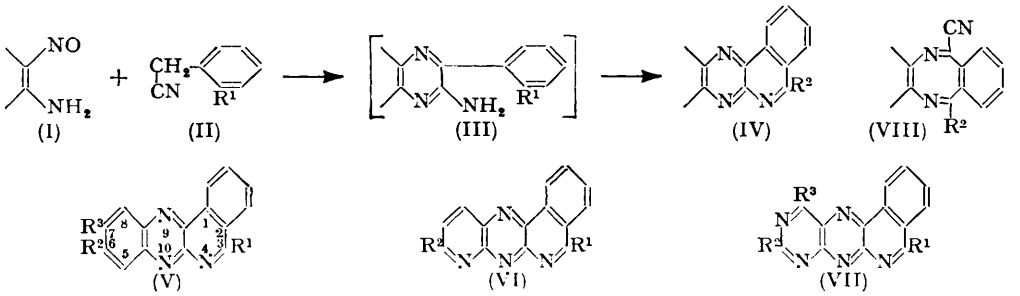
The Synthesis of Compounds with Potential Anti-folic Acid Activity. Part VI. Polyaza-1 : 2-benzanthracene Derivatives.*

By T. S. OSDENE and G. M. TIMMIS.

[Reprint Order No. 6144.]

Several derivatives of 4 : 9 : 10-triaza-, 4 : 5 : 9 : 10-tetra-aza-, and 4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene have been prepared unambiguously by condensation of *o*-aminonitroso-derivatives of the benzene, pyridine, and pyrimidine series with suitably *o*-substituted benzyl cyanide derivatives, involving a double ring-closure. The two last-mentioned ring systems are new. Sodium alkoxides in the appropriate alcohol were effective catalysts in most cases.

ALTHOUGH antagonists of folic acid have been usually found amongst analogous pteridines we have investigated considerably more complex ring systems which, however, still embody the pteridine or a closely related structure. Since, for example, Daniel, Norris, Scott, and Heuser (*J. Biol. Chem.*, 1947, **169**, 689) have found high antifolic activity in 6 : 8-diamino-5 : 7 : 9 : 10-tetra-aza-1 : 2 : 3 : 4-dibenzanthracene and Felton, Osdene, and Timmis (*J.*, 1954, 2895) have reported activity in 6 : 8-diamino-5 : 7 : 9 : 10-tetra-aza-1 : 2-benzanthracene, a pentacyclic or tetracyclic structure is not inconsistent with activity. In another field Woolley and Shaw (*J. Biol. Chem.*, 1953, **203**, 979) have found potent antagonists of serotonin, 3-2'-aminoethyl-5-hydroxyindole, amongst simple indole derivatives and an even more potent antagonist in the pentacyclic structure yohimbine; other structures of intermediate complexity containing the indole nucleus are also antagonists. Since we have found that antifolic activity, although of a low degree, is associated with the 6-amino-5-arylpyridino(2' : 3'-2 : 3)pyrazine (personal communication from Dr. H. O. J. Collier) and 7-amino-6-arylpteridine structures (Spickett and Timmis, *J.*, 1954, 2887) we have now embodied these structures and also that of the corresponding quinoxaline, into more complex types (V, VI, and VII) by completing a six-membered ring between the pyrazine amino-group and the phenyl residue.



Of the ring systems, 4 : 9 : 10-triaza- (V), 4 : 5 : 9 : 10-tetra-aza- (VI) and 4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene (VII), only examples of the first have hitherto been prepared. Gabriel (*Ber.*, 1904, **37**, 4316) and Manuelli and Silvestri (*Gazzetta*, 1904, **34**, I, 493) condensed *o*-phenylenediamine with phthalonimide or phthalonic acid respectively and obtained 3-hydroxy-4 : 9 : 10-tri-aza-1 : 2-benzanthracene (V; R^1 = OH, R^2 = R^3 = H); Manuelli and Moselli (*ibid.*, 1905, **35**, II, 572) used 1 : 2-diamino-4-methylbenzene to obtain a product (V; R^1 = OH, R^2 = Me, R^3 = H or *vice versa*). For analogy with the antifolic pyridinopyrazines and pteridines we required a 6-amino-group in our aza-1 : 2-benzanthracenes; by existing synthetic methods, the 1 : 2 : 4-triaminobenzene, 2 : 3 : 6-triaminopyridine, or 2 : 4 : 5-triaminopyrimidine would be condensed with phthalonimide which would in all cases lead to ambiguous structures. Further, by this method only a hydroxy-group can be introduced adjacent to $N_{(4)}$.

* Part V, *J.*, 2036.

We have synthesised unequivocally the required structures by condensing the appropriate *o*-amino-nitroso-compounds with 2-methoxycarbonyl- or 2-carboxy-benzyl cyanide (II; $R^1 = CO_2Me$ or CO_2H) to yield (IV; $R^2 = OH$), or with 2-cyanobenzyl cyanide (II; $R^1 = CN$) to yield (IV; $R^2 = NH_2$). In a preliminary publication (*Chem. and Ind.*, 1954, 404) we briefly reported three of these reactions.

The first stage is assumed to be formation of the intermediate (III) since it has been proved that under similar conditions benzyl cyanides condense with *o*-amino-nitroso-compounds, with loss of water and addition of the amino- to the cyano-group, to form a 2-amino-3-phenylpyrazine (Spickett and Timmis, *J.*, 1954, 2887; Osdene and Timmis, *J.*, 1955, 2032). In order to exclude the unlikely but conceivable alternative structure (VIII) the infrared spectrum of the product (V; $R^1 = OH$, $R^2 = NH_2$, $R^3 = H$) was examined but failed to reveal a band at the frequency 2230 cm.$^{-1}$ characteristic of a cyano-group.

For cyano- or methoxy-benzyl cyanide the reaction is best conducted in boiling ethanol or 2-ethoxyethanol in presence of 1 mol. of the sodium alkoxide. Although 2-carboxybenzyl cyanide does not react appreciably under these conditions, possibly owing to salt formation on the carboxy-group, in boiling acetic acid in presence of sodium acetate this acid with 2 : 4 : 6-triamino-5-nitrosopyrimidine and with 4 : 6-diamino-2-dimethylamino-5-nitrosopyrimidine yields 6 : 8-diamino- (VII; $R^1 = OH$, $R^2 = R^3 = NH_2$) and 8-amino-6-dimethylamino-3-hydroxy-4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene (VII; $R^1 = OH$, $R^2 = NMe_2$, $R^3 = NH_2$) respectively.

For the synthesis of 4 : 9 : 10-triaza-1 : 2-benzanthracene derivatives, 2 : 4-diamino- and 2 : 4-diamino-5-methyl-1-nitrosobenzene were condensed with the ester (II; $R^1 = CO_2Me$) and with the nitrile (II; $R^1 = CN$). The amino-derivatives (V; $R^1 = OH$, $R^2 = NH_2$, $R^3 = Me$) and (V; $R^1 = R^2 = NH_2$, $R^3 = Me$) with boiling acetic anhydride yielded monoacetamido-compounds which were not diazotised by nitrous acid; since both amino-derivatives were diazotised, it is clear that 6-acetamido-derivatives are formed on acetylation.

2 : 6-Diamino-3-nitrosopyridine reacted with the ester (II; $R^1 = CO_2Me$) and nitrile (II; $R^1 = CN$) to give the corresponding 4 : 5 : 9 : 10-tetra-aza-1 : 2-benzanthracene derivatives.

In the preparation of 4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracenes, 4 : 6-diamino-, 2 : 4 : 6-triamino-, 4 : 6-diamino-2-dimethylamino-, 4 : 6-diamino-2-methylthio-, and 6-amino-4-hydroxy-2-phenyl-5-nitrosopyrimidines were condensed with the ester (II; $R^2 = CO_2Me$), to yield the corresponding 3-hydroxy-derivatives; and 4 : 6-diamino- and 2 : 4 : 6-triamino-5-nitrosopyrimidine with the cyano-derivative (II; $R^1 = CN$) yielded the corresponding 3-amino-derivatives.

In general, the reaction of 2-cyanobenzyl cyanide with *o*-amino-nitroso-compounds was faster than that of 2-methoxycarbonylbenzyl cyanide. In the latter case at least 1 mol. of sodium alkoxide was desirable since the sodium salt of the product was readily precipitated in good yield. Less than 1 mol. of sodium alkoxide was adequate in the former case, but in all cases the crude product was precipitated during the reaction.

Experimental

M. p.s (uncorrected) were determined in an electrically heated copper block. Analyses were by Mr. P. R. W. Baker, Beckenham. Purity was established by paper chromatography (butanol–acetic acid). The azabenzanthracenes all fluoresce in ultraviolet light. For good yields the conditions prescribed must be adhered to.

2-Methoxycarbonylbenzyl Cyanide.—2-Carboxybenzyl cyanide (*Org. Synth.*, 1942, **22**, 30) (15 g.) in ether (20 ml.) containing 5 drops of acetone was treated gradually with ethereal diazomethane (200 ml.; from 20·6 g. of methylnitrosourea). After 24 hr. at room temperature and drying (KOH), evaporation gave the *ester* (12 g.), needles (from ether or pentane), m. p. 42° (Found: C, 68·5, 68·7; H, 5·5, 5·4; N, 7·9. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·2; N, 8·0%).

2-Cyanobenzyl Cyanide.—2-Cyanobenzyl bromide (Fuson, *J. Amer. Chem. Soc.*, 1926, **48**, 834) (32·0 g.) and " AnalaR " potassium cyanide (13 g.) in ethanol (250 ml.) and water (50 ml.) were gradually brought to the b. p. Vigorous reaction then occurred. After 45 minutes'

refluxing most of the ethanol was removed and the residue was poured into ice–water. The green solid formed was dissolved in chloroform, dried (Na_2SO_4), and passed through alumina. The solvent was removed and the residue crystallised twice from methanol to give white needles, m. p. 79—80° (12·4 g.).

6-Amino-3-hydroxy-4 : 9 : 10-triaza-1 : 2-benzanthracene (V; $R^1 = OH$; $R^2 = NH_2$, $R^3 = H$).—2 : 4-Diamino-1-nitrosobenzene (1·37 g.; finely ground) and 2-methoxycarbonylbenzyl cyanide (1·9 g.) were added to a solution of sodium (0·3 g.) in dry ethanol (100 ml.) and the mixture was boiled under reflux for 30 min. The thick yellow crystalline precipitate was collected after cooling, and crystallised from glacial acetic acid to yield *6-amino-3-hydroxy-4 : 9 : 10-triaza-1 : 2-benzanthracene* as dark orange needles, containing acetic acid of crystallisation, m. p. 336°, which slowly lost acetic acid yielding yellow needles (Found: C, 63·5; H, 4·45; N, 17·3. $C_{15}H_{10}ON_4,CH_3{\cdot}CO_2H$ requires C, 63·4; H, 4·4; N, 17·4. After drying at 120° *in vacuo*: C, 68·7; H, 3·9. $C_{15}H_{10}ON_4$ requires C, 68·7; H, 3·8%). The solution in ethanol showed an intense yellow-green fluorescence in ultraviolet light.

3 : 6-Diamino-4 : 9 : 10-triaza-1 : 2-benzanthracene (V; $R^1 = R^2 = NH_2$, $R^3 = H$).—To a solution of sodium (0·1 g.) in dry ethanol (100 ml.) were added 2 : 4-diamino-1-nitrosobenzene (1·37 g.) and 2-cyanobenzyl cyanide (1·56 g.) and the mixture was boiled under reflux for 20 min. A thick yellow, crystalline precipitate was deposited at the b. p. After cooling, the precipitate was dried (2·05 g.) and crystallised from glacial acetic acid to yield 3 : 6-diamino-4 : 9 : 10-triaza-1 : 2-benzanthracene as dark orange crystals, containing two molecules of acetic acid of crystallisation, lost *in vacuo* at 190° to give yellow crystals. The orange compound remained unchanged on treatment with ammonia solution but yielded the yellow compound on treatment with dilute sodium hydroxide solution (Found: C, 58·2; H, 4·9; N, 18·2. $C_{15}H_{11}N_5,2CH_3{\cdot}CO_2H$ requires C, 59·2; H, 4·5; N, 18·4. After drying *in vacuo* at 190°: C, 68·8; H, 4·4. $C_{15}H_{11}N_5$ requires C, 68·95; H, 4·2%).

6-Amino-3-hydroxy-7-methyl-4 : 9 : 10-triaza-1 : 2-benzanthracene (V; $R^1 = OH$, $R^2 = NH_2$, $R^3 = Me$).—2 : 4-Diamino-5-methyl-1-nitrosobenzene (1·5 g.), 2-methoxycarbonylbenzyl cyanide (1·8 g.) and sodium (0·3 g.) in dry ethanol (25 ml.), as in the previous case (reflux for 10 min.; crude yield 1·2 g.), gave, after several crystallisations from acetic acid, the *4 : 9 : 10-triaza-1 : 2-benzanthracene* as orange needles, m. p. 334° (Found, after drying *in vacuo* at 180°: C, 69·2; H, 4·2; N, 20·3. $C_{16}H_{12}ON_4$ requires C, 69·55; H, 4·4; N, 20·3%). Diazotisation and coupling with R salt gave a deep red colour. Treatment with hot acetic anhydride yielded the *6-acetamido-derivative* as yellow needles (from *n*-butanol), m. p. 398° (decomp.) (Found, after drying *in vacuo* at 110°: C, 67·8; H, 4·5; N, 17·5. $C_{18}H_{14}O_2N_4$ requires C, 67·9; H, 4·4; N, 17·6%).

3 : 6-Diamino-7-methyl-4 : 9 : 10-triaza-1 : 2-benzanthracene (V; $R^1 = R^2 = NH_2$, $R^3 = Me$).—2 : 4-Diamino-5-methyl-1-nitrosobenzene (1·0 g.), 2-cyanobenzyl cyanide (1·1 g.), and a solution of sodium (0·2 g.) in dry ethanol (20 ml.), as in the previous case, gave, after several crystallisations from dimethylformamide, *3 : 6-diamino-7-methyl-4 : 9 : 10-triaza-1 : 2-benzanthracene* (crude, 1·6 g.), m. p. 363° (Found, after drying *in vacuo* at 180°: C, 69·1; H, 5·3; N, 25·4. $C_{16}H_{13}N_5$ requires C, 69·8; H, 4·8; N, 25·4%). Coupling as before gave a deep red colour.

Hot acetic anhydride yielded the *6-acetamido-derivative* (from *n*-butanol), m. p. 328—329° (decomp.) (dried *in vacuo* at 110°) (Found: C, 69·5; H, 4·6; N, 21·7. $C_{17}H_{15}ON_5$ requires C, 68·1; H, 4·8; N, 22·1%), which failed to diazotise.

6-Amino-3-hydroxy-4 : 5 : 9 : 10-tetra-aza-1 : 2-benzanthracene (VI; $R^1 = OH$, $R^2 = NH_2$).—2 : 6-Diamino-3-nitrosopyridine (1·4 g.) and 2-methoxycarbonylbenzyl cyanide (1·4 g.) were added to a solution of sodium (0·3 g.) in ethanol (100 ml.), and the mixture was boiled under reflux for 1 hr. (yellow precipitate). After cooling, the precipitate was collected and extracted with boiling N-acetic acid (30 ml.) to remove some unchanged nitroso-compound. The residue, crystallised several times from dilute formic acid, gave the *tetra-azabenzanthracene* as yellow needles, m. p. >300° (Found: C, 57·9; H, 3·6; N, 22·1. $C_{14}H_9ON_5,H{\cdot}CO_2H$ requires C, 58·25; H, 3·6; N, 22·65. After drying *in vacuo* at 150°: C, 64·0; H, 3·5; N, 26·3. $C_{14}H_9ON_5$ requires C, 63·9; H, 3·45; N, 26·6%). The formic acid solution showed an intense light blue fluorescence in ultraviolet light.

3 : 6-Diamino-4 : 5 : 9 : 10-tetra-aza-1 : 2-benzanthracene (VI; $R^1 = R^2 = NH_2$).—To a solution of sodium (0·1 g.) in ethanol (100 ml.) was added 2 : 6-diamino-3-nitrosopyridine (1·4 g.), followed by 2-cyanobenzyl cyanide (1·56 g.) and the mixture was boiled under reflux for 1 hr. Several crystallisations from glacial acetic acid yielded the *tetra-azabenzanthracene* as yellow needles (crude, 2·0 g.), m. p. >300° (Found: C, 53·9; H, 5·1; N, 18·9. $C_{14}H_{10}N_6,3CH_3{\cdot}CO_2H$

requires C, 54·3; H, 5·0; N, 19·0. After drying *in vacuo* at 190° : C, 64·3; H, 3·9; loss, 40·8. $C_{14}H_{10}N_6$ requires C, 64·1; H, 3·8; loss, 40·7%).

8-Amino-3-hydroxy-4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene (VII; R^1 = OH, R^2 = H, R^3 = NH_2).—4 : 6-Diamino-5-nitrosopyrimidine (1·4 g.) and 2-methoxycarbonylbenzyl cyanide (1·8 g.) were added to a solution of sodium (0·25 g.) in ethanol (125 ml.) and the mixture was boiled under reflux for 30 min. (yellow precipitate). After cooling, the precipitate was collected, dried (2·4 g.), recrystallised from 80% formic acid, and basified with 2N-sodium carbonate. Crystallisation of the product from glacial acetic acid yielded *8-amino-3-hydroxy-4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene* as light yellow hair-like crystals, m. p. >300° (dried *in vacuo* at 180°) (Found : C, 59·4; H, 2·9; N, 31·6. $C_{13}H_8ON_6$ requires C, 59·1; H, 3·05; N, 31·8%). Hot acetic anhydride yielded the *8-acetamido-derivative* as pale yellow needles, m. p. >300° (dried *in vacuo* at 150°) (Found : C, 58·9; H, 3·2; N, 27·75. $C_{15}H_{10}O_2N_6$ requires C, 58·8; H, 3·3; N, 27·4%).

3 : 8-Diamino-4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene (VII; R^1 = R^3 = NH_2, R^2 = H).—4 : 6-Diamino-5-nitrosopyrimidine (1·4 g.) and 2-cyanobenzyl cyanide (1·56 g.) were added to a solution of sodium (0·25 g.) in ethanol (125 ml.) and the mixture was boiled under reflux for 10 min. (brown precipitate). After cooling, the material was collected and dried (1·8 g.). Several crystallisations from glacial acetic acid yielded the *penta-azabenzanthracene* as yellow crystals (dried *in vacuo* at 190°) (Found : C, 59·65; H, 3·6; N, 36·6. $C_{13}H_9N_7$ requires C, 58·3; H, 3·45; N, 37·25%). The glacial acetic acid solution showed an intense green fluorescence (ultraviolet).

6 : 8-Diamino-3-hydroxy-4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene (VII; R^1 = OH, R^2 = R^3 = NH_2).—(*A*) Finely powdered 2 : 4 : 6-triamino-5-nitrosopyrimidine (0·75 g.) and 2-methoxycarbonylbenzyl cyanide (1·8 g.) were added to a solution of sodium (0·2 g.) in 2-ethoxyethanol (50 ml.), and the mixture was boiled under reflux for 5·5 hr. (yellow precipitate). Next morning the material was collected and dried (0·5 g.). Several crystallisations from 30% formic acid yielded the *penta-azabenzanthracene* as yellow needles, m. p. >300° (dried *in vacuo* at 180°) (Found : C, 54·4; H, 3·3; N, 33·6. $C_{13}H_9ON_7,\frac{1}{2}H_2O$ requires C, 54·2; H, 3·5; N, 34·0%).

(*B*) 2 : 4 : 6-Triamino-5-nitrosopyrimidine (0·4 g.; finely powdered), 2-carboxybenzyl cyanide (0·45 g.) and anhydrous sodium acetate (0·2 g.) were added to glacial acetic acid (10 ml.), and the whole was boiled under reflux for 30 min. After cooling, filtration, and washing with glacial acetic acid and methanol, the product (0·55 g.) was dissolved in hot 80% formic acid, treated with charcoal, filtered, cooled, and made alkaline with dilute ammonia solution. Recrystallisation of the precipitate from dilute aqueous formic acid yielded very small yellow needles, m. p. >360° (dried *in vacuo* at 180°) (Found : C, 54·8; H, 3·6; N, 33·5. $C_{13}H_9ON_7,\frac{1}{2}H_2O$ requires C, 54·2; H, 3·5; N, 34·0%).

3 : 6 : 8-Triamino-4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene (VII; R^1 = R^2 = R^3 = NH_2).—To a solution of sodium (0·25 g.) in 2-ethoxyethanol (150 ml.) was added 2 : 4 : 6-triamino-5-nitrosopyrimidine (1·54 g.) followed by 2-cyanobenzyl cyanide (2·0 g.), and the mixture was boiled under reflux for 1 hr. The dense brown precipitate was collected, dried (*in vacuo* at 180° for analysis), analysed (Found : C, 55·1; H, 3·6; N, 39·15. Calc. for $C_{13}H_{10}N_8$: C, 56·1; H, 3·6; N, 40·3%), and crystallised several times from glacial acetic acid, yielding *3 : 6 : 8-triamino-4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene* as yellow needles, m. p. >300° (Found : C, 44·8; H, 5·1; N, 24·8. $C_{13}H_{10}N_8,2CH_3{\cdot}CO_2H,2H_2O$ requires C, 45·1; H, 5·3; N, 24·8%). The acid solution showed an intense green fluorescence (ultraviolet).

8-Amino-6-dimethylamino-3-hydroxy-4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene (VII; R^1 = OH, R^2 = NMe_2, R^3 = NH_2).—(*A*) 4 : 6-Diamino-2-dimethylamino-5-nitrosopyrimidine (0·95 g.) and 2-methoxycarbonylbenzyl cyanide (0·9 g.) were added to a solution of sodium (0·25 g.) in ethanol (100 ml.), and the mixture was boiled for 12 hr. The yellow precipitate was collected, dried (0·3 g.), and purified by dissolution in hot 10% formic acid followed by basification with concentrated ammonia solution. The precipitate was recrystallised from butan-2-ol to yield *8-amino-6-dimethylamino-3-hydroxy-4 : 5 : 7 : 9 : 10-penta-aza-1 : 2-benzanthracene*, m. p. >300° (dried *in vacuo* at 150°) (Found : C, 58·3; H, 4·35; N, 31·3. $C_{15}H_{13}ON_7$ requires C, 58·6; H, 4·2; N, 31·9%).

(*B*) 4 : 6-Diamino-2-dimethylamino-5-nitrosopyrimidine (0·5 g.), 2-carboxybenzyl cyanide (0·5 g.), and anhydrous sodium acetate (0·2 g.) were added to glacial acetic acid (10 ml.), and the whole boiled under reflux for 30 min. After cooling and addition of water (20 ml.) the mixture was made alkaline with ammonia solution, the precipitate collected, washed with water and extracted with hot 10% formic acid, the extract treated with charcoal and made alkaline with ammonia solution, and the precipitate collected, washed with methanol, and recrystallised from

butanol, yielding small yellow prisms which did not melt below 360° (dried *in vacuo* at 150° Found : C, 58·8; H, 4·4; N, 31·5%).

8-*Amino*-3-*hydroxy*-6-*methylthio*-4 : 5 : 7 : 9 : 10-*penta-aza*-1 : 2-*benzanthracene* (VII; R^1 = OH, R^2 = MeS, R^3 = NH_2).—4 : 6-Diamino-2-methylthio-5-nitrosopyrimidine (0·9 g.) and 2-methoxycarbonylbenzyl cyanide (0·95 g.) were added to a solution of sodium (0·15 g.) in ethanol (50 ml.), and the mixture was boiled under reflux for 7 min. (yellow precipitate). Several crystallisations from acetic acid afforded the *penta-azabenzanthracene* as yellow needles, m. p. >360° (crude, 1·13 g.) (dried *in vacuo* at 150°) (Found : C, 52·9; H, 3·1; N, 27·0; S, 9·6. $C_{14}H_{10}ON_6S$ requires C, 54·2; H, 3·2; N, 27·1; S, 10·3%). The acetic acid solution showed an intense blue-green fluorescence (ultraviolet).

3 : 8-*Dihydroxy*-6-*phenyl*-4 : 5 : 7 : 9 : 10-*penta-aza*-1 : 2-*benzanthracene* (VII; R^1 = R^3 = OH, R^2 = Ph).—A solution of sodium (0·1 g.) in ethanol (50 ml.), 4-amino-6-hydroxy-5-nitroso-2-phenylpyrimidine (0·5 g.), and 2-methoxycarbonylbenzyl cyanide (0·5 g.) as in the preceding case (reflux 1 hr.) gave the *penta-azabenzanthracene* (crude, 0·54 g.) as pale yellow needles, m. p. >300° (Found : C, 63·1; H, 4·0; N, 17·5. $C_{19}H_{11}O_2N_5,CH_3{\cdot}CO_2H$ requires C, 62·8; H, 3·8; N, 17·5. After drying *in vacuo* at 150° : C, 66·4; H, 3·3; N, 20·2. $C_{19}H_{11}O_2N$ requires C, 66·85; H, 3·2; N, 20·5%). The acetic acid solution showed an intense blue fluorescence (ultraviolet).

We thank Professors A. Haddow and F. Bergel for their interest in this work, Mr. S. F. D. Orr, M.A., for the infrared measurements, and Mr. M. H. Baker for technical assistance. This investigation has been supported by grants to this Institute from the British Empire Cancer Campaign, the Jane Coffin Childs Memorial Fund for Medical Research, the Anna Fuller Fund, and the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service.

CHESTER BEATTY RESEARCH INSTITUTE,
INSTITUTE OF CANCER RESEARCH : ROYAL CANCER HOSPITAL,
FULHAM ROAD, LONDON, S.W.3. [*Received, February 17th*, 1955.]