88. *Synthesis of Some* 1 : 2- *and* 7 : 8-*Benzophenanthridines.*

By K. W. Gopinath, T. R. Govindachari, K. Nagarajan, and K. K. Purushothaman.

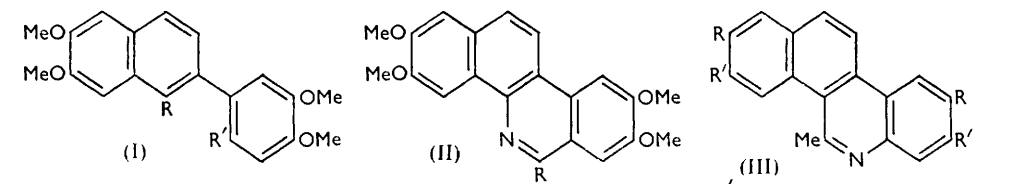
6-(3 : 4-Dimethoxyphenyl)-2 : 3-dimethoxynaphthalene yields a mixture of the 5- and the 6′-mononitro-compound (I) and (Ib), reduced to the corresponding amines. The formyl and acetyl derivatives of the amines are cyclised to tetramethoxybenzophenanthridines. Diazotisation of the amine (Ic) yields the 5 : 6-diazachrysene (IVa). Nitration of 2 : 3-methylenedioxy-6-(3 : 4-methylenedioxyphenyl)naphthalene leads to the 6′-nitro-derivative (V), which through the acetyl derivative of the amine gives the 7 : 8-benzophenanthridine (IIIa). Diazotisation of the amine (Va) yields a diazachrysene (IVb). The dinitration product of the methylenedioxynaphthalene is assigned a probable structure.

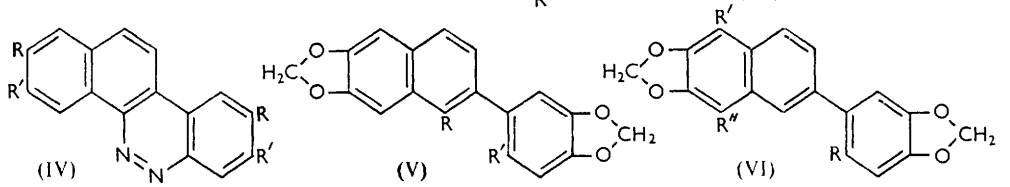
In connexion with work on some 1 : 2-benzophenanthridine alkaloids, we had occasion to study the nitration of 6-(3 : 4-dimethoxyphenyl-2 : 3-dimethoxy)- and 2 : 3-methylenedioxy-6-(3 : 4-methylenedioxyphenyl)-naphthalene which were readily available.[1] We

[1] Gopinath, Govindachari, Nagarajan, and Purushothaman, *J.*, 1957, 1144.

present below an account of the products and the benzophenanthridines obtained from them.

6-(3 : 4-Dimethoxyphenyl)-2 : 3-dimethoxynaphthalene gave two mononitro-derivatives. One is 2-(3 : 4-dimethoxyphenyl)-6 : 7-dimethoxy-1-nitronaphthalene (I), since cyclisation of the formyl derivative of the derived amine (Ia) yielded the known 2′ : 3′ : 6 : 7-tetramethoxy-1 : 2-benzophenanthridine [2] (II). Catalytic reduction of these nitro-compounds proceeded best in benzene solution, use of alcohol or acetic acid as solvent





	R	R′
(I)	NO_2	H
(Ia)	NH_2	H
(Ib)	H	NO_2
(Ic)	H	NH_2
(II)	H	—
(IIa)	Me	—

	R	R′
(III)	OMe	OMe
(IIIa)	$-CH_2O_2-$	
(IV)	H	H
(IVa)	OMe	OMe
(IVb)	$-CH_2O_2-$	

	R	R′ (or R″)
(V)	H	NO_2
(Va)	H	NH_2
(Vb)	NO_2	H
(VI)	NO_2	NO_2
(VIa)	NH_2	NH_2

giving very poor yields. The acetyl derivative of the base (Ia) likewise furnished the 9-methylbenzophenanthridine (IIa). The other product of mononitration is evidently 6-(4 : 5-dimethoxy-2-nitrophenyl)-2 : 3-dimethoxynaphthalene (Ib), since reduction to the amine (Ic), acetylation, and cyclisation yielded 2 : 3 : 2′ : 3′-tetramethoxy-9-methyl-7 : 8-benzophenanthridine (III). The corresponding formamide did not undergo cyclisation, because of insufficient activation at the 1-position of the naphthalene. 2-Acetamidodiphenyl is known to give 9-methylphenanthridine readily whereas the 2-formyl derivative is difficult to cyclise.[3]

An attempted Sandmeyer reaction on 6-(6-amino-3 : 4-dimethoxyphenyl)-2 : 3-dimethoxynaphthalene (Ic) resulted in a compound, $C_{20}H_{18}O_4N_2$, whose ultraviolet spectrum (Fig. 1) showed the presence of an extended chromophore. The compound is assigned the structure, 2 : 3 : 8 : 9-tetramethoxy-5 : 6-diazachrysene (IVa), in analogy with the formation of cinnolines by diazotisation of 2-aminostyrenes.[4] The parent diazachrysene (IV) is unknown.[5]

Nitration of 2 : 3-methylenedioxy-6-(3 : 4-methylenedioxyphenyl)naphthalene has been reported [6] to yield the nitro-derivative (V), m. p. 225—228°. Repetition of the nitration and repeated recrystallisation of the product from acetic acid gave a purer specimen, of m. p. 241—242° which could not be improved further. Reduction to the amine (Va) and cyclisation of the acetyl derivative yielded 9-methyl-2 : 3-2′ : 3′-bismethylenedioxy-7 : 8-benzophenanthridine (IIIa) having an ultraviolet spectrum (Fig. 2) very similar to that of the tetramethoxy-analogue (III). The formyl derivative of the amine (Va), as expected,

[2] Bailey, Robinson, and Staunton, *J.*, 1950, 2277.
[3] Whaley and Govindachari, "Organic Reactions," John Wiley & Sons, Inc., New York, 1951, Vol. VI, p. 131.
[4] Simpson, *J.*, 1943, 447.
[5] Allen, "Six Membered Nitrogen Compounds with Four Condensed Rings," Interscience Publ., New York, 1951, p. 174.
[6] Erdtman and Robinson, *J.*, 1933, 1530.

could not be cyclised. Diazotisation of the amine gave a good yield of 2 : 3 : 8 : 9-bismethylenedioxy-5 : 6-diazachrysene (IVb). From the mother-liquors of the crystallisation of the nitro-compound (V), an impure material was recovered and subjected to catalytic hydrogenation in benzene solution. Chromatography of the product gave a small amount of compound (Va) and a very small amount of a yellow substance, isomeric with the nitro-compound (V). This is probably the nitro-compound (Vb) which had escaped reduction (for lack of material, its identity could not be confirmed).

Nitration of 2 : 3-methylenedioxy-6-(3 : 4-methylenedioxyphenyl)naphthalene under forced conditions gave a moderate yield of a dinitro-compound which was reduced to a diamine. Cyclisation of its diacetyl derivative gave an acetamidobismethylenedioxymethylbenzophenanthridine, whose ultraviolet spectrum (Fig. 2) was similar to those of the

FIG. 1. FIG. 2. FIG. 3.

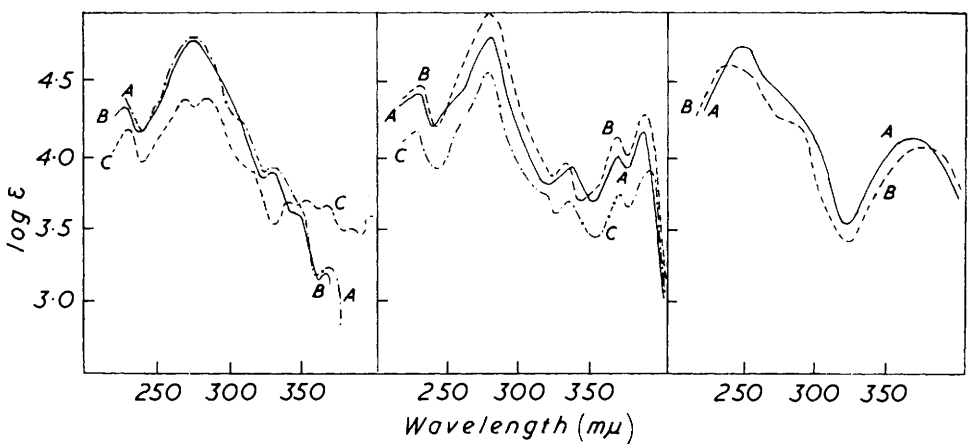


FIG. 1. *Ultraviolet absorption of* (*A*) 2′ : 3′ : 6 : 7-*tetramethoxy- and* (*B*) 2′ : 3′ : 6 : 7-*tetramethoxy*-9-*methyl*-1 : 2-*benzophenanthridine and* (*C*) 2 : 3 : 8 : 9-*tetramethoxy*-5 : 6-*diazachrysene.*

FIG. 2. *Ultraviolet absorption of* (*A*) 2 : 3 : 2′ : 3′-*tetramethoxy-*, (*B*) 2 : 3-2′ : 3′-*bismethylenedioxy-, and* (*C*) 1′(or 4′)-*acetamido*-9-*methyl*-2 : 3-2′ : 3′-*bismethylenedioxy*-7 : 8-*benzophenanthridine.*

FIG. 3. *Ultraviolet absorption of* (*A*) 9 : 10-*dihydro*-2 : 3 : 2′ : 3′-*tetramethoxy*-9 : 10-*dimethyl*-7-8-*dibenzophenanthridine and* (*B*) 9 : 10-*dihydro*-9 : 10-*dimethyl*-2 : 3-2′ : 3′-*bismethylenedioxy*-7 : 8-*dibenzophenanthridine.*

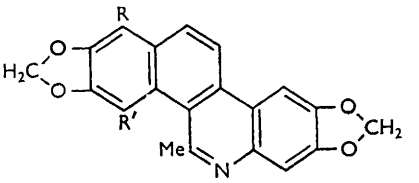
7 : 8-benzophenanthridines (III) and (IIIa), and different from those of the two 1 : 2-benzophenanthridines (II) and (IIa) (Fig. 1). Hydrolysis of this base and deamination yielded the 7 : 8-benzophenanthridine (IIIa), showing thereby that it is an acetamido-9-methyl-2 : 3-2′ : 3′-bismethylenedioxy-7 : 8-benzophenanthridine. One of the nitro-groups in the dinitro-compound must therefore be in the 6′-position. The other cannot be at position 5, since cyclisation should then have yielded a 1 : 2-benzophenanthridine and not a 7 : 8-benzophenanthridine, or at position 2′, since the diacetyl derivative should then have given a mixture of 7 : 8-benzophenanthridines. If positions 7 and 8 are excluded as unlikely, the most probable ones for the second nitro-group are therefore 1 and 4, giving the dinitro-compound structure (VI). The derived diamine is therefore 1-amino-6(or 7)-(6-amino-3 : 4-methylenedioxyphenyl)-2 : 3-methylenedioxynaphthalene (VIa) and the resulting phenanthridine must be 1′(or 4′)-acetamido-9-methyl-2 : 3-2′ : 3′-bismethylenedioxy-7 : 8-benzophenanthridine (VII).

The three 7 : 8-benzophenanthridines (III, IIIa, and VII) whose synthesis and ultraviolet spectra are reported here are of interest because only the parent compound of this group is so far known [7] and its ultraviolet spectrum has not been recorded. The spectra

[7] Graebe, *Annalen*, 1904, **335**, 122.

of members of this group are characteristic and different from those of the 1 : 2-benzophenanthridines. The spectra (Fig. 3) of the dihydro-derivatives obtained by reduction of the quaternary salts of the phenanthridines (III) and (IIIa) also differ remarkably from those reported [2] for similar 1 : 2-benzophenanthridine derivatives.

(VII) R = H, R′ = NH·COMe or *vice versa*.



Experimental

Nitration of 6-(3 : 4-*Dimethoxyphenyl*)-2 : 3-*dimethoxynaphthalene*.—To the naphthalene derivative [1] (5 g.) in acetic acid (20 ml.) cooled in ice–salt and stirred, nitric acid (*d* 1·42; 2·5 ml.) was added during ½ hr. Stirring in ice was continued for 2 hr. and the solid was filtered off and washed with small amounts of acetic acid and with cold alcohol. The dry solid was dissolved in the minimum amount of hot acetic acid and allowed to cool, pale yellow needles (0·2 g.) separating. Recrystallisation from acetic acid yielded greenish-yellow needles of 2-(3 : 4-*dimethoxyphenyl*)-6 : 7-*dimethoxy*-1-*nitronaphthalene*, m. p. 209—210° (Found: C, 64·8; H, 5·2. $C_{20}H_{19}O_6N$ requires C, 65·0; H, 5·1%). The mother-liquor, overnight, deposited reddish crystals. These were redissolved in acetic acid and allowed to cool slowly. A mixture of heavy reddish-yellow prisms and small greenish-yellow needles separated. The latter were washed from the former by small amounts of acetic acid. After two further crystallisations of the yellow needles a further yield (0·6 g.) of the 1-nitronaphthalene, m. p. 209—210°, was obtained. The red solid after two further crystallisations from acetic acid yielded 6-(4 : 5-*dimethoxy*-2-*nitrophenyl*)-2 : 3-*dimethoxynaphthalene* (2·1 g.) as reddish-yellow prisms, m. p. 189—190° (Found: C, 64·7; H, 5·3%).

1-*Amino*-2-(3 : 4-*dimethoxyphenyl*)-6 : 7-*dimethoxynaphthalene*.—The 1-nitro-compound (0·5 g.) in benzene (40 ml.) was reduced catalytically by hydrogen at 50—60 lb./sq. in. after the addition of Adams catalyst (0·2 g.). After 3 hr. the benzene solution was filtered and the catalyst washed several times with benzene. Removal of the solvent yielded the *amine* (0·4 g.), colourless plates (from methanol), m. p. 144—145° (Found: C, 71·0; H, 6·3. $C_{20}H_{21}O_4N$ requires C, 70·8; H, 6·2%). The amine (0·5 g.) in 95% formic acid (2 ml.) was evaporated to dryness and the solid formate heated at 180° for 2 hr. Water was added and the solid obtained washed with dilute hydrochloric acid and water, to yield 1-*formamido*-2-(3 : 4-*dimethoxyphenyl*)-6 : 7-*dimethoxynaphthalene* (0·5 g.) as colourless needles (from ethanol), m. p. 215—216° (Found: C, 68·9; H, 6·0. $C_{21}H_{21}O_5N$ requires C, 68·7; H, 5·7%). The *acetyl derivative* (0·2 g.), prepared from the amine (0·25 g.) by acetic anhydride (5 ml.) in pyridine (0·5 ml.) at 100° for 1 hr., formed colourless needles (from ethanol), m. p. 154—156° (Found: C, 68·9; H, 6·2. $C_{22}H_{23}O_5N$ requires C, 69·3; H, 6·0%).

2′ : 3′ : 6 : 7-*Tetramethoxy*-1 : 2-*benzophenanthridine*.—A solution of the foregoing formamide (0·3 g.) in phosphorus oxychloride (3 ml.) was heated at 100° for 1 hr. After a few minutes a yellow precipitate separated. The excess of phosphorus oxychloride was decomposed with ice-water, the yellow hydrochloride washed with water, then basified with ammonia, and the base recrystallised from pyridine–ethanol to yield 2′ : 3′ : 6 : 7-tetramethoxy-1 : 2-benzophenanthridine (0·2 g.) as colourless plates, m. p. and mixed m. p. (cf. ref. 2) 305—306° (Found: C, 72·6; H, 5·4; N, 4·2. Calc. for $C_{21}H_{19}O_4N$: C, 72·2; H, 5·5; N, 4·0%).

2′ : 3′ : 6 : 7-*Tetramethoxy*-9-*methyl*-1 : 2-*benzophenanthridine*.—The above acetamide (0·2 g.) and phosphorus oxychloride (3 ml.) heated at 100° for 2 hr. yielded, as above, 2′ : 3′ : 6 : 7-*tetramethoxy*-9-*methyl*-1 : 2-*benzophenanthridine* (0·15 g.), m. p. 275—276° (from pyridine–ethanol) (Found: C, 72·6; H, 5·6. $C_{22}H_{21}O_4N$ requires C, 72·7; H, 5·8%).

6-(2-*Amino*-4 : 5-*dimethoxyphenyl*)-2 : 3-*dimethoxynaphthalene*.—The 2′-nitro-compound (1·0 g.) was hydrogenated in benzene (50 ml.) during 3 hr. at 55—60 lb. after addition of Adams catalyst (0·2 g.). Working up as before yielded the *amine* (0·9 g.) as almost colourless prisms (from ethanol), m. p. 201—202° (Found: C, 70·5; H, 6·2%), yielding as before the *formyl derivative* (0·25 g. from 0·3 g.) as colourless needles (from ethanol), m. p. 206—207° (Found:

C, 69·3; H, 5·8%), which was not cyclised by phosphorus oxychloride; the *acetyl derivative* (0·4 g. from 0·5 g.) formed colourless needles (from dioxan), m. p. 204—205° (Found: C, 69·7; H, 6·2%).

2 : 3 : 2′ : 3′-*Tetramethoxy*-9-*methyl*-7 : 8-*benzophenanthridine*.—The above acetyl derivative (0·3 g.) in phosphorus oxychloride (5 ml.) at 100° for 2 hr. yielded, as before, 2 : 3 : 2′ : 3′-*tetramethoxy*-9-*methyl*-7 : 8-*benzophenanthridine* (0·2 g.) as needles (from pyridine–ethanol), m. p. 259—260° (Found: C, 72·8; H, 5·9%). The methosulphate, m. p. 248—250° (decomp.) (prepared by methyl sulphate in hot nitrobenzene) on reduction with lithium aluminium hydride gave the 9 : 10-*dihydro*-10-*methyl derivative*, m. p. 184—185° (from alcohol) (Found: C, 72·2; H, 6·2. $C_{23}H_{25}O_4N$ requires C, 72·8; H, 6·6%).

2 : 3 : 8 : 9-*Tetramethoxy*-5 : 6-*diazachrysene*.—6-(2-Amino-4 : 5-dimethoxyphenyl)-2 : 3-dimethoxynaphthalene (0·2 g.) was dissolved in 48% hydrobromic acid (10 ml.), cooled in ice–salt, and treated dropwise with stirring with sodium nitrite (0·2 g.) in water (5 ml.). Stirring was continued for ½ hr., and to the cold solution was then added with stirring freshly precipitated copper (1·0 g.). The mixture was allowed to rise slowly to room temperature and left overnight. The solid which separated was filtered off and extracted repeatedly with hot chloroform. The chloroform solution was washed with dilute aqueous sodium hydroxide, then with water. The dried (Na_2SO_4) extracts yielded on evaporation a red solid which was washed with cold alcohol and crystallised from acetic acid, to yield yellow 2 : 3 : 8 : 9-*tetramethoxy*-5 : 6-*diazachrysene* (0·04 g.) which blackened at 250° and did not melt at 360° (Found: C, 68·2; H, 5·4; N, 7·4. $C_{20}H_{18}O_4N_2$ requires C, 68·5; H, 5·1; N, 8·0%). Use of cuprous bromide in hydrobromic acid in place of copper led to the same result.

2 : 3-*Methylenedioxy*-6-(4 : 5-*methylenedioxy*-2-*nitrophenyl*)*naphthalene*.—A suspension of 2 : 3-methylenedioxy-6-(3 : 4-methylenedioxyphenyl)naphthalene [1] (2 g.) in acetic acid (10 ml.) was treated at 20—25° with stirring with fuming nitric acid (*d* 1·48; 1 ml.). The naphthalene dissolved but soon a yellow precipitate separated. The mixture was allowed to come to room temperature and stirring continued for 2 hr. The product was filtered off and washed first with a little acetic acid and then with alcohol. One crystallisation from acetic acid yielded yellow crystals, m. p. 220—227°. Two further crystallisations yielded the *nitro-compound* (0·7 g.) as brownish-yellow needles (from acetic acid), m. p. 241—242° (Found: C, 63·9; H, 3·1. $C_{18}H_{11}O_6N$ requires C, 64·1; H, 3·3%). The mother-liquors from crystallisations were diluted with water, and the yellow solid (0·7 g.; m. p. 185—230°) filtered off. It was dissolved in benzene (50 ml.) and hydrogenated at 55—60 lb. for 3 hr. after addition of Adams catalyst (0·2 g.). Working up yielded a yellow solid which was chromatographed over alumina. The yellow band which came down first yielded on evaporation a solid, m. p. 220—225° giving, on two crystallisations, yellow cubes of a *nitro-compound* (0·05 g.), m. p. 225—227° (from ethanol–acetic acid) (Found: C, 64·4; H, 3·2%). The mixed m. p. with the 2′-nitrophenyl isomer was 190—200°. Subsequent fractions yielded a basic solid which after acetylation and crystallisation from ethanol yielded 6-(2-acetamido-4 : 5-methylenedioxyphenyl)-2 : 3-methylenedioxynaphthalene (see below), m. p. and mixed m. p. 204—205°.

6-(2-*Amino*-4 : 5-*methylenedioxyphenyl*)-2 : 3-*methylenedioxynaphthalene*.—The nitro-compound (0·5 g.) was reduced in benzene (100 ml.) at a hydrogen pressure of 55—60 lb. after the addition of Adams catalyst (0·2 g.). Working up gave the *amine* (0·3 g.) as colourless plates (from ethanol), m. p. 201—202° (Found: C, 70·1; H, 4·4. $C_{18}H_{13}O_4N$ requires C, 70·4; H, 4·2%), yielding with formic acid a *formyl derivative* as needles (from ethanol), m. p. 160° (Found: C, 68·3; H, 4·2. $C_{19}H_{13}O_5N$ requires C, 68·1; H, 3·9%) (which could not be cyclised), and with acetic anhydride an *acetyl derivative*, needles (from ethanol), m. p. 204—205° (Found: C, 69·3; H, 4·7. $C_{20}H_{15}O_5N$ requires C, 68·8; H, 4·3%).

9-*Methyl*-2 : 3-2′ : 3′-*bismethylenedioxy*-7 : 8-*benzophenanthridine*.—The above acetamide (0·2 g.) and phosphorus oxychloride (2 ml.), heated at 100° for 2 hr., yielded 9-*methyl*-2 : 3-2′ : 3′-*bismethylenedioxy*-7 : 8-*benzophenanthridine* (0·1 g.), colourless needles (from pyridine–ethanol), m. p. 293—294° (decomp.) (Found: C, 72·8; H, 4·3. $C_{20}H_{13}O_4N$ requires C, 72·5; H, 3·9%). The methosulphate, m. p. 307—310° (decomp.) (prepared by methyl sulphate in hot nitrobenzene), on reduction with lithium aluminium hydride, yielded the yellow 9 : 10-*dihydro*-10-*methyl derivative*, m. p. 209—210° (from benzene–ethanol) (Found: C, 72·4; H, 4·9. $C_{21}H_{17}O_4N$ requires C, 72·6; H, 4·9%).

2 : 3-8 : 9-*Bismethylenedioxy*-5 : 6-*diazachrysene*.—6-(2-Amino-4 : 5-methylenedioxyphenyl)-2 : 3-methylenedioxynaphthalene (0·1 g.) in acetic acid (2·5 ml.) and concentrated hydrochloric

acid (0·5 ml.) was cooled to 0° and diazotised with a solution of sodium nitrite (0·2 g. in water, 2 ml.). The diazonium solution was allowed to rise slowly to room temperature and left overnight. Water was added and the brown solid centrifuged off and washed with water, dilute sodium hydroxide, and finally boiling water, yielding 2 : 3-8 : 9-*bismethylenedioxy*-5 : 6-*diazachrysene* (0·04 g.) as brown needles (from nitrobenzene), which did not melt at 360° (Found: C, 68·2; H, 2·8; N, 8·7. $C_{18}H_{10}O_4N_2$ requires C, 67·9; H, 3·1; N, 8·8%).

2 : 3-*Methylenedioxy*-6(or 7)-(4 : 5-*methylenedioxy*-2-*nitrophenyl*)-1-*nitronaphthalene*.—2 : 3-Methylenedioxy-6-(3 : 4-methylenedioxyphenyl)naphthalene (2 g.), suspended in acetic acid (20 ml.), was treated at 25—30° with nitric acid (*d* 1·48; 4 ml.), with stirring. The naphthalene dissolved but soon a yellow precipitate separated. After 2 hours' stirring at room temperature, the temperature was slowly raised to 60—70° and kept there for 3 hr. The yellow powder which separated was filtered off and washed with acetic acid and then alcohol. The dry solid was twice crystallised from a large volume of acetic acid, to yield the yellow *dinitro-derivative* (0·5 g.), m. p. 286—287° (decomp.) (Found: C, 56·3; H, 2·5. $C_{18}H_{10}O_8N_2$ requires C, 56·5; H, 2·6%).

1-*Amino*-6(or 7)-(2-*amino*-4 : 5-*methylenedioxyphenyl*)-2 : 3-*methylenedioxynaphthalene*.—The foregoing dinitro-compound (0·5 g.), suspended in benzene (70 ml.), was shaken for 3 hr. in hydrogen at 60 lb. after addition of Adams catalyst (0·2 g.). The solid dissolved and the solution became almost colourless. Working up yielded the *diamine* (0·35 g.) as pale brown plates (from ethanol), m. p. 177—178° (Found: C, 67·5; H, 4·6. $C_{18}H_{14}O_4N_2$ requires C, 67·1; H, 4·4%), yielding with formic acid as before a *diformyl derivative* (0·4 g. from 0·5 g.) as colourless crystals (from pyridine–ethanol), m. p. 330° (decomp.) (Found: C, 63·7; H, 4·2. $C_{20}H_{14}O_6N_2$ requires C, 63·2; H, 3·7%), which was not cyclised. The *diacetyl derivative* (1 g. from 1 g.) formed colourless feathery crystals (from pyridine), m. p. 342—343° (decomp.) (Found: C, 65·5; H, 4·6. $C_{22}H_{18}O_6N_2$ requires C, 65·0; H, 4·4%).

1′(*or* 4′)-*Acetamido*-9-*methyl*-2 : 3-2′ : 3′-*bismethylenedioxy*-7 : 8-*benzophenanthridine*.—The foregoing diacetamide (1 g.) and phosphorus oxychloride (5 ml.) were heated together at 100° for 3 hr. The reactant slowly dissolved to a yellow solution with an intense green fluorescence. Working up yielded the *benzophenanthridine* (0·6 g.) as colourless needles (from pyridine–ethanol), m. p. 329—330° (decomp.) (Found: C, 68·5; H, 4·6. $C_{22}H_{16}O_5N_2$ requires C, 68·1; H, 4·1%).

1′(*or* 4′)-*Amino*-9-*methyl*-2 : 3-2′ : 3′-*bismethylenedioxy*-7 : 8-*benzophenanthridine*.—The foregoing acetamidophenanthridine (0·1 g.), ethanol (10 ml.), and concentrated hydrochloric acid (20 ml.) were heated together under reflux for 6 hr. After 3 hr. a further 10 ml. of concentrated hydrochloric acid were added. The original lemon-yellow hydrochloride changed to a fluffy pale yellow solid. The solid was filtered off, washed with a small quantity of alcohol, and basified with ammonia. The pale yellow solid obtained yielded on crystallisation the *aminobenzophenanthridine* (0·06 g.) as pale yellow needles (from pyridine–ethanol), m. p. 281—282° (decomp.) (Found: C, 69·0; H, 4·3. $C_{20}H_{14}O_4N_2$ requires C, 69·4; H, 4·0%).

Deamination of 1′(*or* 4′)-*Amino*-9-*methyl*-2 : 3-2′ : 3′-*bismethylenedioxy*-7 : 8-*benzophenanthridine*.—The preceding amino-compound (0·1 g.) was suspended in water (20 ml.) containing concentrated sulphuric acid (*d* 1·84; 5 ml.), cooled to 0°, and diazotised with sodium nitrite (0·2 g.) in water (5 ml.). The solid gradually went into solution. After ½ hour's stirring 35% hypophosphorous acid (10 ml.) was added in small lots at <0—10°. The mixture was then allowed slowly to reach room temperature. After 1 hr. a yellow precipitate began to separate. Next morning the yellow solid was filtered off, washed with water, and basified with sodium hydroxide solution. The pale brown precipitate was washed with water and crystallised from pyridine–ethanol, yielding 9-methyl-2 : 3-2′ : 3′-bismethylenedioxy-7 : 8-benzophenanthridine (0·06 g.), colourless needles, m. p. and mixed m. p. 293—294° (Found: C, 72·3; H, 4·2%).

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