabenz*[a]*anthracene* (**13**).—These were prepared by the method of Bloomfield[1] and the latter was converted into compound (**38**) by a similar zinc dust distillation. The m.p. of 6-phenyl-5,12-diazabenz[*a*]anthracene was depressed by the material claimed by Moszew as this compound.

7-*Phenyl*-5,12-*diazabenz*[a]*anthracene* (**34**).—A suspension of palladium catalyst (10% Pd; 0.15 g) in ethanol (30 ml) containing potassium hydroxide (0.1 g) was equilibrated with hydrogen and then a solution of 6-chloro-7-phenyl-5,12-diazabenz[*a*]anthracene [0.2 g, derived from compound (**7**)] in toluene (20 ml) was introduced. When the hydrogen uptake ceased the suspension was filtered, the solvent removed, and the residue dissolved in toluene and chromatographed on alumina. Elution with ether (5%)–toluene gave a pale yellow solution which, on evaporation and crystallisation from light petroleum (b.p. 100—120 °C) gave 7-phenyl-5,12-diazabenz[*a*]anthracene (0.15 g, 82%) as colourless prisms, m.p. 200—201 °C, un-

depressed on admixture with an authentic sample prepared from 2-aminobenzophenone and 1,2,3,4-tetrahydroquinolin-4-one.

References

1 Part 25, D. G. Bloomfield, C. Upton, and H. J. Vipond, *J. Chem. Soc., Perkin Trans 1*, 1986, 857.
2 M. W. Partridge, J. M. Sprake, and H. J. Vipond, *J. Org. Chem.*, 1966, **31**, 1245.
3 'Replacement Nomenclature,' taken from Rule B-4 in I.U.P.A.C. 'Nomenclature of Organic Chemistry,' Pergamon Press, 1979, is used.
4 J. Moszew, *Bull. Acad. Pol. Sci. Ser. Sci. Chim., Geol., Geogr.*, 1938, **A98**, 42.
5 B. Adamczyk and J. Moszew, *Zesz. Nauk. Univ. Jagiellon, Pr. Chem.*, 1966, **11**, 27.
6 K. Butler and M. W. Partridge, *J. Chem. Soc.*, 1959, 2396; M. W. Partridge, H. J. Vipond, and J. A. Waite, *J. Chem. Soc.*, 1962, 2549; R. W. Baldwin, G. J. Cunningham, M. W. Partridge, and H. J. Vipond, *Br. J. Cancer*, 1962, **16**, 276.
7 J. Moszew, *Rocz. Chem.*, 1947, **21**, 46.
8 M. Bala and J. Moszew, *Rocz. Chem.*, 1965, **39**, 853; M. Bala and J. Moszew, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, 1964, **12**, 393.
9 M. W. Partridge and H. J. Vipond, *J. Chem. Soc.*, 1962, 632.
10 C. R. Hauser and C. A. Reynolds, *J. Am. Chem. Soc.*, 1948, **70**, 2402.
11 E. A. Fehnel, *J. Org. Chem.*, 1966, **31**, 2899.
12 H. Johns, *J. Prakt. Chem.*, 1931, **131**, 266.
13 N. P. Buu-Hoi and O. Perin-Rousell, *J. Chem. Soc.*, 1972, 234.
14 G. R. Clemo and W. H. Perkin, *J. Chem. Soc.*, 1949, 3525.
15 F. S. H. Curd, C. G. Raisen, and F. L. Rose, *J. Chem. Soc.*, 1947, 899.

Received 14*th October* 1985; *Paper* 5/1766