11. *Comparison of the Directive Powers of Elements having Consecutive Atomic Numbers. Part VI. Examination of Further Possible Comparative Cases, and Conclusions.*

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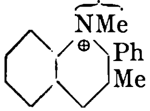
Sections (a) to (e) record results of examinations of other possible comparisons of the types indicated in earlier papers of this series.

(a) *3-Phenyl-2-methyl- and 2-Phenyl-3-methyl-benzopyrylium and* -N-*methylquinolinium Salts*.—With the intention of supplementing work previously reported (J., 1929, 2771; 1930, 2236) we have studied salts of the kations (I), (II), (III), and (IV).

(I.)



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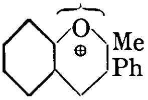

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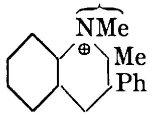
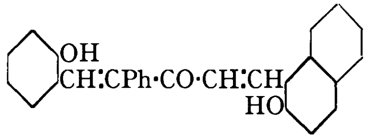


(IV.)

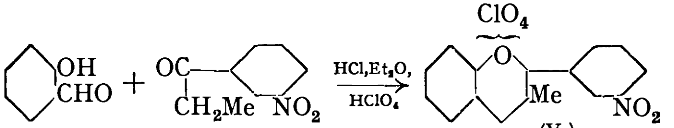
The chloride and the ferrichloride of (I) have been obtained by treatment of 3-methylcoumarin with phenylmagnesium bromide (Heilbron, Hill, and Walls, J., 1931, 1701). The direct interaction of salicylaldehyde and propiophenone by the method first described by Löwenbein and Katz (*Ber.*, 1926, **59**, 1377) for the condensation of *o*-hydroxy-aldehydes and β-ketonic esters has now been utilised to produce the perchlorate of (I) conveniently in one operation.

Application of this and other standard procedures to 2-hydroxy-α-phenylstyryl methyl ketone (the "2-hydroxystyryl benzyl ketone" of Dickinson, J., 1926, 2234), however, did not effect ring closure to give the perchlorate of (III). This failure was unexpected, because Heilbron and Irving (J., 1929, 936) had reported the preparation of 3-phenylbenzo-β-naphtha*spiro*pyran by saturation of an alcoholic solution of salicylaldehyde, benzyl methyl ketone, and 2-naphthol-1-aldehyde with dry hydrogen chloride. This reaction was considered as involving the preliminary formation of Dickinson's ketone, from which 3-phenyl-2-methylbenzopyrylium chloride was produced, which in turn then condensed with the naphthol-aldehyde. Our result implies a slightly different interpretation, *viz.*, that the 2-naphthol-1-aldehyde joined the complex at the *second*, rather than the third, stage, giving β-*o*-hydroxyphenyl-α-phenyl-β′-2-hydroxy-1-naphthyldivinyl ketone (annexed formula), which then underwent ring formation to the pyrylium salt, from which the *spiro*pyran, m. p. 208—209°, was obtained by treatment with dilute ammonia solution, etc.

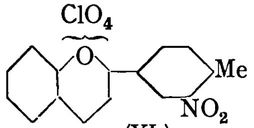


The direct condensation of phenylacetone with salicylaldehyde in ethereal hydrogen chloride–perchloric acid gave a salt which from its analyses appeared to be the desired 3-*phenyl-2-methylbenzopyrylium perchlorate* (III). We are unable to explain the non-formation of an *o*-hydroxystyryl derivative in this reaction. It would appear (see Experimental) that salicylaldehyde and 2-naphthol-1-aldehyde differ considerably as regards the relative reactivities of their aldehydic functions; possibly chelation in the former molecule (Sidgwick and Callow, J., 1924, **125**, 527) causes a more complete suppression of carbonyl activity than in the latter case. The kations (II) and (IV) were readily accessible from isatin and the appropriate *ar*-ketone by Pfitzinger's general quinoline synthesis (*J. pr. Chem.*, 1897, **56**, 314).

The perchlorate of (I) resembled 2-phenylbenzopyrylium perchlorate (J., 1927, 2771) in giving by direct nitration a single mononitro-derivative (V), whose constitution was established by (1) analysis and (2) synthesis as formulated from salicylaldehyde, *m*-nitropropiophenone (Commanducci and Pescitelli, *Gazzetta*, 1906, **36**, ii, 789), hydrogen chloride, and ethereal perchloric acid :



(V.)



(VI.)

The nitration of the *methopicrate* of (II) was not investigated closely, because the high percentage of meta-nitration obtained with (I) clearly made any comparison impossible.

Salts of (III) and (IV) were attacked by nitric acid, but a pure nitro-salt has not yet been isolated.

(b) 2-p-*Tolylbenzopyrylium and Corresponding Methoquinolinium Salts.*—Salicylaldehyde and *p*-methylacetophenone in the presence of caustic potash solution afforded p-*tolyl*-2-*hydroxystyryl ketone*, from which 2-p-*tolylbenzopyrylium perchlorate* was obtained. This salt yielded a mononitro-perchlorate, which, being also obtained from salicylaldehyde and 3-nitro-4-methylacetophenone (Errera, *Gazzetta*, 1891, **21**, 92) by standard methods, was evidently (VI). Salts of the corresponding 2-p-*tolyl*-N-*methylquinolinium* kation were obtained from isatin and *p*-methylacetophenone *via* 2-p-*tolylquinoline*-4-*carboxylic acid*, which by decarboxylation produced 2-p-*tolylquinoline*. The *methopicrate* underwent approximate mononitration in fuming nitric acid almost certainly (compare Le Fèvre and Mathur, J., 1930, 2236) to form the *m*-nitro-derivative. This was not synthesised for the reason given above in the case of (II).

No instances having yet been reported of direct substitution in the pyrylium nucleus or a benzo-ring fused thereto, the three following sets of experiments were instituted.

(c) 2-*Methylbenzopyrylium and* 2-*Methyl*-N-*methylquinolinium Salts.*—An ethereal solution of 2-hydroxystyryl methyl ketone (Harries, *Ber.*, 1891, **24**, 3180) containing hydrogen chloride and perchloric acid deposited 2-*methylbenzopyrylium perchlorate*, upon which nitric acid could not be caused to have any action except degradation. Attempts to prepare this pyrylium salt directly from its components gave good specimens of 2-*o*-hydroxystyrylbenzopyrylium perchlorate (Decker and Felsner, *Ber.*, 1908, **41**, 2997, 3755), which rapidly underwent dinitration when dissolved in ordinary nitric acid.

At the outset this comparison was contemplated because the necessary nitroquinaldines had been oriented and described (Döbner and Miller, *Ber.*, 1884, **17**, 1700).

Gerdeissen (*Ber.*, 1889, **22**, 245) performed the nitration of quinaldine by adding its nitrate to an excess of sulphuric acid; the products were 5- and 8-nitroquinaldine in the ratio of 3 : 2 approximately. We find that quaternary salt formation appears to alter this ratio in favour of the first nitro-derivative : quinaldinium methopicrate forms the 5-*nitro*-salt by nitration in yields of *ca.* 75% (by isolation), once again exemplifying the way in which a kationic substituent tends to enter an onium salt as remotely as possible from the positive pole (compare Drumm, Reilly, and Moore, J., 1928, 563; Le Fèvre, J., 1929, 2771).

(d) 2 : 3-*Dimethylbenzopyrylium and* 2 : 3-*Dimethyl*-N-*methylquinolinium Salts.*—This intended comparison failed at the outset because the condensation of salicylaldehyde and methyl ethyl ketone could not be prevented from producing 2-*o*-hydroxystyryl-3-methylbenzopyrylium perchlorate (compare Le Fèvre and Pearson, this vol., p. 1197); from this salt a *dinitro*-derivative was readily obtainable. The same hydroxystyryl salt was also produced from salicylaldehyde and α-methylacetoacetic ester by ethereal hydrogen chloride–perchloric acid treatment, showing that the ketonic, rather than the expected acidic, scission of the ketonic ester is effected by these strongly acidic reagents.

(e) *Benzopyrylium and* N-*Methylquinolinium Salts.*—In view of the fact that Decker (*Ber.*, 1905, **38**, 1274) had examined the nitration of quinolinium methonitrate, substitution experiments with salts of benzopyrylium were essayed, but without success.

Considerable oxidation always occurred when the nitration of benzopyrylium ferrichloride (Decker and von Fellenberg, *Annalen*, 1907, **356**, 297) was attempted, small yields only of nitrosalicylic acid being isolated. The resistance to reagents associated with the 2-phenyl and other substituted benzopyrylium salts studied in this series is thus not exhibited by the parent substance in accordance with a priori expectations. Pyrylium salts manifest in solution the equilibria : salt $\rightleftharpoons$ oxonium base $\rightleftharpoons$ pyranol base $\rightleftharpoons$ open-chain ketone. In the majority of cases the last-named is an aromatic ketone and not therefore particularly unstable towards nitric acid (especially if separate oxonium salt formation occurs at the carbonyl group; Baker and others, J., 1931, **307**, **314**; 1932, **1226**, **2917**). From benzopyrylium salts, however, *o*-hydroxycinnamaldehyde would be produced and the subsequent isolation of nitrosalicylic acids, etc., can be readily understood.

Attempted ring closure of 3- and 5-nitro-2-hydroxycinnamaldehydes (Miller and Kinkelin, *Ber.*, 1897, **20**, 1933) to form salts of 8- and 6-nitrobenzopyrylium respectively were unsuccessful, although *6-nitro-2-phenylbenzopyrylium perchlorate* was obtained from 5-nitrosalicylaldehyde and acetophenone without difficulty.

Conclusion.—It is now obvious that a satisfactory experimental comparison of an oxonium salt with an ammonium salt is impracticable. It is not proposed to continue this series. The following is a statement of the position reached in the present and previous papers.

The meta-directive influence of oxygen in the onium condition has been demonstrated most clearly in the cases of 2-phenyl-, 2-phenyl-3-methyl-, and 2-*p*-tolyl-benzopyrylium perchlorates and 2 : 4 : 6-triphenylpyrylium perchlorate.

The contrast between the activating effect of bivalent oxygen and the deactivating effect of " quadrivalent " oxygen was demonstrated by the observations that (a) xanthylium salts were not nitrated under conditions which adequately sufficed to dinitrate xanthone, and (b) 9-phenylxanthylium salts underwent mono-*p*-nitration in the 9-phenyl group only.

Qualitative indications were that oxonium oxygen forms a stronger deactivating positive pole than does ammonium nitrogen (when this element is co-valently bound to a methyl group, as has been the case in all our experiments).

These investigations have been of added interest because oxygen was the last atom whose orienting ability in the onium valency state required determination, and the results now summarised thus complete and support the general conclusion of Vorländer (*Ber.*, 1919, **52**, 262) regarding orientation by positive poles.

EXPERIMENTAL.

(a) *2-Phenyl-3-methylbenzopyrylium Perchlorate.*—Dry hydrogen chloride was passed through a solution of propiophenone (1·3 g.), salicylaldehyde (1·2 g.), and perchloric acid (70%, 5 c.c.) in ether (20 c.c.), until the mixture was saturated at 0°. After a few days the solution had become a magma of crystals; these were washed with ether (yield, 2·8 g.) and recrystallised from acetic acid, forming orange-coloured needles, m. p. 174—177° (Found : C, 60·0; H, 4·1. $C_{16}H_{13}O_5Cl$ requires C, 59·9, H, 4·0%).

Nitration. The substance was unaffected by treatment with nitric acid (*d* 1·42) at room temperature for 30 minutes. After preliminary experiments with fuming nitric acid the following procedure was found to yield maximum amounts of mononitro-derivative : the perchlorate (5 g.) was dissolved in nitric acid (*d* 1·5, 100 c.c.) at 0° and left for 3 minutes. The solution was diluted with ice to twice its volume, and an excess of perchloric acid (*d* 1·12) added. The precipitate was dried (4·3 g., m. p. 218—220°) and recrystallised from acetic acid containing a little perchloric acid, yellow microcrystalline plates, m. p. 239—240° (not depressed by admixture with the synthetic m-*nitro-perchlorate* below) (Found : C, 52·1; H, 3·2; N, 3·8. $C_{16}H_{12}O_7NCl$ requires C, 52·5; H, 3·3; N, 3·8%), being obtained.

2-m-*Nitrophenyl-3-methylbenzopyrylium Perchlorate.*—A mixture of salicylaldehyde (1·2 g.), *m*-nitropropiophenone (Commanducci and Pescitelli, *Gazzetta*, 1906, **36**, ii, 789) (1·8 g.), and perchloric acid (70%, 2 g.) was dissolved in dry ether (40 c.c.), and the solution saturated with hydrogen chloride. After 24 hours the yellow crystalline deposit was filtered off, washed with ether, and dried (m. p. 242—243°). After several recrystallisations from acetic acid–perchloric acid aq., it had m. p. 248—249° (Found : C, 52·0; H, 3·2; N, 3·9. Calc. : C, 52·5; H, 3·3; N, 3·8%).

2-Phenyl-3-methylquinoline Methopicrate.—Isatin (10 g.), water (150 c.c.), sodium hydroxide (30% aq., 70 c.c.), and propiophenone (10 g.) were heated under reflux for 8 hours, the excess of ketone then distilled in steam, and the solution diluted with water to 400 c.c. and made exactly neutral by the addition of dilute hydrochloric acid. The copious white precipitate formed, after drying (m. p. over 300°; yield, 10 g.), was thoroughly mixed with slaked lime (75 g.) and distilled from an iron tube fitted with a delivery tube carrying a water jacket. The oily distillate, extracted in ether, was distilled in a vacuum, the fraction, b. p. 230—240°/15 mm. —which set to a solid on standing, m. p. 50°—being collected. The quinoline (5·5 g.) so obtained was dissolved in dry benzene (10 c.c.) and refluxed for 10 minutes with methyl iodide (5 g.). On cooling, a yellow solid was deposited (1 g. m. p. 215°). The filtrate from this was evaporated until free from benzene, and the residue refluxed for 15 minutes with excess of methyl iodide. On cooling, a further 2 g. of *methiodide* were formed. The total yield was dissolved in the minimum quantity of ethyl alcohol, and an excess of warm saturated picric acid solution added. 2-*Phenyl*-3-*methyl*-N-*methoquinolinium picrate* was slowly deposited as yellow needles, which, after recrystallisation from alcohol–picric acid, had m. p. 169—170° (yield, 2·5 g.) (Found : N, 12·2. $C_{23}H_{18}O_7N_4$ requires N, 12·1%).

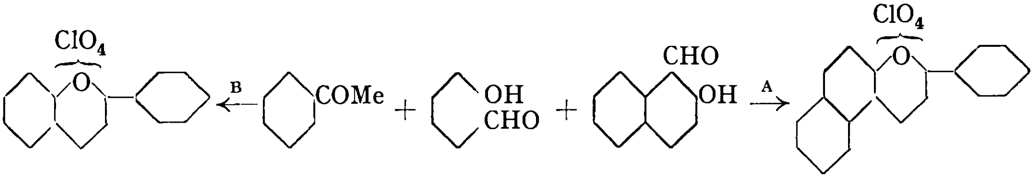
2-*Hydroxy*-α-*phenylstyryl Methyl Ketone.*—This was prepared by the method given by Dickinson (J., 1926, 2234) for " 2-hydroxystyryl benzyl ketone." Benzyl methyl ketone (52 g.), salicylaldehyde (48 g.), alcohol (100 c.c.), and piperidine (10 drops per day for a week) yielded after one crystallisation from dilute alcohol 48 g. of the required styryl methyl ketone, m. p. 180—181° (Found : C, 81·0; H, 6·0. Calc. : 80·7; H, 5·9%).

Attempted Ring Closure of the Preceding Compound.—A solution of the ketone in boiling acetic acid was treated with concentrated hydrochloric acid and reboiled. Addition of excess of perchloric acid precipitated the original material. Similarly, the saturation of a solution of the ketone in dry ether, ethyl acetate, or anhydrous formic acid, alone or in presence of 70% perchloric acid, failed to produce any pyrylium salt.

3-*Phenyl*-2-*methylbenzopyrylium perchlorate* was eventually isolated by the following procedure : equimolecular portions of salicylaldehyde and benzyl methyl ketone (1·8 g. of salicylaldehyde), with perchloric acid (70%, 5 c.c.), were dissolved in dry ether (10 c.c.) and saturated with hydrogen chloride. A red-blue crystalline product was formed, which was washed with ether and recrystallised from acetic acid; m. p. 189—191° (Found : C, 59·4; H, 4·1. $C_{16}H_{13}O_5Cl$ requires C, 59·9; H, 4·1%. $C_{23}H_{17}O_6Cl$ requires C, 65·0; H, 4·0%). Attempted nitrations of this substance produced only black masses.

2-*Phenyl*-α-*naphthapyrylium Perchlorate.*—2-Naphthol-1-aldehyde (1·7 g.), acetophenone (1·2 g.), and perchloric acid (70%, 5 c.c.) were dissolved in anhydrous ether (40 c.c.) and saturated at 0° with dry hydrogen chloride. After 24 hours, 2 g. of 2-*phenyl*-α-*naphthapyrylium perchlorate*, m. p. 208—212°, had separated. Crystallisation of the salt from acetic acid gave long yellow needles, m. p. 216—220° (Found : C, 63·6; H, 3·7. $C_{19}H_{13}O_5Cl$ requires C, 64·0; H, 3·6%). The total insoluble material obtained by filtration after this perchlorate had been stirred with an excess of sodium acetate solution was dissolved in acetic acid, and the product treated with solid ferric chloride. The ferrichloride described by Decker and von Fellenberg (*Annalen*, 1909, **364**, 42) was precipitated quantitatively, m. p. 187—188° (Found : C, 50·5; H, 3·0. Calc. : C, 50·1; H, 2·9%).

Relative Reactivities of Salicylaldehyde and 2-*Naphthol*-1-*aldehyde.*—We attempted to demonstrate this point by setting the two aldehydes in competition for a deficiency of acetophenone :



A solution of 2-naphthol-1-aldehyde (1·7 g.), salicylaldehyde (1·2 g.), and acetophenone (1·2 g.) in anhydrous ether (150 c.c.) was saturated with dry hydrogen chloride at 0° and left for 48 hours at room temperature. The dark-coloured solution had then deposited about 1 g. of bronze-coloured needles, m. p. 160—175° (mixed with 2-phenylbenzopyrylium perchlorate of m. p. 177—178°, m. p. 155—158°; mixed with 2-phenyl-α-naphthapyrylium perchlorate described above, m. p. 160—180°).

The result shows that reaction A apparently predominated and suggests that salicylaldehyde is inferior to the naphthalene compound in reactivity. Relevant also in this connection is the observation of Das and Ghosh (J., 1919, **115**, 820) that salicylaldehyde will not condense with deoxybenzoin in an alkaline medium, although according to Singh and Mazumdar (*ibid.*, p. 822) 2-naphthol-1-aldehyde easily does so.

3-*Phenyl*-2-*methylquinoline*.—A mixture of phenylacetone (9·2 g.), isatin (8 g.), and the other reagents in quantities as in the case of 2-phenyl-3-methylquinoline (above) was boiled for 8 hours. After steam-blowing, the hot solution was made just acid; on cooling, 3-*phenyl*-2-*methylquinoline*-4-*carboxylic acid* was obtained as a cream-coloured powder (8 g.), m. p. above 250°. The total yield was mixed with slaked lime (80 g.) and distilled, about 30 c.c. of distillate appearing. This was extracted with benzene, dried with potassium hydroxide, and distilled. The fraction (4 g.) passing over at 220—230°/33 mm. was dissolved in excess of methyl iodide and refluxed for 3 hours. Evaporation afforded a gum, which was dissolved in water and treated with saturated aqueous picric acid. The yellow picrate of (IV) was precipitated in a crystalline condition, m. p. 170—175° (Found : N, 12·3. Calc. : N, 12·1%).

(b) *Salicylidene*-4-*methylacetophenone*.—A hot solution of potassium hydroxide (30 g.) in water (25 c.c.) was added to a mixture of salicylaldehyde (25 g.), *p*-methylacetophenone (18 g.), and rectified spirit (100 c.c.). A vigorous reaction ensued and in a few minutes the solution had filled with crystals of a red potassium salt. After 24 hours these were collected, dissolved in water, and acidified with carbon dioxide. The *chalkone* was thus produced as a yellow powder, which after crystallisation from dilute alcohol formed yellow needles (2 g.), m. p. 158—159° (Found : C, 80·6; H, 6·0. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%). By dilution, acidification, etc., of the filtrate from the potassium salt a further 20 g. of product could be obtained (total yield, 22 g.).

Ring closure of the previous compound. A solution of the chalkone (0·5 g.) in acetic acid (25 c.c.) was boiled as quickly as possible and treated with two drops of concentrated hydrochloric acid. Boiling was continued until the initial yellow colour decreased in intensity and did not reappear when a further drop was added. The mixture was then added to perchloric acid (*d* 1·2, 25 c.c.) and water (25 c.c.), from which, on cooling, yellow needles separated. In this way, from 3 g. of the chalkone, 3·1 g. of the *pyrylium perchlorate* were obtained (attempted preparations on larger scales failed because of a strong development of a green colour in the solutions during the boiling; this difficulty has been experienced before, J., 1932, 1990). The compound crystallised well from acetic acid containing perchloric acid, forming stout yellow needles, m. p. 148—150°, with previous darkening from 120° onwards (Found : C, 59·9; H, 4·2. $C_{16}H_{13}O_5Cl$ requires C, 59·9; H, 4·1%).

Nitration of 2-p-*Tolylbenzopyrylium Perchlorate*.—The perchlorate (1 g.) was slowly dissolved in nitric acid (*d* 1·5, 20 c.c.) at a temperature not above 0°, and the solution kept for 2 minutes. The temperature being maintained as low as possible, water (10 c.c.), followed by aqueous perchloric acid (*d* 1·2, 30 c.c.), was added, and the mixture kept for some time before filtration; a lime-coloured *mononitro*-derivative (about 1 g.) was produced, m. p. 199°, with previous shrinking from 150° onwards (Found : N, 4·0. $C_{16}H_{12}O_7NCl$ requires N, 3·8%). A mixture with the synthetic substance described below exhibited the same behaviour in m. p. determinations.

Synthesis of 3′-*Nitro*-2-*phenyl*-4′-*methylbenzopyrylium Perchlorate*.—A mixture of salicylaldehyde (1·2 g.), nitromethylacetophenone (1·8 g.), perchloric acid (70%, 3 c.c.), and anhydrous ether (40 c.c.) was saturated with hydrogen chloride and left for 2 days. The crystalline magma produced had m. p. 200—205° (decomp. after blackening from *ca.* 180°) after purification (Found : N, 3·9. Calc. : N, 3·8%).

Preparation of 2-p-*Tolylquinoline and Derivatives thereof*.—Isatin (10 g.), water (150 c.c.), caustic soda solution (30%, 70 c.c.), and *p*-methylacetophenone (12 g.) were heated together under reflux for 9 hours, the excess of ketone then removed by steam-blowing, and the solution made up to 400 c.c. with water. *Exact* neutralisation with dilute hydrochloric acid then gave 2-*p*-tolylquinoline-4-carboxylic acid (20 g.), m. p. 180—181°. This was distilled with slaked lime (200 g.). The oily distillate, which solidified (*ca.* 8 g.), crystallised from dilute alcohol in pale yellow plates (6 g.) of 2-p-*tolylquinoline*, m. p. 82—83° (Found : N, 6·5. $C_{16}H_{13}N$ requires N, 6·4%).

Methosulphate. 2-*p*-Tolylquinoline (1 g.) and methyl sulphate (3 c.c.) were refluxed for 5 hours in benzene (10 c.c.) After 12 hours, the white needles were separated, washed with benzene, dried (yield, 90%; m. p. 154—155°), and recrystallised from absolute ether and alcohol; m. p. 158—159° (Found : C, 62·7; H, 5·6. $C_{18}H_{19}O_4NS$ requires C, 62·6; H, 5·5%). The *methosulphate* is readily soluble in water and the common organic solvents.

The *methopicrate*, precipitated when an excess of cold saturated aqueous picric acid was added to the methosulphate (1 g.) in dilute aqueous alcohol, and recrystallised from water containing picric acid, formed hair-like needles, m. p. 157—158° (Found : N, 12·3. $C_{23}H_{18}O_7N_4$ requires N, 12·1%).

Nitration of the foregoing methopicrate. The methopicrate (5 g.) was dissolved in nitric acid (50 c.c., *d* 1·5) at 0° to — 10°, the solution left at 0° for 1 hour and poured on ice, the excess of nitric acid partly neutralised by ammonia, more picric acid added (as saturated solution), and the whole left at 0° for 24 hours. The *product* (7 g.), once crystallised from 95% alcohol, had m. p. 192—194° (Found : N, 14·4. $C_{23}H_{17}O_9N_5$ requires N, 13·8%. $C_{23}H_{16}O_{11}N_6$ requires N, 15·2%).

(c) 2-*Methylbenzopyrylium Perchlorate.*—A solution of *o*-hydroxystyryl methyl ketone (2 g.), ether (40 c.c.), and perchloric acid (70%, 3 c.c.) which had been saturated with dry hydrogen chloride at 0° was filtered after 24 hours. The perchlorate was then obtained as compact orange prisms, (2·1 g.), m. p. 153—158°.

An attempt to prepare this salt by passing hydrogen chloride through a solution of salicylaldehyde (2·5 g.), acetone (0·6 g.), and perchloric acid (70%, 3 c.c.) in dry ether gave after 2 days 1·5 g. of dark crystals (Found : C, 58·3; H, 4·0. Calc. for $C_{17}H_{13}O_6Cl$: C, 58·5; H, 3·7%). 2-Hydroxy-2-styrylbenzopyrylium perchlorate was also obtained quantitatively from dicoumaroketone (Decker and Felsner, *Ber.*, 1908, **41**, 2997, 3755), 70% perchloric acid, and anhydrous ether in the usual manner. Both products had m. p. 188—194°, separately or mixed (Buck and Heilbron, J., 1922, **121**, 1198, record m. p. 196°).

Dinitration of 2'-*Hydroxy*-2-*styrylbenzopyrylium Perchlorate.*—The substance was dissolved in 20 times its weight of nitric acid (*d* 1·42) at 0° and immediately poured on ice. The chocolate-brown powder produced, which could not be crystallised without apparent decomposition, was washed with very dilute perchloric acid, followed by ether, and dried in a vacuum (Found : N, 6·7. $C_{17}H_{11}O_{10}N_2Cl$ requires N, 6·4%).

Nitration of Quinaldine Methosulphate.—The methosulphate (m. p. 148—150°) (10 g.) was slowly added to nitric acid (*d* 1·5, 100 c.c.) below 0°, and the mixture kept for 1 hour at 0°, and poured into 1·5 l. of saturated aqueous picric acid containing ice. The precipitate (11·5—12 g.) had m. p. 148—150° after recrystallisation (Found : N, 16·4. $C_{17}H_{13}O_9N_5$ requires N, 16·2%).

Synthesis of 5-*Nitroquinaldine Methopicrate.*—5- and 8-Nitroquinaldines were prepared from quinaldine nitrate as described by Gerdeissen (*Ber.*, 1889, **22**, 245). The former compound was heated with methyl sulphate for 2 hours on the steam-bath, the cooled product extracted with water–alcohol, and aqueous alcoholic picric acid added to the extract. The precipitate obtained crystallised from alcohol in yellow needles, m. p. 149—151° (Found : N, 16·3. Calc. : N, 16·2%). This nitro-compound raised the m. p. of the preceding one.

(d) *Dinitration of* 2-o-*Hydroxystyryl*-3-*methylbenzopyrylium Perchlorate.*—The perchlorate (0·5 g.) was dissolved in nitric acid (*d* 1·5, 20 c.c.) and left at 0° for 3 minutes. Dilution of the solution with acetic acid (20 c.c.) followed by perchloric acid (*d* 1·12, 50 c.c.), produced a yellow precipitate, which, after filtration, washing with acetic acid, and drying, had an indefinite decomp. point above 150° (Found : N, 6·1. $C_{18}H_{13}O_{10}N_2Cl$ requires N, 6·2%).

Condensation of Salicylaldehyde and Ethyl α-Methylacetoacetate.—Löwenbein and Katz (*Ber.*, 1926, **59**, 1377) have reported that by application of their hydrogen chloride–perchloric acid–ether treatment, salicylaldehyde and α-methylacetoacetic ester condense to give 2-*o*-hydroxystyryl-3-methylbenzopyrylium perchlorate. In view of the fact that we now find that ethyl acetoacetate itself and certain of its aryl derivatives do not lose the carbethoxy-group during this procedure we have repeated this reaction. The result is in entire agreement with the description given by the above authors; in addition we find that the carbethoxy-group is similarly lost when pyrylium chloride formation is carried out in 98% formic acid, or acetic acid, solution.

(e) *Benzopyrylium Ferrichloride.*—The directions of Decker and von Fellenberg (*Annalen*, 1909, **364**, 21) for the preparation of this substance from salicylaldehyde and acetaldehyde were followed, but bakelite-like substances were always produced. The working-up was therefore performed as follows : The reaction product was cooled, and the clear liquid decanted. Dilution to about $\frac{3}{4}$ l. with 10% hydrochloric acid caused a further precipitation of resins, which were removed. Any excess of salicylaldehyde was extracted from the filtrate with benzene. Solid ferric chloride hydrate was now stirred in to saturation, and the solution cooled and saturated with hydrogen chloride. As soon as yellow crystals began to form, the extra resinous material thrown out by the hydrogen chloride was removed, the filtrate cooled in ice-salt, and the hydrogen chloride dissolution continued. By proceeding in this way we have obtained yields of *ca.* 4% of benzopyrylium ferrichloride, m. p. 197—199° (Found : C, 32·6;

H, 2·4. Calc. for $C_9H_7OCl_4Fe$: C, 32·8; H, 2·2%). By following as far as possible the brief directions of Decker and von Fellenberg (*loc. cit*), only traces of the ferrichloride could be isolated.

Action of Nitric Acid on Benzopyrylium Ferrichloride.—The ferrichloride (1 g.) was added to nitric acid (*d* 1·42 or 1·5; 20 g.) at various temperatures. Red fumes always appeared, indicating oxidation. In a typical case, an attempted nitration which had stood at room temperature for 24 hours was diluted with ice, a clear reddish solution being obtained. Iron was removed as hydroxide, and the filtrate evaporated to a small bulk, cooled, and acidified with hydrochloric acid. The cream-coloured precipitate produced had m. p. *ca.* 150° (dried at 130°) and in aqueous solution gave a deep red ferric chloride reaction (Found : N, 12·8. Calc. for $C_7H_4O_7N_2$: N, 12·3%). The m. p. was raised by admixture with authentic dinitrosalicylic acid (Hübner, *Annalen*, 1879, **195**, 46) of m. p. 172—173° (also dehydrated at 130°).

Attempted Syntheses of 6- *and* 8-*Nitro*-2-*phenylbenzopyrylium Perchlorates.*—(a) 5-Nitrosalicylaldehyde (1·7 g.), acetophenone (1·2 g.), anhydrous ether (40 c.c.), and perchloric acid (70%, 3 c.c.) were mixed and saturated with hydrogen chloride. The red crystalline precipitate was collected after 3 days (yield, 1·4 g.; m. p. 180—185°). The *salt* could not be crystallised from common solvents without apparent decomposition (Found : N, 4·2. $C_{15}H_{10}O_7NCl$ requires N, 4·0%). The substance, by addition to fuming nitric acid, underwent nitration without any sign of oxidation. (b) Exact duplication of the above conditions in the case of 3-nitrosalicylaldehyde produced 2 g. of long yellow needles, m. p. 163—164° (Found : N, 5·3. $C_{15}H_{11}O_4N$ requires N, 5·2%). From its analysis and mode of production this compound is probably 3-*nitro*-2-*hydroxychalkone*, the slow cyclisation of which might be expected from steric considerations.

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