Synthesis of 4,5-Bridged Carbazoles

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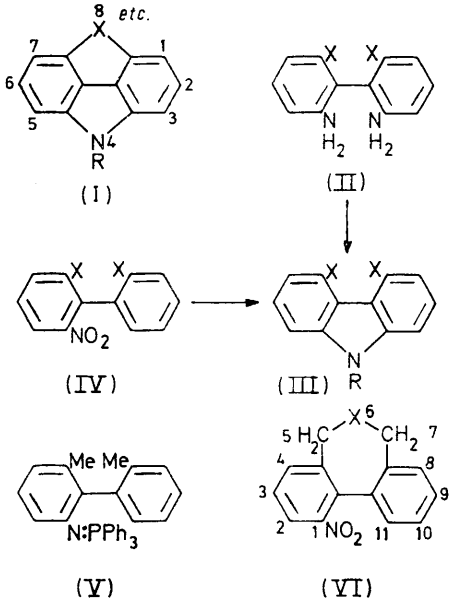
Condensation of 2,2′-bis(bromomethyl)-6-nitrobiphenyl with sodium sulphide gives 5,7-dihydro-1-nitrodibenzo-[*c,e*]thiepin which, on heating with triphenylphosphine, undergoes reductive cyclisation through a nitrene intermediate to form 8,10-dihydrothiepino[3,4,5,6-*def*]carbazole. The *N*-diethylaminoethyl derivative was prepared for pharmacological examination. This route is extended to the synthesis of analogous oxepino-, azepino-, and cyclohepta-carbazoles. 1-Benzamido-5,7-dihydrodibenzo[*c,e*]thiepin is dehydrated by polyphosphoric acid to form 6,8-dihydro-2-phenylthiepino[3,4,5,6-*lmn*]phenanthridine but oxepino- and azepino-phenanthridines could not be prepared similarly.

THE preparations of *N*-acetylbenzo[*def*]carbazole (I; R = Ac, X = CH:CH) [1] and of a related dihydromethyl compound [2] have been reported, but apparently no other carbazoles with a 4,5-bridging group have been described. 8,10-Dihydrothiepino[3,4,5,6-*def*]carbazole (I; R = H, X = CH_2·S·CH_2) shows some resemblance to phenothiazine, and derivatives of this system have therefore been prepared for pharmacological examination.

4,5-Disubstituted carbazoles, possible intermediates for the synthesis of structures (I), have not been studied extensively but several have been obtained by cyclisation of 2,2′-diaminobiphenyls in hydrochloric acid.[3,4] Application of this reaction to 2,2′-diamino-6,6′dimethylbiphenyl (II; X = Me) gave 4,5-dimethylcarbazole (III; R = H, X = Me) in 20% yield, but it proved difficult to reproduce this preparation as some batches gave a second dimethylcarbazole, apparently formed by a rearrangement. 4,5-Dimethylcarbazole was also prepared from 2,2′-dimethyl-6-nitrobiphenyl (IV; X = Me) *via* the corresponding nitrene.[5] Cyclisation by reaction with triethyl or trimethyl phosphite gave low yields of 4,5-dimethylcarbazole and of its 9-alkyl derivative [6] which was formed by the alkylating action of the trialkyl phosphate even when purified cumene was used as solvent.[7] Deoxygenation of the nitro-compound by triphenylphosphine avoided *N*-alkylation but again the yield of 4,5-dimethylcarbazole was low and the iminophosphine (V) was a major product. Reductive cyclisation of 2-nitrobiphenyl with triethyl phosphite gives carbazole (87%) and a little 9-ethylcarbazole;[8]



presumably the low yields of 4,5-dimethylcarbazole are due to the conformations of the nitro-compound and nitrene being unfavourable for ring closure.

[1] J. W. Cook and J. S. Moffatt, *J. Chem. Soc.*, 1951, 2487.
[2] P. G. Sammes, D. H. R. Barton, and G. G. Weingarten, *J. Chem. Soc.* (*C*), 1971, 729.
[3] S. Sako, *Bull. Chem. Soc. Japan*, 1934, **9**, 55; 1936, **11**, 144.
[4] R. B. Carlin and W. O. Forshey, *J. Amer. Chem. Soc.*, 1950, **72**, 793.
[5] J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.
[6] *Cf.* I. Puskas and E. K. Fields, *J. Org. Chem.*, 1968, **33**, 4237.
[7] *Cf.* J. I. G. Cadogan, S. Kulik, C. Thomson, and M. J. Todd, *J. Chem. Soc.* (*C*), 1970, 2437.
[8] J. I. G. Cadogan and M. Cameron-Wood, *Proc. Chem. Soc.*, 1962, 361.

Attempts to convert 4,5-dimethylcarbazole into a 4,5-bridged carbazole (I) were unsuccessful. Bromination in acetic acid gave a product which was probably 1,3,6,8-tetrabromo-4,5-dimethylcarbazole, and treatment with *N*-bromosuccinimide gave a complex mixture which could not be separated and which did not give any sulphide (I; R = H, X = CH_2·S·CH_2) on treatment with sodium sulphide. No identifiable products were isolated when 4,5-dimethylcarbazole was heated with sulphur or oxidised with potassium permanganate. In another attempt to prepare carbazole-4,5-dicarboxylic acid, the diamine (II; X = CO·NEt_2) was heated in a sealed tube with hydrochloric acid, but only the dilactam of 6,6′-diaminodiphenic acid was isolated. Similar treatment of 2,2′,6,6′-tetraminobiphenyl (II; X = NH_2) gave only a small amount of an amino-hydroxycarbazole.

As an alternative approach to structures of type (I), ring closure of a 2,2′-bridged 6-nitrobiphenyl was examined. 2,2′-Bis(bromomethyl)-6-nitrobiphenyl [9] was readily converted into 5,7-dihydro-1-nitrodibenzo[*c*,*e*]thiepin (VI; X = S) in 90% yield by heating with sodium sulphide solution.[10] The nitro-compound was heated with triphenylphosphine in cumene [7] to give 8,10-dihydrothiepino[3,4,5,6-*def*]carbazole (I; R = H, X = CH_2·S·CH_2) in 60% yield. Evidently the bridging group holds the aromatic rings in the nitro-compound (VI; X = S) and in the intermediate nitrene in a favourable conformation for cyclisation to the carbazole. The spectroscopic properties of the product were consistent with structure (I; X = CH_2·S·CH_2, R = H) and the mass spectrum showed a molecular ion peak at *m/e* 225, which excludes the possibility of dimeric structures for the nitro-compound and the carbazole, formed by condensation of two molecules of dihalide with two of sodium sulphide. The structure was confirmed by desulphurisation with ' nickel boride ' [11] to form 4,5-dimethylcarbazole. Conversion of the 4,5-bridged carbazole into the sodio-derivative and condensation with 2-diethylaminoethyl chloride gave 4-(2-diethylaminoethyl)-8,10-dihydrothiepino[3,4,5,6-*def*]carbazole (I; R = CH_2·CH_2·NEt_2, X = CH_2·S·CH_2).

Oxidation of the sulphide (VI; X = S) with hydrogen peroxide in acetic acid gave the sulphone (VI; X = SO_2) which, on reductive cyclisation with triphenylphosphine in cumene, yielded the sulphone (I; R = H, X = CH_2·SO_2·CH_2). 5,8-Dihydro-1-nitrodibenzo[*d*,*f*][1,2]dithiocin (VI; X = S·S) was prepared by condensation of 2,2′-bis(bromomethyl)-6-nitrobiphenyl (IV; X = CH_2Br) with thiourea, and hydrolysis of the bisisothiouronium salt under mild conditions [12] to give the dithiol (IV; X = CH_2·SH), which was oxidised to the cyclic disulphide by air or by iodine and sodium carbonate solution.[13] Treatment of this dithiocin with triphenylphosphine in cumene gave triphenylphosphine sulphide (70%); a little of the thiepinocarbazole (I; R = H, X = CH_2·S·CH_2) was also isolated. Analogous conversions of dialkyl disulphides into sulphides have been reported [14] although benzylic disulphides did not react under the milder conditions used.

This route to 4,5-bridged carbazoles was extended to the oxepino-, azepino-, and cyclohepta-analogues. Thus the nitro-oxepin (VI; X = O) [15] on prolonged heating with triphenylphosphine in cumene gave 8,10-dihydro-oxepino[3,4,5,6-*def*]carbazole (I; R = H, X = CH_2·O·CH_2), the sodio-derivative of which condensed with 2-diethylaminoethyl chloride and with 2-(4-methylpiperazin-1-yl)ethyl chloride to give basic derivatives. Since the oxepinocarbazole was obtained in good yield (45% overall from 6-nitrodiphenic acid), attempts were made to cleave the ether group to form 4,5-disubstituted carbazoles. However, the oxepinocarbazole was unaffected by prolonged boiling with hydrobromic acid, action of hydrogen bromide in acetic and sulphuric acids gave a tetrabromo-derivative of the oxepinocarbazole, and treatment with acetyl methyl sulphonate [16] gave a tar.

For the synthesis of azepinocarbazoles of type (I), 2,2′-bis(bromomethyl)-6-nitrobiphenyl was condensed with an amine to give the nitrodibenzazepine (VI; X = NMe or N·CH_2Ph) (*cf.* ref. 9). Reductive cyclisation with triphenylphosphine formed the corresponding azepinocarbazoles [I; R = H, X = CH_2·NMe·CH_2 or CH_2·N(CH_2Ph)·CH_2] in good overall yields. Attempts to obtain the parent compound (I; R = H, X = CH_2·NH·CH_2) by catalytic hydrogenation of the *N*-benzyl compound were unsuccessful.

Condensation of the nitro-dibromide (IV; X = CH_2Br) with diethyl malonate in the presence of sodium ethoxide (2 mol equiv.) [17] gave diethyl 5,7-dihydro-1-nitrodibenzo[*a*,*c*]cycloheptene-6,6-dicarboxylate [VI; X = C(CO_2Et)$_2$]. Reductive cyclisation with triphenylphosphine furnished diethyl 8,10-dihydrocyclohepta-[1,2,3,4-*def*]carbazole-9,9-dicarboxylate. Treatment with sodium cyanide in dimethyl sulphoxide [18] removed one ethoxycarbonyl group. The corresponding monocarboxylic acid was obtained from the diester by alkaline hydrolysis followed by thermal decarboxylation.

Attempts to condense 2,2′-bis(bromomethyl)-6-nitrobiphenyl (IV; X = CH_2Br) with ethane-1,2-dithiol, with 2-aminobenzenethiol, and with the disodio-derivative of tetraethyl ethane-1,1,2,2-tetracarboxylate were unsuccessful, but condensation with catechol and sodium hydride in dimethoxyethane gave a small amount of a product which appeared to be a hydrated

[9] D. M. Hall and T. M. Poole, *J. Chem. Soc.* (*B*), 1966, 1034.
[10] *Cf.* W. E. Truce and D. D. Emrick, *J. Amer. Chem. Soc.*, 1956, **78**, 6130.
[11] W. E. Truce and F. M. Perry, *J. Org. Chem.*, 1965, **30**, 1316; W. E. Truce and F. E. Roberts, *ibid.*, 1963, **28**, 961.
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[13] *Cf.* R. L. Frank and J. R. Blegen, *Org. Synth.*, Coll. Vol. III, 1955, p. 116.
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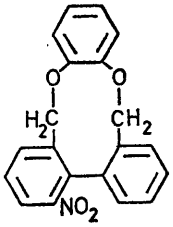
[16] I. O. Sutherland and M. V. J. Ramsay, *Tetrahedron Letters*, 1965, 3401.
[17] *Cf.* J. Kenner, *J. Chem. Soc.*, 1913, 621.
[18] A. P. Krapcho, G. A. Glynn, and B. J. Grenon, *Tetrahedron Letters*, 1967, 215.

form of 9,16-dihydro-4-nitrotribenzo[*b,f,h*][1,4]dioxecin (VII).

It has been shown that phenanthraquinone forms stable adducts (VIII; X = H) with trialkyl or triaryl phosphites [19] or with triphenylphosphine.[20] 4-Nitrophenanthraquinone was therefore treated with triphenylphosphine in cumene, in the hope that reductive cyclisation would form the carbazole system while the quinone was protected as the dioxaphospholene, but no product was isolated.

6-Nitrodiphenic acid was heated with lead tetra-acetate in pyridine–acetonitrile [21] until evolution of carbon dioxide ceased. The product is formulated as the lactone (IX; X = NO_2, Y = H) rather than



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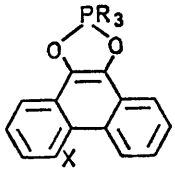

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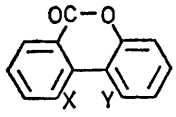

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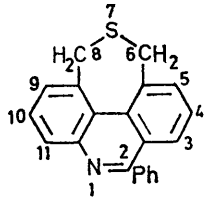

(X)

the isomer (IX; X = H, Y = NO_2) because permanganate oxidation gave 3-nitrophthalic acid. This conclusion was supported by n.m.r. spectroscopic evidence: the protons adjacent to the nitro-group and to the lactone carbonyl each appeared as an ABX system (J_{ortho} 7, J_{meta} 2 Hz), at τ 1·45 and 2·15, respectively, slightly separated from the complex absorption due to the remaining aromatic protons. The presence of the peaks due to both these protons downfield of the aromatic multiplet appears to be consistent with structure (IX; X = NO_2, Y = H) in which the nitro- and carbonyl groups are attached to the same aromatic ring, whereas in the isomer (IX; X = H, Y = NO_2) the lactone oxygen atom would be expected to counteract the strong deshielding effect of the nitro-group in the same ring. When the nitro-lactone was heated with triphenylphosphine, the only product isolated was the phosphorane (IX; X = N:PPh_3, Y = H).

Conversion of the intermediates of type (VI) into 1,10-bridged phenanthridines was also examined. 1-Nitro-5,7-dihydrodibenzo[*c,e*]thiepin (VI; X = S), on reduction with tin(II) chloride followed by benzoylation, gave the corresponding 1-benzamido-compound. Attempted cyclisation with phosphoryl chloride in nitrobenzene [22] failed but treatment with polyphosphoric acid [23] gave 6,8-dihydro-2-phenylthiepino[3,4,5,6-*lmn*]-phenanthridine (X). In the n.m.r. spectrum, the methylene protons give rise to two sharp singlets separated by 0·04 p.p.m. As it appears that there is no geminal coupling between these protons, the molecule must be planar or nearly planar. Only in this conformation are the two hydrogen atoms of the separate methylene groups in the same magnetic environment. Reduction and benzoylation of the nitro-compounds (VI; X = O or NMe) gave the corresponding benzamido-derivatives but attempts to cyclise these to phenanthridines failed.

EXPERIMENTAL

Evaporations were carried out under reduced pressure; petroleum refers to light petroleum of b.p. 60—80°. ^{1}H N.m.r. spectra were measured on a Perkin-Elmer R10 spectrometer at 60 MHz. Where possible deuteriochloroform was used as solvent, with tetramethylsilane as internal standard; with [$^2H_6$]dimethyl sulphoxide or trifluoroacetic acid as solvent sodium 3-trimethylsilylpropane-1-sulphonate was used. U.v. spectra were recorded on a Perkin-Elmer 137 spectrophotometer.

Action of Hydrochloric Acid on Substituted Biphenyls (with N. D. Griffiths).—(i) *2,2′-Diamino-6,6′-dimethylbiphenyl.* The diamine [24] (3 g) in 2N-hydrochloric acid (40 ml) was heated in a sealed tube at *ca.* 210° for 7 h. The material which separated on cooling was crystallised from ethanol to give *4,5-dimethylcarbazole* (1·1 g), m.p. 170—171° (Found: C, 85·4; H, 6·8; N, 7·9. $C_{14}H_{13}N$ requires C, 86·1; H, 6·7; N, 7·2%), $\lambda_{max.}$ (EtOH) 221, 245, 253, 293, 330, and 343 nm (log ε 4·29, 4·51, 4·38, 4·07, 3·45, and 3·51), τ[$(CD_3)_2SO$] 2·2br (1H, s, NH), 2·6—3·2 (6H, m. ArH), 7·05 (6H, s, 4-Me and 5-Me). When the reaction mixture was heated at *ca.* 270° for 7 h, a mixture of two isomeric dimethylcarbazoles was obtained in 85% yield. This had m.p. 141—142° (Found: C, 86·1; H, 7·0; N, 7·0%) and contained about 20% of the 4,5-dimethyl compound (τ 7·09) and 80% of an isomer (τ 7·2 and 7·5; Me groups). Some batches of product obtained by reaction at *ca.* 210° were contaminated with some of the isomer.

(ii) *6,6′-Diamino-NNN′N′-tetraethyldiphenamide.* 2-Iodo-3-nitrobenzoic acid [25] (3 g) and phosphorus pentachloride (2·1 g) were heated at 110° (bath temp.) for 10 min and then at 150° for 15 min. Crystallisation from benzene–petroleum gave *2-iodo-3-nitrobenzoyl chloride* (2 g), m.p. 70—71° (Found: C, 26·9; H, 0·9; N, 5·1. $C_7H_3ClINO_3$

[19] F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, 1963, **85**, 3285.
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[23] E. C. Taylor and N. W. Kalenda, *J. Amer. Chem. Soc.*, 1954, **76**, 1699.
[24] W. Dethloff and H. Mix, *Chem. Ber.*, 1949, **82**, 534.
[25] C. W. James, J. Kenner, and W. V. Stubbings, *J. Chem. Soc.*, 1920, **87**, 776.

requires C, 27·0; H, 1·0; N, 4·5%). The acid chloride (4·1 g) was added to diethylamine (52 ml); the mixture was left overnight, and filtered. Evaporation and crystallisation from benzene–petroleum gave NN-*diethyl*-2-*iodo*-3-*nitrobenzamide* (2·5 g), m.p. 123—124° (Found: C, 38·2; H, 3·7; N, 8·0. $C_{11}H_{13}IN_2O_3$ requires C, 38·0; H, 3·8; N, 8·1%).

Activated copper powder (1 g) was added gradually to the stirred, molten amide (1·65 g) (bath at 160°). After 1 h, the mass was cooled and extracted with acetone; evaporation and crystallisations from acetone gave *NNN'N'-tetraethyl-6,6'-dinitrodiphenamide* (0·53 g), m.p. 210—212° (Found: C, 59·9; H, 6·0; N, 12·7. $C_{22}H_{26}N_4O_6$ requires C, 59·7; H, 5·9; N, 12·7%). This (0·36 g) in ethanol (200 ml) was hydrogenated over palladised charcoal (0·4 g; 10%) until absorption ceased. Filtration, evaporation, and crystallisation from acetone–ether yielded the *diaminodiamide* (30 mg), m.p. 180° (Found: C, 68·9; H, 7·8; N, 14·3. $C_{22}H_{30}N_4O_2$ requires C, 69·1; H, 7·9; N, 14·7%), $\lambda_{max.}$ (EtOH) 212 and 303 nm (log ε 4·64 and 3·73). The diamine in 2N-hydrochloric acid was heated in a sealed tube at 195° for 6 h. Filtration of the cooled mixture gave a little grey solid which was identified as the dilactam of 6,6'-diaminodiphenic acid by comparison (i.r. and u.v. spectra) with authentic material;[26] $\lambda_{max.}$ (EtOH) 245, 295, 306, 336, 352, and 370 nm (log ε 4·55, 3·75, 3·72, 3·75, 4·10, and 4·29).

(iii) 2,2',6,6'-*Tetra-aminobiphenyl*. The tetra-amine (0·3 g) in 2N-hydrochloric acid (10 ml) in a sealed tube was heated at 190° for 5 h. Orange crystals, which separated on cooling, were collected and dissolved in water; basification, extraction with ethyl acetate, and chromatography on alumina in ethyl acetate–petroleum gave a brown solid which was sublimed at 0·1 mmHg (bath at 175°) to give an *amino-hydroxycarbazole* (presumably the 4,5-isomer), m.p. 200° (decomp.) (from ethyl acetate–petroleum) (Found: C, 72·0; H, 5·1; N, 13·9. $C_{12}H_{10}N_2O$ requires C, 72·7; H, 5·1; N, 14·1%), $\nu_{max.}$ 3400, 3380 (NH_2), 3290 (NH), and 3100br cm^{-1} (OH), $\lambda_{max.}$ (EtOH) 223, 250, 288, 324, and 337nm (log ε 4·57, 4·78, 3·94, 3·70, and 3·85), τ [$(CD_3)_2SO$] 1·7 (1H, s, ring NH), 2·5—3·3 (6H, m, ArH), and 5·0br (H_2O and possibly OH,NH_2).

Reductive Cyclisation of 2,2'-*Dimethyl*-6-*nitrobiphenyl*.—(a) *With triethylphosphite*. The nitro-compound[27] (1·8 g) and triethyl phosphite (25 ml) were heated under reflux (N_2) for 22 h. Triethyl phosphite and phosphate were removed by distillation at 1 mmHg and the residue was dissolved in petroleum (300 ml) and chloroform (30 ml). The solution was applied to a column of alumina (100 g; type O). Elution with petroleum containing increasing proportions of ethyl acetate yielded (i) 9-*ethyl*-4,5-*dimethylcarbazole* (100 mg), m.p. 111—113° (Found: C, 86·8; H, 7·4; N, 6·8. $C_{16}H_{17}N$ requires C, 86·1; H, 6·7; N, 7·2%), $\lambda_{max.}$ (EtOH) 248, 257, 265, 295, 337, and 352 nm (log ε 4·64, 4·50, 4·27, 4·17, 3·59, and 3·75), τ ($CDCl_3$) 2·52—3·12 (6H, m, ArH), 5·65 (2H, q, *J* 7 Hz, N·CH_2·CH_3), 6·98 (6H, s, 4- and 5-Me), and 8·60 (3H, t, *J* 7 Hz, N·CH_2·CH_3); (ii) 2-amino-2',6-dimethylbiphenyl (360 mg), oil [*p*-nitrobenzoyl derivative, m.p. 119—121° (from aqueous ethanol) (lit.,[28] 121—122°)]; and (iii) 4,5-dimethylcarbazole (70 mg), m.p. and mixed m.p. 170—171° (from benzene).

(b) *With trimethyl phosphite*. Similar products were obtained: 4,5,9-*trimethylcarbazole* (2%), m.p. 101—103° (from benzene–petroleum) (Found: C, 85·6; H, 7·5; N, 7·0. $C_{15}H_{15}N$ requires C, 85·2; H, 7·7; N, 7·1%), $\lambda_{max.}$ (MeOH) 248, 256, 265, 295, 336, and 352 nm (log ε 4·25, 4·08, 3·84, 3·77, 3·15, and 3·34); aminodimethylbiphenyl (10%); and 4,5-dimethylcarbazole (12%).

(c) *With triphenylphosphine*. The nitro-compound (2·27 g) and triphenylphosphine (5·27 g) were heated under reflux (N_2) for 26 h. The mass was boiled with ethanol (100 ml) and the cooled mixture filtered to give 2',6-*dimethylbiphenyl*-2-*yliminotriphenylphosphorane* (1·3 g), m.p. 179—181° (from chloroform) (Found: C, 84·0; H, 6·1; N, 3·1. $C_{32}H_{28}NP$ requires C, 84·0; H, 6·2; N, 3·1%), $\lambda_{max.}$ (MeOH) 214, $\lambda_{infl.}$ 265 nm (log ε 4·62 and 3·88), τ ($CDCl_3$) 2·20—3·60 (22H, m, ArH) and 8·00 (6H, s, 2C–Me). Evaporation of the combined filtrates and chromatography of the residue as described above yielded (i) a little triphenylphosphine, (ii) 2,2'-dimethyl-6-nitrobiphenyl (256 mg), m.p. and mixed m.p. 38—40°; (iii) 2-amino-2',6-dimethylbiphenyl (identified by t.l.c.); (iv) the phosphorane (100 mg); (v) 4,5-dimethylcarbazole (190 mg), m.p. and mixed m.p. 169—170°; and (vi) triphenylphosphine oxide (3·7 g), m.p. 153—155°.

In similar experiments (*a*) an excess of triphenylphosphine was used, and (*b*) the reaction was carried out in cumene. In each case, the yield of 4,5-dimethylcarbazole was even lower.

Reductive Cyclisation of 2-*Nitrobiphenyl*.—The nitro-compound (3·98 g) and triethyl phosphite (14 ml) were heated at 160° under reflux (N_2) for 19 h. Evaporation at 1 mmHg and crystallisation from acetone–petroleum gave carbazole (2·9 g, 87%), m.p. 243—245° (lit.,[8] 247—248°). Chromatography as in the preceding experiment yielded 9-ethylcarbazole (255 mg, 7%), m.p. 64—66°, identical with a sample prepared by alkylation of carbazole.[29]

Bromination of 4,5-*Dimethylcarbazole* (with N. D. Griffiths).—Bromine (0·5 ml) was added to a suspension of the compound (1 g) in carbon tetrachloride (10 ml). Decolourisation and evolution of hydrogen bromide occurred rapidly to give 1,3,6,8-*tetrabromo*-4,5-*dimethylcarbazole*, m.p. 234—236°, after repeated recrystallisation from 2-ethoxyethanol (Found: C, 33·1; H, 1·7; Br, 61·7; N, 2·6. $C_{14}H_9Br_4N$ requires C, 32·9; H, 1·8; Br, 62·6; N, 2·6%), τ ($CDCl_3$) 2·18 (2H, s, ArH) and 7·18 (6H, s, 4- and 5-Me). The singlet at τ 2·18 was not affected by addition of deuterium oxide and is therefore attributed to 2- and 7-H not to NH.

5,7-*Dihydro*-1-*nitrodibenzo*[c,e]*thiepin* (VI; X = S).—2,2'-Bis(bromomethyl)-6-nitrobiphenyl (11·6 g) was dissolved in warm methanol (600 ml) and treated with sodium sulphide nonahydrate (20 g) in water (60 ml). The mixture was boiled under reflux for 2 h and left overnight. The product was collected by filtration and a second crop was obtained by addition of water to the filtrate. The *thiepin* (6·9 g) formed yellow needles, m.p. 146—148° (from ethanol) (Found: C, 65·9; H, 4·4; N, 5·4. $C_{14}H_{11}NO_2S$ requires C, 65·4; H, 4·3; N, 5·5%), $\lambda_{max.}$ (MeOH) 231—237, $\lambda_{infl.}$ 244mn (log ε 4·11 and 4·08), τ ($CDCl_3$) 2·05—3·10 (7H, m,

[26] J. Kenner and W. V. Stubbings, *J. Chem. Soc.*, 1921, 593; F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci, and K. Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 476.

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ArH), 6·43 (2H, q, *J* 11 Hz, 5-CH_2), and 6·65 (2H, q, *J* 11Hz, 7-H_2).

General Procedure for Preparation of 4,5-Bridged Carbazoles by Reductive Cyclisation.—The foregoing nitro-compound (5·14 g, 0·02 mol) and triphenylphosphine (15·75 g, 0·06 mol) (each dried at 25° and 0·5 mmHg) in purified cumene (200 ml) were heated under reflux (N_2) for 72 h. After removal of solvent by distillation at 100° and 20 mmHg, the residue, in a little chloroform, was applied to a column of alumina (500 g; type O) in petroleum. Elution with petroleum–ethyl acetate gave: triphenylphosphine (1·8 g); nitro-compound (0·4 g); 5,7-*dihydrodibenzo*[c,e]*thiepin*-1-*yliminotriphenylphosphorane* (0·5 g), yellow, m.p. 168—170° (from ethyl acetate–benzene) (Found: C, 79·2; H, 5·6; N, 2·6. $C_{32}H_{26}NPS$ requires C, 78·8; H, 5·4; N, 2·9%), τ ($CDCl_3$) 2·30—3·52 (22H, m, ArH) and 6·46—7·00 (4H, m, CH_2·S·CH_2); 8,10-*dihydrothiepino*[3,4,5,6-def]*carbazole* (2·5 g), m.p. 222—224° (from ethanol or benzene–petroleum) (Found: C, 74·5; H, 4·9; N, 6·1; S, 14·3. $C_{14}H_{11}NS$ requires C, 74·7; H, 4·9; N, 6·2; S, 14·2%), $\lambda_{max.}$ (MeOH) 246, 253, 298, 330, and 344 nm (log ε 4·49, 4·47, 4·06, 3·67, and 3·70), τ ($CDCl_3$) 1·85 (1H, s, NH, exchanges with D_2O), 2·65—3·10 (6H, m, ArH), and 5·69 (4H, s, CH_2·S·CH_2), *m/e* 225 (M^+), 210 (M^+ —NH), 193 (M^+ —S), and 165 (M^+ — CH_2·S·CH_2); and finally triphenylphosphine oxide (7·0 g).

Lower yields of thiepinocarbazole were obtained in the absence of solvent (24%) or when triethyl phosphite was used (1%). Reaction with triethyl phosphite also gave 4-*ethyl*-8,10-*dihydrothiepino*[3,4,5,6-def]*carbazole* (5%), m.p. 202—203° (from ethyl acetate–petroleum) (Found: C, 75·9; H, 6·1; N, 5·2. $C_{16}H_{15}NS$ requires C, 75·9; H, 6·0; N, 5·5%), $\lambda_{max.}$ (EtOH) 248, 257, 266, 288, 299, 338, and 353 nm (log ε 4·52, 4·51, 4·48, 3·92, 4·11, 3·78, and 3·88), τ ($CDCl_3$) 2·60—3·10 (6H, m, ArH), 5·60 (2H, q, *J* 7 Hz, N·CH_2·CH_3) with superimposed 5·68 (4H, s, CH_2·S·CH_2), and 8·57 (3H, t, *J* 7 Hz, N·CH_2·CH_3).

Desulphurisation of 8,10-*Dihydrothiepino*[3,4,5,6-def]*carbazole.*—The compound (23 mg) was dissolved in ethanol (20 ml) and treated with nickel(II) chloride dihydrate (238 mg), boric acid (500 mg), and sodium borohydride (102 mg) under nitrogen. The mixture was stirred at 20° for 16 h.[11] The solid was filtered off and washed with hot ethanol and the combined filtrates were evaporated. The residue in a little chloroform was applied to a column of alumina (10 g; type O) in petroleum and eluted with petroleum–ethyl acetate to give 4,5-dimethylcarbazole (10 mg), m.p. and mixed m.p. 168—170°.

4-(2-*Diethylaminoethyl*)-8,10-*dihydrothiepino*[3,4,5,6-def]-*carbazole.*—Sodium hydride (288 mg; 50%) was added to a solution of the thiepinocarbazole (450 mg) in 1,2-dimethoxyethane (50 ml) and the mixture was stirred and heated (bath 100°) under reflux for 1·5 h. A solution of (2-chloroethyl)diethylamine [from the hydrochloride (1·03 g)] in dry ether was added and the mixture was stirred and heated under reflux for 4 h, cooled, and treated with 6N-hydrochloric acid (50 ml) and ether (25 ml). The separated aqueous layer was washed with more ether (25 ml) and basified with solid sodium carbonate. Isolated with chloroform, 4-(2-*diethylaminoethyl*)-8,10-*dihydrothiepino*[3,4,5,6-def]*carbazole* (500 mg) formed needles, m.p. 123—124° (from methanol) (Found: C, 74·1; H, 7·6; N, 8·5. $C_{20}H_{24}N_2S$ requires C, 74·0; H, 7·5; N, 8·6%), $\lambda_{max.}$ (MeOH) 231, 247, 265, 298, 337, and 351 nm (log ε 4·27, 4·36, 4·23, 3·91, 3·56, and 3·69), τ ($CDCl_3$) 2·73—3·20 (6H, m, ArH), 5·67 (2H, t, *J* 7 Hz, N·CH_2·CH_2·NEt_2), 5·75 (4H, s, CH_2·S·CH_2), 7·25 (2H, t, *J* Hz, CH_2·CH_2·NEt_2) overlaid by 7·40 (4H, q, *J* 7 Hz, 2 N·CH_2·CH_3), and 8·96 (6H, t, *J* 7 Hz, N·CH_2·CH_3).

5,7-*Dihydro*-1-*nitrodibenzo*[c,e]*thiepin* 6,6-*Dioxide.*—A solution of 5,7-dihydro-1-nitrobenzo[*c,e*]thiepin (257 mg) in acetic acid (5 ml) was warmed to 90° and hydrogen peroxide (0·3 ml; 30%) was added. After 15 min, more hydrogen peroxide (0·2 ml) was added and the solution was kept at 90° for 10 min, then boiled under reflux for 1 h, and poured on ice. Filtration and crystallisation from benzene–1,2-dimethoxyethane gave the *sulphone* (184 mg), m.p. 266—268° (Found: C, 58·6; H, 3·8; N, 4·7. $C_{14}H_{11}NO_4S$ requires C, 58·1; H, 3·8; N, 4·8%), $\lambda_{infl.}$ 238 nm (log ε 4·04), τ ($CDCl_3$) 1·96—2·75 (7H, m, ArH), 5·80 (2H, s, 5-H_2), and 5·96 (2H, s, 7-H_2).

8,10-*Dihydrothiepino*[3,4,5,6-def]*carbazole* 9,9-*Dioxide.*—The nitro-sulphone (145 mg) and triphenylphosphine reacted by the general procedure to give the *sulphone* (55 mg), m.p. >330° (from 1,2-dimethoxyethane) (Found: C, 64·8; H, 4·1; N, 5·3. $C_{14}H_{11}NO_2S$ requires C, 65·4; H, 4·3; N, 5·5%), $\lambda_{max.}$ (MeCN) 246, 253, 298, 329, and 343 nm (log ε 4·50, 4·51, 4·12, 3·71, and 3·71), $\nu_{max.}$ 3390 (NH), 1290 and 1118 cm^{-1} (·SO_2·).

5,8-*Dihydro*-1-*nitrodibenzo*[d,f][1,2]*dithiocin.*— 2,2′-Bis-(bromomethyl)-6-nitrobiphenyl (3·85 g) and thiourea (1·6 g) in dimethyl sulphoxide (100 ml) were stirred for 18 h under nitrogen and stirring was continued similarly for 1·5 h after addition of 2N-sodium hydroxide (300 ml). The solution was cooled at 0° while it was carefully neutralised by dropwise addition of 6N-hydrochloric acid. Isolation with ether and chromatography on alumina (30 g) gave the *dithiocin* (1·37 g), m.p. 137—138° (from ethanol) (Found: C, 58·2; H, 3·9; N, 4·7. $C_{14}H_{11}NO_2S_2$ requires C, 58·1; H, 3·8; N, 4·8%), $\lambda_{infl.}$ (MeOH) 254 nm (log ε 3·81), τ ($CDCl_3$) 2·20 (1H, dd, J_{ortho} 7, J_{meta} 3 Hz, 2-H), 2·40—3·15 (6H, m, other ArH), and 6·00—6·55 (4H, m, CH_2·S·S·CH_2). In other experiments the crude dithiol in ether was shaken with iodine and sodium carbonate solution to form the disulphide.

Treatment of the disulphide with triphenyl phosphine in cumene by the general procedure gave triphenylphosphine sulphide (60%), m.p. 161—162° (from ethanol) (lit.,[14] 160—162°) (Found: C, 73·7; H, 5·2. Calc. for $C_{18}H_{15}PS$: C, 73·5; H, 5·1%), and 8,10-dihydrothiepinocarbazole (18%), m.p. and mixed m.p. 220—221°.

8,10-*Dihydro-oxepino*[3,4,5,6-def]*carbazole.*— Reductive cyclisation of 5,7-dihydro-1-nitrodibenzo[*c,e*]oxepin [15] according to the general procedure gave the *oxepinocarbazole* (71%), m.p. 247—248° (from chloroform) (Found: C, 80·6; H, 5·3; N, 6·5. $C_{14}H_{11}NO$ requires C, 80·4; H, 5·3; N, 6·7%), $\lambda_{max.}$ (MeOH) 243, 252, 296, 327, and 340 nm (log ε 4·53, 4·51, 4·10, 3·67, and 3·67), τ ($CDCl_3$–CF_3·CO_2H) 2·75—3·27 (6H, m, ArH), and 4·65 (4H, s, 2 CH_2). Condensation with (2-chloroethyl)diethylamine as before gave 4-(2-*diethylaminoethyl*)-8,10-*dihydro-oxepino*[3,4,5,6-def]*carbazole* (54%), m.p. 53—54° (from aqueous methanol) (Found: C, 77·7; H, 8·1; N, 8·8. $C_{20}H_{24}N_2O$ requires C, 77·9; H, 7·8; N, 9·1%), $\lambda_{max.}$ 247, 256, 263, 297, 333, and 347 nm (log ε 4·55, 4·50, 4·33, 4·09, 3·57, and 3·66), τ ($CDCl_3$) 2·60—3·15 (6H, m, ArH), 4·68 (4H, s, CH_2·O·CH_2), 5·60 (2H, t, *J* 7 Hz, N·CH_2·CH_2·NEt_2), 7·15 (2H, t, *J* 7 Hz, N·CH_2·CH_2·NEt_2), 7·36 [4H, q, *J* 7 Hz, $N(CH_2·CH_3)_2$], and 8·92 [6H, t, *J* 7 Hz, $N(CH_2·CH_3)_2$]. Similarly condensation with 1-(2-chloroethyl)-4-methylpiperazine gave

8,10-*dihydro*-4-[2-(4-*methylpiperazin*-1-*yl*)*ethyl*]*oxepino*-[3,4,5,6-def]*carbazole* (67%), m.p. 123—125° (from ether) (Found: C, 75·7; H, 7·7; N, 12·4. $C_{21}H_{25}N_3O$ requires C, 75·2; H, 7·5; N, 12·5%).

When the oxepino-carbazole (100 mg) in acetic acid (10 ml) was treated successively at 0° with hydrogen bromide in acetic acid (8 ml; 50%) and concentrated sulphuric acid (2 ml) and left at room temperature for 72 h, a grey solid separated. Filtration and recrystallisations from 2-methoxyethanol gave 1,3,5,7-*tetrabromo*-8,10-*dihydro*-*oxepino*[3,4,5,6-def]*carbazole*, m.p. 282—285° (Found: C, 32·2; H, 1·5; N, 2·7. $C_{14}H_7Br_4NO$ requires C, 32·0; H, 1·3; N, 2·7%).

5,7-*Dihydro*-6-*methyl*-1-*nitrodibenzo*[c,e]*azepine*.— 2,2′-Bis(bromomethyl)-6-nitrobiphenyl (3·85 g) in ethanol (200 ml) at 30° was treated dropwise with ethanolic methyl amine (10 ml; 33%) over 5 min. The solution was then boiled under reflux for 4 h, more methylamine solution (5 ml) being added after 2 h. Evaporation gave a residual solid which was dissolved in chloroform and washed with N-sodium carbonate and water. The yellow *nitro-amine* (2·0 g), m.p. 105—107°, was obtained by evaporation and recrystallisations from methanol (Found: C, 70·5; H, 5·6; N, 11·1. $C_{15}H_{14}N_2O_2$ requires C, 70·8; H, 5·6; N, 11·0%); τ ($CDCl_3$) 2·00—2·90 (7H, m, ArH), 6·20—7·10 (4H, m, 5- and 7-H_2), and 7·59 (3H, s, N-CH_3).

Similarly reaction with benzylamine in ethanol gave 6-*benzyl*-5,7-*dihydro*-1-*nitrodibenzo*[c,e]*azepine* (95%), m.p. 119—121° (from methanol) (Found: C, 76·2; H, 5·5; N, 8·3. $C_{21}H_{18}N_2O_2$ requires C, 76·3; H, 5·5; N, 8·5%), $\lambda_{max.}$ (MeOH) 233 nm (log ε 4·33), τ ($CDCl_3$) 2·10—3·15 (12H, m, ArH) and 6·10—6·90 [6H, m, CH_2·N(CH_2Ph)·CH_2].

8,10-*Dihydro*-9-*methylazepino*[3,4,5,6-def]*carbazole*.— 5,7-Dihydro-6-methyl-1-nitrodibenzo[*c*,*e*]azepine was reductively cyclised by the general procedure. Recrystallisations of the crude product from methanol gave the *azepinocarbazole* (50%), m.p. 232—234° (Found: C, 81·4; H, 6·5; N, 12·6. $C_{15}H_{14}N_2$ requires C, 81·1; H, 6·4; N, 12·6%), $\lambda_{max.}$ (MeOH) 245, 253, 286, 296, 327, and 341 nm (log ε 4·53, 4·50, 3·94, 4·12, 3·65, and 3·69), τ ($CDCl_3$) 1·90br (1H, s, NH), 2·40—3·15 (6H, m, ArH), 5·47 (4H, s, CH_2·N·CH_2), and 7·57 (3H, s, NMe).

9-*Benzyl*-8,10-*dihydroazepino*[3,4,5,6-def]*carbazole* (77%), prepared similarly and isolated by chromatography on alumina with petroleum–ethyl acetate, had m.p. 220—222° (Found: C, 84·4; H, 6·1; N, 9·4. $C_{21}H_{18}N_2$ requires C, 84·5; H, 6·1; N, 9·4%), $\lambda_{max.}$ (MeOH) 245, 253, 296, 328, and 342 nm (log ε 4·43, 4·42, 4·02, 3·61, and 3·67), τ [$CDCl_3$–$(CD_3)_2SO$] 2·48—3·45 (11H, m, ArH), 5·50 (4H, s, CH_2·N·CH_2), 6·40 (2H, s, N·CH_2Ph), and 7·02 (1H, s, NH, some exchange with D_2O).

Diethyl 5,7-*Dihydro*-1-*nitrodibenzo*[a,c]*cycloheptene*-6,6-*dicarboxylate*.—Diethyl malonate (3·2 g) in ether (5 ml) and 2,2′-bis(bromomethyl)-6-nitrobiphenyl (7·7 g) in ether (120 ml) were added successively to sodium ethoxide solution [from sodium (0·92 g) and ethanol (20 ml)] and the mixture was stirred and heated under reflux for 4·5 h. After addition of ether (500 ml), the filtered solution was evaporated; crystallisation of the residue from ethanol gave the *diester* (5·67 g), m.p. 124—126° (Found: C, 65·3; H, 5·5; N, 3·6. $C_{21}H_{21}NO_6$ requires C, 65·8; H, 5·5; N, 3·6%), $\lambda_{max.}$ (MeOH) 241 nm (log ε 4·15), τ ($CDCl_3$) 2·33—3·05 (7H, m, ArH), 5·78 (4H, q, *J* 7 Hz, 2 CO_2·CH_2·CH_3), 6·64 and 7·01 (2H, AB pattern, *J* 13·2 Hz, 5- or 7-H_2), 6·69 and 7·25 (2H, AB pattern, *J* 13·8 Hz), and 8·71 (6H, t, *J* 7 Hz, 2 CO_2·CH_2·CH_3).

Diethyl 8,10-*Dihydrocyclohepta*[1,2,3,4-def]*carbazole*-9,9-*dicarboxylate*.—Prepared by the general procedure, followed by chromatography on alumina with ethyl acetate–petroleum, the *carbazole* (78%) had m.p. 165—166° (from benzene–petroleum (Found: C, 71·7; H, 6·2; N, 4·2. $C_{21}H_{21}NO_4$ requires C, 71·8; H, 6·0; N, 4·0%), $\lambda_{max.}$ (MeOH) 243, 292, 326, and 420 nm (log ε, 4·51, 4·00, 3·50, and 3·60), τ ($CDCl_3$) 1·98br (1H, s, NH), 2·57—3·06 (6H, m, ArH), 5·96 (4H, q, *J* 7 Hz, 2 CO_2·CH_2·CH_3), 6·17 (4H, s, 8- and 10-H_2), and 8·97 (6H, t, *J* 7 Hz, 2 CO·CH_2·CH_3).

Ethyl 8,10-*Dihydrocyclohepta*[1,2,3,4-def]*carbazole*-9-*carboxylate*.—The diethyl ester (0·35 g) was stirred at 160° with sodium cyanide (0·1 g) in dimethyl sulphoxide (20 ml) for 8 h.[18] Addition of water and isolation with ethyl acetate gave the *monoester* (0·14 g), m.p. 122—124° (from ethanol) (Found: C, 77·3; H, 6·3; N, 5·0. $C_{18}H_{17}NO_2$ requires C, 77·4; H, 6·1; N, 5·0%), τ ($CDCl_3$) 2·00br (1H, s, NH), 2·70—3·10 (6H, m, ArH), 5·82 (2H, q, *J* 7 Hz, CO_2·CH_2·CH_3), 6·4—6·8 (5H, m, CH_2·CH·CH_2), and 8·75 (3H, t, *J* 7 Hz, CO_2·CH_2·CH_3).

8,10-*Dihydrocyclohepta*[1,2,3,4-def]*carbazole*-9-*carboxylic Acid*.—The diethyl ester (0·35 g) in ethanol (30 ml) and potassium hydroxide (1 g) in water (1 ml) were heated under reflux for 1 h. After addition of water (50 ml), ethanol was removed by distillation; acidification and isolation with ether gave the crude diacid which was heated (bath at 250°) for 30 min. Crystallisation from aqueous ethanol yielded the *acid* (0·14 g), m.p. 234—237° (Found: C, 76·4; H, 5·3; N, 5·6. $C_{16}H_{13}NO_2$ requires C, 76·5; H, 5·2; N, 5·6%), τ (C_5D_5N) −2·08 (1H, s, CO_2H, exchanges with D_2O), 0·90br (1H, s, NH, exchanges with D_2O), 2·40—3·05 (6H, m, ArH), and 6·04—6·30 [5H, m, CH_2·CH(CO_2H)·CH_2, some exchange of CH·CO_2H with D_2O].

9,16-*Dihydro*-4-*nitrotribenzo*[b,f,h][1,4]*dioxecin*.— Catechol (0·11 g) in 1,2-dimethoxyethane (5 ml) was added to sodium hydride (0·1 g; 50%) in the same solvent (10 ml). The mixture was stirred for 15 min, then treated with 2,2′-bis(bromomethyl)-6-nitrobiphenyl (0·39 g) in dimethoxyethane (10 ml), heated under reflux for 6 h, cooled, and poured into water. Isolated by extraction with toluene and chromatography on alumina in petroleum–ethyl acetate, the *dioxecin* (80 mg) was dried at 40° and 0·5 mmHg but remained partially hydrated. It had m.p. 88—91° (Found: C, 69·2; H, 5·0; N, 3·8. $C_{20}H_{15}NO_4$,0·67H_2O requires C, 69·6; H, 4·7; N, 4·1%), $\nu_{max.}$ 3500—3250w,br cm^{-1} (bonded OH), τ ($CDCl_3$) 2·10—3·30 (11H, m, ArH), 4·70—5·44 (4H, m, 9- and 16-H_2), and 8·50 (1·3H, s, H_2O, exchanged by D_2O).

10-*Nitrodibenzo*[b,d]*pyran*-6-*one*.—6-Nitrodiphenic acid (7·2 g), lead tetra-acetate (16·6 g), pyridine (6 ml), and acetonitrile (50 ml) were heated at 120° and stirred vigorously until evolution of carbon dioxide ceased.[21] The mixture was extracted with benzene (7 × 300 ml) and the combined extracts were washed with 2N-hydrochloric acid and water. Evaporation and crystallisation from methanol gave the *pyranone* (1·43 g) (Found: C, 64·7; H, 3·1; N, 5·8. $C_{13}H_7NO_4$ requires C, 64·7; H, 2·9; N, 5·8%), $\lambda_{max.}$ 317 nm (log ε 3·60), τ ($CDCl_3$) 1·45 (1H dd, J_{ortho} 7, J_{meta} 2 Hz, 9-H), and 2·05—2·95 (6H, m, other ArH). Oxidation of the lactone with potassium permanganate in refluxing sodium hydroxide solution gave, on acidification, 3-nitrophthalic acid, identified by t.l.c. in methanol.

When the nitro-lactone was heated with triphenylphosphine in cumene, according to the general procedure for cyclisation, chromatography on alumina with petroleum–ethyl acetate yielded only 6-*oxodibenzo*[b,f]*pyran*-10-*yliminotriphenylphosphorane* (0·24 g), m.p. 222—224° (Found: C, 79·6; H, 4·8; N, 3·0. $C_{32}H_{22}NO_2P$ requires C, 79·4; H, 4·7; N, 3·0%).

1-*Benzamido*-5,7-*dihydrodibenzo*[c,e]*thiepin*.— 5,7-Dihydro-1-nitrodibenzo[*c,e*]thiepin (2·57 g) was added to a stirred solution of tin(II) chloride dihydrate (7·8 g) in concentrated hydrochloric acid (20 ml) at 5°. The mixture was stirred and heated (steam-bath) for 1·5 h, cooled, and filtered. The complex was washed with water and decomposed by boiling with 10N-potassium hydroxide (5 ml) and methanol (10 ml) for 10 min. Addition of water and isolation with ether gave the oily amine, which was shaken with benzoyl chloride, ether, and 2N-sodium hydroxide to form the *benzamido-compound* (2·03 g), m.p. 186—188° (from ethanol) (Found: C, 76·6; H, 5·2; N, 4·0. $C_{21}H_{17}NOS$ requires C, 76·1; H, 5·2; N, 4·2%), $\lambda_{max.}$ 246 nm (log ε 4·40), τ ($CDCl_3$) 1·50 (1H, dd, J_{ortho} 8, J_{meta} 2 Hz, 2-H), 1·94 (1H, s, NH), 2·28—2·92 (11H, m, ArH), and 6·35—6·80 (4H, m, $CH_2{\cdot}S{\cdot}CH_2$).

6,8-*Dihydro*-2-*phenylthiepino*[3,4,5,6-lmn]*phenanthridine*.—The amide (1·99 g) was added over 10 min to stirred, freshly-prepared polyphosphoric acid (120 g) at 170—180°. Heating and stirring were continued for 1 h and the slightly-cooled mixture was then added to ice–water (300 g). Basification, filtration, and crystallisations from ethanol gave the *thiepinophenanthridine* (0·97 g), m.p. 230—232° (Found: C, 80·3; H, 4·8; N, 4·2. $C_{21}H_{15}NS$ requires C, 80·5; H, 4·8; N, 4·5%), $\lambda_{max.}$ (MeOH) 222, 253, and 360—369 nm (log ε 4·53, 4·51, and 3·41), τ ($CDCl_3$) 1·80—2·75 (12H, m, ArH), 6·11 (2H, s, 8-H_2), and 6·15 (2H, s, 6-H_2).

1-*Benzamido*-5,7-*dihydrodibenzo*[c,e]*oxepin*.—The nitrodibenzo-oxepin (241 mg) in ethanol (50 ml) was hydrogenated over Raney nickel (W2) [30] until absorption ceased. Filtration, evaporation, and benzoylation as above, gave the *benzamido-compound* (280 mg), m.p. 147—148° (from ethanol) (Found: C, 79·8; H, 5·3; N, 4·4. $C_{21}H_{17}NO_2$ requires C, 80·0; H, 5·4; N, 4·4%), $\lambda_{max.}$ 230—238 nm (log ε 4·36), τ ($CDCl_3$) 1·48 (1H, dd, J_{ortho} 7, J_{meta} 2 Hz, 2-H), 1·76br (1H, s, NH), 2·20—2·88 (11H, m, other ArH), 5·63 (2H, q, J 11 Hz, δ_{AB} 24 Hz, geminal coupling, 5-H_2), and 5·75 (2H, q, J 11 Hz δ_{AB} 32 Hz, 7-H_2).

Similar reduction and benzoylation of 5,7-dihydro-6-methyl-1-nitrodibenzo[*c,e*]azepine gave 1-*benzamido*-5,7-*dihydro*-6-*methyldibenzo*[c,e]*azepine* as the *benzoate salt*, m.p. 176—178° (from ethyl acetate) (Found: C, 77·3; H, 5·8; N, 6·2. $C_{29}H_{26}N_2O_3$ requires C, 77·3; H, 5·8; N, 6·2%), τ ($CDCl_3$) 1·22 (1H, s, NH^+, exchanges with D_2O), 1·52 (1H, dd, J_{ortho} 8, J_{meta} 2 Hz, 2-H), 1·80—2·80 (12H, m, other ArH and amide NH which exchanges with D_2O), 5·92—6·75 (4H, m, 5- and 7-H_2), and 7·40 (3H, s, NMe).

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