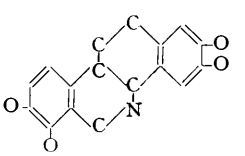
282. *Synthetical Experiments in the Chelidonine–Sanguinarine Group of the Alkaloids. Part II.*

By A. S. Bailey and Sir Robert Robinson.

The method described in Part I for the synthesis of substituted benzphenanthridines related to the sanguinarine group could only be applied to the preparation of 4 : 5-disubstituted catechol ethers of the series. An attempt to overcome this disability by blocking a reactive position with a bromine atom broke down at a late stage in the process.

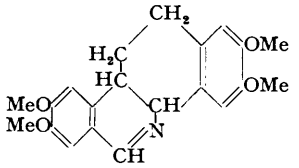
The required orientation (1 : 2 : 3 : 4-) was secured by starting with opianic acid, a route which has already been studied in a preliminary way by R. D. Haworth and abandoned owing to the failure to achieve a necessary step in the synthesis. This difficulty has been surmounted and a derivative possessing the skeletal system (annexed) of the natural alkaloids of the group has been obtained.

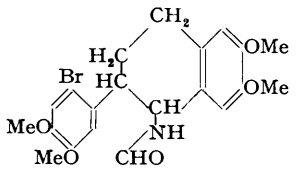


A summary of the results has already been published (*Nature*, 1949, **164**, 402), and a preliminary announcement has also been made in collaboration with R. S. Staunton (*Nature*, 1950, **165**, 235) of the conversion of the end-product described in this communication into a reference compound obtained by Späth and Kuffner (*Ber.*, 1931, **64**, 2034) from both sanguinarine and chelerythrine.

Part I of this investigation (Richardson, Robinson, and Seijo, *J.*, 1937, 835) included an account of the preparation of a tetramethoxytetrahydro-1 : 2-benzphenanthridine (I), the

last stage being the cyclisation of a substituted formamide. In resuming the research we proposed to apply this method to the brominated derivative (II) with the object of inducing

(I.) 

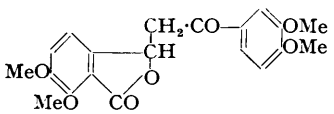
 (II.)

ring-closure in the *ortho*-position to methoxyl, and so to obtain the orientation of the catechol nuclei which occurs in all the known alkaloids of the group. The substance (II) was prepared by following the methods of Part I (cf. the Experimental section) but cyclodehydration could not be brought about, despite many trials.

It occurred to us that a series of reactions similar to those of Part I (but also differing in some obvious respects) might well be based on the use of opianic acid instead of veratraldehyde as the starting point, and this scheme would automatically ensure the correct orientation of catechol nuclei.

After working on this project for some months we found that R. D. Haworth (*J.*, 1937, 1312) had initiated work on the same lines and abandoned it because of the failure of the stage of addition of the elements of hydrogen cyanide. In our experience too, this proved extremely troublesome and the idea was set aside for a time.

Fortunately the difficulty was eventually surmounted by the use of special conditions, which must be strictly observed.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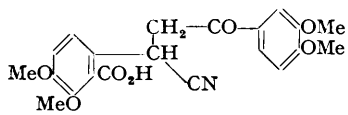
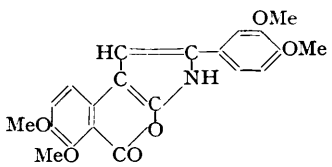
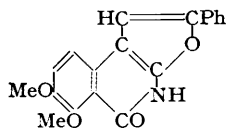

(IV.)

6 : 7-Dimethoxy-3-(3 : 4-dimethoxyphenacyl)phthalide (III) (Haworth, *loc. cit.*) was treated with potassium cyanide in 2-methoxyethanol solution at 100°, in the presence of sodium acetate, to form β-(3 : 4-dimethoxybenzoyl)-α-(2-carboxy-3 : 4-dimethoxyphenyl)propionitrile (IV). On treatment with alkaline hydrogen peroxide the related amide was obtained, and this could be further hydrolysed by hot alkali to the dibasic acid (IV; CN ⟶ CO_2H).

Another route to the same substance starts with the dehydration of (IV) by heat, or by treatment with hot hydrochloric acid in acetic acid. This produces a yellow compound, $C_{21}H_{19}O_6N$, believed to be (V); on hydrolysis with hot aqueous sodium hydroxide, the above dibasic acid is obtained. Haworth (*loc. cit.*) obtained a similar yellow substance from 6 : 7-di-

(V.) 

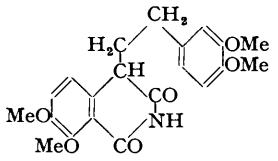
 (VI.)

methoxy-3-phenacylphthalide (Goldschmidt, *Monatsh.*, 1891, **12**, 476) by the action of potassium cyanide (intermediate not characterised) followed by concentrated hydrochloric acid at 100°. He considered the product to be a furan derivative (VI). We prefer the transposition of O and NH, as in (V) because the lactone structure provides a better explanation of the ease of hydrolysis. 2-Pyridones are notably difficult to hydrolyse by means of alkalis. Moreover the experiments of Rogers (*J.*, 1943, 590; B.P. 544,101), Rogers and Davies (*J.*, 1944, 126), and Knott (*J.*, 1947, 1196) exemplify the ready conversion of β-acylpropionitriles into pyrrole derivatives. There can be little doubt but that (V) is the dimethoxy-derivative of Haworth's substance, $C_{19}H_{15}O_4N$, and yet the behaviour on alkaline hydrolysis of the two is different. Haworth (*loc. cit.*) obtained an alkali-soluble substance in colourless prisms, m. p. 184—185° (decomp.) (Found: C, 61·3; H, 5·0. Calc. for $C_{12}H_{12}O_5$: C, 61·0; H, 5·1. Calc. for $C_{17}H_{16}O_7$: C, 61·4; H, 4·8. Calc. for $C_{19}H_{18}O_8$: C, 61·0; H, 4·8%).

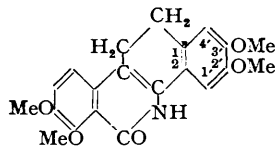
The keto-dibasic acid (IV; CN in place of CO_2H) was reduced by Clemmensen's method

to γ-(3 : 4-dimethoxyphenyl)-α-(2-carboxy-3 : 4-dimethoxyphenyl)butyric acid which is readily converted into its imide (VII). This homophthalimide derivative was found to be convertible in good yield into 7 : 8 : 2′ : 3′-tetramethoxy-3 : 4-dihydro-1 : 2-benzphenanthridone (VIII) by the action of a mixture of phosphoric anhydride and glacial phosphoric acid. Many other methods were tried with much inferior results.

(VII.)



(VIII.)



Various attempts have been made to transform the anhydrocryptopine structure into that of sanguinarine type, but up to the present without success, probably because the vinyl group is reactive at the α- and not at the β-position.

Experimental.

3 : 4-*Dimethoxyphenyl* 2-*Bromo*-4 : 5-*dimethoxystyryl Ketone*.—2N-Sodium hydroxide (120 c.c.) was added to a solution of 6-bromoveratraldehyde (110 g.) and acetoveratrone (85 g.) in boiling ethanol (1000 c.c.). A yellow solid separated almost immediately and next day this was collected, washed with alcohol, and dried; it had m. p. 160—163° (120 g., 66%). 3 : 4-*Dimethoxyphenyl* 2-*bromo*-4 : 5-*dimethoxystyryl ketone* crystallised from acetone as stout, pale yellow rods, m. p. 165—166° (Found : C, 55·8; H, 4·5. $C_{19}H_{19}O_5Br$ requires C, 56·1; H, 4·7%). The 2 : 4-*dinitrophenylhydrazone* separated from xylene in red, woolly needles, m. p. 240—242° (Found : N, 9·8. $C_{25}H_{23}O_8N_4Br$ requires N, 9·6%).

β-(3 : 4-*Dimethoxybenzoyl*)-α-(2-*bromo*-4 : 5-*dimethoxyphenyl*)*propionitrile*.—The addition of hydrogen cyanide to the unsaturated ketone could not be accomplished either by an adaptation of the method given in *Org. Synth.*, 1930, **10**, 80, or by Richardson, Robinson, and Seijo's method (*loc. cit.*).

A solution of the above chalkone (41 g.) in boiling 2-methoxyethanol (150 c.c.) and glacial acetic acid (6 g.) was heated in boiling water and stirred mechanically, and sodium cyanide (11 g.) in water (25 c.c.) added dropwise during 5 minutes. The solid, at first precipitated, disappeared after 5 minutes and a white solid soon began to separate. Ten minutes after all the cyanide had been added the boiling water-bath was removed, water (75 c.c.) added, and the solution allowed to cool slowly to room temperature and then placed in the refrigerator. Next day the solid was collected, washed with water, and dried; it had m. p. 167—169° (42 g., 96%). β-(3 : 4-*Dimethoxybenzoyl*)-α-(2-*bromo*-4 : 5-*dimethoxyphenyl*)*propionitrile* crystallised from acetone in colourless, hard prisms, m. p. 170—171° (Found : C, 55·6; H, 4·3; Br, 18·8. $C_{20}H_{20}O_5NBr$ requires C, 55·3; H, 4·6; Br, 18·4%).

β-(3 : 4-*Dimethoxybenzoyl*)-α-(2-*bromo*-4 : 5-*dimethoxyphenyl*)*propionamide*.—Concentrated sulphuric acid (35 c.c.) was gradually added during 15 minutes to the stirred suspension of the nitrile (43 g.) in acetic acid (300 c.c.). After 15 minutes the solution was poured into water (1·5 l.) and the solid *amide* collected (43 g.; m. p. 176—178°) was pure enough for the next stage. Crystallised from ethanol and then from ethyl acetate, it formed colourless rhombs, m. p. 186—187° (Found : N, 2·9. $C_{20}H_{22}O_5NBr$ requires N, 3·1%).

β-(3 : 4-*Dimethoxybenzoyl*)-α-(2-*bromo*-4 : 5-*dimethoxyphenyl*)*propionic Acid*.—A solution of the above mentioned amide (43 g.) in ethanol (300 c.c.), along with 2N-sodium hydroxide solution (300 c.c.), was refluxed until evolution of ammonia ceased (13—15 hours). Most of the alcohol was distilled off and water (300 c.c.) and excess of 5N-hydrochloric acid were added to the filtered liquid. The solid (36·1 g., 80%) which separated was crystallised from alcohol, and β-(3 : 4-*dimethoxybenzoyl*)-α-(2-*bromo*-4 : 5-*dimethoxyphenyl*)*propionic acid* so obtained in colourless prisms which melted partly at 160—164°, resolidified, and remelted at 174—175° (Found : C, 53·2; H, 4·7; Br, 17·2. $C_{20}H_{21}O_7Br$ requires C, 53·0; H, 4·6; Br, 17·7%).

1-*Keto*-6 : 7-*dimethoxy*-2-(2-*bromo*-4 : 5-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—A mixture of (dimethoxybenzoyl)(bromodimethoxyphenyl)propionic acid (45 g.), amalgamated zinc (150 g.), water (75 c.c.), glacial acetic acid (5 c.c.), concentrated hydrochloric acid (150 c.c.), and toluene (250 c.c.) was refluxed for 48 hours, concentrated hydrochloric acid (25 c.c.) being added every 12 hours. After cooling, the toluene layer was washed with water, and then extracted with 2N-sodium carbonate solution (3 × 40 c.c.). The combined extracts were boiled and acidified with dilute hydrochloric acid. The oil that separated became a glass when cold, and this was soluble in organic solvents but could not be crystallised. A small quantity of the substance was distilled (b. p. 200°/0·01 mm.), yielding again an uncrystallisable glass.

The crude product, dried by heating at 100° *in vacuo* for an hour, was refluxed with phosphoryl chloride (150 c.c.) for 5 minutes; the resulting dark green solution was cooled and then poured on ice. A gum separated which rapidly solidified. Next day the solid was collected, washed well with water, and crystallised from methanol; it had m. p. 135—137° (34·8 g., 84% calc. on the keto-acid). 1-*Keto*-6 : 7-*dimethoxy*-2-(2-*bromo*-4 : 5-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene* was obtained in colourless plates, m. p. 138—139° after recrystallisation (Found : C, 57·4; H, 5·2; Br, 18·4. $C_{20}H_{21}O_5Br$ requires C, 57·1; H, 5·0; Br, 19·0%). The 2 : 4-*dinitrophenylhydrazone* crystallised from dioxan as clusters of red, prismatic needles, m. p. 254—256° (Found : N, 9·3. $C_{26}H_{25}O_8N_4Br$ requires N, 9·4%). The *oxime* (prepared in pyridine) crystallised from methanol in colourless prisms which lost solvent at 120° and then had m. p. 158—159° (Found : N, 3·5. $C_{20}H_{22}O_5NBr$ requires N, 3·2%).

1-*Formamido*-6 : 7-*dimethoxy*-2-(2-*bromo*-4 : 5-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene* (II).—The foregoing ketone (5 g.) and formamide (25 c.c.) were heated together for an hour at 160°. Ammonium sulphate (2 g.) was added and the mixture heated for 4 hours at 180—190° (oil-bath). The warm mixture was poured into ice-water, the solid which separated was extracted with chloroform, the chloroform extract washed with water, dried (Na_2SO_4), and the solvent removed. The residual oil was boiled with methanol (10 c.c.), and the solid collected, washed with methanol, and dried (2·6 g., 49%). 1-*Formamido*-6 : 7-*dimethoxy*-2-(2-*bromo*-4 : 5-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene* crystallised from dioxan–ethanol in fine needles, m. p. 241—243° (Found : C, 55·6; H, 5·4; N, 3·1. $C_{21}H_{24}O_5NBr$ requires C, 56·0; H, 5·3; N, 3·1%).

Attempts to cyclise this amide with phosphoryl chloride alone, or in toluene or xylene, failed. The desired reaction could not be effected by the use of phosphoric anhydride in xylene, or by syrupy phosphoric acid, or by phosphorus pentachloride in chloroform solution.

β-(3 : 4-*Dimethoxybenzoyl*)-α-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*propionitrile* (IV).—The experimental conditions described below are critical.

6 : 7-Dimethoxy-3-(3 : 4-dimethoxyphenacyl)phthalide (50 g.; m. p. 168—169°; Haworth, *loc. cit.*, gives m. p. 165—167°) was dissolved in boiling 2-methoxyethanol (150 c.c.), and crystallised sodium acetate (20 g.) added; the solution then became yellow. The flask containing the solution was immersed in a boiling water-bath, and potassium cyanide (20 g.) in water (30 c.c.) added during 2 minutes from a funnel, the stem of which reached to the bottom of the flask. The solution was occasionally stirred and after 10 minutes 2N-hydrochloric acid (250 c.c.) was added, and the liquid then seeded and allowed to cool slowly. Next day a few drops of concentrated hydrochloric acid were added and the very pale yellow solid collected, washed, and dried. This material (*A*) was used directly for the next stage (see below). A small quantity was crystallised thrice from methanol and once from ethyl acetate. β-(3 : 4-*Dimethoxybenzoyl*)-α-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*propionitrile* was thus obtained in clusters of rhombs which become pale yellow at 122°, shrink slightly at 133°, melt at 156—158° with gas evolution, and resolidify to an orange solid which then melts at 229—231° (Found : C, 63·2; H, 5·5. $C_{21}H_{21}O_7N$ requires C, 63·2; H, 5·3%).

The substance is soluble in cold dilute sodium carbonate solution. When a solution of the nitrile in a drop of aqueous ammonia (*d* 0·88) is heated at 100° for 5 minutes a deep-green solution is produced. Also, when heated at 100° in formamide the substance rapidly gives a deep-green solution.

Lactone of 2-*Hydroxy*-5-(3 : 4-*dimethoxyphenyl*)-3-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*pyrrole* (V).—(*a*) The last-mentioned nitrile was heated in an oil-bath at 140° for half an hour *in vacuo*. Gas was evolved and the orange residue had m. p. 228—230°. Crystallisation from dioxan gave clusters of fine rods, m. p. 234—236° (decomp.) (Found : C, 65·8; H, 5·0; N, 3·2. $C_{21}H_{19}O_6N$ requires C, 66·2; H, 5·0; N, 3·7%).

(*b*) The crude material (*A*) (see above) was dissolved in boiling acetic acid (120 c.c.), the source of heat removed, and concentrated hydrochloric acid (20 c.c.) added. The heat of the reaction caused the deep-red solution to boil, and an orange-red solid began to separate from the solution. After the mixture had been heated for 5 minutes on a steam-bath, warm water (30 c.c.) was added. Next day, the solid was collected, washed with water and with aqueous methanol, and dried, m. p. 227—229° (46 g., 88% on the two stages). Crystallisation from acetic acid and then from dioxan gave the *lactone* in clusters of pale yellow rods, m. p. and mixed m. p. with the product prepared as in (*a*), 234—236°. *X*-Ray powder photographs confirmed the identity of the two specimens (Found : C, 66·3; H, 5·2; N, 3·6%).

The substance is insoluble in cold sodium hydroxide solution and in dilute mineral acid. It forms a deep-red solution in cold concentrated sulphuric acid which becomes brown on warming. With *p*-dimethylaminobenzaldehyde in boiling acetic acid containing a drop of concentrated hydrochloric acid, a deep green colour rapidly developed. The substance was recovered unchanged after being refluxed for 30 minutes with *p*-nitrophenylhydrazine in acetic acid solution.

β-(3 : 4-*Dimethoxybenzoyl*)-α-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*propionic Acid* (IV; CN in place of CO_2H).—The above lactone (30 g.) was refluxed with 2N-sodium hydroxide (300 c.c.). A dark green solution was formed as the solid slowly dissolved, ammonia was evolved, and the solution gradually became pale yellow. After the evolution of ammonia had ceased (1—2 hours), the filtered liquid was acidified with dilute hydrochloric acid. A gum separated, which rapidly solidified and was collected, washed with water, and crystallised from 90% acetic acid; it had m. p. 192—196° (decomp.) (25 g., 76%). A further 2 g. were recovered from the mother-liquors. Three crystallisations from acetic acid gave β-(3 : 4-*dimethoxybenzoyl*)-α-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*propionic acid* in colourless rhombs, m. p. 198—200° (decomp.) [Found : C, 60·1; H, 5·3; *M* (cryoscopic in camphor), 420; equiv. (by titration), 218. $C_{21}H_{22}O_9$ requires C, 60·3; H, 5·3%; *M*, 418; equiv., 209].

The acid gave the potentiometric titration curve expected for a dibasic acid. The 2 : 4-*dinitrophenylhydrazone* crystallised from dioxan–ethanol in orange-red prisms, m. p. 225—227° (decomp.) (Found : N, 9·1. $C_{27}H_{26}O_{12}N_4$ requires N, 9·4%).

The acid (1 g.) was refluxed with acetic anhydride (6 c.c.) for 15 minutes. Excess of acetic anhydride was removed *in vacuo* on the steam-bath, and the residue crystallised twice from ethyl acetate containing a trace of acetic anhydride. The *anhydride* formed fine needles, m. p. 167—168° (Found : C, 63·1; H, 4·9. $C_{21}H_{20}O_8$ requires C, 63·0; H, 5·0%), soluble in cold 2N-sodium hydroxide forming a yellow solution.

A suspension of the anhydride (0·3 g.) in 2N-sodium carbonate solution (3 c.c.) was heated on a steam-bath. A yellow solution was formed which became colourless in 5 minutes. Excess of hydrochloric acid was added, and the precipitate collected and crystallised from 90% acetic acid; m. p. and mixed m. p. with the original dibasic acid, 200—202° (decomp.).

β-(3 : 4-*Dimethoxybenzoyl*)-α-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*propionamide*.—A solution of the above (dimethoxybenzoyl)(carboxydimethoxyphenyl)propionitrile (4 g.) in cold N-sodium hydroxide (10 c.c.) was mixed with aqueous hydrogen peroxide (2 c.c. of 30%) and water (20 c.c.). After 6 hours at room temperature, the mixture was acidified with hydrochloric acid. The solid, which separated, was

collected, washed with water, and crystallised from ethanol. The *amide* formed clusters of fine rods, m. p. 178—180° (decomp.) (Found: C, 60·3; H, 5·7; N, 3·6. $C_{21}H_{23}O_5N$ requires C, 60·5; H, 5·5; N, 3·4%).

A solution of the amide (0·5 g.) in 2N-sodium hydroxide (5 c.c.) was heated on a steam-bath until evolution of ammonia ceased (30 minutes). The acid was precipitated with dilute hydrochloric acid and crystallised from acetic acid, m. p. and mixed m. p. 196—198° (decomp.) (Found: C, 59·8; H, 5·2%).

γ-(3 : 4-*Dimethoxyphenyl*)-α-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*butyric Acid* [*Dibasic Acid related to* (VII)].—A mixture of toluene (300 c.c.), glacial acetic acid (5 c.c.), water (50 c.c.), concentrated hydrochloric acid (150 c.c.), amalgamated zinc (200 g.), and the keto-dibasic acid (50 g.) was refluxed for 60 hours, concentrated hydrochloric acid (50 c.c.) being added every 12 hours. After 12 hours' refluxing most of the keto-acid had disappeared, and after 24 hours a new solid began to separate from the toluene layer. After 60 hours' refluxing the mixture was distilled until approx. 150 c.c. of toluene had been removed, then allowed to cool and the white solid collected, and washed well with water. The zinc residues were extracted with boiling 50% acetic acid (100 c.c.), and the solid also dissolved in this extract. The solution was filtered and cooled; the product, collected and washed with 50% acetic acid, had m. p. 169—170° (38·5 g., 80%). γ-(3 : 4-*Dimethoxyphenyl*)-α-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*butyric acid* crystallised from 50% acetic acid as colourless, diamond-shaped prisms, m. p. 171—172° (decomp.) [Found: C, 62·4, 62·6; H, 6·0, 5·8; *M* (cryoscopic in camphor), 417. $C_{21}H_{24}O_8$ requires C, 62·4; H, 5·9%; *M*, 404]. Potentiometric titration gave the curve expected for a dibasic acid. The *anhydride*, prepared by refluxing the acid with acetic anhydride, crystallised from ethyl acetate as large rhombs, m. p. 155—156°, soluble in cold 2N-sodium hydroxide to a yellow solution (Found: C, 64·8; H, 5·6. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%).

7 : 8-*Dimethoxy*-4-[2-(3 : 4-*dimethoxyphenyl*)*ethyl*]*homophthalimide* (VII).—A solution of (carboxydimethoxyphenyl)(dimethoxyphenyl)butyric acid (10 g.) in aqueous ammonia (15 c.c.; *d* 0·880) was evaporated to dryness *in vacuo* on the steam-bath. Ammonium carbonate (3 g.) was added to the crystalline residue, and the mixture heated for 45 minutes *in vacuo* at 160—170° (oil-bath). The temperature of the bath was then raised to 190—200° for 15 minutes and the resulting pale orange glass crystallised from ethyl acetate, m. p. 126—127° (8·3 g., 87%). The *imide* separated from ethyl acetate as colourless rhombs, m. p. 127—127·5° (Found: C, 65·7; H, 6·1; N, 3·3. $C_{21}H_{23}O_6N$ requires C, 65·6; H, 6·0; N, 3·6%), soluble in cold aqueous sodium hydroxide to a yellow solution.

Heating the methylammonium salt of the acid *in vacuo* gave 7 : 8-*dimethoxy*-N-*methyl*-4-[2-(3 : 4-*dimethoxyphenyl*)*ethyl*]*homophthalimide* as clear, hexagonal prisms [from benzene–light petroleum (b. p. 60—80°)], m. p. 110—111° (Found: C, 65·8; H, 6·2. $C_{22}H_{25}O_6N$ requires C, 66·2; H, 6·3%).

7 : 8 : 2′ : 3′-*Tetramethoxy*-3 : 4-*dihydro*-1 : 2-*benzphenanthridone* (VIII).—(*a*) The above homophthalimide (1 g.), finely powdered, was slowly added to 10 c.c. of sulphuric acid (4 vols. of concentrated acid, 1 vol. water). The resulting deep-red solution was left at the room temperature for 40 hours and then poured on ice, and the mixture shaken with chloroform. The chloroform extract was washed with sodium carbonate solution and water and then dried (Na_2SO_4), and the solvent removed. Crystallisation of the residue from dioxan and then from chloroform–ethanol gave a small quantity (*ca.* 100 mg.) of a pale yellow solid, m. p. 257—259° (decomp.), not depressed by admixture with the substance prepared as below.

(*b*) Phosphoric anhydride (40 g.) was stirred with syrupy phosphoric acid (100 c.c.), and the above homophthalimide (20 g.) (finely powdered) was added to the hot solution. The mixture was then heated at 120° (oil-bath) for an hour, cooled, and poured on ice. A yellow gum separated and this became solid in a few minutes on trituration at *ca.* 90°. The washed product was crystallised from pyridine, giving 14·6 g. (77%) of a pale yellow solid, m. p. 254—257°. 7 : 8 : 2′ : 3′-*Tetramethoxy*-3 : 4-*dihydro*-1 : 2-*benzphenanthridone* was very sparingly soluble in the usual organic solvents, except chloroform and acetic acid. It crystallised from *n*-butanol (100 vols.) as long, cream-coloured needles, m. p. 260—262° (decomp.) (Found: C, 68·4; 68·6; H, 5·8, 5·8; N, 3·8. $C_{21}H_{21}O_5N$ requires C, 68·7; H, 5·7; N, 3·8%). The substance is insoluble in dilute acids; it dissolves in concentrated sulphuric acid to a red solution, and in concentrated hydrochloric acid to a yellow solution. It gives a green colour with ferric chloride in alcoholic solution.

The *perchlorate* crystallised from acetic acid containing perchloric acid as yellow clusters of rods, m. p. 219—221° (decomp.) (Found: C, 53·5; H, 4·8; N, 2·4. $C_{21}H_{21}O_5N,HClO_4$ requires C, 53·9; H, 4·7; N, 3·0%). The salt was decomposed by water, regenerating the phenanthridone.

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