959. *Synthesis of Some* 1 : 2-*Benzophenanthridines.*

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Syntheses of 7 : 2′ : 3′- and 6 : 2′ : 3′-trimethoxy-, 7-methoxy-2′ : 3′-methylenedioxy-, and 6-methoxy-2′ : 3′-methylenedioxy-9-methyl-1 : 2-benzophenanthridine (V) are reported.

For work on some 1 : 2-benzophenanthridine alkaloids, we have prepared four new compounds of this group, by a modification of the method of Richardson *et al.*[1]

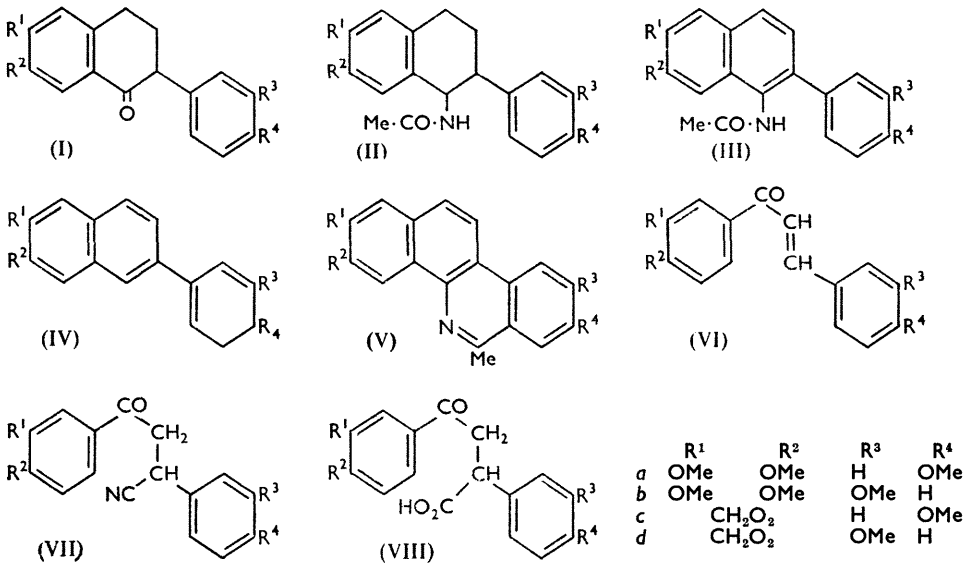
Reduction of the oxime of 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethoxy-2-*p*-methoxyphenyl-1-oxonaphthalene[2] (I*a*) with sodium amalgam and acetylation of the resulting amine yielded the acetamide (II*a*) which on dehydrogenation over palladised charcoal gave a mixture of 6 : 7-dimethoxy-2-*p*-methoxyphenylnaphthalene (IV*a*) and its 1-acetamido-derivative (III*a*), identified by analysis and ultraviolet spectra (Fig. 1). A similar partial removal of the amide group has been observed in the dehydrogenation of 1-acetamido-1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethoxynaphthalene.[3] Cyclisation of the amide (III*a*) with phosphorus oxychloride gave a good yield of 7 : 2′ : 3′-trimethoxy-9-methyl-1 : 2-benzophenanthridine (V*a*). To our knowledge the cyclisations of the amides (III*a* and *c*) (reported below) are the only instances where cyclisation has proceeded *meta* to an alkoxy-group, illustrating the great facility of the Morgan–Walls reaction:[4] Bischler–Napieralski reaction[4] of phenethylamides with alkoxy-groups *meta* to the point of cyclisation either fails or yields only traces of *iso*quinolines.

An attempt to prepare the benzophenanthridine (V*a* but with H in place of Me) was unsuccessful because, although a Leuckart reaction with the tetralone (I*a*) gave a satisfactory yield of the formamide analogous to (II*a*), dehydrogenation of the latter gave only the naphthalene (IV*a*) and not the desired formamide analogous to (III*a*).

Addition of hydrogen cyanide to 3 : 3′ : 4′-trimethoxychalkone (VI*b*) gave the keto-nitrile (VII*b*), which was hydrolysed in two steps to the benzoylpropionic acid (VIII*b*).

[1] Richardson, Robinson, and Seijo, *J.*, 1937, 835.
[2] Golberg and Robinson, *J.*, 1941, 575.
[3] Govindachari and Arumugam, *J.*, 1955, 2534.
[4] Whaley and Govindachari, "Organic Reactions," John Wiley & Sons, Inc., 1951, Vol. VI, p. 131.

Clemmensen reduction, and cyclisation of the resulting γ-phenylbutyric acid, gave 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethoxy-2-*m*-methoxyphenyl-1-oxonaphthalene (I*b*), converted into the acetamide (II*b*) through its oxime. Dehydrogenation of this amide yielded,

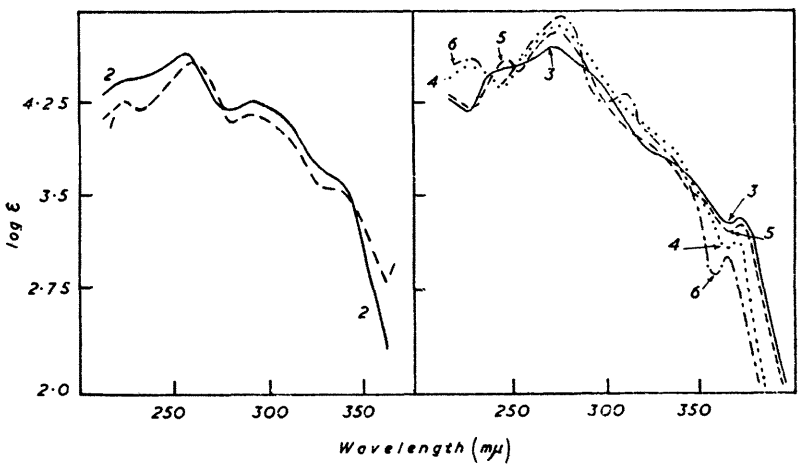


	R¹	R²	R³	R⁴
a	OMe	OMe	H	OMe
b	OMe	OMe	OMe	H
c	CH_2O_2		H	OMe
d	CH_2O_2		OMe	H

as before, a mixture of the naphthalene derivative (IV*b*) and the acetamide (III*b*). Cyclisation of the last compound gave 6 : 2′ : 3′-trimethoxy-9-methyl-1 : 2-benzophenanthridine (V*b*).

Synthesis of 7-methoxy-9-methyl-2′ : 3′-methylenedioxy-1 : 2-benzophenanthridine (V*c*) was achieved by starting with 4-methoxy-3′ : 4′-methylenedioxychalkone (VI*c*). The

FIG. 1. FIG. 2.



Absorption spectra of (1) 6 : 7-*dimethoxy*-2-p-(IV*a*) *and* (2)-m-*methoxyphenylnaphthalene* (IV*b*) *and* (3) 7 : 2′ : 3′-*trimethoxy*- (V*a*), (4) 6 : 2′ : 3′-*trimethoxy*- (V*b*), (5) 7-*methoxy*-2′ : 3′-*methylenedioxy*- (V*c*), *and* (6) 6-*methoxy*-2′ : 3′-*methylenedioxy*- (V*d*) 9-*methyl*-1 : 2-*benzophenanthridine, all in* EtOH.

acetyl derivative required for preparation of the chalkone was conveniently obtained by the action of dimethylcadmium on piperonoyl chloride. The chalkone (VI*c*) was then converted through the nitrile (VII*c*) into the benzoylpropionic acid (VIII*c*). Reduction

to the phenylbutyric acid for cyclisation to the tetralone (I*c*) was found to proceed better by hydrogenation over palladium–charcoal in presence of perchloric acid than by the Clemmensen procedure. As the oxime of the tetralone (I*c*) gave only poor yields of the required acetamide (II*c*), its acetate was subjected to the Schroeter reaction [5] (for conversion of a tetralone oxime into an α-naphthylamine derivative). Acetylation of the amine from this reaction gave the acetamide (III*c*) which was cyclised in good yield to the benzophenanthridine (V*c*).

6-Methoxy-9-methyl-2′ : 3′-methylenedioxy-1 : 2-benzophenanthridine (V*d*) was prepared by a similar sequence of reactions, starting with 3-methoxy-3′ : 4′-methylenedioxychalkone (VI*d*), through the keto-nitrile (VII*d*), the benzoylpropionic acid (VIII*d*), the tetralone (I*d*), and the acetamide (III*d*).

The ultraviolet spectra of the benzophenanthridines are recorded in Fig. 2.

Experimental

7 : 2′ : 3′-*Trimethoxy*-9-*methyl*-1 : 2-*benzophenanthridine* (V*a*).—(i) 1 : 2 : 3 : 4-*Tetrahydro*-1-*hydroxyimino*-6 : 7-*dimethoxy*-2-p-*methoxyphenylnaphthalene*. The tetralone [2] (I*a*) (1 g.), hydroxylamine hydrochloride (1 g.), and dry pyridine (5 ml.), heated at 100° for 5 hr. and poured into water, yielded the *oxime* (0·9 g.), cubes [from light petroleum (b. p. 40—60°)], m. p. 215—216° (Found: C, 70·3; H, 6·4. $C_{19}H_{21}O_4N$ requires C, 69·7; H, 6·4%).

(ii) 1-*Acetamido*-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-*dimethoxy*-2-p-*methoxyphenylnaphthalene* (II*a*). The above oxime (1 g.) in absolute alcohol (150 ml.) was reduced at 60—65° with 5% sodium amalgam (150 g.), added in small lots with shaking, the solution being kept almost neutral by intermittent addition of 50% acetic acid. The alcoholic solution was decanted off, the solvent evaporated under reduced pressure, and the residual solid extracted with hot water containing concentrated hydrochloric acid (10 ml.). After filtration, the acid solution was extracted once with benzene, then basified, and the base extracted with benzene. The dried (K_2CO_3) extract was evaporated and the residual oil heated with acetic anhydride (2 ml.) and dry pyridine (0·2 ml.) for 1 hr. at 100°. Addition of water and crystallisation of the precipitate from dilute alcohol yielded the *acetamide* (0·63 g.) as flakes, m. p. 193—195° (Found: C, 70·7; H, 6·7. $C_{21}H_{25}O_4N$ requires C, 71·0; H, 7·0%).

(iii) *The benzophenanthridine* (V*a*). The foregoing amide (0·3 g.) in dry *p*-cymene (50 ml.) was dehydrogenated over 30% palladium–charcoal (0·3 g.) at 240—260°. The solution was filtered hot from the catalyst which was washed several times with hot benzene. The combined extracts were evaporated and the residue was chromatographed on benzene over alumina. The first 3 fractions of the eluate (collected in 5 ml. portions) yielded, on evaporation, 6 : 7-*dimethoxy*-2-p-*methoxyphenylnaphthalene* (IV*a*) (0·1 g.), needles (from benzene–ethanol), m. p. 158—159° (Found: C, 77·7; H, 6·4. $C_{19}H_{18}O_3$ requires C, 77·6; H, 6·1%). Further elution with benzene containing 1% of ethanol gave 1-acetamido-6 : 7-dimethoxy-2-*p*-methoxyphenylnaphthalene (III*a*) (0·15 g.), m. p. 205—208°, which was heated with phosphorus oxychloride (1 ml.) for 2 hr. at 100° and decomposed with ice-water. Basification of the yellow precipitate with sodium hydroxide gave the *benzophenanthridine* (V*a*) (0·09 g.), needles (from pyridine–ethanol), m. p. 229—230° (Found: C, 75·4; H, 5·7. $C_{21}H_{19}O_3N$ requires C, 75·7; H, 5·7%).

(iv) 1-*Formamido*-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-*dimethoxy*-2-p-*methoxyphenylnaphthalene*. The tetralone (I*a*) (2 g.) in formamide (5 ml.) containing formic acid (0·25 ml.) and ammonium sulphate (0·25 g.) was heated under reflux at 180° for 3 hr., formic acid (0·25 ml.) being added every 1 hr. The cold mixture was diluted with water and extracted with chloroform. The dried (Na_2SO_4) chloroform extract gave, on removal of the solvent, a solid which was triturated with methanol (5 ml.) and then digested with acetone (5 ml.). The insoluble fraction gave the *formamide* (0·6 g.), m. p. 199—200° (from dioxan–ethanol) (Found: C, 71·0; H, 6·5. $C_{20}H_{23}O_4N$ requires C, 70·4; H, 6·7%). The formamide (0·5 g.) was heated in *p*-cymene (50 ml.) with 30% palladium–charcoal: chromatography of the product in benzene over alumina gave only the naphthalene (IV*a*) (0·35 g.), m. p. and mixed m. p. 158—159°.

6 : 2′ : 3′-*Trimethoxy*-9-*methyl*-1 : 2-*benzophenanthridine* (V*b*).—(i) γ-(3 : 4-*Dimethoxyphenyl*)-α-m-*methoxyphenyl*-γ-*oxobutyronitrile* (VII*b*). A mixture of acetoveratrone (20 g.), *m*-methoxybenzaldehyde (15 g.), alcohol (75 ml.), and 10% aqueous sodium hydroxide (20 ml.) was shaken

[5] Schroeter, *Ber.*, 1930, **63**, 1317.

for a few minutes, left overnight, diluted with water and extracted with chloroform. The dried (Na_2SO_4) chloroform extract, on evaporation and distillation, yielded 3 : 3′ : 4′-trimethoxychalkone (VI*b*) (25 g.), b. p. 218—220°/0·08 mm. A solution of the chalkone (25 g.) in boiling methanol (70 ml.) was treated with sodium cyanide (12 g.) and 3 drops of phenolphthalein, then slowly with acetic acid (5 ml.) and water (25 ml.) at such a rate that the solution remained pink. After boiling for 10 min., the solution was poured into ice. The gummy product, when washed with water, yielded the *nitrile* (VII*b*) (21 g.), pale yellow cubes (from acetone), m. p. 153—154° (Found: C, 70·4; H, 5·3. $C_{19}H_{19}O_4N$ requires C, 70·2; H, 5·7%).

(ii) *γ-(3 : 4-Dimethoxyphenyl)-α-m-methoxyphenyl-γ-oxobutyric acid* (VIII*b*). A stirred suspension of the above nitrile (20 g.) in glacial acetic acid (100 ml.) was treated with concentrated sulphuric acid (20 ml.) in small lots, kept for 15 min., poured into ice, and extracted with chloroform. The extract was washed with sodium carbonate solution and water, dried (Na_2SO_4), and evaporated. The residual oil was rubbed with methanol and the solid crystallised from the same solvent, to give *γ-(3 : 4-dimethoxyphenyl)-α-m-methoxyphenylbutyramide* (14 g.) as plates, m. p. 129—130° (Found: C, 66·2; H, 6·2. $C_{19}H_{21}O_5N$ requires C, 66·5; H, 6·1%). The amide (13 g.) was refluxed in alcohol (50 ml.) and 10% aqueous sodium hydroxide (70 ml.) for 15 hr., diluted with water (120 ml.), and extracted once with chloroform. The aqueous layer, on acidification, yielded the *acid* (10 g.), plates (from dilute alcohol), m. p. 153—154° (Found: C, 66·1; H, 6·2. $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·8%).

(iii) *1 : 2 : 3 : 4-Tetrahydro-6 : 7-dimethoxy-2-m-methoxyphenyl-1-oxonaphthalene* (I*b*). The above keto-acid (10 g.), toluene (40 ml.), concentrated hydrochloric acid (53 ml.), zinc amalgam (22 g.), and 5% acetic acid (15 ml.) were refluxed for 48 hr., concentrated hydrochloric acid (10 ml.) being added every 10 hr. The toluene layer was separated, the aqueous layer was extracted once with benzene and the combined toluene–benzene extracts were shaken with sodium carbonate solution. Acidification of the aqueous layer, followed by extraction with chloroform, gave *α-m*-methoxyphenyl-*γ*-(3 : 4-dimethoxyphenyl)butyric acid (8 g.) as a pale yellow oil. This was refluxed with phosphorus oxychloride (15 ml.) for 5 min. and the red solution poured on ice. The pink precipitate was filtered off, washed with sodium carbonate solution and water, dried, and chromatographed in benzene over alumina, the eluate being collected in 10 ml. fractions. The 3 initial fractions gave a substance, m. p. 112—114° (from methanol) (Found: C, 69·0; H, 5·6%). Later fractions gave the *tetralone* (I*b*) (4 g.), plates (from methanol), m. p. 143—145° (Found: C, 73·4; H, 6·2. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%), yielding an *oxime* (pyridine method) as cubes [from benzene–light petroleum (b. p. 40—60°)], m. p. 173—175° (Found: C, 69·6; H, 6·6%).

(iv) *1-Acetamido-1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethoxy-2-m-methoxyphenylnaphthalene* (II*b*). The above oxime (2 g.) in absolute alcohol (150 ml.) was reduced with 5% sodium amalgam (300 g.), and the product worked up as above, yielding the *acetamide* (1·2 g.) as needles (from dilute alcohol), m. p. 172—173° (Found: C, 71·6; H, 7·1%).

(v) *The benzophenanthridine* (V*b*). The foregoing acetamide (1·2 g.) in *p*-cymene (70 ml.), dehydrogenated over 30% palladium–charcoal (0·8 g.) at 230—250° and chromatographed in benzene over alumina, yielded in the initial fractions *6 : 7-dimethoxy-2-m-methoxyphenylnaphthalene* (IV*b*) (0·5 g.), needles (from methanol), m. p. 129—130° (Found: C, 77·7; H, 6·1%). Elution with benzene containing ethanol gave 1-acetamido-6 : 7-dimethoxy-2-*m*-methoxyphenylnaphthalene (III*b*) (0·6 g.) as a gum which was cyclised with phosphorus oxychloride (3 ml.) to the *benzophenanthridine* (V*b*) (0·4 g.), needles (from pyridine–ethanol), m. p. 183—185° (Found: C, 75·2; H, 5·5%).

7-Methoxy-9-methyl-2′ : 3′-methylenedioxy-1 : 2-benzophenanthridine (V*c*).—(i) To an ice-cooled solution of methylmagnesium bromide [from magnesium (9·8 g.) in ether (200 ml.) and excess of methyl bromide] was added, in a nitrogen atmosphere, during 5 min., powdered anhydrous cadmium chloride (38 g.; dried at 110° to constant wt.). Stirring under reflux was continued for 1 hr. After removal of the ether, benzene (60 ml.) was added and an additional 25 ml. of benzene was distilled off. After addition of more solvent (240 ml.), the mixture was cooled to 50° and a solution of piperonoyl chloride [6] (36 g.) in benzene (50 ml.) was added dropwise, considerable heat being evolved. The mixture was refluxed for 1 hr., left overnight, then decomposed with dilute sulphuric acid. The aqueous layer was extracted with more solvent. The combined benzene extracts were washed with sodium carbonate solution and water, dried

[6] Barger, *J.*, 1908, **93**, 567.

(Na_2SO_4), and evaporated. The residue, on cooling, gave 4-acetyl-1 : 2-methylenedioxybenzene (32 g.) as a pale yellow solid, m. p. and mixed m. p. (with a sample [1] obtained by oxidation of 1-piperonoylethanol) 84—85°.

(ii) 4-*Methoxy*-3′ : 4′-*methylenedioxychalkone* (VI*c*). *p*-Methoxybenzaldehyde (15 g.) with the preceding ketone (18·2 g.) in alcohol (86 ml.) containing 10% aqueous sodium hydroxide (20 ml.) yielded the *chalkone* (28 g.) as pale yellow needles (from methanol), m. p. 142° (Found: C, 72·0; H, 4·9. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%).

(iii) α-p-*Methoxyphenyl*-γ-(3 : 4-*methylenedioxyphenyl*)-γ-*oxobutyronitrile* (VII*c*). A stirred solution of the above chalkone (20·5 g.) in 2-ethoxyethanol (80 ml.) containing acetic acid (4·5 ml.) was treated at 100°, during 3 min., with potassium cyanide (9·3 g.) in water (17 ml.). Heating was continued for a further 10 min. and water (100 ml.) added, to give the *nitrile* (15 g.), pale yellow needles (from alcohol), m. p. 130° (Found: C, 70·3; H, 5·3. $C_{18}H_{15}O_4N$ requires C, 69·9; H, 4·9%).

(iv) α-p-*Methoxyphenyl*-γ-(3 : 4-*methylenedioxyphenyl*)-γ-*oxobutyric acid* (VIII*c*). The above nitrile (18 g.) in acetic acid (120 ml.) with concentrated sulphuric acid (18 ml.) gave the *amide* (15 g.), needles (from methanol), m. p. 169° (Found: C, 66·3; H, 5·3. $C_{18}H_{17}O_5N$ requires C, 66·1; H, 5·2%), which with 7% aqueous sodium hydroxide (200 ml.) and alcohol (80 ml.) gave in 6 hr. the *acid* (VIII*b*) (12·5 g.), needles (from methanol), m. p. 169° (Found: C, 65·6; H, 5·4. $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%).

(v) 1 : 2 : 3 : 4-*Tetrahydro*-2-p-*methoxyphenyl*-6 : 7-*methylenedioxy*-1-*oxonaphthalene* (I*c*). The above keto-acid (2·5 g.) in acetic acid (20 ml.) containing 70% perchloric acid (0·5 ml.) was reduced at 60° with hydrogen at 1 atm. in presence of 5% palladium–charcoal (0·5 g.) during 1 hr. The catalyst was filtered off and washed with acetic acid. After removal of the solvent *in vacuo*, the residue was extracted with chloroform. The chloroform was washed with water, dried (Na_2SO_4), and evaporated, to yield α-*p*-methoxyphenyl-γ-(3 : 4-methylenedioxyphenyl)-butyric acid as a yellow oil (2 g.) which with boiling phosphorus oxychloride (5 ml.) for 5 min. yielded as the single product the *tetralone* (I*c*) (1·5 g.), pale yellow prisms (from methanol), m. p. 144—145° (Found: C, 72·6; H, 5·3. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%). Clemmensen reduction of the keto-acid (2·5 g.) and cyclisation with phosphorus oxychloride gave only 0·8 g. of the tetralone. The *oxime* (0·8 g. from 1 g. of the tetralone; pyridine method) formed needles (from alcohol), m. p. 160° (Found: C, 69·3; H, 5·7. $C_{18}H_{17}O_4N$ requires C, 69·5; H, 5·5%), and gave, with acetic anhydride (1·2 ml.) in pyridine (1 ml.) at 100°, the *acetate* (0·8 g.), needles (from alcohol), m. p. 151—152° (Found: C, 68·1; H, 5·4; N, 4·3. $C_{20}H_{19}O_5N$ requires C, 68·0; H, 5·4; N, 4·0%).

(vi) 1-*Acetamido*-1 : 2 : 3 : 4-*tetrahydro*-2-p-*methoxyphenyl*-6 : 7-*methylenedioxynaphthalene* (II*c*). The oxime (1 g.) in absolute ethanol (150 ml.) was reduced at 60—65° with sodium amalgam (150 g.), to the *acetamide* (0·2 g.), needles (from dilute alcohol), m. p. 191—192° (Found: C, 71·3; H, 6·4. $C_{20}H_{21}O_4N$ requires C, 70·8; H, 6·2%).

(vii) *The phenanthridine* (V*c*). A solution of the oxime acetate (0·5 g.) in acetic acid (5 ml.) and acetic anhydride (1·5 ml.) was saturated with dry hydrogen chloride at 0° and heated at 90—95° in a sealed tube for 8 hr., then decomposed with water. The yellow solid obtained was dissolved in hot water and filtered. The filtrate was extracted with benzene, basified with sodium hydroxide, and again extracted with benzene. The final, dried (Na_2SO_4) benzene solution yielded a yellow oil (0·25 g.) which with acetic anhydride (1 ml.) and pyridine (0·5 ml.) at 100° gave 1-acetamido-2-(*p*-methoxyphenyl)-6 : 7-methylenedioxynaphthalene (III*c*) (0·25 g.), m. p. 166—169°, cyclised with phosphorus oxychloride (2·5 ml.) at 100° to the *phenanthridine* (V*c*) (0·12 g.), needles (from pyridine–ethanol), m. p. 185—186° (Found: C, 75·9; H, 5·0. $C_{20}H_{15}O_3N$ requires C, 75·7; H, 4·7%).

6-*Methoxy*-9-*methyl*-2′ : 3′-*methylenedioxy*-1 : 2-*benzophenanthridine* (V*d*).—(i) 3-*Methoxy*-3′ : 4′-*methylenedioxychalkone* (VI*d*). A mixture of *m*-methoxybenzaldehyde (7·5 g.), 4-acetyl-1 : 2-methylenedioxybenzene (9·1 g.), alcohol (43 ml.), and 10% aqueous sodium hydroxide (10 ml.) gave the *chalkone* (14 g.), pale yellow needles (from alcohol), m. p. 100° (Found: C, 72·0; H, 4·9%).

(ii) α-m-*Methoxyphenyl*-γ-(3 : 4-*methylenedioxyphenyl*)-γ-*oxobutyronitrile* (VII*d*). The foregoing chalkone (10 g.) in 2-ethoxyethanol (45 ml.) containing glacial acetic acid (5·25 ml.) was treated with potassium cyanide (4·65 g.) in water (8·5 ml.), yielding the *nitrile* (9 g.), needles (from dilute acetic acid), m. p. 76—77° (Found: C, 69·6; H, 4·9%).

(iii) α-m-*Methoxyphenyl*-γ-(3 : 4-*methylenedioxyphenyl*)-γ-*oxobutyric acid* (VIII*d*). The

foregoing nitrile (9 g.) in acetic acid (45 ml.) was treated with concentrated sulphuric acid (7·5 ml.), to yield the *amide* (8·5 g.), needles (from methanol), m. p. 140° (Found: C, 65·7; H, 4·8%). The amide (7·5 g.) in alcohol (45 ml.) and 7% aqueous sodium hydroxide (90 ml.), refluxed for 5 hr., yielded the *acid* (6·5 g.), needles (from dilute alcohol), m. p. 145° (Found: C, 65·7; H, 5·2%).

(iv) 1 : 2 : 3 : 4-*Tetrahydro*-2-m-*methoxyphenyl*-6 : 7-*methylenedioxy*-1-*oxonaphthalene* (I*d*). The above acid (2 g.) in acetic acid (15 ml.) containing 70% perchloric acid (0·5 ml.) was reduced at 1 atm. over 5% palladised charcoal (0·5 g.) to α-*m*-methoxyphenyl-γ-(3 : 4-methylenedioxyphenyl)butyric acid (1·8 g.), a yellow oil. With phosphorus oxychloride at 100° (15 min.) this gave, after chromatography in benzene over alumina, the *tetralone* (I*d*) (0·7 g.), prisms (from alcohol), m. p. 98—99° (Found: C, 72·8; H, 5·5%). The *oxime* (0·8 g. from 1 g. of the tetralone; pyridine method) formed needles (from alcohol), m. p. 164—165° (Found: C, 69·3; H, 5·6%), and with acetic anhydride and pyridine at 100° gave an *acetate* (0·6 g.), needles (from alcohol), m. p. 132—133° (Found: C, 67·7; H, 5·5%).

(v) *The phenanthridine* (V*d*). The foregoing oxime acetate (0·4 g.) in acetic acid (4 ml.) and acetic anhydride (1·5 ml.) was saturated with hydrogen chloride at 0° and heated at 90—95° in a sealed tube for 8 hr., yielding a brownish oily base, which, with acetic anhydride (1·5 ml.) and pyridine (0·5 ml.) at 100° yielded a dark brown gum. Chromatography in benzene over alumina yielded 1-acetamido-2-*m*-methoxyphenyl-6 : 7-methylenedioxynaphthalene (III*d*) (0·06 g.), cyclised with phosphorus oxychloride (1 ml.) to the *phenanthridine* (0·04 g.), pale yellow needles (from pyridine–ethanol), m. p. 197—198° (Found: C, 76·0; H, 4·7%).

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