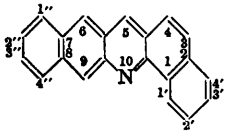
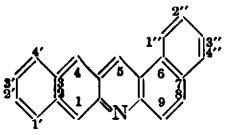
658. *Carcinogenic Nitrogen Compounds. Part IX.* The Use of Aminotetralins for the Synthesis of Dibenzacridines and Related Compounds.*

By Ng. Ph. Buu-Hoï and Pierre Jacquignon.

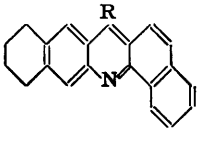
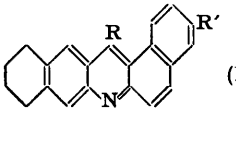
The use is described of 5 : 6 : 7 : 8-tetrahydro-2-naphthylamine for the synthesis of some 1 : 2-7 : 8- and 3 : 4-7 : 8-dibenzacridines; 3-ethyl-5 : 6 : 7 : 8-tetrahydro-2-naphthylamine has similarly been applied to the preparation of 9-ethyl-1 : 2-6 : 7- and 1-ethyl-3 : 4-6 : 7-dibenzacridine. In addition to these acridines, various other polycyclic nitrogenous compounds have been prepared for biological investigation.

1 : 2-6 : 7- and 3 : 4-6 : 7-Dibenzacridine have repeatedly been found carcinogenic both on skin painting and on subcutaneous injection (Barry, Cook, Haslewood, Hewett, and Kennaway, *Proc. Roy. Soc.*, 1935, *B*, **117**, 318; Badger, Cook, Hewett, Kennaway, Martin, and Robinson, *ibid.*, 1940, *B*, **129**, 439; Rondoni and Corbellini, *Tumori*, 1936, **10**, 106). Some homologues of these two dibenzacridines are similarly active (Lacassagne, Buu-Hoï, Lecocq, and Rudali, *Bull. Cancer*, 1946, **33**, 48), and 1 : 2-8 : 9-dibenzacridine is now under test in this Institute. It was also deemed of interest to investigate the activity of the two remaining angular dibenzacridines,

(I)   (II)

the 1 : 2-7 : 8- and the 2 : 3-6 : 7- isomers (I) and (II). Of these two aza-derivatives of 1 : 2-benzotetracene, the former was unknown, and the latter had been prepared by Strohbach (*Ber.*, 1901, **34**, 3157) by distillation of the corresponding acridone with zinc.

We have now found that 5 : 6 : 7 : 8-tetrahydro-2-naphthylamine readily underwent Ullmann–Fetvadjian reactions (*Ber.*, 1903, **36**, 1029) with paraformaldehyde and both α- and β-naphthol, to give 1″ : 2″ : 3″ : 4″-tetrahydro-1 : 2-7 : 8- (III; R = H) and 1′ : 2′ : 3′ : 4′-tetrahydro-2 : 3-6 : 7-dibenzacridine (IV; R = R′ = H) respectively; 6-*tert.*-butyl-2-naphthol led to 2″-*tert.*-butyl-1′ : 2′ : 3′ : 4′-tetrahydro-2 : 3-6 : 7-dibenzacridine (IV; R = H, R′ = Bu^t). Dehydrogenation of the first two compounds to 1 : 2-7 : 8- and 2 : 3-6 : 7-dibenzacridine was

(III)   (IV)

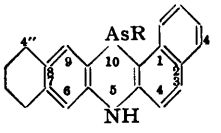
successfully effected with selenium; this showed the high degree of stability of the acridine nucleus, for in most of the reported cases of selenium dehydrogenation of nitrogen-containing heterocyclic compounds, widespread destruction of the molecular structure ensued (see, for instance, Rössner, *Z. physiol. Chem.*, 1937, **249**, 267). Had the Ullmann–Fetvadjian reactions with 5 : 6 : 7 : 8-tetrahydro-2-naphthylamine taken an angular course, the known 1 : 2-6 : 7- and 2 : 3-5 : 6-dibenzacridines would have been obtained. The linear cyclisation is parallel to the preferential formation of 6 : 7-*cyclo*hexenoquinoline in the Skraup reaction (von Braun and Gruber, *Ber.*, 1922, **55**, 1713), and to the Friedel–Crafts chloroacetylation of aceto-5 : 6 : 7 : 8-tetrahydro-2-naphthalide which occurred at position 7 (Schofield, Swain, and Theobald, *J.*, 1949, 2399).

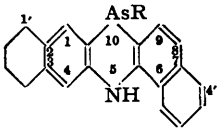
5 : 6 : 7 : 8-Tetrahydro-2-naphthylamine readily gave Knoevenagel reactions with α- and β-naphthol in the presence of iodine, giving *N*-(5 : 6 : 7 : 8-tetrahydro-2-naphthyl)-α- and β-naphthylamine respectively. These secondary amines underwent modified Bernthsen reactions (see Buu-Hoï, *J.*, 1950, 1146) with acetic anhydride, to yield (III; R = Me) and (IV; R = Me, R′ = H), and similar compounds were obtained with propionic anhydride. These substances could be considered as belonging to the trialkyl-1 : 2- and -3 : 4-benzacridine class, in which many carcinogenic representatives have already been found (Zajdela and Buu-Hoï, *Acta Unio Intern. contra Cancrum*, 1950, **7**, 184).

The ability of certain polycyclic arsines to give transient tumours on skin painting (Visser and

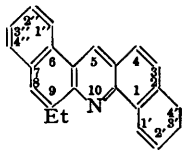
* Part VIII, *J.*, 1951, 2871.

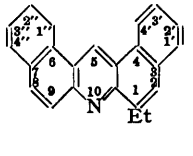
ten Seldam, *Geneesk. Tijdschr. Nederl.-Indië*, 1938, **78**, 3280; Buu-Hoï and Royer, *J.*, 1951, 795) led us to synthesise 10-chloro-5 : 10 : 1″ : 2″ : 3″ : 4″-hexahydro-1 : 2-7 : 8- (V; R = Cl) and -5 : 10 : 1′ : 2′ : 3′ : 4′-hexahydro-2 : 3-6 : 7-dibenzophenarsazine (VI; R = Cl) from arsenic trichloride and the two above-mentioned *N*-tetralylnaphthylamines in the usual way (Burton and Gibson, *J.*, 1926, 2243; Buu-Hoï and Royer, *loc. cit.*). The action of methyl- and ethyl-magnesium iodides on these orange-yellow, sternutatory chloroarsines led to the corresponding colourless, non-irritant 10-alkyl-5 : 10 : 1″ : 2″ : 3″ : 4″-hexahydro-1 : 2-7 : 8- (V; R = Me or Et) and -5 : 10 : 1′ : 2′ : 3′ : 4′-hexahydro-2 : 3-6 : 7-dibenzophenarsazines (VI; R = Me or Et).

(V) 

 (VI)

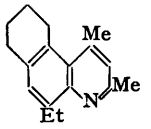
The 5 : 6 : 7 : 8-tetrahydro-2-naphthylamine used in this work was conveniently prepared from tetralin by Friedel–Crafts acetylation, and Beckmann rearrangement of 6-acetyltetralin oxime. It was found that a similar sequence of reactions, starting from 7-ethyltetralin, readily yielded 3-ethyl-5 : 6 : 7 : 8-tetrahydro-2-naphthylamine *via* 6-acetyl-7-ethyltetralin. The fact that Friedel–Crafts acetylation of 7-ethyltetralin involved position 6 and not position 8 was proved by the ability of the parent amine to undergo cyclisation reactions, and is also in accord with similar cases reported in the literature (Fleischer and Siefert, *Ber.*, 1920, **53**, 1259; Schroeter, *Annalen*, 1922, **426**, 66). 3-Ethyl-5 : 6 : 7 : 8-tetrahydro-2-naphthylamine was found a convenient intermediate for the synthesis of homologues of the bisangular 1 : 2-6 : 7- and 3 : 4-6 : 7-dibenzacridine. The Ullmann–Fetvadjian reaction with α- and β-naphthol gave 9-ethyl-1″ : 2″ : 3″ : 4″-tetrahydro-1 : 2-6 : 7- and 1-ethyl-1′ : 2′ : 3′ : 4′-tetrahydro-3 : 4-6 : 7-dibenzacridine respectively; dehydrogenation of these to 9-ethyl-1 : 2-6 : 7- (VII) and 1-ethyl-3 : 4-

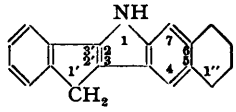
(VII) 

 (VIII)

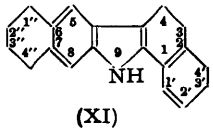
6 : 7-dibenzacridine (VIII) could, surprisingly, be effected by selenium without the loss of the ethyl group, which in both instances is linked to a "*meso*-phenanthrene" carbon atom. It was previously known that alkyl groups located on regions of high π-electron density are easily removed in high-temperature reactions (see, *e.g.*, Fieser, "Organic Reactions," 1942, Vol. I, 129).

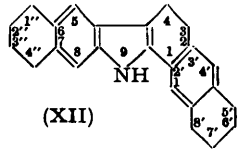
Several other nitrogenous heterocyclic compounds were prepared from 5 : 6 : 7 : 8-tetrahydro-2-naphthylamine and its 3-ethyl derivative, for biological testing. Knorr–Paal condensation (Knorr, *Ber.*, 1885, **18**, 2254) with acetonylacetone gave 2 : 5-dimethyl-1-2′-tetralylpyrroles. Combes's reaction (*Compt. rend.*, 1886, **106**, 1536) between acetylacetone and the ethyl-amine yielded (IX); 5 : 6 : 7 : 8-tetrahydro-2-naphthylamine gave a liquid product,

(IX) 

 (X)

probably a mixture of the two possible isomers (cf. Lindner, Djulgerowa, and Mayer, *Monatsh.*, 1923, **44**, 340). Finally, it was found that 5 : 6 : 7 : 8-tetrahydro-2-naphthylhydrazones of cyclic ketones readily underwent Fischer–Borsche cyclisation; from indan-1-one was thus


(XI)


(XII)

obtained 1″ : 2″ : 3″ : 4″-tetrahydro-5 : 6-benzindeno(3′ : 2′-2 : 3)indole (X); from 1-tetralone, 3 : 4 : 1″ : 2″ : 3″ : 4″-hexahydro-1 : 2-6 : 7-dibenzocarbazole (XI); and from 1-keto-

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene (Kroffpfeiffer and Schäfer, *Ber.*, 1923, **56**, 620), 3 : 4 : 5′ : 6′ : 7′ : 8′ : 1″ : 2″ : 3″ : 4″-decahydro-6 - 7-benzonaphtho(2′ : 3′-1 : 2)carbazole (XII). There was no rigid proof here for linear cyclisation, but this was made probable by the high melting points of the products and by the evidence given above for the acridine cyclisations.

Experimental.

Preparation of 5 : 6 : 7 : 8-*Tetrahydro-2-naphthylamine.*—6-Acetyltetralin (220 g.; b. p. 180°/19 mm.) was obtained from tetralin (270 g.), acetyl chloride (165 g.), and aluminium chloride (325 g.) in carbon disulphide in the usual way, the reaction mixture being kept at room temperature for only 6 hours to avoid side-condensations. Beckmann rearrangement of 6-acetyltetralin oxime (85 g.; m. p. 106°) was performed (at variance with the MacLeish and Campbell, *J.*, 1937, 1107; see also Schofield, Swain, and Theobald, *loc. cit.*) with phosphorus pentachloride (112 g.) at 0° in anhydrous ether. The reaction was instantaneous and gave a 98% yield of aceto-5 : 6 : 7 : 8-tetrahydro-2-naphthalide, b. p. 244°/19 mm., m. p. 106°. The *toluene*-p-*sulphonyl* derivative of the free amine, prepared in pyridine, formed from ethanol large leaflets, m. p. 137° (Found: N, 4·5. $C_{17}H_{19}O_2NS$ requires N, 4·6%); the *N-acetylsulphanilyl* derivative, similarly prepared, formed from ethanol shiny needles, m. p. 216° (Found: N, 8·1. $C_{18}H_{20}O_3N_2S$ requires N, 8·1%).

6-*Acetyl*-7-*ethyltetralin.*—6-Ethyltetralin (70 g.; b. p. 239°) prepared from 6-acetyltetralin (100 g.) (cf. Huang-Minlon, *loc. cit.*). It (100 g.) was acetylated with acetyl chloride (50 g.) and aluminium chloride (100 g.) in carbon disulphide, as for tetralin; the *ketone* was a pale yellow oil, b. p. 188°/17 mm. (Found: C, 83·0; H, 9·1. $C_{14}H_{18}O$ requires C, 83·1; H, 8·9%). The *semicarbazone* formed silky needles, m. p. 134—135°, from ethanol (Found: C, 69·1; H, 8·0. $C_{15}H_{21}ON_3$ requires C, 69·5; H, 8·1%), the *thiosemicarbazone* microscopic needles, m. p. 123°, from methanol (Found: C, 65·8; H, 7·8. $C_{15}H_{21}N_3S$ requires C, 65·5; H, 7·6%), and the *oxime* fine needles, m. p. 128°, from methanol (Found: N, 6·2. $C_{14}H_{19}ON$ requires N, 6·4%).

3-*Ethyl*-5 : 6 : 7 : 8-*tetrahydro-2-naphthylamine.*—Beckmann rearrangement of the foregoing oxime (33 g.) by means of phosphorus pentachloride (30 g.) in ether (80 c.c.) gave *acet*-3-*ethyl*-5 : 6 : 7 : 8-*tetrahydro-2-naphthalide* (32·5 g.), crystallising from ethanol in fine needles, m. p. 166° (Found: N, 6·3. $C_{14}H_{19}ON$ requires N, 6·4%). A suspension of this amide (32 g.) in hydrochloric acid (100 c.c.) was refluxed for 30 minutes; after cooling, the solid amine hydrochloride (m. p. 147° after recrystallisation from water) gave on basification the free *amine* (20 g.) as a pale yellow viscous oil, b. p. 175°/16 mm. (Found: C, 82·3; H, 9·9. $C_{12}H_{17}N$ requires C, 82·3; H, 9·7%). Its *toluene*-p-*sulphonyl* derivative formed leaflets, m. p. 130°, from ethanol (Found: N, 4·3. $C_{19}H_{23}O_2NS$ requires N, 4·4%). Its *N*-acetylsulphanilyl derivative formed shiny needles, m. p. 201°.

1″ : 2″ : 3″ : 4″-*Tetrahydro*-1 : 2-7 : 8-*dibenzacridine* (III; R = H).—To a boiling mixture of 5 : 6 : 7 : 8-tetrahydro-2-naphthylamine (5 g.) and α-naphthol (5 g.), paraformaldehyde (0·75 g.) was added in small portions; the reaction mixture was subsequently boiled for some minutes and then fractionated in a vacuum. The portion boiling at 340—345°/18 mm. (2 g.) gave, after repeated crystallisation from a mixture of ethanol and benzene, fine pale yellow needles, m. p. 118° (Found: C, 88·8; H, 6·1. $C_{21}H_{17}N$ requires C, 89·0% H, 6·0%). The picrate formed from nitrobenzene shiny orange-red prisms, m. p. 257° (decomp. >232°).

1 : 2-7 : 8-*Dibenzacridine* (I).—The foregoing tetrahydro-compound (0·5 g.) was heated with selenium powder (0·3 g.) at 350° for 3 hours. After cooling, the reaction product was extracted several times with ethanol; the residue (0·4 g.) left on evaporation gave, on repeated recrystallisation from ethanol, fine pale yellow needles, m. p. 129° (Found: C, 89·7; H, 4·6. $C_{21}H_{13}N$ requires C, 90·0; H, 4·6%). The picrate formed from nitrobenzene brick-red needles, m. p. 266° (decomp. >242°).

1′ : 2′ : 3′ : 4′-*Tetrahydro*-2 : 3-6 : 7-*dibenzacridine* (IV; R = R′ = H).—Obtained similarly from β-naphthol, the portion of the product boiling at 340—345°/17 mm. (4 g.) gave, after repeated recrystallisation from ethanol and benzene, fine pale yellow prisms, m. p. 145°, giving with sulphuric acid a deep yellow colour as did the isomer (III) (Found: C, 88·6; H, 6·0. $C_{21}H_{17}N$ requires C, 89·0; H, 6·0%).

2 : 3-5 : 7-*Dibenzacridine* (II).—Formed from ethanol in fine yellow prisms, m. p. 209° (lit., m. p. 206°), this gave with sulphuric acid a vermilion colour (Found: C, 89·7; H, 4·6. Calc. for $C_{21}H_{13}N$: C, 90·0; H, 4·6%). The picrate formed orange-red needles, m. p. 295° (decomp. >266°), from nitrobenzene.

3′-tert.-*Butyl*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2 : 3-6 : 7-*dibenzacridine.*—Obtained in the usual way from the amine (2 g.), 6-*tert.*-butyl-2-naphthol (Buu-Hoï *et al.*, *J. Org. Chem.*, 1950, **15**, 1060) (2·2 g.), and paraformaldehyde (0·5 g.), the portion of the product boiling at 350—355°/17 mm. (3 g.) was transformed into a picrate which crystallised from benzene in fine shiny orange needles, decomposing at >231—232°. Treatment with aqueous ammonia gave the free *acridine* which formed pale yellow needles, m. p. 128°, from ethanol (Found: C, 88·2; H, 7·3. $C_{25}H_{25}N$ requires C, 88·6; H, 7·4%).

N-(5 : 6 : 7 : 8-*Tetrahydro-2-naphthyl*)-α-*naphthylamine.*—α-Naphthol (12·5 g.), 5 : 6 : 7 : 8-tetrahydro-2-naphthylamine (7·5 g.), and iodine (0·1 g.) were heated for 5 hours at 240—245°. The reaction mixture gave, on fractionation in a vacuum, the secondary *amine* as a yellow viscous oil (12 g.) b. p. 285—290°/16 mm. (Found: N, 5·0. $C_{20}H_{19}N$ requires N, 5·1%).

The β-*isomer*, obtained as above from β-naphthol (25 g.), had b. p. 304—305°/16 mm., and crystallised from ethanol in colourless needles, m. p. 96° (Found: N, 4·9%).

1″ : 2″ : 3″ : 4″-*Tetrahydro*-5-*methyl*-1 : 2-7 : 8-*dibenzacridine* (III; R = Me).—The foregoing secondary α-amine (2 g.), acetic anhydride (2 g.), and fused zinc chloride (2 g.) was heated at 180—190° for 6 hours; the product was treated with hot aqueous sodium hydroxide, and the *acridine* taken up in toluene. The toluene solution was dried (Na_2SO_4), the solvent removed, and the residue distilled in a vacuum.

The portion boiling at 340—350°/16 mm. (1·5 g.) was transformed into a picrate, crystallising from toluene in orange-yellow needles, m.p. 251°. Decomposition of the picrate with ammonia yielded the free *base* which formed pale yellow prisms, m. p. 130°, from ethanol (Found : C, 88·4; H, 6·3. $C_{22}H_{19}N$ requires C, 88·8; H, 6·4%).

5-*Ethyl*-1'' : 2'' : 3'' : 4''-*tetrahydro*-1 : 2-7 : 8-*dibenzacridine* (III; R = Et).—Similarly obtained with propionic anhydride (2 g.), this compound formed an orange-yellow picrate (from toluene), m. p. 223° (decomp. at >200°); the free *acridine* crystallised from ethanol in yellowish silky needles, m. p. 114° (Found : C, 88·4; H, 6·6. $C_{23}H_{21}N$ requires C, 88·7; H, 6·7%).

1' : 2' : 3' : 4'-*Tetrahydro*-5-*methyl*-2 : 3-6 : 7-*dibenzacridine* (IV; R = Me, R' = H).—The reactants were *N*-5 : 6 : 7 : 8-tetrahydro-2-naphthyl-β-naphthylamine (5 g.), acetic anhydride (5 g.), and zinc chloride (5 g.); the portion of the product boiling at 335—360°/16 mm. (3 g.) gave a picrate crystallising from nitrobenzene in fine brownish-red prisms, m. p. 272—273° (decomp. at >240°); the free *acridine* formed fine pale yellow prisms, m. p. 166°, from ethanol (Found : C, 88·4; H, 6·2%). The 5-*ethyl* homologue (IV; R = Et, R' = H) gave a picrate, shiny brick-red leaflets (from nitrobenzene), m. p. 253° (decomp. at >236—240°), and crystallised from ethanol in pale yellow needles, m. p. 171° (Found : C, 88·5; H, 6·5%).

10-*Chloro*-5 : 10 : 1' : 2' : 3' : 4'-*hexahydro*-2 : 3-6 : 7-*dibenzophenarsazine* (VI; R = Cl).—A solution of *N*-5 : 6 : 7 : 8-tetrahydro-2-naphthyl-α-naphthylamine (4 g.) and arsenic trichloride (2 g.) in *o*-dichlorobenzene (20 c.c.) was gently refluxed for 2 hours. After cooling, the precipitated *chlorophenarsazine* (3·7g.) was collected and washed with benzene; it crystallised from toluene in orange-yellow needles, m. p. 264° (decomp. at >256°), giving with sulphuric acid a blood-red colour (Found : C, 62·5; H, 4·2. $C_{20}H_{17}NClAs$ requires C, 62·9; H, 4·4%).

5 : 10 : 1' : 2' : 3' : 4'-*Hexahydro*-10-*methyl*-2 : 3-6 : 7-*dibenzophenarsazine* (VI; R = Me).—The foregoing chloro-compound (0·5 g.) was added in small portions to an ethereal solution of a Grignard reagent (from methyl iodide, 0·5 g.). After 15 minutes' refluxing on a water-bath, the reaction mixture was treated with an ice-cooled aqueous ammonium chloride, and the ethereal solution washed with water and dried (Na_2SO_4). After evaporation of the solvent, the residue crystallised from methanol, giving fine colourless prisms (0·3 g.), m. p. 226° (Found : C, 69·3; H, 5·4. $C_{21}H_{20}NAs$ requires C, 69·8; H, 5·5%). The 10-*ethyl* homologue (VI; R = Et), similarly prepared with ethylmagnesium iodide, formed from methanol colourless needles, m. p. 157°, giving an orange colour with sulphuric acid (Found : C, 70·0; H, 5·7. $C_{22}H_{22}NAs$ requires C, 70·4; H, 5·8%).

10-*Chloro*-5 : 10 : 1'' : 2'' : 3'' : 4''-*hexahydro*-2 : 3-6 : 7-*dibenzophenarsazine* (V; R = Cl).—Prepared from *N*-(5 : 6 : 7 : 8-tetrahydro-2-naphthyl)-β-naphthylamine (4 g.), as was the isomer, the *chloroarsine* formed fine orange-yellow needles (3·7 g.) (from toluene), m. p. 260° (decomp. at >252°), giving with sulphuric acid a brown-red colour (Found : C, 62·6; H, 4·1%).

5 : 10 : 1'' : 2'' : 3'' : 4''-*Hexahydro*-10-*methyl*-2 : 3-6 : 7-*dibenzophenarsazine* (V; R = Me).—This *methylarsine* formed colourless prisms (0·3 g.), m. p. 200°, from methanol, and gave with sulphuric acid an orange colour (Found : C, 69·2; H, 5·4%). The 10-*ethyl* homologue crystallised from ligroin in fine shiny needles, m. p. 146° (Found : C, 70·0; H, 5·8%).

9-*Ethyl*-1'' : 2'' : 3'' : 4''-*tetrahydro*-1 : 2-6 : 7-*dibenzacridine*.—The portion, b. p. 340—345°/17 mm., of the product obtained from α-naphthol (4 g.), 3-ethyl-5 : 6-7 : 8-tetrahydro-2-naphthylamine (4 g.), and paraformaldehyde (0·75 g.) gave this *acridine* as shiny pale greenish-yellow needles, m. p. 132° (from ethanol) (Found : C, 88·5; H, 6·6. $C_{23}H_{21}N$ requires C, 88·7; H, 6·7%). The picrate formed orange-red needles, m. p. 173°, from toluene; such a low m. p. is characteristic of the picrates of 1 : 2-benzacridines bearing an alkyl substituent at position 9 (cf. Buu-Hoï, *J.*, 1949, 670; 1950, 1146).

9-*Ethyl*-1 : 2-6 : 7-*dibenzacridine* (VII).—Obtained from the foregoing tetrahydro-compound (0·4 g.) with selenium powder (0·3 g.) at 350° for 3 hours, this *compound* formed fine pale yellow needles, m. p. 110°, from ethanol and gave with sulphuric acid a yellow colour (Found : C, 89·2; H, 5·5. $C_{23}H_{17}N$ requires C, 89·8; H, 5·5%). The picrate formed light orange needles (from nitrobenzene), m. p. 256° (decomp. at >232°).

1-*Ethyl*-1' : 2' : 3' : 4'-*tetrahydro*-3 : 4-6 : 7-*dibenzacridine*.—Obtained from β-naphthol (3 g.), the ethyl-amine (3 g.), and paraformaldehyde (0·6 g.), this *isomer* formed fine yellowish needles (from ethanol), m. p. 140°, giving with sulphuric acid an orange-yellow colour (Found : C, 88·9; H, 6·5%). The picrate formed from nitrobenzene orange leaflets, m. p. 289°.

3''-tert.-*Butyl*-1' : 2 : 3' : 4'-*tetrahydro*-3 : 4-6 : 7-*dibenzacridine*.—Prepared from 6-*tert*.-butyl-2-naphthol (2 g.), the ethyl-amine (2 g.), and paraformaldehyde (0·5 g.), by way of a picrate, orange-yellow leaflets (from ethanol), m. p. 257—258° (decomp. at >232°), the *butyl* derivative crystallised from ethanol in fine yellowish needles, m. p. 154° (Found : C, 88·0; H, 7·7. $C_{27}H_{29}N$ requires C, 88·3; H, 7·9%).

1-*Ethyl*-3 : 4-6 : 7-*dibenzacridine* (VIII).—The corresponding tetrahydro-compound (0·5 g.) and selenium powder (0·3 g.) gave this *compound* as fine pale yellow needles (0·3 g.) (from ethanol), m. p. 158° (Found : C, 89·3; H, 5·4%). The picrate formed yellow leaflets, m. p. 276°, from ethanol.

2 : 5-*Dimethyl*-1-(5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl*)*pyrrole*.—5 : 6 : 7 : 8-Tetrahydro-2-naphthylamine (5 g.), acetonylacetone (5 g.), and acetic acid (3 drops) were heated for 16 hours at 170—180°, and the reaction product fractionated in a vacuum. The *pyrrole* (5 g.) was a pale yellow oil, b. p. 200—202°/16 mm., $n^{21\cdot5}$ 1·5790, giving a positive reaction in the pinewood test (Found : C, 85·2; H, 8·5. $C_{16}H_{19}N$ requires C, 85·3; H, 8·4%).

2 : 5-*Dimethyl*-1-(3-*ethyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl*)*pyrrole* (5 g.) formed a viscous pale yellow oil, b. p. 215—216°/17 mm. (Found : C, 85·2; H, 9·0. $C_{18}H_{23}N$ requires C, 85·4; H, 9·1%).

8-*Ethyl*-1' : 2' : 3' : 4'-*tetrahydro*-2 : 4-*dimethyl*-5 : 6-*benzoquinoline* (IX).—3-Ethyl-5 : 6 : 7 : 8-tetrahydro-2-naphthylamine (2 g.) and acetylacetone (2 g.) were refluxed for 2 hours; sulphuric acid (12 c.c.)

was added to the cold mixture, and the whole heated on a water-bath for 1 hour, poured on ice, and basified with aqueous ammonia. The reaction product was taken up in ether and yielded, on vacuum-fractionation in a vacuum, an oil (1·8 g.), b. p. 210—212°/16 mm., which solidified, then formed from light petroleum (b. p. 60—80°) prisms, m. p. 50° (Found: C, 85·0; H, 9·0. $C_{17}H_{21}N$ requires C, 85·3; H, 8·8%). Its picrate formed shiny yellow needles, m. p. 97°, from ethanol.

This reaction similarly yielded 1′ : 2′ : 3′ : 4′-*tetrahydro*-5 : 6-*benzoquinoline* as a pale yellow oil, b. p. 214—216°/17 mm., $n^{21·5}$ 1·6125 (Found: N, 6·5. $C_{15}H_{17}N$ requires N, 6·6%). This material did not solidify on prolonged storage in the refrigerator, but a yellow picrate, m. p. 223—224°, could be prepared.

1″ : 2″ : 3″ : 4″-*Tetrahydro*-5 : 6-*benzindeno*(3′ : 2′-2 : 3)*indole* (X).—5 : 6 : 7 : 8-Tetrahydro-2-naphthylhydrazine hydrochloride was prepared by reduction of the appropriate diazo-compound (from the base, 5 g.) with stannous chloride (25 g.) in hydrochloric acid. A solution of this (1 g.), indan-1-one (1 g.), and sodium acetate (1 g.) in ethanol (20 c.c.) was refluxed for 1 hour, and the crude hydrazone precipitated on dilution with water was heated for a few seconds with a solution of hydrogen chloride in acetic acid. The *indole* obtained on dilution with water formed colourless needles (1 g.), m. p. 297°, from ethanol (Found: C, 87·9; H, 6·4. $C_{19}H_{17}N$ requires C, 88·0; H, 6·5%).

3 : 4 : 1″ : 2″ : 3″ : 4″-*Hexahydro*-1 : 2-6 : 7-*dibenzocarbazole* (XI).—Prepared as above from the hydrazine hydrochloride (1 g.) and 1-tetralone (1 g.), this *compound* formed fine colourless prisms (1·2 g.) (from ethanol), m. p. 190° (Found: C, 87·6; H, 6·6. $C_{20}H_{19}N$ requires C, 87·9; H, 6·9%). The picrate formed brown-violet leaflets, m. p. 175°, from ethanol.

3 : 4 : 5′ : 6′ : 7′ : 8′ : 1″ : 2″ : 3″ : 4″-*Decahydro*-6 : 7-*benzonaphtho*(2′ : 3′-1 : 2)*carbazole* (XII).—Prepared from 1-keto-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene (1 g.) and the hydrazine hydrochloride (1 g.), this hexacyclic compound formed fine colourless prisms (1·5 g.) (from ligroin), m. p. 208° (Found: C, 87·9; H, 7·3. $C_{24}H_{25}N$ requires C, 88·0; H, 7·6%). The picrate formed deep violet needles, m. p. 203°, from ethanol.

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