317. *Extrusion of Sulphur. Part III.* Polycyclic 1 : 4-Thiazepines.*

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Pyrolysis of 9-aryl-9-azidothioxanthens yields mainly anils of thioxanthones and only small amounts of 9-aryldibenzo[*b*,*f*]-1 : 4-thiazepines. Extrusion of sulphur from the thiazepine derivative (IV), obtained by condensing 1-chloroanthraquinone with *o*-aminothiophenol, yields 8-oxodibenzo-[*c*,*mn*]acridine (VII). Similarly, from the bisthiazepines prepared from 1 : 5-dichloro- and 1-chloro-4-nitro-anthraquinone, respectively, the polycyclic diaza-compounds (VIII) and (IX) are synthesised.

Dibenzo[*b*,*f*]-1 : 4-thiazepines (as I; X = S) were first prepared by Brodrick, Nicholson, and Short [1] who applied a Bischler–Napieralski type of ring-closure to 2-benzamidodiaryl sulphides. A different route was taken by Jarrett and Loudon (Part II) who condensed *o*-aminothiophenol with reactive *o*-chlorophenyl-aldehydes or -ketones. We have now extended this method to include reagents of the chloroanthraquinone type and have also examined expansion of the central ring of thioxanthhydrols.

9-Arylxanthhydrols (as II; X = O) and 9-arylthioxanthhydrols (as II; X = S) are readily accessible [2,3] and transformation of the derived azides offers a possible route to dibenzoxazepines (as I; X = O) and dibenzothiazepines (as I; X = S), respectively. By analogy with triphenylmethyl azide [4] such azides should be stable towards mineral acids and, indeed, they were conveniently prepared by adding sodium azide to a solution of the appropriate xanthylium or thioxanthylium sulphate in sulphuric acid. The Schmidt reaction is consequently inoperative although it may be noted that by this means, and presumably under the driving force of central-ring aromatisation, 9-phenylfluoren-9-ol is converted in high yield into 9-phenylphenanthridine.[5] On the other hand pyrolysis of triphenylmethyl azide yields benzophenone anil [6] and we now find that azides derived from carbinols of type (II; X = O or S) are transformed by heat into mixtures of the compounds (I; X = O or S) and (III; X = O or S). Since, however, in these mixtures anils (III) usually predominate and require wasteful separation, the method does not provide an attractive synthesis of oxazepine and thiazepine derivatives.

Condensation of *o*-aminothiophenol with 1-chloroanthraquinone in presence of alkali should yield 1-(*o*-aminophenylthio)anthraquinone. However the immediate product proved to be susceptible to dehydration and it was therefore directly converted by boiling acetic acid into the thiazepine (IV; R = R′ = H). Similarly 1 : 5-dichloroanthraquinone yielded the compound (IV; R = Cl, R′ = H) and, either thence or directly, with a further mol. of *o*-aminothiophenol furnished the bisthiazepine (V). By the same procedure 1-chloro-4-nitroanthraquinone afforded first the chloro-thiazepine (IV; R = H, R′ = Cl) —the nitro-group rather surprisingly being replaced in preference to the chloro-substituent —and then the bisthiazepine (VI).

Brodrick *et al.*[1] report the conversion of 2 : 8-dibromo- and of 2 : 8-dicyano-11-phenyldibenzo[*b*,*f*]-1 : 4-thiazepine into corresponding phenanthridines by cuprous salts in boiling quinoline. The yields were poor and similar extrusion of sulphur from the parent compound (I; X = S) was not detected. We now find that this compound (I; X = S) when

* Part II, *J.*, 1957, 3818.

[1] Brodrick, Nicholson, and Short, *J.*, 1954, 3857. We thank Dr. C. I. Brodrick for drawing our attention to this paper which regrettably we had overlooked: in it dibenzo[*b*,*f*]-1 : 4-thiazepines are named as 2 : 3-6 : 7-dibenzo-1-thia-4-aza*cyclo*hepta-2 : 4 : 6-trienes.

[2] Loudon, Robertson, and Watson, *J.*, 1950, 55.

[3] Campbell, Dick, Ferguson, and Loudon, *J.*, 1941, 747.

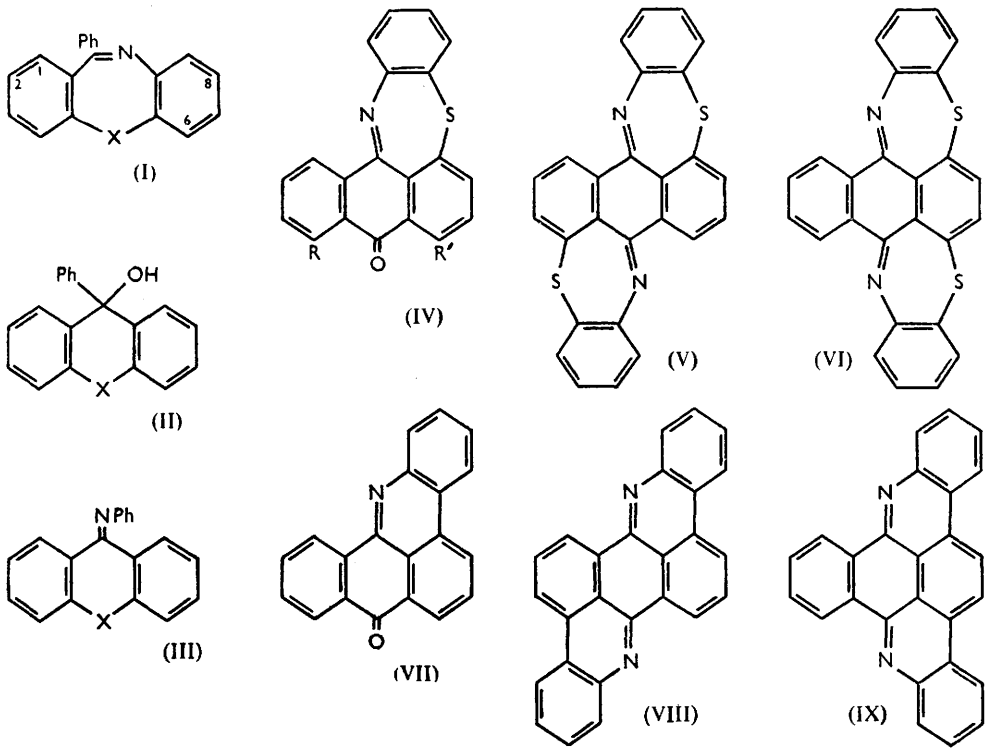
[4] Wieland, *Ber.*, 1909, **42**, 3020; Arcus and Mesley, *J.*, 1953, 178; Newman and Hay, *J. Amer. Chem. Soc.*, 1953, **75**, 2322.

[5] Arcus and Coombs, *J.*, 1954, 4319.

[6] Senior, *J. Amer. Chem. Soc.*, 1916, **38**, 2718.

heated with copper in diethyl phthalate (cf. Part II) affords 9-phenylphenanthridine in over 90% yield. Under the same conditions the thiazepine (IV; R = R′ = H) yielded 8-oxodibenz[*c*,*mn*]acridine (VII) and the bisthiazepines (V) and (VI) gave the polycyclic diaza-compounds, (VIII) and (IX), respectively, all in high yield. On the other hand the chloro-compounds (IV; R = Cl, R′ = H) and (IV; R = H, R′ = Cl) gave ill-defined products from which no pure compound was isolated. The dibenzacridine (VII) and 8 : 16-diazadibenzo[*b*,*k*]perylene (VIII) had the properties recorded by Braude and Fawcett [7] who synthesised these compounds *via* the adducts of *o*-nitrophenylbutadiene with naphthaquinone and benzoquinone, respectively. The ultraviolet absorption spectrum of the hitherto unknown 11 : 16-diazatribenzo[*a*,*e*,*i*]pyrene (IX) resembles that of its carbocyclic analogue.[8]

At least in favourable cases extrusion of sulphur from thiazepines in boiling diethyl phthalate appears to be largely a thermal decomposition, only slightly better yields being obtained in presence of copper. Thus the thiazepine (IV; R = R′ = H) gave the acridine



(VII) in 71% yield in this solvent alone, in 75% yield in presence of hydrogen-free Raney nickel, and in 83% yield in presence of copper bronze. The Raney nickel catalyst in boiling xylene [9] was ineffective, as was simple heating in phosphoryl chloride, in phosphoryl chloride–dimethylformamide,[10] or in acetic acid. Heating the thiazepine in acetic acid with hydrogen peroxide gave the acridine (VII) in 67% yield. This is the third type of product to be obtained from 11-aryldibenzothiazepines with this reagent which, in other cases, has oxidised the thiazepine to the *S*-dioxide [1] or broken the heterocycle as in the formation of 2-benzoyl-2′ : 4-dinitrodiphenyl sulphone from the 2-nitro-derivative of

[7] Braude and Fawcett, *J.*, 1951, 3117; cf. Koelsch, *J. Amer. Chem. Soc.*, 1936, **58**, 1325.
[8] Clar, *J.*, 1949, 2168.
[9] Hauptmann and Wladislaw, *J. Amer. Chem. Soc.*, 1950, **72**, 707, 711.
[10] Parham and Traynelis, *ibid.*, 1954, **76**, 4960.

compound (I; X = S) (Part II). It recalls the ring-contraction to thiophens accompanying similar oxidation of *p*-dithiins.[10] Moreover in the present instance some hydrogen sulphide was evolved and this may suggest the elimination of sulphur monoxide from an intermediate thiazepine *S*-monoxide, followed by the disproportionation: $3SO + H_2O \longrightarrow 2SO_2 + H_2S$.

Experimental

Light petroleum refers to the fraction of b. p. 60—80°.

9-Azido-9-phenylxanthen, m. p. 110° (from light petroleum), was obtained almost quantitatively when a solution of sodium azide (10 g.) in water (40 c.c.) was added (7 min.) to a cold solution of 9-phenylxanthhydrol (5·0 g.) in sulphuric acid (50 c.c.)–water (100 c.c.) (Found: C, 76·1; H, 4·1; N, 13·9. $C_{19}H_{13}ON_3$ requires C, 76·2; H, 4·4; N, 14·0%). When heated for a few min. in ethanol it afforded 9-ethoxy-9-phenylxanthen, m. p. and mixed m. p. 103°.[11]

Xanthone Anil and 11-*Phenyldibenz*[b,f]-1 : 4-*oxazepine*.—A solution of the preceding azide (1 g.) in decalin (2 c.c.; distilled from sodium) was heated under reflux for 20 min. by which time the theoretical volume of nitrogen had been evolved. The solution, diluted with benzene, was filtered through charcoal and treated with a hot solution of picric acid (0·4 g.) in benzene (total volume, 15 c.c.). The resultant orange-coloured picrate was collected (filtrate-*A*) and crystallised from benzene (filtrate-*B*), affording the *picrate* (0·4 g.), m. p. 227°, of xanthone anil (Found: C, 60·3; H, 3·5. $C_{25}H_{16}O_8N_4$ requires C, 60·0; H, 3·2%). The anil itself, liberated by passing a hot solution of the picrate in benzene through alumina, was identical in m. p. (135°; from light petroleum) and infrared spectrum with an authentic sample.[12] It was hydrolysed to xanthone, m. p. and mixed m. p. 174°, by 5N-hydrochloric acid in acetic acid (1 : 1) at 100°.

The residue obtained by evaporating filtrate-*A* was dissolved in methanol (10 c.c.) and treated with methanolic picric acid (0·4 g. in 5 c.c.). The rather discoloured picrate which slowly separated was passed in benzene through alumina and reconverted into the picrate, now obtained as canary-yellow needles, m. p. 150—152°, from methanol. This, combined with similar material recovered from filtrate-*B* (total yield, 0·92 g.), was passed in benzene through alumina affording 11-phenyldibenz[*b,f*]-1 : 4-oxazepine, m. p. 108° (from light petroleum) (depressed to 90—97° by admixture with xanthone anil) (Found: C, 84·4; H, 4·8; N, 5·1. Calc. for $C_{19}H_{13}ON$: C, 84·1; H, 4·8; N, 5·2%). Brodrick *et al.*[13] record m. p. 81° for the base (for which their carbon analysis is poor) and this may indicate polymorphism: their picrate had m. p. 150°.

Thioxanthone Anil and 11-*Phenyldibenzo*[b,f]-1 : 4-*thiazepine*.—To a stirred solution of 9-phenylthioxanthhydrol (4 g.) in concentrated sulphuric acid (10 c.c.), sodium azide (4 g.) was added at 0° and, after 12 hr. at 18°, the resultant suspension was added to ice and extracted with benzene. The recovered red, viscous oil (4·13 g.) was heated under reflux with decalin (8 c.c.) for 7 min. (nitrogen-evolution, 95% of theory). The crystals which separated from the cold solution were collected, washed with light petroleum (combined in filtrate-*A*) and crystallised twice from ethanol (combined filtrates-*B*). *Thioxanthone anil* (1·81 g.), so obtained, was further purified in benzene on alumina affording golden-yellow needles, m. p. 153° (from ethanol) (Found: C, 79·5; H, 4·9; N, 5·0. $C_{19}H_{13}NS$ requires C, 79·4; H, 4·6; N, 4·9%). It was hydrolysed by 5N-hydrochloric acid–acetic acid (1 : 2) at 100° (30 min.) to thioxanthone, identified by mixed m. p. 214° and comparison of its infrared spectrum with that of an authentic sample.[14]

The residue obtained by evaporating filtrates-*B* was added to filtrate-*A* and the whole was extracted with 5N-hydrochloric acid (5 × 20 c.c.). The extract was heated at 100° (1 hr.), cooled, and filtered from thioxanthone (0·75 g.), and the filtrate concentrated at 100° *in vacuo*. Aqueous sodium carbonate was then added and a benzene extract, after chromatography on alumina, afforded 11-phenyldibenzo[*b,f*]-1 : 4-thiazepine (0·52 g.), m. p. 117° (from methanol) (Found: C, 79·7; H, 4·4; N, 5·0. Calc. for $C_{19}H_{13}NS$: C, 79·4; H, 4·6; N, 4·9%): Brodrick *et al.*[1] give m. p. 117—118°.

3′ : 5-Dinitro-2-(phenylthio)benzophenone.—To a hot stirred suspension of 2-chloro-3′ : 5-dinitrobenzophenone (1 g.) in ethanol–water (2 : 1; 7·5 c.c.) a solution of thiophenol (0·5 g.) and

[11] Büntzly and Decker, *Ber.*, 1904, **37**, 2931.
[12] Schönberg and Asker, *J.*, 1942, 725; Graebe and Röder, *Ber.*, 1899, **32**, 1688.
[13] Brodrick, Donaldson, Nicholson, Short, and Wibberley, *J.*, 1953, 1079.
[14] Gomberg and Britton, *J. Amer. Chem. Soc.*, 1921, **43**, 1945.

sodium hydroxide in the same solvent (6 c.c.) was added portionwise during 65 min. After each addition the mixture was heated under reflux and heating was continued finally for 15 min. 3′ : 5-*Dinitro*-2-(*phenylthio*)*benzophenone* formed pale yellow needles, m. p. 124° (from ethanol) (Found: C, 60·2; H, 3·4. $C_{19}H_{12}O_5N_2S$ requires C, 60·0; H, 3·2%).

2-*Nitrothioxanthone* m-*Nitroanil and* 2-*Nitro*-11-m-*nitrophenyldibenzo*[b,f]-1 : 4-*thiazepine*.—To an ice-cooled solution of 3′ : 5-dinitro-2-(phenylthio)benzophenone (0·5 g.) in concentrated sulphuric acid (2 c.c.) sodium azide (0·5 g.) was added and, after 12 hr., the mixture was poured on ice. The resultant precipitate was washed with water, aqueous sodium carbonate, and then water, dried *in vacuo*, and extracted with boiling benzene (charcoal). Addition of light petroleum to the concentrated extract gave a crystalline azide (0·4 g.; m. p. 147°) which was heated (7 min.) with decalin (5 c.c.) under reflux. The solid obtained from the cooled solution was crystallised from benzene (charcoal) affording, as the first crop (filtrate-*A*), yellow needles (0·176 g.) of 2-*nitrothioxanthone* m-*nitroanil*, m. p. 259° (Found: C, 60·5; H, 2·9; N, 11·3. $C_{19}H_{11}O_4N_3S$ requires C, 60·5; H, 2·9; N, 11·1%). When hydrolysed by acid, it gave 2-nitrothioxanthone identical in m. p. 225—227° and in infrared spectrum with an authentic sample.[15]

A second crop of crystals, obtained from filtrate-*A*, was chromatographed in benzene on alumina and afforded in the first eluate 2-nitro-11-*m*-nitrophenyldibenzo[*b*,*f*]-1 : 4-thiazepine (0·013 g.) identified by m. p. 274—278° and infrared spectrum with an authentic sample (Part II).

2-*Nitro*-9-*phenylthioxanthhydrol*.—To a refluxing solution of 2-chloro-5-nitrobenzophenone (1·3 g.) and thiophenol (0·55 g.) in ethanol (17 c.c.) and water (5 c.c.) there was added a hot solution of sodium hydroxide (0·27 g.) in ethanol–water (1 : 1; 10 c.c.) and then ethanol (10 c.c.). Heating was continued for 1 hr., then the oil, which formed in the cooled mixture, was separated, taken into ether, the ethereal solution washed with water and dried, and the product recovered and dissolved in concentrated sulphuric acid. After 12 hr. the red solution was poured into ice–water, affording 2-*nitro*-9-*phenylthioxanthhydrol*, m. p. 155° (from benzene–light petroleum) (Found: C, 68·3; H, 4·1. $C_{19}H_{13}O_3NS$ requires C, 68·1; H, 3·9%).

2-*Nitrothioxanthone Anil*.—A solution of the foregoing xanthhydrol (0·5 g.) in concentrated sulphuric acid (1 c.c.) was treated with sodium azide (0·5 g.) and, after 12 hr., the whole was added to ice-water. The precipitate was dried and crystallised from benzene–light petroleum (1 : 4). The resultant azide (0·42 g.; m. p. 120°) was decomposed (7 min.) in boiling decalin (1 c.c.) from which after cooling 2-*nitrothioxanthone anil*, m. p. 205° (from benzene), was obtained in 86% yield (based on the azide) (Found: C, 68·75; H, 3·5; N, 8·75. $C_{19}H_{12}O_2N_2S$ requires C, 68·7; H, 3·6; N, 8·4%). Although probably present, no thiazepine was detected. The anil was identified by hydrolysis to 2-nitrothioxanthone.

2-*Methyl*-7-*nitrothioxanthone Anil*.—Essentially as described for the foregoing compound, 5-nitro-2-*p*-tolylthiobenzophenone in concentrated sulphuric acid was converted into an azide which by decomposition in decalin yielded 2-*methyl*-7-*nitrothioxanthone anil*, m. p. 200—202° (from benzene), in 74% yield (Found: C, 69·7; H, 4·2; N, 8·65. $C_{20}H_{14}O_2N_2S$ requires C, 69·4; H, 4·1; N, 8·1%). Again no thiazepine was detected and hydrolysis of the anil gave 2-methyl-7-nitrothioxanthone which was identified by m. p. 264° [3] and infrared spectrum.

9-*Oxoanthra*[9,1-ef]*benzo*[b]*thiazepine* (IV; R = R′ = H).—To a solution of 1-chloroanthraquinone (0·22 g.) in peroxide-free dioxan (4 c.c.) were added *o*-aminothiophenol hydrochloride (0·18 g.) and then, dropwise, a solution of sodium hydroxide (0·1 g.) in ethanol–water (1 : 1; 2 c.c.). The whole was heated at 100° for 30 min., then cooled and water added. An acetic acid solution of the resultant red solid was heated under reflux for 1 hr., affording the thiazepine (IV; R = R′ = H) as yellow needles (0·2 g.), m. p. 218° (from acetic acid) (Found: C, 76·35; H, 4·05. $C_{20}H_{11}ONS$ requires C, 76·7; H, 3·55%).

10-*Chloro*-9-*oxoanthra*[9,1-ef]*benzo*[b]*thiazepine* (IV; R = Cl, R′ = H).—1 : 5-Dichloroanthraquinone (0·35 g.) in dioxan (8 c.c.) was treated as for the 1-chloro-compound (but for 3 hr.) with sodium *o*-aminophenyl sulphide (1 mol.) generated as before. The immediate product, after being heated (2 hr.) in acetic acid, gave an insoluble yellow solid (0·05 g., m. p. >360°; cf. below) and the more soluble *thiazepine* (IV; R = Cl, R′ = H) as orange-red needles (0·29 g.), m. p. 239° (from acetic acid) (Found: C, 68·7; H, 2·85; N, 4·4. $C_{20}H_{10}ONSCl$ requires C, 69·1; H, 2·7; N, 4·0%).

Anthra[9,1-ef, 10,5-e′f′]*bisbenzo*[b]*thiazepine* (V).—When two mols. of sodium *o*-aminophenyl sulphide were used in the preceding reaction, or when the thiazepine (IV; R = Cl, R′ = H)

[15] Mayer, *Ber.*, 1909, **42**, 3046.

was treated with one mol. of this reagent, the procedure described gave the yellow solid (m. p. >360°) in *ca.* 75% yield. This afforded the *bisthiazepine* (V) as yellow needles from ethylene glycol (Found: C, 74·3; H, 3·7; N, 6·8. $C_{26}H_{14}N_2S_2$ requires C, 74·6; H, 3·4; N, 6·7%).

8-*Chloro*-9-*oxoanthra*[9,1-ef]*benzo*[b]*thiazepine* (IV; R = H, R′ = Cl) *and Anthra*[9,1-ef, 10,4-e′f′]*bisbenzo*[b]*thiazepine* (VI).—By the procedures described above 1-chloro-4-nitroanthraquinone was converted into the *monothiazepine* (IV; R = H, R′ = Cl), m. p. 229° (from acetic acid), in 50% yield (Found: C, 68·9; H, 3·0; N, 4·6%), and the *bisthiazepine* (VI), m. p. 262° (from acetic acid), in 51% yield (Found: C, 74·4; H, 3·2; N, 6·9%).

9-*Phenylphenanthridine*.—11-Phenyldibenzothiazepine (0·15 g.), copper bronze (0·15 g.), and diethyl phthalate (1 c.c.) were heated (65 min.) under reflux in an atmosphere of nitrogen. The mixture was diluted with benzene and filtered (warm) through charcoal. A hot solution of picric acid (0·15 g.) in benzene was added to the filtrate and 9-phenylphenanthridine picrate (0·24 g., 94% yield), m. p. 250—252°, collected: Arcus and Coombs [5] record m. p. 251°. The base, liberated from the picrate, was identical in m. p. 105° and infrared spectrum with an authentic sample[16] (Found: C, 89·1; H, 5·05; N, 5·6. Calc. for $C_{19}H_{13}N$: C, 89·4; H, 5·1; N, 5·5%). After a reaction time of 7 min. the base was isolated (by fractional crystallisation from admixture with the thiazepine) in 33% yield; and after 20 min. the picrate was obtained in 80% yield.

8-*Oxodibenzo*[c,mn]*acridine* (VII).—(*a*) A solution of the thiazepine (IV; R = R′ = H) (0·3 g.) in diethyl phthalate (4 c.c.) was boiled under nitrogen with copper bronze for 5—7 min. The cooled mixture was diluted with benzene, heated with charcoal, filtered, and concentrated, affording the acridine [7] (0·22 g.), m. p. 224° (from acetic acid); $\lambda_{max.}$ 363 (shoulder), 303, 382 mμ (log ε 4·465, 4·19 and 4·15) in chloroform (Found: C, 85·1; H, 3·9; N, 5·3. Calc. for $C_{20}H_{11}ON$: C, 85·4; H, 3·9; N, 5·0%).

(*b*) A solution of the thiazepine (0·2 g.) in acetic acid (25 c.c.) containing hydrogen peroxide (30%; 0·6 c.c.) was heated under reflux for 45 min., during which hydrogen sulphide was evolved. The solution was concentrated, the residue treated with water, and the resultant solid chromatographed on alumina in benzene–light petroleum (2 : 1) affording the acridine in 67% yield.

8 : 16-*Diazadibenzo*[b,k]*perylene* (VIII).—This compound, m. p. ~370°, was obtained in 78% yield when procedure (*a*) was applied to the bisthiazepine (V) and the solid product was recovered in chloroform from a Soxhlet thimble (Found: C, 88·2; H, 3·9; N, 7·95. Calc. for $C_{26}H_{14}N_2$: C, 88·1; H, 4·0; N, 7·9%); $\lambda_{max.}$ 258 (shoulder), 273 (sh), 282, 294, 370, 390, 410, and 435 mμ (log ε 4·38, 4·47, 4·57, 4·68, 4·15, 4·33, 4·59, and 4·65) in dioxan.[7]

11 : 16-*Diazatribenzo*[a,e,i]*pyrene* (IX).—This compound, m. p. 311° (from xylene), was similarly obtained in 76% yield from the bisthiazepine (VI) (Found: C, 87·9; H, 3·7; N, 7·9. $C_{26}H_{14}N_2$ requires C, 88·1; H, 4·0; N, 7·9%); $\lambda_{max.}$ 267, 283, 292, 323, 368, 382, 388, and 408 mμ (log ε 4·67, 4·71, 4·86, 4·17, 4·39, 4·37, 4·38, and 3·90) in dioxan.

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[16] Morgan and Walls, *J.*, 1931, 2447; Walls, *J.*, 1945, 294.