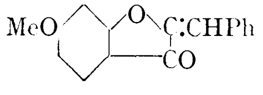
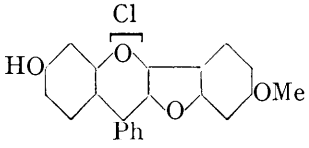
213. *A New Synthesis of Chromylium Salts. Part II.*

By Robert Robinson and James Walker.

The method described in Part I (J., 1934, 1435), consisting essentially of the condensation of an unsaturated ketone with resorcinol in alcoholic solution in presence of hydrogen chloride and chloranil, has not been modified because no better conditions have been found. New applications, using resorcinol, have demonstrated the general character of the synthesis for a wide variety of unsaturated ketones. 6-Methoxy-2-benzylidenecoumaranone (I) yields (II), which has been demethylated.

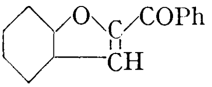
(I.)



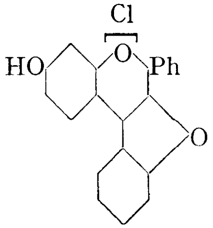


(II.)

2-Benzoylcoumarone (III) similarly affords the pyrylium salt (IV), and (V) is obtained from 2-*p*-dimethylaminobenzylidene-1-hydrindone.



(III.)



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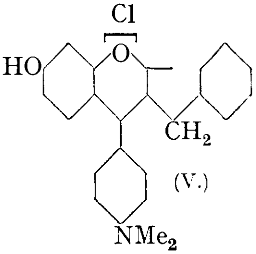
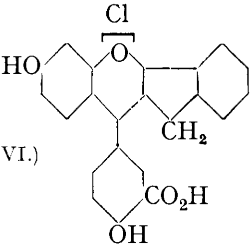
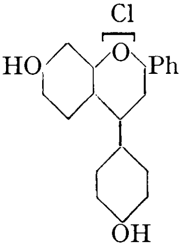


(V.)

In order to examine the lake-forming properties of the product, the salicylic acid residue has been introduced into an oxonium salt, the example (VI) being derived from the *ester* of 2-(3′-*carboxy*-4′-*hydroxybenzylidene*)-1-*hydrindone* and resorcinol.



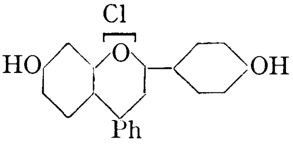
(VI.)



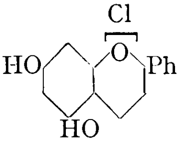
(VII.)

The salts (VII) and (VIII) have been prepared by demethylation of known substances (cf. Part I, *loc. cit.*), whereas (IX), (X), (XI), (XII) and (XIII) were prepared in order to show that the reactive phenol component can be varied within the usual limits.

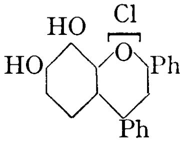
Comments may be made on the following points: The colour-base derived from (VIII) has a bluer tone than that derived from (VII); this is a special case of the general rule that substituents in the 2-substituted phenyl group have a larger influence in deepening the colour of flavylium salts and their derivatives than have similar substituents in other positions. The salt (X) was obtained by Bülow and von Sicherer (*Ber.*, 1901, **34**, 3921)



(VIII.)

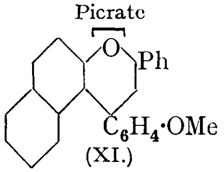


(IX.)

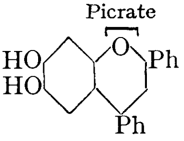


(X.)

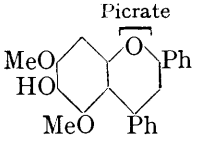
by the condensation of pyrogallol, dibenzoylmethane, and hydrogen chloride. They describe, however, a monohydrate, whereas in our experience the salt always crystallised as a *trihydrate*. Bülow and Sicherer did not describe the characteristic reactions of this salt. It readily yields a blue quinone-colour-base and a pseudo-base, and the following reactions can be realised:



(XI.)



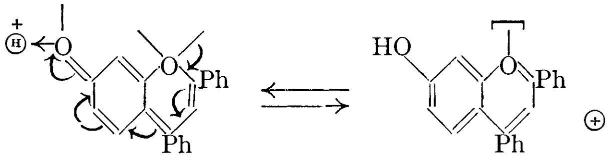
(XII.)



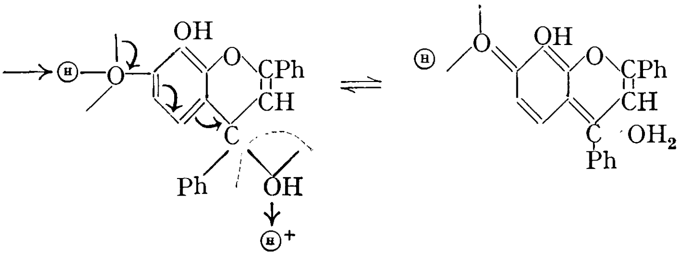
(XIII.)

$$\text{Pyrylium salt} \rightleftharpoons \underset{\xleftarrow{\text{decreasing } p_{\text{H}}}}{\overset{\xrightarrow{\text{increasing } p_{\text{H}}}}{\text{colour-base}}} \rightleftharpoons \text{pseudo-base}$$

Most of these changes have often been described previously, but the conversion of the pseudo-base into the colour-base on the addition of acid without formation of the oxonium chloride appears to be novel. It supplements the direct removal of a proton from the kation of the pyrylium salt with formation of the colour-base or its realised converse, as in the example,



by the direct removal of carbinol hydroxyl from a pyranol (the pyranol may also be an α-pyranol).



In the case of the dimethylamino-substituted salt (V) the usual effect of neutralisation of the auxochrome by salt-formation is recognisable. Solution of the *yellow* pyrylium salt hydrochloride in methyl alcohol causes hydrolysis to the dimethylamino-pyrylium salt, which is reddish-violet; the quinone-base also is red. This salt was not obtained free from tetrachloroquinol, which crystallised in combination with it.

EXPERIMENTAL.

7-*Hydroxy*-4-p-*hydroxyphenylflavylium Chloride* (VII).—A mixture of 7-hydroxy-4-anisylflavylium chloride (J., 1934, 1437) (1 g.), phenol (6 g.), and colourless hydriodic acid (60 c.c., *d* 1·7) was boiled gently under reflux for ½ hour in a stream of carbon dioxide. Water (150 c.c.) and ether (150 c.c.) were added to the cooled mixture and a heavy black periodide was precipitated; on shaking, this appeared to give place to golden needles of the iodide; these were collected, washed with ether, and dried. The crude iodide (1·1 g.) was added to a large excess of freshly precipitated silver chloride suspended in ethyl alcohol (80 c.c.) and the mixture was boiled for 10 minutes and filtered hot. An equal volume of dilute hydrochloric acid was added to the filtrate, which deposited needles of the chloride on standing (0·85 g.). The *chloride*, recrystallised from 85% methyl alcohol containing 2% of hydrogen chloride, formed fine, reddish-orange needles (Found in material dried in a vacuum over sulphuric acid and potassium hydroxide : C, 63·3; H, 5·3; Cl, 9·2. $C_{21}H_{15}O_3Cl,2{\cdot}5H_2O$ requires C, 63·7; H, 5·1; Cl, 9·0%).

The salt dissolves in concentrated sulphuric acid to a yellow solution exhibiting a green, not very intense, fluorescence; on warming, the colour darkens slightly and the fluorescence is almost discharged, but the initial properties return on cooling. The anhydronium base dissolves sparingly in ether to an orange-red solution; apparently it is incompletely extracted from water by ether. When the salt is shaken with ether–aqueous sodium carbonate, the ether remains colourless and the aqueous solution has a reddish-orange colour.

7 : *4′-Dihydroxy-4-phenylflavylium Chloride* (VIII).—7-Hydroxy-4′-methoxy-4-phenylflavylium chloride (J., 1934, 1438) (1 g.) was demethylated precisely as described above; the alcoholic solution of the *chloride* was, however, concentrated to about one-third of its bulk before being treated with dilute hydrochloric acid (50 c.c.); fine orange needles (0·9 g.) were then obtained. The salt crystallised from 70% methyl alcohol, containing 2% of hydrogen chloride, in orange prisms and from 80% methyl alcohol, containing 1·5% of hydrogen chloride, in fine reddish-orange needles (Found in a specimen dried in a vacuum over sulphuric acid : C, 65·2; H, 4·7; Cl, 9·2. $C_{21}H_{15}O_3Cl,2H_2O$ requires C, 65·2; H, 4·9; Cl, 9·2%).

The yellow solution of the chloride in concentrated sulphuric acid shows a strong green fluorescence, slightly weaker, however, than that of the methoxylated salt under the same conditions. The orange solution in methyl alcohol is devoid of fluorescence in contrast to the parent substance. Addition of sodium acetate to an aqueous-alcoholic solution precipitates reddish-violet flocks of the quinone-base, which is sparingly soluble in ether or benzene. When the salt is treated with sodium acetate in a little methyl alcohol and then distributed between ether and water, the water retains a magenta colour and the ethereal layer has a red colour. When the chloride is shaken with a mixture of ether and sodium carbonate solution, no colour passes into the ether and the aqueous layer has a deep bluish-red colour. This reaction proves that the demethylation was complete.

7-Hydroxy-6′-methoxy-4-phenyl-2 : 3-coumareno(3′ : 2′)-chromylium * *Chloride* (II).—6-Methoxy-2-benzylidenecoumaranone (5·0 g.) (v. Auwers and Pohl, *Annalen*, 1914, **405**, 268) was condensed with resorcinol (2·2 g.) in ethyl alcohol (70 c.c.) containing 10% of hydrogen chloride in presence of chloranil (4·9 g.). After 6 hours the chloranil had disappeared and after 16 hours the bright brick-red powder was precipitated with ether (500 c.c.), filtered off, and dried in a vacuum (8·4 g.; 98% yield). It was shaken with anisole containing hydrogen chloride, collected, washed with ether, and crystallised from 80% methyl alcohol containing 1—2% hydrogen chloride, forming reddish-orange, microscopic, very sparingly soluble prisms (Found in a specimen dried over sulphuric acid and potassium hydroxide in a vacuum : C, 60·8; H, 3·7; Cl, 20·9. $C_{22}H_{15}O_4Cl,1{\cdot}5HCl$ requires C, 60·9; H, 3·8; Cl, 20·5%). The composition suggested is unusual but not unique, as in the related group of the anthocyanins the appearance of hydrogen chloride as an addendum has frequently been noticed.

The *salt* is very sparingly soluble in the usual solvents for the type and its yellow solution in concentrated sulphuric acid has a strong yellowish-green fluorescence; on warming, the colour of the solution becomes orange, and the fluorescence gradually diminishes, but returns sharply on continued heating as a darker green shade, which, when the liquid is cold, is even more intense than the initial fluorescence. The fluorescence in sulphuric acid is markedly diminished on 12-fold dilution with water, but is still perceptible; it is not affected on 12-fold dilution of the solution with acetic acid; also the solution of the salt in acetic acid exhibits green fluorescence. The quinone-base is crimson and dissolves in ether or benzene to bluish-red solutions which are bluer in thin layers.

7 : *6′-Dihydroxy-4-phenyl-2 : 3-coumareno(3′ : 2′)-chromylium Chloride.*—The above salt (1 g.) was demethylated as in the previous cases and the filtered alcoholic solution of the chloride was mixed with an equal volume of dilute hydrochloric acid; the bright orange-red, microscopic, diamond-shaped crystals that separated were collected, washed, and dried (0·65 g.). The *chloride* was extremely sparingly soluble in the usual solvents and was analysed without further purification (Found : C, 68·9; H, 3·7; Cl, 9·5. $C_{21}H_{13}O_4Cl$ requires C, 69·1; H, 3·6; Cl, 9·7%). Addition of sodium acetate to an aqueous-alcoholic solution precipitates purple flocks of the quinone-base, which is insoluble in benzene, ether or ethyl acetate. Addition of sodium acetate to a methyl-alcoholic solution of the salt develops a bluish-red coloration and a very

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* The expression " flavylium " for " 2-phenylbenzopyrylium " has proved useful and is generally understood. Hence, since benzo-γ-pyrone is well known as chromone, there seems to be no reason why the somewhat shorter " chromylium " should not replace " benzo-γ-pyrylium."

intense red fluorescence. Under the same conditions the parent methylated compound gives a red non-fluorescent solution which is bluer in thin layers. In concentrated sulphuric acid the behaviour of this salt is very similar to that of the parent compound except that the green fluorescence is slightly bluer in tone.

Chrysinidin Chloride (5 : 7-*Dihydroxyflavylium Chloride*) (IX).—Phloroglucinol (6·0 g.) was condensed with a crude specimen (10 g.; *ca.* 30% excess) of phenyl vinyl ketone (Mannich and Heilner, *Ber.*, 1922, **55**, 356) in presence of chloranil (12 g.) in ethyl alcohol containing *ca.* 12% of hydrogen chloride; a vigorous exothermic reaction took place, accompanied by the separation of much solid. After 15 hours the product was precipitated with ether (500 c.c.), collected, washed with ether, and dried (10 g.; 87% yield). The crude reddish-brown product was shaken with anisole–benzene (1 : 1) containing a little hydrogen chloride in order to remove the last traces of chloranil; it then crystallised from acetic acid–hydrochloric acid in clusters of dark red prisms (Found : C, 59·0; H, 4·7. Calc. for $C_{15}H_{11}O_3Cl,2H_2O$: C, 58·0; H, 4·8%) (Pratt, Robertson, and Robinson, J., 1927, 1977, found C, 58·7; H, 4·7%). A few mg. of the perchlorate were prepared; it had m. p. 230° (decomp.) without recrystallisation (Pratt, Robertson, and Robinson, *loc. cit.*, give m. p. 244° decomp.). The colour reactions of this salt were precisely as described by these authors.

7-*Hydroxy*-3 : 4-*coumareno*(2″ : 3″)-*flavylium Chloride* (IV).—A mixture of 2-benzoylcoumarone (4·5 g.) (Rap, *Gazzetta*, 1895, **25**, ii, 286), resorcinol (2·3 g.), chloranil (4·9 g.), and ethyl-alcoholic hydrogen chloride (70 c.c. of 12%) was kept at room temperature for 7 days, and ether (500 c.c.) then added. The finely powdered crude product was shaken with anisole (60 c.c.) containing dissolved hydrogen chloride and after 3 hours the solid was collected and washed with ether. The light reddish-brown powder (4·0 g.) was very readily soluble in ethyl and methyl alcohols; on warming with alcoholic hydrogen chloride, tars resulted, so the usual methods of recrystallisation were useless. The *salt* was dissolved in methyl alcohol and precipitated as a sandy brown powder by the careful addition of a little concentrated hydrochloric acid (Found in a specimen dried in a vacuum : C, 69·2; H, 4·4. $C_{21}H_{13}O_3Cl,H_2O$ requires C, 68·8; H, 4·1%).

This salt readily loses its hydrogen chloride on exposure and an old specimen did not give the characteristic colour reaction with sodium acetate until it had been moistened with concentrated hydrochloric acid. Addition of sodium acetate to an aqueous-alcoholic solution precipitates a bluish-violet quinone-base, the solution of which in ether or benzene is deep bluish-violet; the colour fades through light violet (5 minutes) to pale yellow (*ca.* 20 minutes). The orange solution in concentrated sulphuric acid exhibits an intense green fluorescence.

7-*Hydroxy*-4-p-*dimethylaminophenyl*-2 : 3-*indeno*(3′ : 2′)-*chromylium Chloride Hydrochloride* (V).—A mixture of *p*-dimethylaminobenzylidenehydrindone (5·2 g.) (Feuerstein, *Ber.*, 1901, **34**, 415), resorcinol (2·2 g.), chloranil (4·9 g.), and ethyl-alcoholic hydrogen chloride (70 c.c. of 12%) was warmed to about 60° in order to dissolve the hydrochloride of the first-named component. On cooling, khaki-coloured material was deposited and after 2 days ether (150 c.c.) was added and the greenish-yellow powder was washed with ether and dried (6·5 g.). After treatment with anisole in the usual way it crystallised from 25% acetic acid, containing 15% of hydrogen chloride, in clusters of short yellow prisms [Found in material dried in a vacuum : C, 45·7; H, 3·0; Cl, 38·3. $C_{24}H_{21}O_2NCl_2,2C_6H_2O_2Cl_4,2H_2O$ (*i.e.*, $C_{36}H_{29}O_8NCl_{10}$) requires C, 45·7; H, 3·0; Cl, 37·6; N, 1·5%]. On recrystallisations from 25% acetic acid containing 3% of hydrogen chloride, clusters of darker crystals were obtained (Found : C, 43·2; H, 2·9; Cl, 40·4, 39·9; N, 1·2%). When the salt (*ca.* 100 mg.) was heated under diminished pressure, a white sublimate of monoclinic prisms was obtained, m. p. 210—213°; this was recrystallised once from benzene and had then m. p. 220—222° (Found on 0·9 mg. : Cl, 52·3. Calc. for $C_6H_2O_2Cl_4$: Cl, 57%). The recrystallisation was very wasteful and further purification was impracticable. Tetrachloroquinol has m. p. 232—236°.

The yellow solution in concentrated sulphuric acid shows a strong apple-green fluorescence; on warming, the colour deepens somewhat and the fluorescence is diminished. The solution in methyl alcohol is deep reddish-violet, becoming yellow on the addition of hydrochloric acid and pink on the addition of a trace of sodium acetate.

7 : 8-*Dihydroxy*-4-*phenylflavylium Chloride* (X).—A mixture of pyrogallol (2·5 g.), benzylideneacetophenone (4·2 g.), chloranil (4·9 g.), and ethyl-alcoholic hydrogen chloride (50 c.c. of 12%) was kept for 15 hours at room temperature, ether (500 c.c.) was then added, and the precipitate was collected, washed with ether, and dried. The crude product (4 g.) was a granular maroon-coloured powder, which, after being washed with anisole containing a little dissolved hydrogen chloride, separated from 40% methyl alcohol, containing 1—2% of hydrogen chloride,

in needles 7—8 mm. in length and about 0·5 mm. in thickness; these were dark orange-brown under the microscope by transmitted light and appeared to be purplish-black with a steel-blue reflex by reflected light (Found in air-dried material: C, 62·7, 62·0; H, 5·5, 5·5; Cl, 8·5, 9·0. $C_{21}H_{15}O_3Cl,3H_2O$ requires C, 62·3; H, 5·2; Cl, 8·8%).

The *salt* was practically insoluble in water, but was readily soluble in alcohol to a deep reddish-orange solution. Addition of sodium acetate to an aqueous-alcoholic solution precipitated a blue colour-base which had a purple reflex; it was soluble in ether or benzene to a deep ultramarine solution. Addition of a little sodium acetate to a solution of the salt in methyl alcohol gave a pure deep blue solution; on addition of a little sodium carbonate, rapid decolorisation took place due to the formation of a colourless pseudo-base. Dilute hydrochloric acid was then added carefully, whereupon the deep blue colour was assumed once more and addition of an excess of the acid gave the reddish-orange solution of the oxonium salt. The orange solution in concentrated sulphuric acid was not fluorescent.

7-*Hydroxy*-4-(4″-*hydroxy*-3″-*carboxyphenyl*)-2 : 3-*indeno*(3′ : 2′)-*chromylium Chloride* (VI).—5-Aldehydosalicylic acid (4 g.; 1 mol.) (Duff and Bills, J., **1932**, 1987; **1934**, 1306) was mixed with α-hydrindone (3·3 g.; 1 mol.) in alcohol (35 c.c.), and aqueous potassium hydroxide (5·6 g., 4 mols., in 5 c.c.) was added with shaking. The deep orange-red solution was kept at room temperature for 12 hours and the resulting semi-solid mass was dissolved in water and extracted with ether. The dissolved ether was removed from the separated aqueous solution in a current of air, the deep orange-brown solution was then acidified with hydrochloric acid, and the somewhat gelatinous acid was collected, washed with water, and dried in a vacuum (yield, quantitative). Crystallisation from glacial acetic acid afforded cream-coloured rectangular prisms, m. p. 285° (Found: C, 73·1; H, 4·4. $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%).

The *acid* was soluble in concentrated sulphuric acid with a greenish-yellow colour and in aqueous alkalis with an intense orange colour. The *ethyl* ester was prepared by prolonged refluxing of the acid with ethyl alcohol and a few c.c. of concentrated sulphuric acid; the length of the operation is due to the sparing solubility of the acid in boiling alcohol. The product was added to water and shaken with chloroform, and the chloroform solution washed with aqueous sodium carbonate several times, dried, and evaporated. The ester separated from ethyl acetate in fine, almost colourless needles, m. p. 172° (Found: C, 73·6; H, 5·4. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%).

This substance was far too sparingly soluble to allow of its application to the pyrylium salt synthesis under the standard conditions; the only solvent that could be used was dioxan. The above ester (2·7 g.), resorcinol (1·0 g.), and chloranil (2·2 g.) dissolved in dioxan (50 c.c.) containing hydrogen chloride (4 g.) to a clear reddish-brown solution. After 6 days the mixture, with solid in suspension, was added to ether (350 c.c.) and the reddish-orange crude product was collected and dried (2·0 g.). It was immediately treated with hydriodic acid and phenol as described above and the iodide (1·5 g.) was converted into the chloride in the usual way. The crude chloride (1·0 g.) was boiled with ethyl alcohol containing about 2% of hydrogen chloride and the residue consisted of a deep brick-red, granular, crystalline powder (Found: C, 66·7; H, 3·9. $C_{23}H_{15}O_5Cl,0{\cdot}5H_2O$ requires C, 66·4; H, 3·9%).

The *salt* is very sparingly soluble in the usual solvents and insoluble in water; it dissolves in neutral alcohol to a deep orange solution, which becomes bright orange-red on the addition of a trace of sodium acetate. The salt is all but insoluble in alcohol containing a trace of hydrogen chloride. It dissolves in concentrated sulphuric acid to a yellow solution with an intense green fluorescence; on warming, the colour deepens somewhat and the fluorescence is rapidly discharged; on cooling again, the fluorescence returns, but to a less brilliancy and a darker tone.

2-*Phenyl*-4-*anisyl*-5 : 6-*naphtha*(1′ : 2′)-*pyrylium Picrate* (XI).—A mixture of β-naphthol (2·9 g.), anisylideneacetophenone (4·8 g.), and chloranil (4·9 g.) in ethyl alcohol (50 c.c.) containing 12% of hydrogen chloride was kept at room temperature for 7 weeks. The light brown solution was then filtered from unchanged chloranil (3·2 g.), which was washed with alcohol, and ether (500 c.c.) was added, precipitating a brown liquid. The ether was decanted, and the brown liquid washed with fresh ether. On addition of an excess of a saturated alcoholic solution of picric acid a brick-red crystalline substance separated; this was dried (2·0 g.), and crystallised from half-saturated ethyl-alcoholic picric acid, forming fine red prisms, m. p. 204° (Found: C, 64·8; H, 3·6; N, 7·1. $C_{32}H_{21}O_9N_3$ requires C, 65·0; H, 3·6; N, 7·1%).

6 : 7-*Dihydroxy*-4-*phenylflavylium Picrate* (XII).—Hydroxyquinol (2·5 g.), benzylideneacetophenone (4·2 g.), and chloranil (4·9 g.) were mixed in ethyl alcohol (50 c.c.) containing 12% of hydrogen chloride. Chloranil could no longer be seen in the dark reddish-brown solution

after 12 hours at room temperature. Addition of ether (500 c.c.) to the alcoholic solution precipitated a dark brown viscous liquid, which was washed with ether, dissolved in a little alcohol, and mixed with a large excess of aqueous sodium acetate. The crimson quinone-base precipitated was collected, washed with water, and dried in a vacuum. The crude base (1·2 g.) was dissolved in ethyl alcohol (15 c.c.) and mixed with alcoholic picric acid (25 c.c., saturated at room temperature); on cooling, brownish-yellow needles of the picrate separated. Recrystallisation from half-saturated alcoholic picric acid gave brownish-yellow needles, m. p. 235° (Found: C, 58·4; H, 3·2; N, 7·5. Calc. for $C_{27}H_{17}O_{10}N_3,0{\cdot}5H_2O$: C, 58·7; H, 3·3; N, 7·6%). Bülow and v. Sicherer (*Ber.*, 1901, **34**, 3929) describe this derivative as "rothen Nädelchen" of m. p. 236° and record N, 7·44% only.

The quinone-base dissolved in concentrated sulphuric acid to an orange solution with a faint green fluorescence.

6-*Hydroxy*-5 : 7-*dimethoxy*-4-*phenylflavylium Picrate* (XIII).—2 : 6-Dimethoxyquinol (3·4 g.), benzylideneacetophenone (4·2 g.), and chloranil (4·9 g.) were mixed in ethyl alcohol (50 c.c.) containing *ca.* 12% of hydrogen chloride. Separation of a copious sand-coloured crystalline precipitate occurred soon after mixing (quinhydrone-type substance), but next day this had redissolved, giving a reddish-brown solution. The alcoholic solution was filtered and mixed with ether (500 c.c.). The black tarry liquid precipitated was treated with a large excess of saturated alcoholic picric acid, producing deep reddish-brown microscopic crystals (6·5 g.). Recrystallisation from half-saturated alcoholic picric acid, in which the compound was rather sparingly soluble, gave a dark reddish-brown microcrystalline powder, m. p. 220° (decomp.) (Found: C, 58·5; H, 4·1; N, 6·8. $C_{29}H_{21}O_{11}N_3,0{\cdot}5H_2O$ requires C, 58·4; H, 3·7; N, 7·0%).

Miscellaneous Trials.—Arsenic acid was tried as an oxidising agent, under the same conditions as chloranil, in an attempt to condense resorcinol with styryl anisyl ketone, but the reaction was very slow and gave a very impure specimen of the desired salt. Styryl anisyl ketone was selected because it condenses readily with resorcinol under the standard conditions and also because the resulting salt can be quickly recognised owing to the striking fluorescence in concentrated sulphuric acid. Lead peroxide as oxidising agent gives extremely poor yields, probably because it is too powerful in the presence of hydrogen chloride to be of value in a slow reaction of polyhydric phenols.

Ethyl benzylidenepyruvate (6·1 g.) (the method of Reimer, *J. Amer. Chem. Soc.*, 1924, **46**, 785, gives a monomeric product; cf. Musajo, *Gazzetta*, 1932, **62**, 901), resorcinol (3·3 g.), and chloranil (7·4 g.) were mixed in ethyl alcohol (75 c.c.) containing hydrogen chloride (11 g.). The formation of an oxonium salt was detected by exchange between benzene or ether (light pink), sodium acetate, and hydrochloric acid (yellow), but after 12 days at room temperature a large proportion of the chloranil (5·3 g.) was recovered and the usual methods of isolation failed.

No condensation occurred with benzylidene-*N*-methyloxindole (Stollé, *J. pr. Chem.*, 1930, **128**, 5) under the usual conditions.

Pyrogallol and 6-methoxy-2-benzylidenecoumaranone gave a very poor yield of a condensation product, which was not investigated further. The quinone-base had a deep pure blue colour in methyl-alcoholic solution and this became light green on addition of a drop of aqueous ferric chloride.

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