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The Chemotherapy of Tuberculosis. Part V.

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The Chemotherapy of Tuberculosis. Part V. Some
5-Amino-benzacridines and -dibenzacridines.*

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5-Amino-9-methyl-1:2- and -3:4-benzacridine, and 5-amino-1:2-8:9- and -2:3-6:7-dibenzacridine have been synthesised from the corresponding acridones, obtained by the Chapman rearrangement and simultaneous thermal cyclisation of 2-methoxycarbonyl-1-aryl *N*-aryl-benzimidates. Attempted preparation of 1:2-3:4-8:9-tribenzacridone failed. Reduction of 9-methyl-1:2-benzacridone by sodium in pentyl alcohol gave 1':2':3':4'-tetrahydro-9-methyl-1:2-benzacridine. The basic strengths of the aminoacridines have been determined.

THE preparation of 5-amino-9-methyl-1:2- and -3:4-benzacridine was undertaken to supply strong bases with large planar surface areas, required for work on the relation between physicochemical properties and antituberculous activity.

• Part IV, *J.*, 1953, 1490.

9-Methyl-1 : 2-benzacridone has been obtained previously (Reed, *J.*, 1945, 186) in low yield. Attempted Jourdan-Ullmann reaction of 1-bromo-2-naphthoic acid and *o*-toluidine caused reductive debromination to 2-naphthoic acid (cf. Acheson and Robinson, *J.*, 1953, 232). Preparation of 1-chloro-2-naphthoic acid from 1-hydroxy-2-naphthoic acid (Strohbach, *Ber.*, 1901, 34, 4158; Cairns and Kermack, *J.*, 1950, 1323) gave poor yields and this route was abandoned.

The Chapman rearrangement (*J.*, 1927, 1743) has been used for the preparation of acridones by Jamison and Turner (*J.*, 1937, 1954) who report one instance of direct thermal cyclisation of the *N*-benzoyl-2-methoxycarbonyldiphenylamine (with loss of methyl benzoate) to give the acridone. This direct synthesis has now been extended to benz- and dibenz-acridones.

Condensation of *N*- α -naphthylbenzimidoyl chloride with the sodium salt of methyl 2-hydroxy-6-methylbenzoate gave 6-methoxycarbonyl-2-methylphenyl *N*- α -naphthylbenzimidate (I) which rearranged and cyclised smoothly to 9-methyl-1 : 2-benzacridone (II). In the conversion of this into 5-chloro-9-methyl-1 : 2-benzacridine the use of chloroform and ice in the final hydrolysis (Bachman and Picha, *J. Amer. Chem. Soc.*, 1946, 68, 1599) was found unnecessary, the chloroacridine being stable (Albert, "The Acridines," Arnold and Co., London, 1951, p. 26). Amination then gave 5-amino-9-methyl-1 : 2-benzacridine after 1.5 hours; reaction for half this time furnished much of the 5-phenoxy-compound, a known intermediate in this reaction (Dupre and Robinson, *J.*, 1945, 549; Albert, Brown, and Duewell, *J.*, 1948, 1284).

Confirmation of the structure of the acridone was sought by reduction to the known 9-methyl-1 : 2-benzacridine (von Braun and Wolff, *Ber.*, 1922, 55, 3575) but both zinc dust distillation (Graebe and Lagodzinski, *Ber.*, 1892, 25, 1733) of 9-methyl-1 : 2-benzacridone and Albert and Royer's method (*J.*, 1949, 1148) were unsuccessful.

Reduction of the acridone with sodium and pentyl alcohol, followed by ferric chloride oxidation (Reed, *J.*, 1944, 679), gave a tetrahydrobenzacridine, which must be 1' : 2' : 3' : 4'-tetrahydro-9-methyl-1 : 2-benzacridine (III) from the similarity of its ultraviolet absorption spectrum (Table 1) to that of acridine (Badger, Pearce, and Pettit, *J.*, 1951, 3199), with the expected bathochromic shift (*ca.* 100 Å) due to the alkyl substituents in the acridine system, and also to that of the carbocyclic analogue 1' : 2' : 3' : 4'-tetrahydro-10-methyl-1 : 2-benzanthracene (Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1938, 60, 940).

TABLE 1. *Absorption spectra in 95% ethanol.*

Substance	λ_{\max} (Å)	$\log \epsilon$	λ_{\min} (Å)	$\log \epsilon$
1' : 2' : 3' : 4'-Tetrahydro-9-methyl-1 : 2-benzacridine	2585, 3580	5.24, 3.87	3020	3.09
Acridine ^a	2475, 3560	5.29, 4.0	2910	2.88
1' : 2' : 3' : 4'-Tetrahydro-10-methyl-1 : 2-benzanthracene ^b	2585, 3510	5.28, 3.76	3020	2.82
9-Methyl-1 : 2-benzacridone	2780, 2870, 3480	4.78, 4.72, 3.79	3100	3.50
3 : 4-Benzacridine ^a	2780, 2860, 3480	4.78, 4.73, 3.87	3080	3.48

^a Badger, Pearce, and Pettit, *J.*, 1951, 3199. ^b Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1938, 60, 940.

Reduction of 9-methyl-1 : 2-benzacridone to the acridine was achieved with sodium amalgam (Clemo, Perkin, and Robinson, *J.*, 1924, 1751).

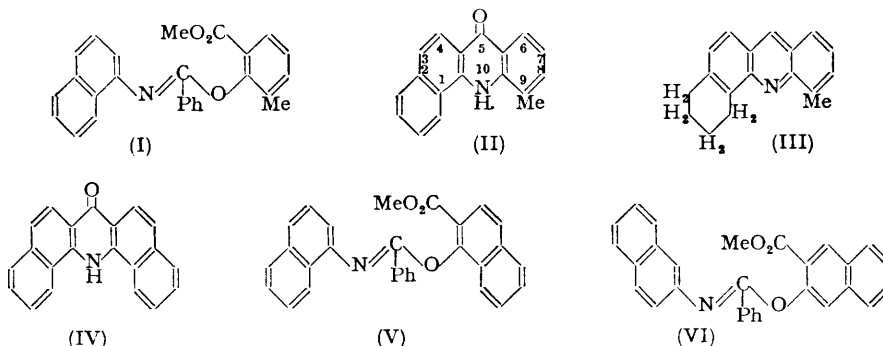
Use of *N*- β -naphthylbenzimidoyl chloride gave the β -naphthyl analogue of the benzimidate (I). This eliminated methyl benzoate to yield 9-methyl-3 : 4-benzacridone, converted, *via* the 5-chloroacridine, into 5-amino-9-methyl-3 : 4-benzacridine. Reduction of the acridone with sodium amalgam furnished the known 9-methyl-3 : 4-benzacridine having a somewhat higher m. p. than that reported (Ullmann, D.-R.P. 123,260; Friedlander, 6, 462).

Ullmann condensation of 1-bromo-2-naphthoic acid and α -naphthylamine gave only 2-naphthoic acid, but the synthesis of 1 : 2-8 : 9-dibenzacridone (IV) was carried out from 2-methoxycarbonyl-1-naphthyl *N*- α -naphthylbenzimidate (V).

The dibenzacridone (IV) gave a particularly inert chloro-derivative, aminated only at

180°. Sodium amalgam reduction of the acridone gave the known 1 : 2-8 : 9-dibenzacridine (Senier and Austin, *J.*, 1906, 1387).

In order to obtain a 5-aminodibenzacridine unsubstituted in the 1- and the 9-position, preparation of 2 : 3-6 : 7-dibenzacridone was undertaken. This was obtained from 3-methoxycarbonyl-2-naphthyl *N*-β-naphthylbenzimidate (VI), and was converted, *via* the reactive 5-chloro-compound, into 5-amino-2 : 3-6 : 7-dibenzacridine.



Attempted synthesis of 1 : 2-3 : 4-8 : 9-tribenzacridone by condensation of *N*-9-phenanthrylbenzimidoyl chloride with methyl 1-hydroxy-2-naphthoate was unsuccessful.

The relative basic strengths of the foregoing aminoacridines were determined in 50% alcoholic solution by potentiometric titration; the exceedingly low solubility of the bases in water precluded the use of spectrophotometric methods to obtain absolute values. The abnormally low basic strength of 1 : 9-disubstituted 5-aminoacridines has been ascribed (Craig, *J.*, 1946, 534) to steric blocking of protonation, and the reduced basicity of 5-amino-9-methyl-1 : 2-benzacridine and 5-amino-1 : 2-8 : 9-dibenzacridine, compared with their isomers having free 1- and 9-positions, may be due to the same cause.

The antituberculous activities of the aminoacridines were kindly determined by Professor S. D. Rubbo against *Mycobact. tuberculosis* H37Rv *in vitro*, and are recorded in Table 2. It is seen that the weakly basic 5-amino-1 : 2-8 : 9-dibenzacridine had greatly reduced activity; a full account of the bacteriological aspects will be given elsewhere.

TABLE 2. *Ionisation in 50% alcohol at 20°.*

Substance	pK _a	Antituberculous activity *
5-Amino-1 : 2-benzacridine	8.15 ^a	256,000
5-Amino-9-methyl-1 : 2-benzacridine	7.26	128,000
5-Amino-3 : 4-benzacridine	8.41 ^b	256,000
3-Amino-9-methyl-3 : 4-benzacridine	8.59	128,000
5-Amino-1 : 2-8 : 9-dibenzacridine	5.36, ^c 5.30 ^d	32,000
5-Amino-2 : 3-6 : 7-dibenzacridine	8.94	256,000

* Highest dilution, expressed as 1/molarity, completely inhibiting growth in Youmans's medium after 14 days at 37°, in presence of 10% of serum.

^a Albert, Goldacre, and Phillips (*J.*, 1948, 2240) find 8.13. ^b *Idem*, *loc. cit.* ^c In 50% alcohol from half-neutralisation point. ^d In 66% alcohol by potentiometric titration.

EXPERIMENTAL

Methyl 2-Hydroxy-6-methylbenzoate.—This ester had b. p. 124–126°/21 mm., n_D^{20} 1.5350. Behal and Tiffeneau (*Bull. Soc. chim.*, 1908, 3, 730) give b. p. 111°/11 mm.

2-Methoxycarbonyl-6-methylphenyl N-α-Naphthylbenzimidate.—To a cooled solution of sodium (2.23 g.) in ethanol (110 c.c.) was added methyl 2-hydroxy 6-methylbenzoate (19.5 g.), followed rapidly by *N*-α-naphthylbenzimidoyl chloride (20.6 g.; Just, *Ber.*, 1886, 19, 979) in dry ether. Reaction began immediately with precipitation of sodium chloride, and the solution was set aside overnight. Removal of solvents *in vacuo* and trituration of the residue (water, then light petroleum) gave the *benzimidate*, crystallising from benzene–light petroleum (b. p. 40–60°) as pale yellow prisms (21.3 g., 70%), m. p. 109.5° (Found : N, 3.8. C₂₆H₂₁O₃N requires N, 3.55%).

9-Methyl-1 : 2-benzacridone.—A vigorous reaction occurred when the foregoing benzimidate (30 g.) was heated to 275°, the temperature rising to 300° and methyl benzoate refluxing. The internal temperature was maintained at 280–300° for 0.75 hr., and the cooled residue then boiled with ethanol (25 c.c.) and filtered hot. The insoluble solid was washed (ethanol, then ether) and purified by Soxhlet extraction with pyridine, giving 9-methyl-1 : 2-benzacridone (14.18 g., 72%), as pale straw-coloured needles, m. p. 274° (Found : N, 5.7. Calc. for $C_{18}H_{13}ON$: N, 5.4%). Reed (J., 1945, 186) gives m. p. 265°.

5-Chloro-9-methyl-1 : 2-benzacridine.—(a) 9-Methyl-1 : 2-benzacridone (7.58 g.) and phosphorus oxychloride (50 c.c.) were refluxed for 2 hr. After removal of most of the phosphorus oxychloride *in vacuo*, the viscous residue was poured into a mixture of ice, ammonia solution, and chloroform, sufficient to dissolve the product after 0.5 hr. with a further 0.5 hour's stirring without cooling. The solution was kept alkaline to phenolphthalein throughout. Filtration and distillation of the chloroform layer gave 5-chloro-9-methyl-1 : 2-benzacridine (6.44 g., 79%) as pale yellow needles, m. p. 156.5° (from benzene) (Found : N, 5.05. $C_{18}H_{12}NCl$ requires N, 5.05%).

(b) In a second experiment the chloroform and ice were omitted in the alkaline hydrolysis, the solid being vigorously stirred for 1 hr. Filtration and drying gave a quantitative yield, m. p. 155–156°.

5-Amino-9-methyl-1 : 2-benzacridine.—A stirred solution of 5-chloro-9-methyl-1 : 2-benzacridine (5.32 g.) in phenol (29 g.) was heated to 70° with powdered "AnalaR" ammonium carbonate (3.7 g.) as fast as possible. The solution was stirred at 120° for 1.5 hr. and poured into 10N-sodium hydroxide, and the solid was filtered off and washed. A solution of the crude product in N-acetic acid was adjusted to pH 6 and filtered from a trace of weakly basic material, and the filtrate basified with sodium hydroxide, giving 5-amino-9-methyl-1 : 2-benzacridine (4.76 g., 82%), crystallising from toluene as yellow prisms, m. p. 148° (decomp.) (rapid heating) (Found : N, 11.15. $C_{18}H_{14}N_2$ requires N, 10.85%). The analytical specimen was dried in the dark at 56°, slow decomposition occurring in light at 100°. The *hydrochloride* crystallised from methanol in yellow needles, m. p. 378° (decomp.) (Found : 9.75. $C_{18}H_{14}N_2 \cdot HCl$ requires N, 9.5%).

9-Methyl-5-phenoxy-1 : 2-benzacridine.—(a) Treatment of 5-chloro-9-methyl-1 : 2-benzacridine with ammonium carbonate in phenol as described above but for only 0.75 hr. gave 57% of the aminobenzacridine and a weakly basic fraction insoluble in N-acetic acid. This was chromatographed in benzene on alumina and crystallised from alcohol as pale fawn prisms of 9-methyl-5-phenoxy-1 : 2-benzacridine, m. p. 158–159° (Found : 4.55. $C_{22}H_{17}ON$ requires N, 4.2%). Mixed m. p.s with the chloro- and the amino-benzacridine were 128–138° and 128–135° respectively.

(b) A mixture of 5-chloro-9-methyl-1 : 2-benzacridine (2.14 g.), sodium hydroxide (0.46 g.) and phenol (7.2 g.) was heated at 100° for 3 hr., the clear solution poured into 2.5N-sodium hydroxide solution (60 c.c.) and filtered, and the solid washed with water and dried at 120°, to give the phenoxy-compound (2.47 g., 96%), which crystallised from ethyl acetate as fawn-coloured prisms, m. p. 159°, undepressed on admixture with the material obtained as in (a).

Attempted Preparation of 9-Methyl-1 : 2-benzacridine.—(a) A saturated solution of 5-chloro-9-methyl-1 : 2-benzacridine and toluene-*p*-sulphonylhydrazide in chloroform was treated with dry hydrogen chloride for 10 sec. and the mixture set aside for 7 days. Filtration and washing (alcohol) of the precipitate gave the adduct (37% yield) as a yellow powder. Attempted decomposition of this by Albert and Royer's method (J., 1949, 1148) gave only tar insoluble in N-hydrochloric acid.

(b) A suspension of powdered 9-methyl-1 : 2-benzacridone (3.88 g.) in refluxing pentyl alcohol (150 c.c.) was treated with sodium (8.25 g.) in 6 portions, complete dissolution occurring after addition of the first portion. The cold solution was diluted with water (150 c.c.), the pentyl alcohol removed in steam, and the yellow acridan filtered off, suspended in 10N-hydrochloric acid (40 c.c.), and refluxed with excess of ferric chloride for 2 hr. The suspension was neutralised with concentrated ammonia solution and extracted with chloroform. Basic material, taken through 2N-hydrochloric acid and chromatographed on alumina in light petroleum (b. p. 40–60°), crystallised from ethanol as pale yellow needles of 1' : 2' : 3' : 4'-tetrahydro-9-methyl-1 : 2-benzacridine (1.73 g., 44%), m. p. 64° (Found : C, 87.0; H, 7.0; N, 6.0. $C_{18}H_{17}N$ requires C, 87.4; H, 6.95; N, 5.7%). The *picrate* had m. p. 176–177° (orange needles from ethanol) (Found : N, 11.95. $C_{18}H_{17}N \cdot C_6H_3O_7N_3$ requires N, 11.75%).

(c) Reduction of 9-methyl-1 : 2-benzacridone (1.5 g.) with sodium amalgam as described below for 1 : 2.8 : 9-dibenzacridone, and oxidation of the crude acridan with ferric chloride gave

9-methyl-1 : 2-benzacridine (0.58 g., 41%), subliming at 200°/0.5 mm., and crystallising from ethanol as yellow plates, m. p. 114—115° (Found : C, 89.15; H, 5.2. Calc. for $C_{18}H_{13}N$: C, 88.9; H, 5.4%). Von Braun and Wolff (*Ber.*, 1922, 55, 3675) give m. p. 107°. The picrate formed yellow needles, m. p. 156—157°, from methanol. Von Braun and Wolff (*loc. cit.*) give m. p. 155° and Buu-Hoi (*J.*, 1949, 670) reports m. p. 150—151°.

2-Methoxycarbonyl-6-methylphenyl N-β-Naphthylbenzimidate.—Prepared from methyl 2-hydroxy-6-methylbenzoate (48 g.), *N*-β-naphthylbenzimidoyl chloride (50 g.; Just, *Ber.*, 1886, 19, 979), and sodium (5.5 g.) in ethanol (270 c.c.), the *benzimidate* (63%) crystallised from benzene–light petroleum (b. p. 60—90°) as prisms, m. p. 120—121° (Found : C, 78.8; H, 5.5. $C_{26}H_{21}O_3N$ requires C, 78.95; H, 5.35%).

9-Methyl-3 : 4-benzacridone.—The preceding benzimidate (22 g.) gave little acridone at 300°. At 360° in nitrogen reaction took place in 0.5 hr., liberating methyl benzoate. The washed (benzene) *acridone* crystallised from nitrobenzene as yellow needles (5.49 g., 38%), m. p. 264—265° (Found : C, 83.2; H, 5.05; N, 5.45. $C_{18}H_{13}ON$ requires C, 83.35; H, 5.05; N, 5.4%).

5-Chloro-9-methyl-3 : 4-benzacridine.—Reaction of the acridone (4 g.) and phosphorus oxychloride gave the *chloro-acridine* (3.25 g., 76%), crystallising from benzene as yellow needles, m. p. 137° (Found : C, 77.5; H, 4.35; N, 4.95. $C_{18}H_{12}NCl$ requires C, 77.8; H, 4.35; N, 5.05%).

5-Amino-9-methyl-3 : 4-benzacridine.—The preceding chloroacridine (2 g.) was aminated in phenol at 120° for 1.5 hr. in the usual manner. After precipitation of impurities at pH 6, the *aminoacridine* (1.41 g., 76%) crystallised from benzene as red needles, m. p. 182—183° (Found : C, 83.9; H, 5.4; N, 10.8. $C_{18}H_{14}N_2$ requires C, 83.7; H, 5.45; N, 10.85%).

9-Methyl-3 : 4-benzacridine.—Reduction of 9-methyl-3 : 4-benzacridone (1.4 g.) with sodium amalgam as described below for 1 : 2.8 : 9-dibenzacridone gave, apart from recovered acridone (0.28 g.), the acridine (0.61 g., 58%), crystallising from benzene–light petroleum (b. p. 60—90°) as pale cream needles, m. p. 155° (Found : C, 88.9; H, 5.4; N, 5.3. Calc. for $C_{18}H_{13}N$: C, 88.9; H, 5.4; N, 5.7%). Ullmann (*D.-R.P.* 123,260; Friedlander, 6, 462) gives m. p. 143°. The *picrate* formed yellow needles (from acetone), m. p. 289° (decomp.) (Found : C, 60.8; H, 3.4. $C_{18}H_{13}N.C_6H_5O_7.N_3$ requires C, 61.0; H, 3.4%).

Methyl 1-Hydroxy-2-naphthoate (cf. Cameron, Jeskey, and Baine, *J. Org. Chem.*, 1950, 15, 233).—A mixture of α-naphthol (0.2 mole), anhydrous potassium carbonate (0.4 mole), and solid carbon dioxide (1 mole) was heated in an autoclave (500 c.c.) for 8 hr. at 130—140° (internal). The solid was dissolved in boiling water, the solution filtered, and the acid precipitated from the hot filtrate with 10*N*-hydrochloric acid, washed (water), and dried (100°), giving 1-hydroxy-2-naphthoic acid (80%), m. p. 192°. Refluxing with methanol and sulphuric acid for 12 hr. gave the methyl ester as prisms, m. p. 78°, from ethanol. Schmitt and Burkard (*Ber.*, 1887, 20, 2699) give m. p.s 187° and 78° for the acid and ester respectively.

2-Methoxycarbonyl-1-naphthyl N-α-Naphthylbenzimidate.—To a cooled solution of sodium (2.03 g.) in ethanol (100 c.c.) was added methyl 1-hydroxy-2-naphthoate (22 g.), followed rapidly by *N*-α-naphthylbenzimidoyl chloride (19.4 g.), each in dry ether. The *benzimidate* was washed with ethanol and crystallised from benzene as pale yellow prisms (23.17 g., 74%), m. p. 141—142° (Found : N, 3.1. $C_{29}H_{21}O_3N$ requires N, 3.25%).

1 : 2.8 : 9-Dibenzacridone.—The preceding benzimidate was heated to 280°, whereupon reaction set in, the temperature rising to 310°. Methyl benzoate was formed, and during 0.5 hr. at 280—300°, the *acridone* (47% yield) was deposited as a solid, crystallising from pyridine (by Soxhlet extraction) as straw-coloured needles, m. p. 331—332° (Found : N, 5.0. $C_{21}H_{13}ON$ requires N, 4.75%).

5-Chloro-1 : 2.8 : 9-dibenzacridine.—The preceding acridone (6.53 g.), after brief heating with phosphorus oxychloride (45 c.c.), gave the *chloroacridine* (6.45 g., 92%) as yellow needles from benzene, m. p. 240—241° (Found : N, 4.8. $C_{21}H_{12}NCl$ requires N, 4.5%).

5-Amino-1 : 2.8 : 9-dibenzacridine.—No reaction occurred when 5-chloro-1 : 2.8 : 9-dibenzacridine (2.52 g.) was treated with ammonium carbonate in phenol as described previously, but after 2 hr. at 180° with regular further addition of ammonium carbonate, working up as before gave 5-amino-1 : 2.8 : 9-dibenzacridine soluble in *N*-acetic acid and crystallising from benzene as pale yellow needles, m. p. 238—239° (1.72 g., 73%) (Found : C, 85.35; H, 4.8; N, 9.7. $C_{21}H_{14}N_2$ requires C, 85.7; H, 4.8; N, 9.5%).

5-Phenoxy-1 : 2.8 : 9-dibenzacridine.—(a) The material (0.88 g.) insoluble in *N*-acetic acid in the previous preparation crystallised from ethyl acetate as pale yellow prisms, m. p. 254—255°, of the *phenoxyacridine* (Found : N, 4.0. $C_{27}H_{17}ON$ requires N, 3.8%). (b) 5-Chloro-1 : 2.8 : 9-dibenzacridine (0.92 g.), phenol (3 g.), and sodium hydroxide (0.19 g.) were heated at 180°

for 2 hr. Working up as above gave the phenoxyacridine (1.07 g., 100%), m. p. and mixed m. p. identical with the product obtained as in (a). Attempted preparation at 100° for 3 hr. gave 92% recovery of unchanged chloro-compound.

1 : 2-8 : 9-Dibenzacridine.—1 : 2-8 : 9-Dibenzacridone (1 g.) was dissolved in alcohol (100 c.c.) and water (50 c.c.) by adding sodium hydroxide (0.3 g.) with heating and stirring. Sodium amalgam (60 g.; 2.5%) was added during 1 hr. with stirring at 60°, carbon dioxide being passed through at such a rate that the solution remained slightly alkaline. After a further hour's refluxing with continued stirring, the flow of gas was increased; the acridone was then no longer precipitated. Removal of mercury and dilution with water gave the acridan, oxidised by refluxing with excess of ferric chloride in 3*N*-hydrochloric acid. Treatment with potassium carbonate and extraction of the dried precipitate with benzene gave the acridine (0.67 g., 71%) as pale cream needles, m. p. 188°, undepressed on admixture with a specimen (m. p. 188°) made by Senier and Austin's method (*J.*, 1906, 1387). These authors give m. p. 185.5° and Kermack, Slater, and Spragg (*Proc. Roy. Soc. Edinburgh*, 1930, 50, 243) give m. p. 185°. A stable picrate could not be formed, nor could the methosulphate be prepared even in nitrobenzene at 160°. Kermack, Slater, and Spragg (*loc. cit.*) mention this methosulphate but do not describe its preparation or properties.

3-Methoxycarbonyl-2-naphthyl N-β-Naphthylbenzimidate.—Prepared from *N*-β-naphthylbenzimidoyl chloride (58 g.), methyl 3-hydroxy-2-naphthoate (66 g.), and sodium (6 g.) in absolute ethanol (300 c.c.), the *benzimidate* was washed with water and alcohol and crystallised from benzene as pale yellow prisms, m. p. 175° (47.8 g., 51%) (Found : C, 80.7; H, 4.9; N, 3.15. $C_{29}H_{21}O_3N$ requires C, 80.7; H, 4.9; N, 3.25%).

2 : 3-6 : 7-Dibenzacridone.—The preceding benzimidate (10 g.) was cyclised at 350–360° during 0.5 hr. and the acridone washed with ether and benzene and crystallised from nitrobenzene as golden-red plates (3.69 g., 54%), m. p. 372° (Found : C, 85.45; H, 4.3. Calc. for $C_{21}H_{13}ON$: C, 85.4; H, 4.45%). Strohbach (*Ber.*, 1901, 34, 4146) gives m. p. >300°.

10-Ethyl-2 : 3-6 : 7-dibenzacridone, prepared by Strohbach's method (*loc. cit.*), formed yellow needles from acetone, m. p. 204.5–205° (Strohbach, *loc. cit.*, gives m. p. 204.5–205°).

5-Chloro-2 : 3-6 : 7-dibenzacridine.—The acridone (4 g.) was converted as above into the *chloroacridine* (3.67 g., 86%), crystallising from chloroform as orange needles, m. p. 254–255° (Found : C, 80.1; H, 3.85. $C_{21}H_{12}NCl$ requires C, 80.4; H, 3.85%).

5-Amino-2 : 3-6 : 7-dibenzacridine.—Amination of the preceding chloroacridine in phenol at 120° for 1 hr., then at 180° for 0.5 hr., gave a product sparingly soluble in *N*-acetic acid. The *base* (89%) was chromatographed on alumina in chloroform and formed red needles (from chlorobenzene), m. p. 226.5° (Found : C, 85.5; H, 4.75. $C_{21}H_{14}N_2$ requires C, 85.7; H, 4.8%).

5-Phenoxy-2 : 3-6 : 7-dibenzacridine.—Treatment of the chloroacridine (0.5 g.) with phenol (3 g.) and sodium hydroxide (0.1 g.) at 100° for 1.5 hr gave the *phenoxy-compound* (0.48 g., 81%), crystallising from benzene as yellow prisms, m. p. 253–254° (Found : N, 3.4. $C_{27}H_{17}ON$ requires N, 3.75%).

***N*-9-Phenanthrylbenzimidoyl Chloride.**—An equimolecular mixture of *N*-9-phenanthrylbenzimidoyl chloride (Schmidt and Heinle, *Ber.*, 1911, 44, 1501) and phosphorus oxychloride was heated at 100–110° for 1 hr. Removal of phosphorus oxychloride *in vacuo* and extraction of the residue with benzene–light petroleum (b. p. 60–80°) gave the *benzimidoyl chloride* as yellow prisms, m. p. 118.5° (Found : N, 4.7. $C_{21}H_{14}NCl$ requires N, 4.45%).

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