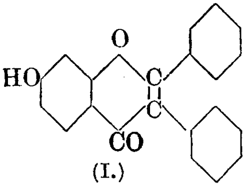
XXXIX.—*Colloidal Phenoxides. Part II. Some Phenanthraxanthones.*

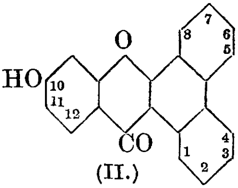
By Wilson Baker.

A number of derivatives of 7-hydroxybenzo-γ-pyrone containing aromatic groups in positions 2 and 3 dissolve in hot aqueous alkaline solutions and yield gels on cooling. The relationships existing between the chemical constitution and the capability of forming gels in these compounds was established in Part I (Baker and Eastwood, J., 1929, 2897), and the ultimate object of the work was indicated. Briefly, this was to prepare a substance which should give a gel in alkaline solutions and at the same time exhibit fluorescence, so that by examination in ultra-violet light the structure of the gel might be visible.

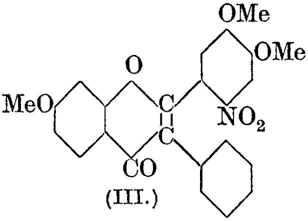
The simplest derivative of benzo-γ-pyrone which gives a gel is 7-hydroxy-2 : 3-diphenylbenzo-γ-pyrone (I), and the attempt to make the molecule fluoresce while retaining the colloidal properties is described in this paper. The work recorded in Part I showed that only minor changes could be made in the molecule (I) without destroying the desired physical properties of the alkali salts. Such changes as can be made within these limitations consist of alteration of the substituents in positions 2 and 3 (introduction of a *p*-methoxy-group, replacement of phenyl by styryl) and the introduction of a further hydroxyl group in position 5. No such changes can be expected, nor are found, to increase appreciably the fluorescence of the substance (I), and it was obvious that some other type of simple alteration to the molecule was necessary. Attention was therefore directed to the synthesis of 10-*hydroxyphenanthraxanthone** (II), in which the two phenyl nuclei are united, so that the substance, being a phenanthrene derivative, might be expected to possess an enhanced fluorescence.



(I.)



(II.)



(III.)

This synthesis has now been achieved, but both the physical and the optical properties of the alkali salts of the substance are such that it is very doubtful if it will serve the purpose for which it was intended. The gels are unstable and without appreciable fluorescence.

The ring closure between the two phenyl nuclei was effected by means of Pschorr's phenanthrene synthesis, and in order to study the conditions of the reaction use was made of the readily accessible 7-*methoxy*-3-*phenyl*-2-(6-*nitro*-3 : 4-*dimethoxyphenyl*)*benzo*-γ-*pyrone* (III). This substance was prepared by the nitration of 7-methoxy-3-phenyl-2-(3 : 4-dimethoxyphenyl)benzo-γ-pyrone (Part I, *loc. cit.*) in acetic acid solution, the position of the nitro-group being inferred from the great reactivity of the veratryl nucleus in position 6, and the success of the subsequent ring closure. Reduction with tin and hydrochloric acid gave 7-*methoxy*-3-*phenyl*-2-(6-*amino*-3 : 4-*dimethoxyphenyl*)*benzo*-γ-*pyrone*, and a methyl-alcoholic solution of the sulphate of this base, when diazotised and subsequently boiled, deposited the very sparingly soluble 6 : 7 : 10-*trimethoxyphenanthraxanthone* (IV) in 70% yield. This compound was demethylated by boiling with hydrobromic acid and acetic acid, giving 6 : 7 : 10-*trihydroxyphenanthraxanthone*. The high yield of (IV) is doubtless to be attributed to the spatial arrangement of the *o*-nitrophenyl and

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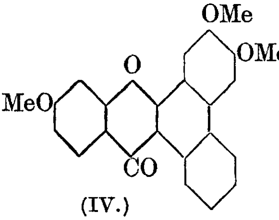
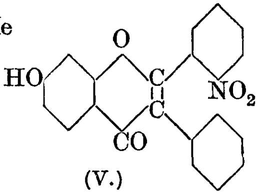
* At the suggestion of the Editor the parent substance has received the name "phenanthraxanthone" with the numbering shown. The formula (II) should be inverted, but in order not to confuse the relation of the substance to the diphenylbenzo-γ-pyrone from which it is prepared, the representation above is adopted in this paper.

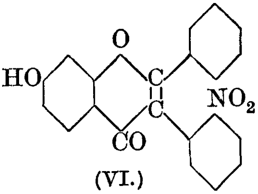
the phenyl group, *cis-trans* isomerism about the ethylenic linkage being impossible.



(IV.)



(V.)



(VI.)

The synthesis of (II) was effected as follows. When 2 : 4-dihydroxyphenyl benzyl ketone was heated under carefully defined conditions with *o*-nitrobenzoic anhydride and sodium *o*-nitrobenzoate and the product was hydrolysed with alcoholic potassium hydroxide, 7-*hydroxy*-3-*phenyl*-2-o-*nitrophenylbenzo*-γ-*pyrone* (V) was obtained. The *methyl* ether of this compound was reduced with tin and hydrochloric acid to the base 7-*methoxy*-3-*phenyl*-2-o-*aminophenylbenzo*-γ-*pyrone*, and diazotisation of this substance in the manner described above yielded 10-*methoxyphenanthraxanthone*, from which 10-*hydroxyphenanthraxanthone* (II) was obtained by demethylation with hydrobromic acid in acetic acid.

Owing to difficulties encountered in the preparation of (V), the synthesis of (II) was attempted in another way. *o*-Nitrophenylacetonitrile was condensed with resorcinol under the conditions of the Hoesch reaction, giving 2 : 4-*dihydroxyphenyl* o-*nitrobenzyl ketone*; this, when heated with benzoic anhydride and sodium benzoate, yielded a product which gave 7-*hydroxy*-2-*phenyl*-3-o-*nitrophenylbenzo*-γ-*pyrone* (VI) on hydrolysis. The corresponding *methyl* ether, however, when reduced with tin and hydrochloric acid or with ferrous sulphate and ammonia, yielded, not a primary base, but an uncrystallisable substance showing some of the properties of a secondary amine. It is possible that ring closure may occur between the amino-group first produced and the carbonyl group, and that further reduction then takes place.

EXPERIMENTAL.

7-*Methoxy*-3-*phenyl*-2-(6-*nitro*-3 : 4-*dimethoxyphenyl*)*benzo*-γ-*pyrone* (III).—7-Hydroxy-3-phenyl-2-(3 : 4-dimethoxyphenyl)benzo-γ-pyrone (Part I, *loc. cit.*) (10 g.) was dissolved in warm glacial acetic acid (75 c.c.), and to the cooled solution was added a mixture of glacial acetic acid (50 c.c.) and concentrated nitric acid (50 c.c.; *d* 1·42). After 2 hours, the red solution was poured into water, and the precipitated *nitro*-compound collected; it crystallised from alcohol, in which it was sparingly soluble, in light yellow, thick, diamond-shaped plates (or hexagonal plates), m. p. 222° (Found : C, 66·0 ; H, 4·6 ; N, 3·5. $C_{24}H_{19}O_7N$ requires C, 66·5 ; H, 4·4 ; N, 3·2%). In contrast to the unnitrated substance, this compound shows no basic properties towards hydrochloric acid.

7-*Methoxy*-3-*phenyl*-2-(6-*amino*-3 : 4-*dimethoxyphenyl*)*benzo*-γ-*pyrone*.—The finely powdered nitro-compound (III) (10 g.), alcohol (300 c.c.), finely divided granulated tin (25 g.), and concentrated hydrochloric acid (60 c.c.) were gently boiled for 6 hours; alcohol (100 c.c.) was then removed by distillation. The filtered solution deposited thick, hexagonal, light yellow plates of the *stannichloride*, which were collected after 12 hours and washed with a little alcohol (yield, 8·7 g.). The substance slowly darkens from 200° and melts with decomposition at about 240° [Found : C, 49·6 ; H, 4·2. $(C_{24}H_{19}O_5NH_2,HCl)_2SnCl_4$ requires C, 50·5 ; H, 3·9%]. The stannichloride (2·5 g.) was dissolved in hot 50% alcohol (50 c.c.) containing concentrated hydrochloric acid (1 c.c.) and a rapid stream of hydrogen sulphide was passed through the hot solution. When the filtered, tin-free liquid was treated with an excess of concentrated aqueous ammonia, the free *amino*-compound separated in small, sulphur-yellow, diamond-shaped plates, m. p. 208° (Found : C, 71·3 ; H, 5·4 ; N, 3·7. $C_{24}H_{21}O_5N$ requires C, 71·4 ; H, 5·3 ; N, 3·5%). Yield, 7 g. from 10 g. of the nitro-compound. The *hydrochloride* separates from 50% alcoholic hydrochloric acid in very pale yellow, hexagonal plates (Found : N, 3·2 ; Cl, 7·7. $C_{24}H_{21}O_5N,HCl$ requires N, 3·2 ; Cl, 8·1%). It slowly becomes more yellow at 100° owing to loss of hydrogen chloride ; the same change takes place on heating with water or organic solvents or in a vacuum over sodium hydroxide.

6 : 7 : 10-*Trimethoxyphenanthraxanthone* (IV).—The preceding amino-compound (1 g.) was dissolved in a warm mixture of methyl alcohol (120 c.c.) and concentrated sulphuric acid (2 g.) and cooled to —10°. A 5% aqueous solution of sodium nitrite (13·9 c.c.) was then added during ½ hour, and the solution subsequently kept at 0° for 2 days. The liquid, which now contained a small amount of crystalline material, was boiled under reflux for ½ hour, colourless needles being deposited. These were separated from the hot liquid by filtration, washed with much alcohol and with water, and dried (yield, 0·7 g.) ; m. p. 232—233° (Found : C, 74·3 ; H, 4·8. $C_{24}H_{18}O_5$ requires C, 74·6 ; H, 4·7%). 6 : 7 : 10-*Trimethoxyphenanthraxanthone* is almost insoluble in most organic solvents. It separates from a large volume of boiling glacial acetic acid in hair-like needles. It dissolves in concentrated sulphuric acid to an orange-yellow solution which exhibits no fluorescence, and

shows feebly basic properties towards concentrated hydrochloric acid.

6 : 7 : 10-*Trihydroxyphenanthraxanthone.*—The attempted demethylation of the trimethoxyphenanthraxanthone (IV) with hydriodic acid, or hydriodic acid in acetic acid, was unsatisfactory, owing to the precipitation of an insoluble dark-green hydriodide of the methylated compound.

6 : 7 : 10-Trimethoxyphenanthraxanthone (0·5 g.) was boiled with glacial acetic acid (25 c.c.) and hydrobromic acid (25 c.c.; *d* 1·5) for 8 hours. After 2½ hours, the solution began to deposit orange crystals of a hydrobromide, which gradually increased in amount, and were finally collected and washed with very dilute sodium bicarbonate solution and with water; the free trihydroxyphenanthraxanthone was then obtained as a pale yellow powder. By dissolving it in a large volume of boiling alcohol and filtering and concentrating the solution, it was obtained in small blunt-ended prisms, which when rapidly heated melted at 318—319° with much darkening. The substance contains alcohol of crystallisation which is lost at 110°, the crystals becoming opaque (Found: C, 70·9; H, 5·3. Found in material dried at 110°: C, 72·9; H, 3·9. $C_{21}H_{12}O_5$,EtOH requires C, 70·8; H, 4·7%. $C_{21}H_{12}O_5$ requires C, 73·3; H, 3·5%). 6 : 7 : 10-*Trihydroxyphenanthraxanthone* as a xanthone derivative with vicinal hydroxyl groups is a weak mordant dye. On cotton mordanted with iron, aluminium and tin, it gives greyish-brown, pale lemon-yellow, and bright yellow shades respectively. Its alcoholic solution develops an intense dull bluish-green colour with ferric chloride.

o-*Nitrobenzoic Anhydride.*—This was prepared by a modification of the method of D.R.-P. 201325 (compare Robinson and Venkataraman, J., 1929, 63). *o*-Nitrobenzoic acid (33·4 g.) was dissolved in a mixture of dry ether (50 c.c.) and pyridine (15·8 g.), and a solution of thionyl chloride (11·9 g.) in ether (50 c.c.) was added with vigorous shaking. After 24 hours, ice and dilute hydrochloric acid were added and the solid product was collected, washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and much water, and dried at first in the air, then at 100°. The anhydride (24 g.) formed a white crystalline powder, m. p. 126—128°. Bischoff and Rach (*Ber.*, 1884, **17**, 2789) state that the substance is explosive, but the author is unable to confirm this. The anhydride can be heated to 200° without decomposition, and when heated as rapidly as possible to very high temperatures in a small tube it decomposes suddenly but without explosion.

7-*Hydroxy*-3-*phenyl*-2-o-*nitrophenylbenzo*-γ-*pyrone* (V).—The interaction of *o*-nitrobenzoic anhydride, 2 : 4-dihydroxyphenyl benzyl ketone, and sodium *o*-nitrobenzoate under the ordinary conditions of the chromone synthesis (180° for 10 hours) gives a negligible yield of the desired product. After many failures, the following method was found to give fairly satisfactory results and the *o*-nitrobenzoic acid was recoverable.

2 : 4-Dihydroxyphenyl benzyl ketone (4 g.), *o*-nitrobenzoic anhydride (16 g.), and sodium *o*-nitrobenzoate (4 g.) were heated at 153° (anisole vapour bath) for 2½ hours. The product was dissolved in hot 90% alcohol (60 c.c.) and boiled with potassium hydroxide (8 g.), dissolved in a little water, for 2 minutes. The solution was diluted with water (200 c.c.) and saturated with carbon dioxide and the precipitate was collected, washed, and crystallised from alcohol (charcoal) (yield, 1·1 g.). A further recrystallisation from alcohol yielded pale yellow prisms, m. p. 268° (Found : N, 3·9. $C_{21}H_{13}O_5N$ requires N, 3·9%). The *methyl* ether, prepared quantitatively by the action of methyl sulphate and alkali upon a 50% acetone–alcohol solution of the compound, crystallised from alcohol in pale yellow, highly refracting, four-sided bi-pyramids, m. p. 183° (Found : C, 70·8; H, 4·1. $C_{22}H_{15}O_5N$ requires C, 70·8; H, 4·1%).

7-*Methoxy*-3-*phenyl*-2-o-*aminophenylbenzo*-γ-*pyrone*.—The preceding methyl ether (3·5 g.), alcohol (200 c.c.), granulated tin (20 g.), and concentrated hydrochloric acid (50 c.c.) were boiled for 6 hours. The solution was diluted with water and treated while hot with hydrogen sulphide and the tin-free filtrate was rendered alkaline with excess of ammonia solution and at once filtered from a small amount of flocculent material. The *base* crystallised completely on further dilution (yield, 3·2 g.); on recrystallisation from alcohol it formed thin, pale-yellow, diamond-shaped plates, m. p. 213° (Found : N, 4·4. $C_{22}H_{17}O_3N$ requires N, 4·1%).

10-*Methoxyphenanthraxanthone*.—The preceding base (1 g.) was dissolved in warm methyl alcohol (120 c.c.) containing concentrated sulphuric acid (2 g.), cooled to −10°, and diazotised by the gradual addition of 5% aqueous sodium nitrite (10·2 c.c.). The solution was kept for 24 hours at 0° and then boiled for ½ hour and the crystalline precipitate was collected, washed with water and alcohol, and recrystallised from glacial acetic acid, in which it was very sparingly soluble. It separated in very pale yellow prisms, m. p. 248—249° (Found : C, 80·8; H, 4·3. $C_{22}H_{14}O_3$ requires C, 81·0; H, 4·3%). The solution in concentrated sulphuric acid is yellow and slowly develops a strong blue fluorescence.

10-*Hydroxyphenanthraxanthone* (II).—The preceding compound (0·4 g.) was boiled for 12 hours with glacial acetic acid (60 c.c.) and hydrobromic acid (20 c.c.; *d* 1·5). The product which separated on cooling was collected and acetylated by boiling for 1 hour with acetic anhydride and a drop of pyridine. The acetyl derivative subsequently separated in colourless prisms, m. p. 234—235°. Hydrolysis of this compound was effected by boiling its alcoholic suspension with a few drops of aqueous sodium hydroxide; a yellow solution exhibiting a weak green fluorescence was then produced. Acidification threw down a gelatinous precipitate, which, after boiling with water, was collected and pressed on porous earthenware. The substance was now dissolved in a large volume of boiling glacial acetic acid (charcoal); after concentration to a small bulk, the solution deposited bunches of fine colourless needles, m. p. 325—326° with slight darkening (Found: C, 80·5; H, 3·9. $C_{21}H_{12}O_3$ requires C, 80·8; H, 3·9%).

10-*Hydroxyphenanthraxanthone* dissolves in dilute aqueous sodium hydroxide to a yellow solution which sets to a turbid gel on cooling. The gel has no marked fluorescence and, unlike those described in Part I, is not very stable and shows a great tendency to deposit the alkali salt as a fibrous curd. The solution of 10-hydroxyphenanthraxanthone in concentrated sulphuric acid is yellow and slowly develops a greenish-blue fluorescence.

o-*Nitrophenylacetonitrile.*—*o*-Nitrophenylpyruvic acid was prepared by the modification of Reissert's method (*Ber.*, 1897, **30**, 1036) suggested by Gulland and Haworth (J., 1928, 585). The oxime of this acid (Reissert, *Ber.*, 1908, **41**, 3813) was readily converted into *o*-nitrophenylacetonitrile by warming it with its own weight of acetic anhydride; a vigorous reaction rapidly occurred, after a few minutes water was added, and the crystalline nitrile, which separated on shaking, was collected, washed, and dried (yield, almost quantitative).

2 : 4-*Dihydroxyphenyl* o-*Nitrobenzyl Ketone.*—A mixture of *o*-nitrophenylacetonitrile (10 g.) and resorcinol (20 g.) in anhydrous ether (300 c.c.) was saturated with a rapid stream of hydrogen chloride without external cooling until all had dissolved. Powdered zinc chloride (10 g.) was then added and the solution was cooled to 0° and again saturated with hydrogen chloride. After 48 hours, water was added and the ketimine hydrolysed by heating on the steam-bath for 1 hour. The solid *ketone* (10·5 g.), which separated on cooling, was used directly for the preparation of the benzo-γ-pyrone (VI). The pure substance separates from dilute alcohol (charcoal) in very pale yellow, prismatic needles, m. p. 159—161° (Found: N, 5·2. $C_{14}H_{11}O_5N$ requires N, 5·1%). Its alcoholic solution gives a deep reddish-brown coloration with ferric chloride. The solution in aqueous sodium hydroxide is yellow.

7-*Hydroxy*-2-*phenyl*-3-o-*nitrophenylbenzo*-γ-*pyrone* (VI).—The preceding ketone (10 g.), benzoic anhydride (75 g.), and sodium benzoate

(10 g.) were stirred and heated at 180—190° for 6 hours. The product was dissolved in alcohol (200 c.c.), heated for 20 minutes with potassium hydroxide (40 g.) in water (100 c.c.), diluted with a large volume of water, and saturated with carbon dioxide. The *pyrone* was used without further purification for the preparation of its methyl ether. The pure substance separates from a small amount of alcohol in very pale yellow octahedra, m. p. 267° (Found : N, 4·1. $C_{21}H_{13}O_5N$ requires N, 3·9%).

The *methyl* ether, prepared in the same manner as the methyl ether of (V), crystallised from alcohol in colourless prismatic needles, m. p. 178° (Found : C, 70·7 ; H, 3·9. $C_{22}H_{15}O_5N$ requires C, 70·8 ; H, 4·0%). The reduction of this compound in the manner described for the reduction of the methyl ether of (V) gave a light yellow powder, which could not be obtained in the crystalline state. The substance, which is very readily soluble in all the common organic solvents except light petroleum, develops a greenish tint on exposure to light, and cannot be diazotised. It gives a weak Liebermann's nitroso-reaction. A similar result was obtained by reduction with ferrous sulphate and ammonia.

The author wishes to record his thanks to Miss F. M. Eastwood, B.A., B.Sc., for carrying out the preliminary experiments with *o*-nitrobenzoic anhydride, and to Dr. J. M. Gulland for advice in connexion with the phenanthrene ring closure.

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