Combining this with the preceding equation,

$$CO_2(g.) + 2NH_3(g.) = CO(NH_2)_2(s.) + H_2O(l.);\ \Delta F = -1772,$$

gives

$$CO_2(g.) + 2NH_3(g.) = CO(NH_2)_2\ (molal) + H_2O(l.);\ \Delta F = -3334.$$

The Free Energy of Formation of Ammonium Cyanate.

In the experiments of Walker and Hambly,[1] of Walker and Kay,[2] and of Fawsitt,[3] the equilibrium between urea and ammonium cyanate in dilute aqueous solution has been determined. From their several observations the percentage of 0.1 molal urea converted into cyanate is 6.6, 6.2, 6.5; average, 6.5%. Assuming the ammonium cyanate in this very dilute solution to be completely dissociated, we have for the equilibrium constant in the reaction $CO(NH_2)_2 = NH_4^+ + CNO^-$.

$$K = \frac{(0.0065)^2}{0.0935} = 0.00045.$$

The heat of the reaction as given by Walker[4] is 7500 cal. Whence, applying the van't Hoff equation, we find at 25° $K = 0.000035$. Hence, $\Delta F = -RT \ln K = 6100$, where ΔF refers to normal conditions, that is to the reaction,

$$CO(NH_2)_2\ (molal) = NH_4^+\ (molal) + CNO^-\ (molal) + H_2O_1(l.);$$
$$\Delta F = 2766.$$

How we may proceed from this equation to calculate the free energy of formation of hydrocyanic acid and other important compounds will be discussed in another paper.

[Contribution from the Chemical Laboratory of the University of Michigan.]

ON TRIPHENYLMETHYL. XXI. QUINOCARBONIUM SALTS OF THE HYDROXY-XANTHENOLS.

By M. Gomberg and C. J. West.[5]

Received September 4, 1912.

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[1] *J. Chem. Soc.*, **67**, 746 (1895).

[2] *Ibid.*, **71**, 507 (1897).

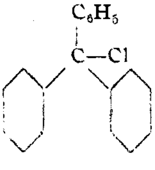
[3] *Z. physik. Chem.*, **41**, 601 (1902).

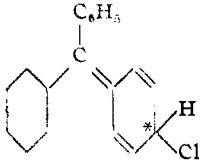
[4] *Ibid.*, **42**, 207 (1902).

[5] This investigation was presented by Mr. West to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

Theoretical.

1. Introduction.—In a preliminary paper[1] we have emphasized the fact that "triphenylchloromethane and its analogs exist in two tautomeric forms: the benzenoid (I) when colorless and the quinoid (II) when colored. The quinoid compounds behave like salts. The salt-like character of these quinocarbonium compounds was attributed to the carbon atom C*,[2] and was inferred from their capacity to conduct the electric current, to form double salts, perhalides and the like.


I.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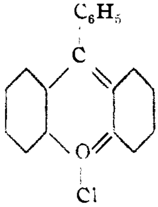
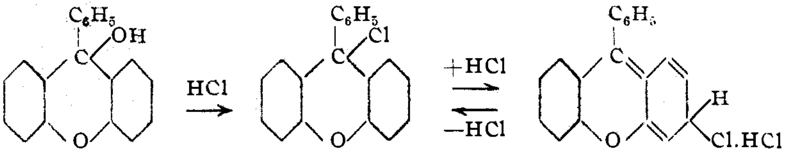

III.

Later, Gomberg and Cone[3] extended the hypothesis of the quinocarbonium salts to the study of the xanthone and thioxanthone derivatives, the salts of which have been usually regarded, prior to this, as possessing the oxonium constitution (III). They showed that there is the closest analogy between triphenylcarbinol and its analogs on the one hand, and the aryl-xanthenols and thio-xanthenols on the other. This analogy consists in (1) that the xanthenols, like the triphenylcarbinols, form *colorless* carbinol halides (IV), an important fact that had been overlooked by the various investigators in this field; (2) these halides show the tendency to unite with a metal halide, a halogen, or even an extra molecule of halogen acid and then exist in a tautomeric, *colored* quinoid form (V); (3) the extra molecule of halogen acid may be readily removed by a stream of dry air in an inert solvent and the *colorless* halide is again regenerated. With phenyl-xanthenol (VI), for instance, these reactions may be formulated as follows:



VI. Phenyl-xanthenol.

IV. Phenyl-xanthenol chloride, colorless.

V. Quinocarbonium salt. Phenyl-quino-xanthenol chloride-hydrochloride, colored.

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[1] This Journal, **33**, 1211 (1911).

[2] Gomberg, *Ber.*, **40**, 1847 (1907); **42**, 406 (1909).

[3] *Ann.*, **370**, 142 (1909); **376**, 183 (1910); cf. also Gomberg and Van Slyke, This Journal, **33**, 532 (1911); Cone and West, *Ibid.*, **33**, 1538 (1911).

(4) The halogen of the normal colorless halide is removed by molecular silver, and there results an unsaturated compound entirely analogous to triphenylmethyl, which, like the latter, is decolorized upon exposure to the air with the formation of the colorless peroxide; (5) the normal halide dissolves in liquid sulfur dioxide with the production of color, thus existing in this solvent in the tautomeric state.

The chief, and, in fact, the only difference between these two classes of compounds, the triphenylcarbinols and the xanthenols, is the readiness with which they are tautomerized to the quinocarbonium form. Thus the triphenylcarbinol halides are tautomerized by means of sulfur dioxide, metal halides, and also in some isolated cases[1] by halogen acids. The aryl-xanthenols, on the other hand, are generally tautomerized by halogen acids just as readily as by the above mentioned reagents, forming double salts and acid salts which are much more stable than the corresponding ones in the triphenylcarbinol series.

The increased reactivity of the xanthenols as compared with the triphenylcarbinols was attributed by Gomberg and Cone to the bridge oxygen of the pyrone ring. "The function of the oxygen of the pyrone ring seems to be two-fold in nature: first, it directs quinoidation towards one of the two nuclei which are in direct union with the pyrone linking; second, it imparts to the xanthenol derivatives a much greater tendency to tautomerize, and consequently a greater stability to the tautomerized product than we find in the triphenylmethane derivatives."[2]

2. *Purpose of This Investigation.*—After it had been shown that the salt-like compounds derived from plain phenyl-xanthenol and from some of its halogen substitution derivatives are true quinocarbonium and not "oxonium" salts, it became necessary to show the same for the various methoxy and hydroxy derivatives of phenyl-xanthenol, which have been described by various investigators as colored oxonium salts.[3] The following work has for its purpose, then, the demonstration of the constitution of these widely discussed colored derivatives. The results of this study would throw, it is hoped, further light upon the base-like behavior of the more complex derivatives of xanthone, such as gentisin, resorcin-benzin, hydrochinon-benzin, fluorescein, hydrochinon-phthalein, and related compounds.

We have used in this paper the system of naming the xanthone deriva-

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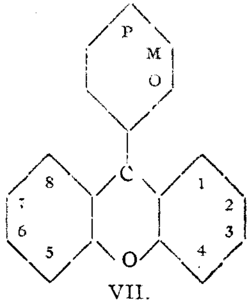
[1] Baeyer and Villiger, *Ber.*, **35**, 1199, 3013 (1902); **36**, 2787 (1903); Gomberg and Cone, *Ann.*, **370**, 191 (1909).

[2] *Ann.*, **370**, 151 (1909).

[3] Baeyer, *Ann.*, **372**, 97 (1910); Decker and Fellenberg, *Ibid.*, **356**, 313 (1907); Kehrmann, *Ibid.*, **372**, 287 (1910); Kehrmann and Dengler, *Ber.*, **41**, 3440 (1908); **42**, 870 (1909); Kehrmann and Knop, *Ibid.*, **44**, 3505 (1911); Kropp and Decker, *Ibid.*, **42**, 578 (1909); Liebig, *J. prakt. Chem.*, **85**, 97, 241 (1912); Pope and Howard, *J. Chem. Soc.*, **97**, 1923 (1910); **99**, 545 (1911).

tives as given by Richter, Lexicon, (3rd Edition) and also in the Index of the *Berichte d. Chem. Ges.*, **1911**, p. 3874. (VII.) (Compare, however, Baeyer, *Ann.*, **372**, 98 (1910)). We have studied, so far, *p*-, 1-, 2-, 3-, 4-methoxy- and hydroxy-xanthenols and also, to some extent, 3,6-dihydroxyxanthenol.



VII.

3. *Influence of the Methoxy and Hydroxy Groups.*—In all the cases where the influence of these groups has been studied as regards the basicity,[1] stability,[2] and color[3] of organic compounds, it has been found that the influence is a positive one, that is, it causes an increase in basicity, stability, or a deepening of color. No strictly general rules can be laid down as to the position that has the greatest influence, though Baeyer found that the *para* position gave the largest increase in basicity in the triphenylcarbinol series, and it is generally recognized that the *ortho* substituent produces the most intense color,[4] while the *para* substituted compound is less strongly colored than the others. In the study of the various methoxy- and hydroxy-xanthenols we have observed the following general characteristics:

a. The color of the quinoid derivatives is deepened in every case from yellow as found in phenyl-xanthenol to deep red, most intense in the phenyl-1-hydroxy-xanthenol derivatives. The 3-derivative presents a peculiar and interesting exception to this, for it possesses, in all its compounds, a pure yellow color. Decker and Fellenberg very curiously report the 3-hydroxy derivatives as being intensely red.[5]

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[1] Baeyer and Villiger, *Ber.*, **35**, 3013 (1902); **36**, 2774 (1903); Gomberg and Cone, *Ann.*, **370**, 191 (1909); **376**, 211 (1910); Schmidt, *Ber.*, **40**, 2331 (1907); Staudinger, *Ibid.*, **44**, 1640 (1911); *Ann.*, **384**, 38 (1911); Stobbe, *Ibid.*, **370**, 93 (1909); Strauss and Ecker, *Ber.*, **39**, 2987 (1906).

[2] Kehrmann, *Ann.*, **372**, 287 (1910); Strauss, *Ibid.*, **374**, 40, 127 (1909); Strauss and Hussy, *Ber.*, **42**, 2172 (1909); Wieland and Wecker, *Ibid.*, **43**, 700 (1910).

[3] O. Fischer, *Ber.*, **14**, 2532 (1881); Decker and Fellenberg, *Ann.*, **356**, 312 (1907); Kaufmann and Fritz, *Ber.*, **41**, 4414 (1908); Kostanecki and Tambor, *Ibid.*, **32**, 1291 (1899); Ley and Englehardt, *Ibid.*, **41**, 2993 (1908); Noelting and Gerlinger, *Ibid.*, **39**, 2041 (1906); Pfeiffer, *Ann.*, **383**, 95 (1911); Stobbe, *Ber.*, **39**, 761 (1906); and others; Wieland and Stenzel, *Ber.*, **40**, 845, 2352, 2360 (1907).

[4] See the work of Gomberg and Van Slyke, and also that of Noelting and Gerlinger.

[5] See also Dengler, Thesis, Zürich, **1910**, p. 39.

b. The stability of the quinoid compounds is increased by the presence of the hydroxy and methoxy groups in the molecule. This may be illustrated by the following: The chloride-hydrochlorides of most of the compounds described in previous papers are readily decomposed into the components by ether at room temperature,[1] or by boiling a benzene suspension of the acid salt on the water bath. On the other hand, the chloride-hydrochlorides of the hydroxy- and methoxy-xanthenols described in this paper are readily obtained from an ether solution of the xanthenol, and do not give off the extra molecule of hydrochloric acid in some cases under a temperature of 125–145°. This increased stability of the colored acid chlorides is also seen in the fact that they may be obtained from a solution of the hydroxy-xanthenols in dilute mineral acids in *water*. The product thus obtained is the same as that from a non-water solution, as from ether or benzene. In view of this fact, the argument of Kehrmann loses all its force as regards the "oxonium" constitution of the colored xanthenol salts when these are obtained from watery solutions instead of from benzene or ether.[2] If they are quinocarbonium in the one case, they must be in the other.

c. The stability of the benzoid salts, chlorides and bromides, of the hydroxy- and methoxy-xanthenols is diminished, naturally, in proportion to their greater tendency towards tautomerization. So pronounced is this tendency towards quinoidation that some of the halides exist largely, if not wholly, only in the quinoid state, even when there is absolutely no excess of acid present. This is particularly true of those derivatives that contain the (OH) group in the *para* position to the carbinol carbon atom, or in the *ortho* position to the bridge oxygen atom. The hydroxyl group is of far greater influence as regards tautomerization than the methoxy group. For this reason, while in certain cases the halide of the hydroxy compound is found to be colored, quinoid, the corresponding halide of the methoxy compound is unquestionably colorless and benzoid. Compare, for instance, the chlorides of phenyl-3-methoxy- and -hydroxy-xanthenol, and of phenyl-4-methoxy- and -hydroxy-xanthenol; also the bromides of the different methoxy- and hydroxy-xanthenols. It is not surprising that all the workers in this field have obtained and described only *colored* salts, having entirely overlooked the existence of the benzoid modification. Indeed, in most instances, where it is not difficult to prove the existence of the benzoid halide so long as the latter is kept under some neutral solvent, it is next to impossible to isolate the solid salt entirely colorless. The slightest trace of moisture or of mineral acids causes the formation of a red coating on the outside of the halide.

d. The reactivity of the xanthones themselves is much enhanced by the

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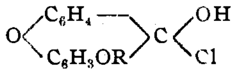
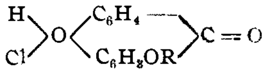
[1] Baeyer, *Ann.*, **372**, 84 (1910); Gomberg and Cone, *Ibid.*, **370**, 165 (1909).

[2] *Ann.*, **372**, 313 (1910); Kehrmann and Knop, *Ber.*, **44**, 3505 (1911).

presence of the hydroxy and methoxy groups. These xanthones are much more prone to form additive compounds with acids, metal halides, etc. Thus, we find that they combine even with hydrochloric acid, forming unstable, easily dissociable, salt-like compounds. A considerable number of these are described in the experimental part. The reasons for considering these additive compounds, as (VIII), in preference to the older conception (IX), have been given in a previous paper.[1].



VIII.



IX.

4. *Influence of Acetoxy and Benzoxy Groups.*—For the sake of comparison, we have also prepared the acetoxy and benzoxy derivatives of certain of the phenyl-hydroxy-xanthenols. We find that the positive influence of the oxygen is entirely obliterated by these acyl groups, and the tendency towards quinoidation is very much diminished. The behavior of these compounds is the same as that already described for the xanthenols containing halogens and other negative groups in the nucleus. Thus, the chloride-hydrochlorides of the acetoxy-xanthenols possess in most cases only a yellow or yellow-red color; they give up the extra molecule of acid quite readily, and are decomposed even by ether. The colorless chlorides and bromides may be obtained without difficulty. In every respect, the colored salts show the behavior of quinocarbonium salts, and, in many instances, it would indeed be difficult to differentiate these salts from the quinocarbonium salts of the triphenylcarbinols.

5. *Hydrobromic Acid as a Tautomerizing Agent.*—Gomberg and Cone have discussed the effects of hydrochloric, sulfuric and perchloric acids as tautomerizing agents. It only remains to add a few words concerning the effects of hydrobromic acid. This acid has been used by them in a few cases, also by Cone and West. The conclusion was drawn that the influence of hydrobromic acid as a tautomerizing agent is greater than that of hydrochloric. Chichibabin[2] believes that he has obtained a quinoid form of the bromide of so simple a substance as trinaphthylcarbinol. In the study of the xanthenols, we have found that the influence of hydrobromic acid is much more marked than that of hydrochloric acid. In the case of the methoxy-xanthenols we obtained bromide-hydrobromides, from which a molecule of hydrobromic acid could be driven off, leaving a colorless bromide. But, in the case of all the hydroxy-xanthenols that have been studied, colored, insoluble, *mono*-bromides were obtained, which have resisted all attempts to prepare them colorless. Whether we

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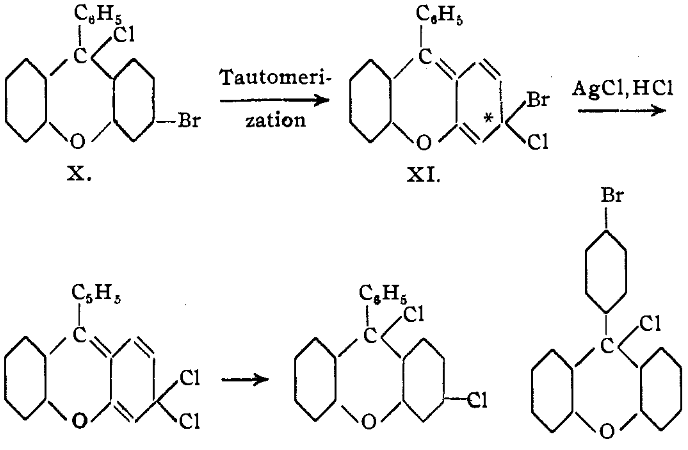
[1] *Ann.*, 376, 217 (1910); Pfeiffer, *Ibid.*, 376, 285 (1910); 383, 95 (1911), accounts for these addition compounds by the use of partial valences; the color, according to him, is due to halochromie.

[2] *J. prakt. Chem.*, 84, 751 (1911).

have not as yet obtained the proper experimental conditions for this remains to be seen. But all the evidence at present indicates that these mono-bromides are true quinoid compounds: they are intensely colored, they are insoluble in benzene, but soluble in nitrobenzene and in chloroform, which is the same behavior as shown by true quinoid compounds such as the perchlorates, sulfates, etc. A similar case was found by Cone and West,[1] who were unable to prepare phenylenediquinoxanthylene bromide colorless. It is, therefore, not surprising that Kehrmann should find phenyl-3,6-dimethyl-xanthenol iodide[2] to be colored in distinction from the colorless chloride. Thus, it is seen that of the chlorides those of 1- and of 2-hydroxy-xanthenol are colorless, and those of *p*,-3,4-hydroxy-xanthenols are colored, while the bromides all tautomerize spontaneously to the quinoid state. Moreover, such quinoidation may occur even under the influence of other groups than the hydroxyl, as evidenced from Kehrmann's experiences.

6. *Localization of Quinoid Nucleus.*—Among the proofs in favor of the quinocarbonium in preference to the oxonium constitution of the xanthenol salts, the behavior of *para*-brominated derivatives deserves particular attention. It was found that the nucleus bromine atom in phenyl-*p*-bromo-xanthenol chloride (X), when the latter is dissolved in liquid sulfur dioxide, or even when dissolved in benzene, becomes labile, and can be readily replaced by chlorine, using either silver chloride or hydrochloric acid. The quinocarbonium constitution alone is capable of explaining consistently the course of this reaction. On the basis of this constitution, the quinoid nucleus in (XI) has lost its aromatic character, the carbon atom C* becomes aliphatic in its function, and consequently the bromine



X. XI. XII. XIII. XIV.

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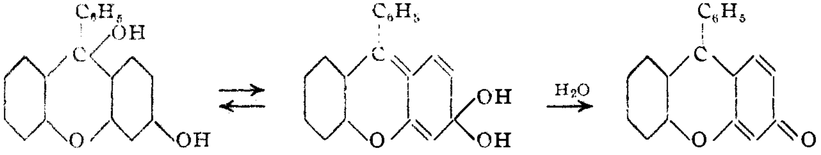
[1] This Journal, 33, 1538 (1911).

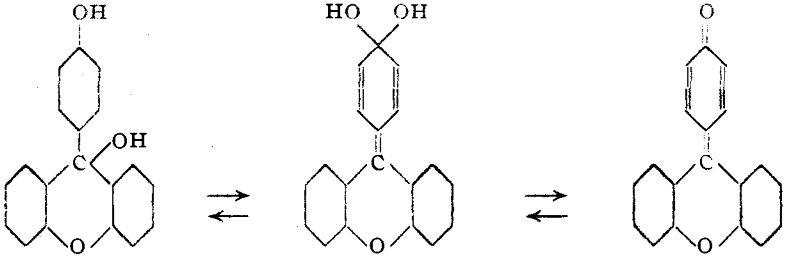
[2] Kehrmann and Knop, *loc. cit.*

linked to it becomes labil. Since the isomeric compound *p*-bromophenylxanthenol chloride (XIV) does not show the same behavior (is, in fact, unaffected by the reagents) it must be concluded that the tautomerization goes to one of the two phenyl rings which is linked to the pyrone oxygen, and not to that phenyl ring which is outside the xanthone nucleus.

The behavior of the various hydroxy-xanthenols, as will be described below, seems to us to lend a very strong additional argument in favor of the quinocarbonium structure of the colored derivatives. All the methoxy-xanthenols described in this paper have been found to yield, on being demethylated, colorless hydroxy-xanthenols, with the exception of phenyl-3-methoxy-xanthenol, which yields fluorone. In view of what has been stated as regards the strong tautomerizing influence of the hydroxyl group when in the *para*-position to the carbinol carbon, there can be little doubt as to the mechanism involved in the formation of the fluorone. It has been shown that all xanthenol sulfates and perchlorates are quinoid; so are many bromides, and so are even some chlorides, and it may reasonably be inferred that some xanthenols in themselves, as such, may possess the tendency towards tautomerization. Now in the case of the 3-hydroxy-xanthenol, the equilibrium between the two tautomers (XV) and (XVI) would naturally be disturbed, due to the splitting off of a molecule of water from the latter with the consequent formation of the fluorone (XVII), this disturbance of equilibrium continuing until the xanthenol is entirely converted into the fluorone. Indeed, the existence of a true and stable quinocarbonium base may be presaged even in the case of such polyhydroxy-xanthenols as contain no hydroxyl group in the *para*-position to the carbinol carbon atom.



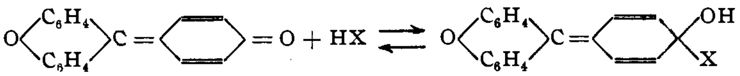
XV. XVI. XVII.



XVIII. XIX. XX.

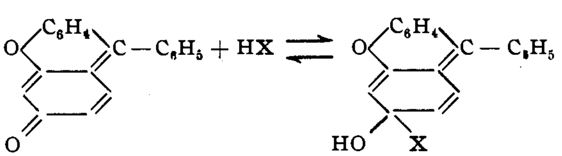
But it may reasonably be asked, if the *para*-hydroxyl group is in the phenyl ring which is not linked to the bridge oxygen, will the tautomerization then be induced to that ring, in virtue of the tautomerizing influence of the hydroxyl group? The answer is, as in the case of the corresponding bromine derivative, no. It is indeed possible to prepare this xanthenol, *p*-hydroxy-phenyl-xanthenol. It is aperfectly colorless stable substance and begins to lose water only when heated near its melting point. The quinone (XX), *xanthylene quinomethane*, resulting through the loss of a molecule of water, has a characteristic green color and is isomeric with *phenyl-fluorone*, but, unlike the latter, is readily changed back to the xanthenol by alkalies or dilute acids. The relative ease with which these two isomeric phenyl-hydroxy-xanthenols, *p*-hydroxy-phenyl- and phenyl-3-hydroxy-xanthenol are changed to their respective quinones, indicates with certainty that normally the tautomerizing influence is towards the xanthone ring.

7. *The Action of Halogen Acids upon the Two Quinones.*—Xanthylene-quinomethane, as mentioned, is readily converted by hydrolyzing agents into benzoid compounds, but, by the action of hydrochloric or hydrobromic acid upon the quinone, the latter yields, upon removing the excess of acid, the colored quinoid *p*-hydroxy-phenyl-xanthenol halide, and this halide is identical with the one obtained by the direct action of the acid upon the *p*-hydroxy-phenyl-xanthenol itself. The mechanism of the reaction must be interpreted as follows:



XXI. XXII.

Fluorone also combines with halogen acids as has been first shown by Kehrmann, who assigns to the salts the oxonium constitution. But the reaction between this quinone and acids cannot, of course, be materially different in its nature from the similar action of its isomer, xanthylene quinomethane. The mechanism is as follows:



XXIII. XXIV.

What has been said about phenyl fluorone applies also to phenyl-3-hydroxyfluorone, the chemical behavior of which has been the subject of much discussion,[1] because of its close relation to fluorescein. In fact the second hydroxyl group imparts to the molecule, as might be expected, a still greater tendency towards tautomerization and the quinoid compounds are still more stable than those obtainable from phenyl fluorone.

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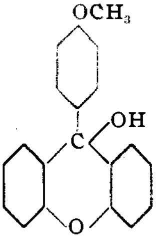
[1] References, page 1568.

Experimental.

I. p-Oxy-phenyl-xanthenol Salts.

p-Methoxy-phenyl-xanthenol,



The Grignard reagent is prepared from one and a half molecules of magnesium (1.2 grams) and a slight excess of *p*-anisyl iodide (12 grams). It takes between two and three hours for the magnesium to go into solution, and the process is hastened by the addition of iodine several times during the course of the reaction.[1] One molecule of xanthone (6.5 grams), finely pulverized or dissolved in about 30 cc. boiling benzene, is then added in small portions to the Grignard reagent. The magnesium addition product separates out in a few minutes as a light yellow powder. The reaction mixture is then heated on the water bath for two hours and decomposed as usual. The dark colored residue, which remains after the steam distillation, is taken up in benzene, the dried solution boiled an hour with animal charcoal and then concentrated. Upon the addition of petroleum ether, white prismatic crystals are obtained. The yield is 90% of the calculated amount. The xanthenol is soluble in the usual organic solvents except petroleum ether. It crystallizes from benzene with one-half molecule of benzene of crystallization. The solvent of crystallization is held very firmly by the xanthenol, and is not driven off by keeping the compound in a vacuum at room temperature. It is, however, removed by heating the compound for an hour at a temperature near its melting point.

Calculated for $C_{20}H_{16}O_3.{}^1/_2C_6H_6(C_{23}H_{19}O_3)$: C_6H_6, 11.37; C, 80.44; H, 5.58.
Found: C_6H_6, 12.19; C, 80.85, 80.80; H, 5.70, 5.75.

Recrystallized from ether or acetone, the xanthenol is obtained as large monoclinic prisms, melting at 120–121°.[2]

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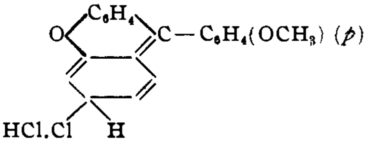
[1] Cf. v. Braun and Sobecki, *Ber.*, **44**, 1925 (1911).

[2] The xanthenol described above was prepared from Kahlbaum's xanthone. Several times in the course of this investigation the anisylxanthenol was prepared from samples of xanthone that were made in our laboratory by Perkin's method (*Ber.*, 16, 339 (1883)). When prepared from the latter source, the xanthenol melted at a higher temperature, namely at 155°. The higher melting form can be converted into the lower melting modification, but we were unable to bring about the reverse transformation. Both modifications yield the same chlorates, perchlorates, etc. We are unable to state positively at present whether or not we have here an actual case of dimorphism as recorded by E. and O. Fischer (*Ber.*, 12, 796 (1879); **37**, 3355 (1904)).

Calculated for $C_{20}H_{16}O_3$: C, 78.89; H, 5.30.
Found: C, 78.99; H, 5.40.

p-Methoxy-phenyl-quinoxanthenol Chloride Hydrochloride,



The chloride-hydrochloride is prepared by saturating a benzene solution of the xanthenol, to which a little acetyl chloride has been added, with dry hydrochloric acid. The hydrochloride precipitates as a dark red oil, which becomes crystallin after standing about two hours. It may also be prepared from an ether solution of the xanthenol, which contains a little acetyl chloride. It is quite hygroscopic and is best dried in an atmosphere of dry hydrochloric acid gas. Dark red crystals, melting between 110–115° with decomposition.

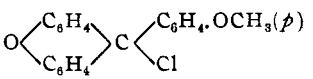
Calculated for $C_{20}H_{15}O_2Cl.HCl$: Cl, 19.76. Found: Cl, 19.78.

When dry air is passed through a suspension of the hydrochloride in dry benzene at 40–50°, the extra molecule of hydrochloric acid is easily and quickly removed. The acid was collected in standard silver nitrate solution.

Calculated for HCl: 10.16. Found: HCl, 10.13.

The clear, colorless benzene solution now contains the carbinol chloride. If dry hydrochloric acid is passed into this colorless solution, the hydrochloride is regenerated and precipitates as bright red crystals, forming into rosets.

p-Methoxy-phenyl-xanthenol Chloride,

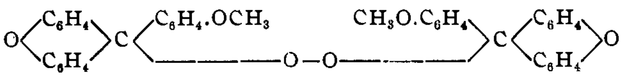


$$O\left\langle\begin{array}{c}C_6H_4\\C_6H_4\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_4.OCH_3(p)\\Cl\end{array}\right.$$

A concentrated solution of the xanthenol chloride, obtained by passing air through a suspension of the chloride-hydrochloride in petroleum ether (b. p. 70–80°), was filtered to remove a few red flakes, then allowed to stand two days. Colorless crystals had formed on the sides of the flask. The mother liquor was decanted, the crystals washed with low boiling petroleum ether and dried in vacuum. It melts at 95–96°. The chloride is quite easily soluble in all ordinary solvents. It is very susceptible to moisture or traces of acids, as it turns pink on the slightest exposure to the air.

Calculated for $C_{20}H_{15}O_2Cl$: Cl, 10.97. Found: Cl, 11.20.

p-Methoxy-phenyl-xanthenol Peroxide,

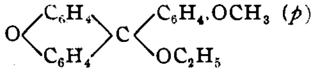


$$O\left\langle\begin{array}{c}C_6H_4\\C_6H_4\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_4.OCH_3\\\text{———}O-O\text{———}\end{array}\right. \left.\begin{array}{r}CH_3O.C_6H_4\\\end{array}\right\rangle C\left\langle\begin{array}{c}C_6H_4\\C_6H_4\end{array}\right\rangle O$$

A concentrated solution of the colorless chloride in dry benzene was shaken with molecular silver for three days. At the end of that time the solution was of a bright red color, and some of the unsaturated triphenylmethyl analog had separated in yellow crystals. After warming to 60°, in order to dissolve these crystals, the solution was decanted and filtered and the residue treated with boiling benzene until the extract was colorless. The red benzene solution changed to pure yellow as soon as exposed to the air, owing to the formation of the peroxide. The red gummy mass, obtained after the spontaneous evaporation of the benzene, was treated with a little ether, placed on a filter, and the crude peroxide was washed with ether until colorless. Recrystallized from benzene with the addition of petroleum ether, it was obtained as a white crystallin powder, melting at 214° with decomposition. It is easily soluble in boiling benzene, toluene, slightly soluble in cold benzene, acetic ester, and glacial acetic acid, insoluble in ether, acetone and petroleum ether.

Calculated for $C_{40}H_{30}O_6$: C, 79.18; H, 4.99. Found: C, 79.36; H, 5.09.

p-Methoxy-phenyl-xanthenol Ethyl Ether,



$$O{<}^{C_6H_4}_{C_6H_4}{>}C{<}^{C_6H_4.OCH_3\ (p)}_{OC_2H_5}$$

The ethyl ethers or ethoxy derivatives are usually prepared by the action of alcohol or sodium alcoholate upon the chlorides.[1] In this instance, the ether was prepared from the perchlorate,[2] which was decomposed by suspending it in absolute alcohol and heating on the water bath. The resulting solution was treated with animal charcoal, filtered and concentrated. The ether separates upon cooling. This was recrystallized twice from absolute alcohol, when it formed white crystals, melting at 156–157°. It is soluble in all the ordinary organic solvents except petroleum ether. The same ether was prepared by using the chloride-hydrochloride and absolute ethyl alcohol.

Calculated for $C_{22}H_{20}O_3$: C, 79.48; H, 6.04. Found: C, 79.17, 79.10; H, 6.02, 5.93.

The *methyl ether* was prepared in the same way as the ethyl ether, using absolute methyl alcohol. Recrystallized twice from methyl alcohol, it forms colorless crystals, melting at 129–130°.

Calculated for $C_{21}H_{18}O_3$: C, 79.21; H, 5.70. Found: C, 79.10; H, 5.64.

Double Salts of the Chloride.

Ferric Chloride Double Salt.—This may be prepared as follows: (1) By adding to an acetic ester solution of the colorless chloride, ferric chloride dissolved in the same solvent. (2) By dissolving the xanthenol in acetyl chloride and adding an acetic acid solution of ferric chloride. (3) By saturating an acetic acid solution of the xanthenol with hydro-

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[1] Cf. Werner, *Ber.*, **34**, 3306 (1901).

[2] See page 1542.

chloric acid, or by dissolving the chloride-hydrochloride in glacial acetic acid, and treating this solution with ferric chloride in the same solvent. It forms bright red, fluffy crystals, which melt at 198–199°.

Calculated for $C_{20}H_{15}O_2Cl.FeCl_3$: Cl, 29.26; Fe, 11.52.
Found: Cl, 29.44, 29.19; Fe, 11.87.

Zinc Chloride Double Salt.—This was prepared in the same three ways as the above described iron salt. It was obtained as orange red crystals, melting at 240–241°.

Calculated for $C_{20}H_{15}O_2Cl.ZnCl_2$: Cl, 23.49. Found: Cl, 23.14.

Mercuric Chloride Double Salt.—This was prepared from the components in absolute acetic ester. A solution of the colorless benzoid chloride is easily prepared by dissolving the xanthenol in acetic ester and adding a little more than the theoretical amount of acetyl chloride. The bright red double salt precipitates immediately upon the addition of the mercuric chloride. After standing an hour, it is filtered and dried in vacuum. Fine orange red crystals, which begin to soften at 180°, and melt at 185–186°.

Calculated for $C_{20}H_{15}O_2Cl.HgCl_2$: Cl, 17.92. Found: Cl, 17.77.

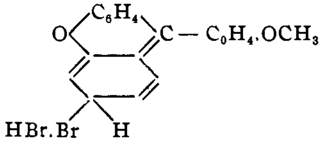
Perbromide.—When a carbon disulfide solution of bromine is added to a benzene solution of the chloride a slight precipitate is formed, which upon the addition of more bromine changes to an oil and adheres to the sides of the flask. In a few minutes this oil begins to crystallize into rosets of small needle-like crystals. After standing an hour, these are filtered and dried in a stream of dry air. Fine light orange needles, melting with decomposition between 159–163°.

Calculated for $C_{20}H_{15}O_2Cl.Br_2$: Br, 34.13. Found: Br, 34.00.

Periodide.—From the components in benzene-carbon disulfide solution the periodide precipitates at once as dark brown crystals.

Calculated for $C_{20}H_{15}O_2Cl.I_2$: Cl, 6.15; I, 44.04. Found: Cl, 6.66; I, 43.90.

p-Methoxy-phenyl-quinoxanthenol Bromide Hydrobromide,



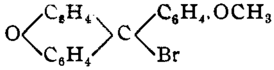
A little acetyl bromide is added to a benzene solution of the xanthenol and dry hydrobromic acid passed into it. The hydrobromide separates as a dark oil, which soon becomes crystallin. Dark brown crystals, which are much darker than the hydrochloride, are formed.

Calculated for $C_{20}H_{15}O_2Br.HBr$: Br, 35.68. Found: Br, 35.74.

If a stream of dry air is passed through the suspension of the hydrobromide in dry benzene, there is gradually given off one molecule of hydrobromic acid and solution results. It is very difficult to get the solution perfectly colorless, owing to the ease of hydrolysis of the bromide. The escaping hydrobromic acid was collected in a solution of standard silver nitrate.

Calculated for: HBr, 18.05. Found: HBr, 17.60.

p-Methoxy-phenyl-xanthenol Bromide,



$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_4.OCH_3\\Br\end{matrix}\right.$$

The solution of the bromide obtained as just mentioned is carefully concentrated and dry petroleum ether added. The bromide separates as colorless crystals, if the moisture is very thoroughly excluded. The mother liquor is decanted and the compound quickly washed and dried. The slightest trace of moisture is sufficient to hydrolyze a part of the bromide with the production of a red coloration on the surface.

Calculated for $C_{20}H_{15}O_2Br$: Br, 21.77. Found: Br, 21.50.

Derivatives of the Bromide. Zinc Bromide Double Salt.—This was obtained from the components in absolute acetic ester as light reddish yellow crystals, which melted at 224–225°.

Calculated for $C_{20}H_{15}O_2Br.ZnBr_2$: Br, 40.48. Found: Br, 41.16.

Mercuric Bromide Double Salt.—Was also prepared from the components in absolute acetic ester. The red double salt precipitated immediately. It melts at 192–194°.

Calculated for $C_{20}H_{15}O_2Br.HgBr_2$: Br, 32.98. Found: Br, 32.75.

The *perbromide* is readily obtained from a benzene-carbon disulfide solution of the components. The bright red crystallin precipitate immediately separated out. This melted at 174–175°.

Calculated for $C_{20}H_{15}O_2Br.Br_2$: Br, 45.51. Found: Br, 45.14.

The *periodide* is prepared as above. A dark red crystallin powder separates immediately upon mixing the components. It melts at 187–189°.

Calculated for $C_{20}H_{15}O_2Br.I_2$: Br, 13.04; I, 41.42. Found: Br, 12.54; I, 41.40.

p-Methoxy-phenyl-xanthenol Perchlorate.—The perchlorate crystallizes from a benzene-acetone solution of the components[1] in large dark red crystals which have a greenish metallic luster. If an ether solution of the xanthenol is used, the perchlorate separates immediately as a dark red, finely divided crystallin powder. It melts at 192–193°. It is very stable, requiring several days to hydrolyze with water. With alcohol it gives the corresponding ether.

Calculated for $C_{20}H_{15}O_2ClO_4$: ClO_4, 25.73. Found: ClO_4, 25.95.

The Acid Sulfate.—One-half gram of the xanthenol is dissolved in about 50 cc. of absolute ether and the calculated amount of concentrated sul-

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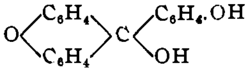
[1] In the preparation of all perchlorates 70% perchloric acid is used. Cf. Gomberg and Cone, *Ann.*, **370**, 193 (1909); **376**, 194 (1910); Hofmann, *Ber.*, **42**, 4856 (1909); **43**, 178, 183, 1080 (1910).

furic acid, also dissolved in ether, added. At each addition of the acid, a red, finely divided precipitate forms, which, when nearly all is added, changes to an oil and settles to the sides of the flask. After standing some hours, it becomes crystallin. Dark red crystals, which melt at 117–118°. The sulfate is immediately decomposed by water or alcohol.

Calculated for $C_{20}H_{15}O_2HSO_4$: SO_4, 25.01. Found: SO_4, 24.50.

The Phosphate.—The xanthenol is dissolved in absolute ether and 85% phosphoric acid added. Upon shaking, the acid goes into solution, and the phosphate which is formed separates out. It forms large clumps of red crystals. They soften at about 115°, and melt at 124–125°. It is decomposed by water or alcohol. It is soluble in boiling nitrobenzene, insoluble in cold nitrobenzene, chloroform, acetone, etc. Like the sulfates, it shows a tendency to crystallize with acid of crystallization.

p-Hydroxy-phenyl-xanthenol,



$$O\left<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right>C\left<\begin{matrix}C_6H_4.OH\\OH\end{matrix}\right.$$

This was prepared from *p*-methoxy-phenyl-xanthenol, using Baeyer's method.[1] Two grams of the xanthenol are added to a cooled solution of two grams of aluminium chloride in twenty grams of antimony trichloride. The green fluorescing solution is heated on the steam bath for ten minutes and then decomposed by ice. Concentrated hydrochloric acid is added until the liquid becomes clear, and the dark red precipitate allowed to settle. This is then filtered off, suspended in dilute sodium hydroxide, and warmed until all the xanthenol has gone into solution. The solution is then filtered, cooled thoroughly, acidified with dilute acetic acid, and allowed to stand several hours, when the light brown precipitate becomes granular. The xanthenol recrystallizes from ether on the addition of a large quantity of petroleum ether, and is obtained in rosets consisting of colorless needles. The total yield is 90% of the calculated amount. Care must be taken in recrystallizing the xanthenol, for if a too concentrated solution of the xanthenol be heated, a partial decomposition takes place, with the formation of the quinone described below. For the same reason, a hot alkalin solution of the xanthenol should not be neutralized with glacial acetic acid. The xanthenol melts with decomposition at 149–150°, water is split off and the quinone is formed.

Calculated for $C_{19}H_{14}O_3$: C, 78.56; H, 4.86. Found: C, 78.42; H, 5.00.

The *perchlorate*, $C_{19}H_{13}O_2.ClO_4$, a red crystallin powder, melts at 255–256°.

The *sulfate*, $C_{19}H_{13}O_2.HSO_4$, red, melts at 240–245°.

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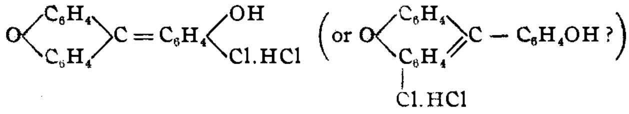
[1] *Ann.*, **372**, 101 (1910).

p-Hydroxy-phenyl-quinoxanthenol Chloride Hydrochloride,

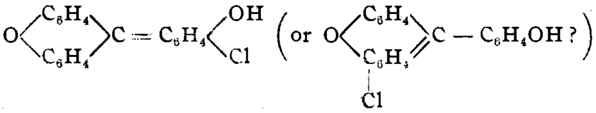


$$O\begin{matrix}C_6H_4\\C_6H_4\end{matrix}C = C_6H_4\begin{matrix}OH\\Cl.HCl\end{matrix} \left(\text{or } O\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\underset{Cl.HCl}{C} - C_6H_4OH\ ?\right)$$

The hydrochloride may be easily prepared by passing a stream of dry hydrochloric acid gas over the surface of an ether solution of the xanthenol. It separates in dark red plates, with a fuchsin-like irridescence. It may also be obtained by treating an acetic acid suspension of the xanthenol with dry hydrochloric acid gas, when the xanthenol first goes into solution and the hydrochloride separates upon cooling the solution. The substance does not show a definit melting point, beginning to soften at 200°, and melting between 235–240°.

Calculated for $C_{19}H_{13}O_2Cl.HCl$: Cl, 20.56. Found: Cl, 20.38.

p-Hydroxy-phenyl-quinoxanthenol Chloride,



$$O\begin{matrix}C_6H_4\\C_6H_4\end{matrix}C = C_6H_4\begin{matrix}OH\\Cl\end{matrix} \left(\text{or } O\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\underset{Cl}{C} - C_6H_4OH\ ?\right)$$

The acid salt, suspended in boiling xylene, loses a molecule of acid when a stream of dry air is passed through the solution, and the red, insoluble powder is the quinoid salt. The latter is, however, best prepared by heating the acid salt, placed in a boat, at 130° in a vacuum. The acid salt loses one molecule of acid, the irridescence disappears, but the crystallin form is retained. The brown red salt shows now the characteristics of a quinoid salt, unlike the benzoid halides, it is insoluble in benzene, ether, but fairly soluble in nitrobenzene and in chloroform. In nitrobenzene it dissolves with an intense purple color, resembling a concentrated solution of potassium permanganate in water. It melts at 235–245°, and at that temperature begins to evolve hydrochloric acid.

Calculated for $C_{19}H_{13}O_2Cl$: Cl, 11.49. Found: Cl, 11.31.

Double salts of the chloride were prepared as follows: The table gives the name of the derivative, the formula as derived from the analysis, the solvent in which the reaction was carried on, etc.

Name.	Formula.	Solvent.	Color.	M. p.
Ferric chloride	$C_{19}H_{13}O_2Cl.FeCl_3$	Acetic acid	Red	156–157°
Zinc chloride	$C_{19}H_{13}O_2Cl.ZnCl_2$	Acetic acid	Red	222–223°
Mercuric chloride	$C_{19}H_{13}O_2Cl.HgCl_2$	Acetic ester	Red	215–216°
Perbromide	$C_{19}H_{13}O_2Cl.Br_2$	Ether	Red	230–235°
Periodide	$C_{19}H_{13}O_2Cl.I_2$	Ether	Purple	

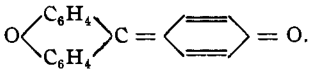
Treated with molecular silver, the nitrobenzene solution of the chloride changes color to a clear red, due, probably, to the production of the triarylmethyl compound.

p-Hydroxy-phenyl-quinoxanthenol Bromide.—(Structural formula like the chloride.) If an absolute ether solution of the xanthenol is treated with dry hydrobromic acid gas, there immediately precipitates a red crystallin powder, leaving the ether above perfectly clear. After standing for half an hour, it is filtered and dried in an atmosphere of dry air for ten minutes. Analysis showed that a little hydrobromic acid, about 0.5%, is held by the bromide. If the substance is dried in an atmosphere of hydrobromic acid, the amount of bromine is not increased, and all attempts to prepare a bromide-hydrobromide were fruitless. If the bromide is suspended in dry benzene and dry air passed through it at room temperature, a small amount of hydrobromic acid is given off (the excess indicated in the above analysis), and even though the benzene be heated to its boiling point there is no indication of the solution of the bromide. After drying, this red insoluble precipitate analyzed as the mono-bromide.

Calculated for $C_{19}H_{13}O_2Br$: Br, 22.65. Found: Br, 22.60.

The bromide, like the quinoid chloride, is insoluble in cold or boiling benzene, toluene, ether, ethyl acetate, etc.; it is soluble in chloroform, nitrobenzene, slightly so in acetic acid. It is slowly decomposed by water, more rapidly by dilute alkalies, instantly by alcohol. It melts with de composition at 258–260°.

Xanthylene Quinomethane,



$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle C = C_6H_4 = O.$$

p-Hydroxy-phenyl-xanthenol, when heated near its melting point for a short time, splits off a molecule of water and forms a quinone. Similar cases have been found in the triphenylmethane series, as in the preparation of fuchsone, or 7,7 -diphenyl-quinomethane[1] and its analogs, and in the xanthenol series in the preparation of phenylfluorone and its derivatives.[2]

The quinone was prepared by heating *p*-hydroxy-phenyl-xanthenol in an air bath at 110–120° for about two hours. During the heating one molecule of water is given off.

Calculated for $C_{19}H_{14}O_3.H_2O$: H_2O, 6.21. Found: loss, 6.96.

The formation of the quinone has also been observed as mentioned above, in heating a concentrated solution of the xanthenol in ether, also to some extent, when a hot alkalin solution of the xanthenol is neutralized with acetic acid.

The quinone as obtained possesses a green color. It is very slightly soluble in nitrobenzene and chloroform and practically insoluble in all other organic reagents. All attempts to find a suitable solvent for recrystallizing the quinone were fruitless. When heated, the quinone

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[1] Auwers and Schröter, *Ber.*, **36**, 3236 (1903); Baeyer and Villiger, *Ber.*, **36**, 2774 (1903); **37**, 2848 (1904); Bistrzycki and Herbst, *Ibid.*, **36**, 2333, 3565 (1903); Bistrzycki and Zurbriggens, *Ibid.*, **36**, 3558 (1903); Sachs and Thonet, *Ibid.*, **37**, 3327 (1904).

[2] For references on the fluorone see pages 1561 and 1568.

melts at 287–288°. The marked insolubility of this quinone in the usual organic solvents, in contrast to similar quinones, suggests that it is probably a polymerized product of the monomolecular quinone. Quinone-imines, as found by Baeyer, possess a decided tendency towards polymerization.[1]

Calculated for $C_{19}H_{12}O_2$: C, 83.79; H, 4.44. Found: C, 83.60, 83.65; H, 4.50, 4.52.

Reactions of the Quinone. Dilute Acetic Acid.—When the quinone is heated with 50% acetic acid on the water bath for half an hour, or boiled a few minutes over a flame, it is completely hydrolyzed back to the hydroxy-xanthenol.

Alcoholic Potash.—If the quinone is suspended in dilute alcoholic potash and allowed to stand, the compound gradually loses its green color, becoming pure white. Upon heating to boiling, solution results. When this solution is diluted with water and acidified with dilute acetic acid, *p*-hydroxy-phenyl-xanthenol is precipitated.

Hydrochloric Acid.—Upon passing dry hydrochloric acid gas over the finely divided quinone in a porcelain boat, or through a suspension of the quinone in benzene, the green color immediately changes to a deep red. After fifteen minutes the gain in weight showed that two molecules of hydrochloric acid had been taken up.

Calculated 2 HCl: gain, 26.07; Found: 27.03.

The compound melts at 240°, with decomposition, and it is identical with *p*-hydroxy-phenyl-quinoxanthenol chloride hydrochloride.

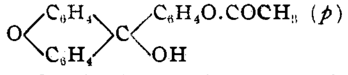
Hydrobromic Acid.—The quinone, treated as above with hydrobromic acid, gives *p*-hydroxy-phenyl-quinoxanthenol bromide.

On boiling with *acetic anhydride*, the quinone is converted into the colorless *p*-acetoxy-phenyl-xanthenol.

Methyl Sulfate.—The quinone dissolves in methyl sulfate with deep red color, and on warming adds on a molecule of the sulfate. On hydrolyzing the addition product, *p*-anisyl-xanthenol is obtained.

Phosphorus Pentachloride.—Heated with phosphorus pentachloride in benzene, the quinone is converted into *p*-chloro-phenyl-xanthenol chloride.[2]

p-Acetoxy-phenyl-xanthenol,



$$O\left\langle\begin{array}{l}C_6H_4\\C_6H_4\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_4O.COCH_3\ (p)\\OH\end{array}\right.$$

One and one-half grams of *p*-hydroxy-phenyl-xanthenol, 2 grams of anhydrous sodium acetate, and 20 cc. acetic anhydride are boiled under the reflux for 10 minutes. To the warm solution about 150 cc. of cold water are added. The acetoxy compound separates as a colorless oil, which solidifies upon standing over night. Recrystallized from a mixture of

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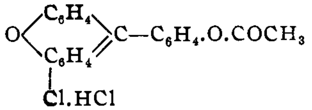
[1] *Ber.*, **37**, 579 (1904).

[2] Gomberg and Cone, *Ann.*, **370**, 174 (1909).

ether and petroleum ether, it is obtained in colorless, long, slender needles melting at 145–146° to a colorless liquid; there is no indication of the formation of a quinone, as is the case with the hydroxy compound. It is soluble in all the usual organic solvents except petroleum ether. Yield, about 1.5 grams or 85% of the theory.

Calculated for $C_{21}H_{16}O_4$: C, 75.86; H, 4.85. Found: C, 75.98; H, 5.00.

p-Acetoxy-phenyl-quinoxanthenol Chloride Hydrochloride,



$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle C{-}C_6H_4.O.COCH_3,\quad Cl.HCl$$

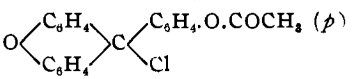
The hydrochloride is best obtained by the use of petroleum ether as a solvent. The xanthenol is suspended in petroleum ether, a few drops of acetyl chloride added and the solution is saturated with dry hydrochloric acid gas. The solid xanthenol changed to a light red oil, which upon standing a short time forms a mass of light red crystals. These are filtered off and dried in an atmosphere of dry air. The hydrochloride is immediately decomposed by alcohol or dilute alkalies, quite readily by water or ether. It begins to soften at 110° and melts with decomposition at 118–122°.

Calculated for $C_{21}H_{15}O_3Cl.HCl$: Cl_2, 18.33. Found: Cl, 18.00.

If a stream of dry air is passed through a suspension of the hydrochloride in dry benzene or petroleum ether, a molecule of hydrochloric acid is easily driven off and a clear, colorless solution results.

Calculated for HCl, 9.42. Found: HCl, 9.30.

p-Acetoxy-phenyl-xanthenol Chloride,

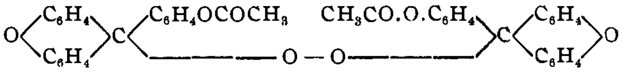


$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_4.O.COCH_3\ (p)\\Cl\end{matrix}\right.$$

The chloride was prepared in two ways: An ether solution of the xanthenol was treated with an excess of acetyl chloride, the solution evaporated in vacuum, and petroleum ether added. The chloride separated as colorless crystals. It was also obtained from the chloride hydrochloride by removing the extra molecule of acid as described above, concentrating the benzene solution of the chloride and adding petroleum ether. It is easily soluble in all organic solvents and quite so even in petroleum ether. All moisture must be excluded, as it is susceptible to the slightest trace.

Calculated for $C_{21}H_{15}O_3Cl$: Cl, 10.11. Found: Cl, 10.00.

p-Acetoxy-phenyl-xanthenol Peroxide,



$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_4OCOCH_3\\ \text{———}\end{matrix}\right. O-O \left.\begin{matrix}CH_3CO.O.C_6H_4\\ \text{———}\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O$$

The peroxide was prepared by shaking a solution of the chloride in dry benzene with molecular silver for two days. The light red solution of the triphenylmethyl analog is immediately decolorized upon exposure to the air, with the formation of the peroxide. The residue obtained by the evaporation of the benzene is washed with ether until colorless. The white crystallin product is the peroxide, which may be further purified by crystallization from benzene with the addition of petroleum ether. It begins to soften at 207° and melts at 211–212° with decomposition.

Calculated for $C_{42}H_{30}O_8$: C, 76.15; H, 4.72. Found: C, 76.02; H, 4.80.

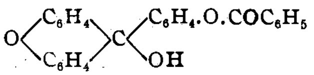
Double salts and perhalides of the chloride were prepared as indicated below:

Name.	Formula.	Color.	M. p.
Ferric chloride	$C_{21}H_{15}O_3Cl.FeCl_3$	Orange yellow	182°
Zinc chloride	$C_{21}H_{15}O_3Cl.ZnCl_2$	Yellow	194°
Stannic chloride	$C_{21}H_{15}O_3Cl.SnCl_4$	Yellow	188°
Mercuric chloride	$C_{21}H_{15}O_3Cl.HgCl_2$	Yellow	215°
Perbromide	$C_{21}H_{15}O_3Cl.Br_2$	Orange	

The *perchlorate* separates immediately as a fine yellow crystallin powder from the components in ether acetone solution. It shows an unsharp melting point, beginning to soften at 150°, and melting between 175–185°.

Calculated for $C_{21}H_{15}O_3ClO_4$: ClO_4, 23.65. Found: ClO_4, 24.01.

p-Benzoxy-phenyl-xanthenol,



$$O\langle{}^{C_6H_4}_{C_6H_4}\rangle C\langle{}^{C_6H_4.O.COC_6H_5}_{OH}$$

This was prepared as follows: *p*-hydroxy-phenyl-xanthenol was dissolved in an excess of 5% sodium hydroxide (if 10% be used the sodium salt precipitates out) and shaken with benzoyl chloride. The reaction product separates very quickly, is filtered off, washed with alkali, then water, dried, dissolved in benzene, boiled with animal charcoal, the solution concentrated and petroleum ether added, when the xanthenol separates as colorless crystals, which melt at 181–182° to a colorless liquid. It is soluble in all the usual organic solvents except petroleum ether.

Calculated for $C_{26}H_{18}O_4$: C, 79.71; H, 4.62. Found: C, 79.52; H, 4.80.

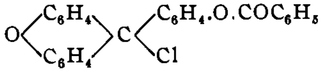
p-Benzoxy-phenyl-quinoxanthenol Chloride Hydrochloride.—(Formula like that of the acetoxy derivative.) When a solution of the xanthenol, dissolved in benzene, is treated with a few drops of acetyl chloride, and then with dry hydrochloric acid gas, a red oil separates, which soon becomes crystallin. The yield is slightly increased if petroleum ether is added. The color of the product varies from a yellow to a deep orange or orange red, depending upon the rapidity with which it is precipitated. It is easily decomposed by water, alkalies, or alcohol, slowly by ether. The hydrochloride begins to soften at 135° and melts with decomposition at 143–145°.

Calculated for $C_{26}H_{17}O_3Cl.HCl$: Cl, 15.79. Found: Cl, 15.50.

The extra molecule of hydrochloric acid may be easily removed by passing a current of dry air through the hydrochloride suspended in dry benzene at 40°, leaving a perfectly clear, colorless solution.

Calculated for HCl, 8.30. Found: HCl, 8.20.

p-Benzoxy-phenyl-xanthenol Chloride,



$$O\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_4.O.COC_6H_5\\Cl\end{matrix}\right.$$

This may be prepared by concentrating the above solution of the colorless chloride, and adding petroleum ether, or it may be prepared by treating a solution of the xanthenol in absolute ether with a slight excess of acetyl chloride. In each case, the chloride is obtained as colorless crystals, which are very susceptible to traces of moisture or acids, and melt at 175–176°.

Calculated for $C_{26}H_{17}O_3Cl$: Cl, 8.59. Found: Cl, 8.70.

The chloride gives a double salt with ferric chloride (m. p. 204–205°) and with zinc chloride.

The *perchlorate*, a yellow crystallin powder, melts at 235–236°.

p-Benzoxy-phenyl-xanthenol Peroxide was prepared by shaking the chloride in benzene solution with molecular silver. The red solution of the unsaturated compound is immediately decolorized by the oxygen of the air. The crude product, after washing with ether, melts at 217–219°. Recrystallized from benzene and petroleum ether, it melts at 218–219° with decomposition.

Calculated for $C_{52}H_{34}O_8$: C, 79.36; H, 4.35. Found: C, 79.18; H, 4.50.

II. Phenyl-1-hydroxy-xanthenol Salts.

The 1-methoxy-xanthone, which was the starting point of this work, was prepared according to the method of Ullmann.[1] 2,6-Dinitrotoluene was reduced by means of hydrogen sulfide and ammonia to 2-amino-6-nitrotoluene,[2] which was changed into 2-chloro-6-nitrotoluene[3] through Sandmeyer's reaction. This was again reduced, using stannous chloride and hydrochloric acid, which gave 6-amino-2-chlorotoluene.[4] By diazotizing and heating with dilute sulfuric acid, the amino-compound was changed into 2-chloro-6-hydroxytoluene[5] which on treatment with methyl sulfate forms 2-chloro-6-methoxytoluene. The latter, by oxidation with neutral permanganate, furnishes 2-chloro-6-methoxybenzoic acid. The xanthone is obtained from this by condensation with phenol, using Ullmann's reaction, and heating the methoxyphenyl ether of salicylic acid

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[1] Ullmann and Panchaud, *Ann.*, **350**, 108 (1906).

[2] Cunerth, *Ann.*, **172**, 225 (1874); C. Ullmann, *Ber.*, **17**, 1958 (1884); Green and Lawson, *J. Chem. Soc.*, **59**, 1014 (1891); Noelting, *Ber.*, **37**, 1018 (1904).

[3] Green and Lawson, *loc. cit.*; Noelting, *loc. cit.*; Cohn, *Monatsh.*, **22**, 475 (1901).

[4] Noelting, *loc. cit.*; Hönig, *Ber.*, **20**, 2417 (1887); Wynne and Greeves, *Proc. Chem. Soc.*, **11**, 151 (1895).

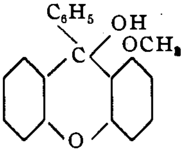
[5] Noelting, *loc. cit.*

with concentrated sulfuric acid. 1-Methoxyxanthone[1] forms colorless crystals from benzene, which melt at 138°.

As mentioned in the theoretical part, the hydroxy- and methoxy-xanthones combine with metal halides much more readily than the simple xanthone itself. So pronounced is the influence of these groups that they combine even with hydrochloric acid and not only with hydrobromic acid, as is the case with xanthone. The halogen acid addition compounds are extremely unstable, can only be prepared in the absence of water, and readily dissociate into the components. In the preparation of the following addition products, a benzene solution of the xanthone was always used while the metal halide was dissolved in acetic ester or ethyl ether:

Name.	Formula.	Color.	M. p.
Stannic chloride	$(C_{14}H_{10}O_3)_2SnCl_4$	Yellow	135–136°
Stannic bromide	$(C_{14}H_{10}O_3)_2SnBr_4$	Yellow	172–173°
Mercuric chloride	$C_{14}H_{10}O_3.HgCl_2$	White	183–184°
Mercuric bromide	$C_{14}H_{10}O_3.HgBr_2$	White	167–168°
Zinc chloride	$C_{14}H_{10}O_3.ZnCl_2$	Yellow	....
Zinc bromide	$C_{14}H_{10}O_3.ZnBr_2$	Yellow	....
Hydrochloride	$C_{14}H_{10}O_3.HCl$	Yellow	110–115°

Phenyl-1-methoxy-xanthenol,

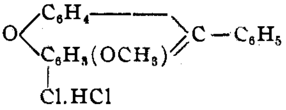


To a solution of phenylmagnesium bromide prepared from 1.5 grams magnesium. 15 grams bromobenzene and 60 cc. absolute ether, 5 grams of 1-methoxy-xanthone, dissolved in 30 cc. boiling benzene, are gradually added. The solution takes on a green fluorescence, and the magnesium addition product gradually separates out as a gray powder. After boiling an hour and a half on the water bath, the mixture is decomposed with ice and distilled with steam. The nearly colorless crystallin residue is taken up in benzene, the dried solution boiled with animal charcoal, concentrated and petroleum ether added. The xanthenol separates as colorless, shining needles, which, upon recrystallization from benzene, melt at 162–163°. The xanthenol is quite easily soluble in all the ordinary organic solvents except petroleum ether.

Calculated for $C_{20}H_{16}O_3$: C, 78.91; H, 5.30. Found: C, 78.81; H, 5.50.

The *perchlorate*, dark red crystals, melts at 225°.

Phenyl-1-methoxy-quinoxanthenol Chloride Hydrochloride,



$$O\left\langle\begin{array}{l}C_6H_4\text{———}\\C_6H_3(OCH_3)\end{array}\right\rangle C-C_6H_5\quad \underset{Cl.HCl}{|}$$

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[1] Tambor, *Ber.*, 43, 1883 (1910).

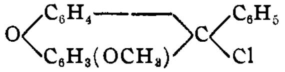
A benzene solution of the xanthenol is treated with a few drops of acetyl chloride and then with dry hydrochloric acid. The hydrochloride precipitates as a dark red oil, which crystallizes after standing about three hours, filling the liquid with a mass of shining, purple needles. These are filtered out, washed with low boiling petroleum ether, and dried a short time in dry air. If the stream of air is continued too long, there is formed a layer of the colorless chloride, and for this reason the drying is completed in an atmosphere of dry hydrochloric acid gas. The crystals are quite hygroscopic. The hydrochloride is very easily decomposed by water, alkalies, alcohol, or ether. The solution in chloroform has a deep red color.

Calculated for $C_{20}H_{15}O_2Cl.HCl$: Cl, 19.76. Found: Cl, 19.52.

The extra molecule of hydrochloric acid is very readily removed by suspending the hydrochloride in dry benzene and passing a stream of dry air through it for a few minutes. It may also be removed by placing the hydrochloride in a vacuum with soda lime for about a week.

Calculated for HCl, 10.16. Found: HCl, 10.10.

Phenyl-1-methoxy-xanthenol Chloride,



$$O\left\langle\begin{array}{l}C_6H_4 \text{———} \\ C_6H_3(OCH_3)\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_5 \\ Cl\end{array}\right.$$

As mentioned above the extra molecule of hydrochloric acid is very easily removed from the hydrochloride. The chloride may be prepared by keeping the hydrochloride in a vacuum for a week. It is best prepared, however, by passing dry air through a suspension of the hydrochloride in petroleum ether. Colorless crystals, which melt at 160–161°, and are soluble in all the ordinary solvents.

Calculated for $C_{20}H_{15}O_2Cl$: Cl, 10.99. Found: Cl, 10.79.

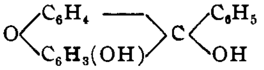
The relative ease with which the above colored xanthenol dichloride dissociates into the *benzoid* chloride and free hydrochloric acid reminds one of the identical behavior of the trianisyl-chloromethane chloride hydrochloride, which is a true triphenylcarbinol salt.

The colorless chloride gives colored salts with metal halides. The double salts with iron, mercury and tin have been analyzed and found to consist of one molecule of each component.

Phenyl-1-methoxy-xanthenol peroxide was prepared in the usual way, by shaking a benzene solution of the chloride with molecular silver. After washing with ether and recrystallizing from benzene, the colorless peroxide melted at 200–201°.

Calculated for $C_{40}H_{30}O_6$: C, 79.18; H, 4.99. Found: C, 79.26; H, 5.29.

Phenyl-1-hydroxy-xanthenol,



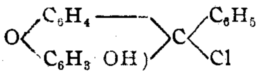
$$O\left\langle\begin{array}{l}C_6H_4 \text{——} \\ C_6H_3(OH)\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_5 \\ OH\end{array}\right.$$

One gram of the methoxy-xanthenol was warmed with a solution of 1 gram of aluminium chloride in 10 grams of antimony trichloride 10 minutes on the water bath. The dark red liquid was then decomposed with ice water and hydrochloric acid added until the product became crystallin. This was then filtered off, the precipitate taken up in alkali, the solution filtered and acidified with dilute acetic acid. The xanthenol separates as a colorless precipitate (sometimes with a bluish tinge), which is dried and recrystallized from ether. It forms colorless crystals, which melt at 148–150° with decomposition, giving a blue melt.

Calculated for $C_{19}H_{14}O_3$: C, 78.56; H, 4.86. Found: C, 78.40; H, 5.23.

The *perchlorate*, $C_{19}H_{13}O_2.ClO_4$, dark purple crystals, melts at 249–250°.

Phenyl-1-hydroxy-xanthenol Chloride,



$$O\left\langle\begin{matrix}C_6H_4 \text{——}\\ C_6H_3(OH)\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5\\ Cl\end{matrix}\right.$$

When hydrochloric acid gas is passed into an ethereal solution of the xanthenol, the solution assumes a deep purple color, but no precipitation of the quinoid acid salt occurs until a considerable excess of the acid is led in. The chloride-hydrochloride separates then as a spongy, dark purple mass, which could not be brought to crystallization. The ether is then decanted, and the residue washed several times with absolute ether containing some hydrochloric acid. It is now covered with pure ether, and through the warm solution dry air is passed. The dichloride loses a molecule of hydrochloric acid, the resulting benzoid chloride then goes into solution, almost entirely without color. The isolation of the solid chloride from this colorless solution is next to impossible, the merest trace of moisture produces enough free acid to color all of it. The presence of the benzoid, colorless chloride in the colorless solution was then proven indirectly. The ethereal solution was treated with molecular silver, whereby the characteristic triarylmethyl compound was produced—red, only slightly soluble in ether, and losing its color on exposure to air through the formation of the peroxide.

Upon warming a benzene solution of the colorless chloride, decomposition occurs, with the production of an intense blue color, suggesting an *ortho*-quinoid formation.

The chloride was further characterized by the preparation of the iron double salt, m. p. 146–147°, and the tin double salt, m. p. 185°.

III. Phenyl-2-hydroxy-xanthenol Salts.

2-Methoxy-xanthone was prepared according to the general method of Ullmann,[1] starting with hydrochinone monomethyl ether and the

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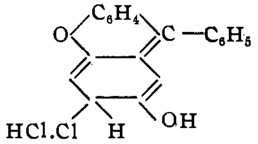
[1] Ullmann and Zlokasoff, *Ber.*, **38**, 2119 (1905); Ullmann and Kipper, *Ibid.*, **38**, 2121 (1905); Baeyer, *Ann.*, **372**, 102 (1910).

potassium salt of *o*-chlorobenzoic acid in the condensation reaction. The reaction is best carried out with small amounts of material, 5 grams of the chloro-acid. Yield, from 28 grams acid, 22 grams of xanthone or 55% of the theoretical amount. Baeyer found that 14 grams of *p*-methoxyphenyl-salicylic acid gave 5 grams of xanthone.

The following addition products of the xanthone were prepared and analyzed:

Name.	Formula.	Color.	M. p.
Stannic chloride	$(C_{14}H_{10}O_3)_2SnCl_4$	Yellow	235–240°
Stannic bromide[1]	$(C_{14}H_{10}O_3)_2SnBr_4$	Yellow	199–200°
Zinc chloride	$C_{14}H_{10}O_3.ZnCl_2$	Yellow	244–245°
Mercuric chloride	$C_{14}H_{10}O_3.HgCl_2$	White	200°
Mercuric bromide	$C_{14}H_{10}O_3.HgBr_2$	White	187–189°
Perchlorate	$C_{14}H_{10}O_3HClO_4$	Yellow	150–155°

Phenyl-2-methoxy-quino-xanthenol Chloride Hydrochloride,



Phenyl-2-methoxy-xanthenol[2] was prepared from the above xanthone and phenyl magnesium bromide. It may be recrystallized from benzene and petroleum ether or from ether. It melts at 134°.

The hydrochloride was prepared by suspending the xanthenol in petroleum ether, adding a little acetyl chloride and thoroughly saturating with dry hydrochloric acid. It is obtained as bright red crystals, which should be dried in an atmosphere of hydrogen chloride. If absolute ether is used as a solvent, instead of petroleum ether, the hydrochloride separates as an oil, which, upon cooling, forms bright red crystals. If benzene or a mixture of benzene and petroleum ether be used, a dark red oil is obtained which refuses to crystallize. The acid chloride begins to soften at 110° and melts with decomposition at 140–144°.

Calculated for $C_{20}H_{15}O_2Cl.HCl$: Cl, 19.76. Found: Cl, 19.56.

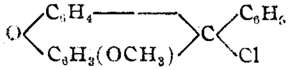
The hydrochloride, suspended in dry benzene, readily gives off a molecule of hydrochloric acid, when a stream of dry air is passed through the suspension and a clear colorless solution results.

Calculated for $C_{20}H_{15}O_2Cl.HCl$: HCl, 10.16. Found: HCl, 10.01.

[1] Dilute solutions of the xanthone, which readily yield precipitates with stannic chloride, give only a coloration with stannic bromide. This is apparently in harmony with the observations of Straus (*Ann.*, **370**, 323 (1909)) and Walden (*Ber.*, **35**, 2028 (1902)) that stannic bromide does not have the same tendency to form complexes as does the chloride. The salt is best prepared by dissolving 1 gram of the xanthone in 10 cc. boiling benzene and adding an *excess* of stannic bromide, also dissolved in benzene.

[2] Decker and Fellenberg, *Ann.*, **356**, 312 (1907); Baeyer, *Ibid.*, **372**, 102 (1910).

Phenyl-2-methoxy-xanthenol Chloride,



$$O\left\langle\begin{array}{l}C_6H_4\text{——}\\C_6H_3(OCH_3)\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_5\\Cl\end{array}\right.$$

The solution of the chloride obtained as above is concentrated and petroleum ether added. Upon standing, the colorless benzoid chloride separates out. This is very susceptible to moisture, and is quickly washed and dried, and analyzed in the original container.

Calculated for $C_{20}H_{15}O_2Cl$: Cl, 10.97. Found: Cl, 11.02.

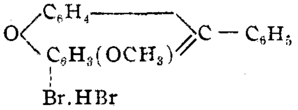
Phenyl-2-methoxy-xanthenol peroxide was prepared by shaking a benzene solution of the chloride with molecular silver for two days. The solution of the unsaturated derivative was a deep red. The peroxide was obtained as described above for other peroxides. Recrystallized from benzene with the addition of petroleum ether, it forms colorless crystals, melting at 198°. It is readily soluble in benzene and toluene, nearly insoluble in ether and petroleum ether.

Calculated for $C_{40}H_{30}O_6$: C, 79.18; H, 4.99. Found: C, 78.96; H, 5.21.

Double salts and perhalides of the chloride were prepared as indicated below, using acetic ester and benzene as solvents:

Name.	Formula.	Color.	M. p.
Ferric chloride	$C_{20}H_{15}O_2Cl.FeCl_3$	Bright red	123–124°
Zinc chloride	$C_{20}H_{15}O_2Cl.ZnCl_2$	Red plates	197–198°
Mercuric chloride	$C_{20}H_{15}O_2Cl.HgCl_2$	Dark red plates	....
Stannic chloride	$C_{20}H_{15}O_2Cl.SnCl_4$	Bright red	147–149°
Perbromide	$C_{20}H_{15}O_2Cl.Br_2$	Red plates	....

Phenyl-2-methoxy-quino-xanthenol Bromide Hydrobromide,



$$O\left\langle\begin{array}{l}C_6H_4\text{——}\\C_6H_3(OCH_3)\\\;\vdots\\Br.HBr\end{array}\right\rangle C-C_6H_5$$

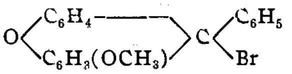
The hydrobromide is prepared from an ether solution of the xanthenol, with or without the addition of acetyl bromide, and dry hydrobromic acid gas. It separates as an oily mass, which soon begins to crystallize. It forms deep red crystals, which begin to soften at 220° and decompose at 223–224°. The hydrobromide is immediately decomposed by alcohol or alkalies, more slowly by water.

Calculated for $C_{20}H_{15}O_2Br.HBr$: Br, 35.68. Found: Br, 35.00.

When a stream of dry air is passed through a suspension of the hydrobromide in boiling toluene, a molecule of hydrobromic acid is driven off and a clear solution results.

Calculated for HBr, 18.05. Found: HBr, 17.60.

Phenyl-2-methoxy-xanthenol Bromide,



$$O\left\langle\begin{array}{l}C_6H_4\text{——}\\C_6H_3(OCH_3)\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_5\\Br\end{array}\right.$$

The clear solution obtained as above was concentrated and dry petroleum ether added. Upon standing, colorless crystals separated.

Calculated for $C_{20}H_{15}O_2Br$: Br, 21.77. Found: Br, 21.39.

The colorless bromide gives the usual double salts with metal halides, intensely colored, and consisting of a molecule of each component.

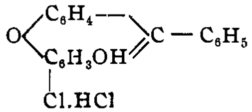
The *perchlorate* was obtained as red crystals, melting at 193–194°, from a benzene-acetone solution of the components.

Calculated for $C_{20}H_{15}O_2ClO_4$: ClO_4, 25.73. Found: ClO_4, 25.72.

The *sulfate* was prepared from the components in absolute ether. A red powder separates at first; this gradually changes to an oil as more acid is added, and again becomes crystallin after standing three days. Bright red crystals, which darken at 85°, and melt unsharply between 110–120°.

Calculated for $C_{20}H_{15}O_2HSO_4$: SO_4, 25.01. Found: SO_4, 26.00.

Phenyl-2-hydroxy-quino-xanthenol Chloride Hydrochloride,



Phenyl-2-hydroxy-xanthenol was prepared from phenyl-2-methoxy-xanthenol according to the directions of Baeyer,[1] by demethylating the latter with aluminium chloride. Recrystallized from ether, it melts at 170°.

The hydrochloride is readily prepared by passing dry hydrochloric acid gas into an ethereal solution of the xanthenol. It precipitates at once as a dark red powder, leaving the ether above it clear and colorless. After standing an hour, it is filtered, dried in a stream of dry air, and, finally, in an atmosphere of dry hydrochloric acid gas. It begins to soften at 220°, and melts at about 240°.

Calculated for $C_{19}H_{13}O_2Cl.HCl$: Cl, 20.56. Found: Cl, 20.31, 20.35.

Upon passing a stream of dry air through a suspension of the dichloride in benzene at 80°, the hydrochloric acid is given off slowly. When the benzene is replaced by xylene, the liberation of acid is more rapid and a clear solution of the benzoid chloride was obtained after one molecule of acid had been driven off.

Calculated for $C_{19}H_{13}O_2Cl.HCl$: HCl, 10.57. Found: HCl, 10.47, 10.52.

In the theoretical part we have called attention to the work of Kehrmann as regards the formation of the so-called "oxonium" salts from water solutions, and mentioned the fact that we were able to prepare the identical derivatives either from benzene by means of dry hydrochloric acid, or from dilute acids in water. We have found that it is indeed very easy to prepare the above described colored hydrochloride also from dilute

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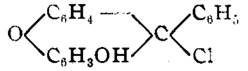
[1] Baeyer, *Ann.*, 372, 103 (1910); Kropp and Decker, *Ber.*, 42, 578 (1909); Dietrich, Inaug. Diss., Berlin, 1911, p. 13.

hydrochloric acid in the presence of water. The colorless xanthenol was treated with concentated hydrochloric acid in excess, and the mixture allowed to stand two days. The deep red precipitate was filtered off and dried in a vacuum. It is a little darker than the hydrochloride obtained from ether, probably due to the rate of precipitation. The compound was shown to be the same as the above by its melting point, by its yielding the normal colorless chloride when a suspension of it in dry xylene is treated with a stream of dry air, and by analysis.

Calculated for Cl, 20.56. Found: Cl, 20.71.

Phenyl-2-hydroxy-xanthenol Chloride,



$$O\left\langle\begin{matrix}C_6H_4 - \\ C_6H_3OH\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5 \\ Cl\end{matrix}\right.$$

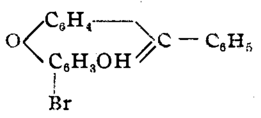
The clear solution obtained as above is concentrated, and dry petroleum ether added. The short exposure to the air causes the solution to become slightly red. Upon standing, crystals separate which are reddish pink on the outside, but which are colorless when broken open. They are very sensitive to all traces of moisture.

Calculated for $C_{19}H_{13}O_2Cl$: Cl, 11.49. Found: Cl, 11.04.

Baeyer considers the red precipitate obtained from the action of hydrochloric acid upon the ethereal solution of the xanthenol as the monochloride. Dietrich also describes this compound—purple red, long needles, which show the melting point 224–225°—as the chloride, and finds it contains only 11.72% of chlorine. From our analyses and the behavior of the compound, there can be no question that the red precipitate obtained by them consisted either entirely of the dichloride, or contained enough of the latter to impart a red color to the otherwise colorless monochloride.

The colorless chloride gives colored salts with metal halides, of the same general composition as is given by other carbinol halides.

Phenyl-2-hydroxy-quinoxanthenol Bromide,[1]



$$O\left\langle\begin{matrix}C_6H_4 - \\ \underset{\displaystyle Br}{\overset{}{C_6H_3}}OH\end{matrix}\right\rangle C - C_6H_5$$

This was prepared by passing dry hydrobromic acid gas over a solution of the xanthenol in absolute ether. The bromide precipitates at once as small red plates. It does not melt at 275°. It is soluble in glacial acetic acid, chloroform, nitrobenzene, and boiling ethylene bromide. It is insoluble in ether, benzene, toluene, acetic ester, etc. Absolute ethyl or methyl alcohol decomposes it immediately.

Calculated for $C_{19}H_{13}O_2Br$: Br, 22.65. Found: Br, 22.50.

We have prepared the bromide also by the action of concentrated hydro-

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[1] Also prepared by Kropp and Decker, *loc. cit.*

bromic acid in water upon the xanthenol. The red crystals were filtered off, washed with dilute hydrobromic acid, and dried in vacuum. The bromide showed the same composition and the same behavior as the compound above described.

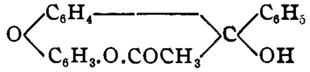
The *perchlorate* was obtained from an ether-acetone solution of the components as a fine red crystallin powder, which melts about 260°.

Calculated for $C_{19}H_{13}O_2ClO_4$: ClO_4, 26.69. Found: ClO_4, 26.60.

The *sulfate* was prepared from the components in absolute ether. It precipitates immediately as fine, bright red crystals. It begins to soften at 120°, and melts at 133–135°. It is instantly decomposed by alcohol, more slowly by cold water and dilute alkalies.

Calculated for $C_{19}H_{13}O_2HSO_4$: SO_4, 25.97. Found: SO_4, 25.40.

Phenyl-2-acetoxy-xanthenol,



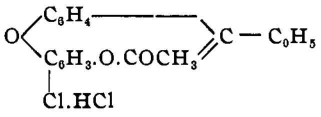
$$O\left\langle\begin{matrix}C_6H_4\text{———} \\ C_6H_3.O.COCH_3\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5 \\ OH\end{matrix}\right.$$

This was prepared by boiling a solution of phenyl-2-hydroxy-xanthenol in acetic anhydride with anhydrous sodium acetate. The acetyl compound was precipitated with water and recrystallized from ether by the addition of petroleum ether. Unless special care is taken to purify the original hydroxy-xanthenol, the acetic anhydride solution develops an intense purple color as it is boiled. This color is carried by the xanthenol into the ether solution, and can only be removed with difficulty by repeated recrystallization of the xanthenol. The color may be removed, however, with some loss of xanthenol, by converting the latter into the sulfate and then hydrolyzing the latter with water. The pure xanthenol is a colorless crystallin compound, which melts at 151–152°. It is very easily soluble in acetic ester and ether, and readily in all other organic solvents except petroleum ether.

Calculated for $C_{21}H_{16}O_4$: C, 75.86; H, 4.85. Found: C, 75.60; H, 4.98.

The *perchlorate*, $C_{21}H_{15}O_3.ClO_4$, orange red, melts at 180–185°.

Phenyl-2-acetoxy-quino-xanthenol Chloride Hydrochloride,



$$O\left\langle\begin{matrix}C_6H_4\text{———} \\ C_6H_3.O.COCH_3\end{matrix}\right\rangle C-C_0H_5 \quad \begin{matrix}| \\ Cl.HCl\end{matrix}$$

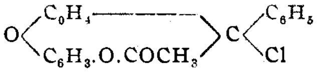
If a benzene solution of the xanthenol is treated with acetyl chloride and dry hydrochloric acid gas, there precipitates a red oil, which does not crystallize even upon standing for several days. An ether solution of the xanthenol, treated in the same way, gives no precipitate at all, as might be expected from the influence of the acetoxy group as compared with the hydroxy or methoxy group. The acid chloride can be prepared when the xanthenol is suspended in petroleum ether, acetyl chloride added, and the mixture treated with dry hydrochloric acid. The dichloride comes down as a mixture of oil and crystals; upon standing, all becomes crystallin, forming a mass of light orange crystals. These are filtered and dried in a stream of dry air. The hydrochloride begins to soften at 110°, and melts at 125–129° with decomposition.

Calculated for $C_{21}H_{15}O_3Cl.HCl$: Cl, 18.33. Found: Cl, 17.91.

A stream of dry air readily removes a molecule of hydrochloric acid from the hydrochloride suspended in benzene, leaving a clear solution.

Calculated for HCl, 9.42. Found: HCl, 9.25.

Phenyl-2-acetoxy-xanthenol Chloride,



$$O\left\langle\begin{matrix}C_6H_4 \\ C_6H_3.O.COCH_3\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5 \\ Cl\end{matrix}\right.$$

This was obtained as colorless crystals from an ether solution of the xanthenol and acetyl chloride. These, however, are very sensitive to moisture and turn pink or red during the process of filtration and drying. They are especially sensitive towards acid fumes.

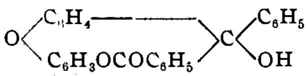
Calculated for $C_{21}H_{15}O_2Cl$: Cl, 10.11. Found: Cl, 9.80.

The colorless chloride gives colored salts with metal halides, which have been found to have the usual composition.

Phenyl-2-acetoxy-xanthenol peroxide was prepared by shaking the chloride with molecular silver. The solution of the unsaturated derivative is light red in color, and is immediately decolorized upon exposure to the air. Recrystallized from benzene, in which it is quite easily soluble, upon the addition of petroleum ether, the peroxide is obtained as a white crystallin product, which melts with decomposition at 128°.

Calculated for $C_{42}H_{30}O_8$: C, 76.15; H, 4.72. Found: C, 76.04; H, 4.90.

Phenyl-2-benzoxy-xanthenol,



$$O\left\langle\begin{matrix}C_6H_4 \\ C_6H_3OCOC_6H_5\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5 \\ OH\end{matrix}\right.$$

This xanthenol was prepared by shaking a solution of the corresponding hydroxy-xanthenol in 10% sodium hydroxide with benzoyl chloride. Recrystallized from benzene and petroleum ether, it is obtained in colorless crystals, melting at 205–206°. It is not very soluble in cold ether or benzene, readily soluble in boiling benzene, and acetic ester. It is not readily hydrolyzed by water or dilute alkalies.

Calculated for $C_{26}H_{18}O_4$: C, 79.71; H, 4.62. Found: C, 79.50; H, 4.90.

The *perchlorate*, $C_{26}H_{17}O_3.ClO_4$, yellow crystals, melting at 210°.

Phenyl-2-benzoxy-quinoxanthenol Chloride Hydrochloride.—The hydrochloride was prepared by suspending the xanthenol in dry petroleum ether, adding a little acetyl chloride, and saturating with dry hydrochloric acid gas. It precipitates as a red oil, which, upon standing several hours, forms a mass of light red crystals. These melt at 147–148°.

Calculated for $C_{26}H_{17}O_3Cl.HCl$: Cl, 15.79. Found: Cl, 15.40.

The extra molecule of hydrochloric acid is readily removed by passing a stream of dry air through the suspension of the hydrochloride in dry benzene.

Calculated for HCl, 8.30. Found: HCl, 8.40.

Phenyl-2-benzoxy-xanthenol Chloride.—As in the case of the acetoxy compound, ether can be used as a solvent in preparing the monochloride. An ether solution of the xanthenol is treated with a little more than the theoretical amount of acetyl chloride, and evaporated in vacuum. When the chloride began to separate, petroleum ether was added, and the solution allowed to stand several hours. The chloride separated as colorless crystals, which, however, began to turn pink as soon as the mother liquor was decanted. It is quickly washed with low boiling petroleum ether and dried. The crude product melted at 190°. It was not recrystallized.

Calculated for $C_{26}H_{17}O_3Cl$: Cl, 8.59. Found: Cl, 8.25.

The colorless chlorides give colored double salts.

The *peroxide* was prepared as usual. Recrystallized from benzene, it melts at 170° with decomposition.

Calculated for $C_{52}H_{34}O_8$: C, 79.36; H, 4.35. Found: C, 79.09; H, 4.60.

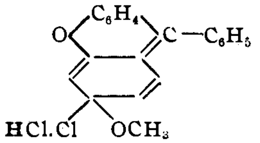
IV. Phenyl-3-hydroxy-xanthenol Salts.

3-Methoxyxanthone.—The 3-methoxyphenylsalicylic acid required for the preparation of this xanthone was prepared by condensing *o*-chlorobenzoic acid with resorcinol monomethyl ether, according to the method of Ullmann.[1] Twenty-eight grams of the chloro-acid, worked up in 5 gram lots, gave 42 grams crude acid, while the calculated amount is 43 grams. The crude product, however, may be used for the condenlsation into the xanthone without any appreciable loss in the final yield. It was found that if the amount of aluminium chloride be decreased sightly, the condensation took place just as readily, but that there was very little hydroxyxanthone formed, while according to Baeyer's directions, about a third of the product is 3-hydroxyxanthone.

It was found that in some experiments this reaction did not give a single reaction product but a mixture, probably of the 1- and 3-methoxy-xanthones. Ullmann has noticed a similar mixture in the preparation of 3-methyl-xanthone.

This xanthone, too, combines readily with metal halides and acids to form additive compounds, of the same composition as given by other xanthones.

Phenyl-3-methoxy-quino-xanthenol Chloride Hydrochloride,



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[1] *Ber.*, **38,** 2111 (1905) cf. Baeyer, *Ann.*, **372,** 99 (1910).

Phenyl-3-methoxy-xanthenol[1] was prepared according to the directions of Baeyer from 3-methoxy-xanthone and phenylmagnesium bromide. Colorless crystals, melting at 125°. The perchlorate, yellow, melts at 215–217°.

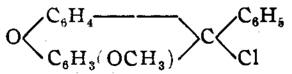
One-half gram of the xanthenol was dissolved in 20 cc. of absolute ether, $^1/_2$ cc. acetyl chloride added, and dry hydrochloric acid gas passed over the surface of the solution. At once, a yellow powder began to precipitate, which, upon standing, yielded small orange yellow needles. These were filtered, washed with low boiling petroleum ether, dried in an atmosphere of dry hydrochloric acid, and the excess of acid finally removed by a stream of dry air. It begins to soften at 122°, and melts with decomposition at 125–126°.

Calculated for $C_{20}H_{15}O_2Cl.HCl$: Cl, 19.76. Found: Cl, 19.33, 19.32.

If a stream of dry air is passed through a suspension of the hydrochloride, one molecule of hydrochloric acid is readily given off at a temperature of 60°, and there remains a clear, nearly colorless solution.

Calculated for HCl, 10.16. Found: HCl, 10.02.

Phenyl-3-methoxy-xanthenol Chloride,



$$O\left\langle\begin{matrix}C_6H_4\text{————}\\C_6H_3(OCH_3)\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5\\Cl\end{matrix}\right.$$

The above solution of the colorless chloride is concentrated, and dry petroleum ether added. Upon standing, the chloride separates. The outside of the crystals are coated with a small amount of a yellow substance, probably some of the hydrochloride formed by hydrolysis.

Calculated for $C_{20}H_{15}O_2Cl$: Cl, 10.97. Found: Cl, 11.26.

The following derivatives were prepared and analyzed:

Name.	Formula.	Color.	M. p.
Ferric chloride[2]	$C_{20}H_{15}O_2Cl.FeCl_3$	Yellow	163–164°
Zinc chloride	$C_{20}H_{15}O_2Cl.ZnCl_2$	Yellow	200–201°
Mercuric chloride	$C_{20}H_{15}O_2Cl.HgCl_2$	Orange	190°

Phenyl-3-methoxy-quino-xanthenol Bromide Hydrobromide.—The hydrobromide precipitates as a yellow orange crystallin powder upon treating a solution of the xanthenol in absolute ether with dry hydrobromic acid gas. It begins to darken at 110°, and melts with decomposition at 112–115°.

Calculated for $C_{20}H_{15}O_2Br.HBr$: Br, 35.68. Found: Br, 35.12.

Upon passing air through a suspension of the hydrobromide in dry,

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[1] Decker and Fellenberg, *Ann.*, **356**, 314 (1907); *Ber.*, **42**, 578 (1909); Baeyer, *Ann.*, **372**, 99 (1910).

[2] This double salt has been described by Decker and Fellenberg, *loc. cit.*, and Dengler, Diss., p. 39, as deep red, large needles, melting at 154°. They prepared it from an acetic acid solution of the components. We have also prepared the salt in this way and find that it is identical with that obtained from acetic ester and starting with the colorless benzoid chloride.

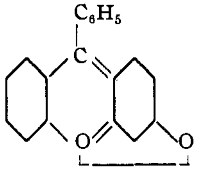
boiling toluene, a molecule of hydrobromic acid is given off by the hydrobromide, leaving a colorless solution of the bromide.

Calculated for $C_{20}H_{15}O_2Br.HBr$: HBr, 18.07. Found: Br, 17.81.

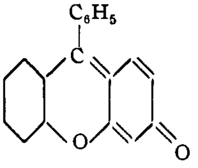
The benzoid bromide was not isolated, but some of its double salts were prepared:

Zinc bromide salt, $C_{20}H_{15}O_2Br.ZnBr_2$ golden yellow, m. p. 190°; mercuric bromide, $C_{20}H_{15}O_2Br.HgBr_2$, orange yellow, melts at 150–155°.

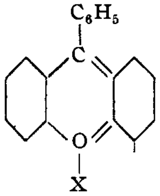
Phenyl-3-hydroxy-xanthenol does not exist, but spontaneously splits off water, giving *phenyl fluorone*. The latter was first prepared by Kehrmann and Dengler[1] by the action of benzotrichloride upon monoacetyl-*m*-aminophenol. They ascribe to it the *ortho*-quinoid structure (I) because of the analogy to the rosamines and apo-safranone. Since then, the compound has been prepared and studied by Kropp and Decker,[2] and by Baeyer[3] from the corresponding methoxy-xanthenol, and by Pope and Howard[4] from phenylhydroxy-xanthene by oxidation. These authors ascribe to the fluorone the *para*-quinoid structure (II) as originally suggested by Mohlau and Koch,[5] but agree with Kehrmann in ascribing an oxonium structure to the salts (III). The reasons for attributing to these salts the quinocarbonium rather than the oxonium constitution has been discussed in the theoretical part of this paper.



I.



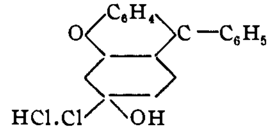
II.



III.

Phenyl fluorone was prepared according to the directions of Baeyer by the action of aluminium chloride upon the corresponding methoxy-xanthenol. Crystallized from benzene, yellow red leaves, melting at 207° to a dark red liquid.

Phenyl-3-hydroxy-quino-xanthenol Chloride Hydrochloride,



This was prepared by the action of dry hydrochloric acid gas upon a

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[1] *Ber.*, 41, 3440 (1908); Kehrmann, *Ann.*, 372, 287 (1910); Dengler, Inaug. Diss., Zürich, 1910, p. 22.

[2] *Ber.*, 42, 578 (1909).

[3] *Ann.*, 372, 101 (1910).

[4] *J. Chem. Soc.*, 97, 1023 (1910); 99, 545 (1911).

[5] *Ber.*, 27, 2887 (1894).

benzene solution of the fluorone, and was obtained as finely divided yellow crystals, which must be dried in an atmosphere of hydrochloric acid gas. It is not very stable and easily loses a part of the second molecule of acid.

Calculated for $C_{19}H_{13}O_2Cl.HCl$: Cl, 20.56. Found: Cl, 20.32, 20.18.

When suspended in dry benzene, one molecule of hydrochloric acid may be removed by passing a stream of dry air through the suspension at room temperature. There still remains in suspension a yellow solid, the monochloride. If the temperature is now raised to the boiling point of benzene and the stream of air continued, the second molecule of acid is given off and there results an orange colored solution of the fluorone, melting point, 207°.

Calculated for $C_{19}H_{13}O_2Cl.HCl$:	1 HCl, 10.57;	2 HCl, 21.13.
Found:	1 HCl, 10.20;	2 HCl, 20.88.

This resembles the behavior of 2,4-diphenyl-7-hydroxybenzopyranole,[1] and is the behavior that was predicted for fluorone before this work was started.[2]

Phenyl-3-hydroxy-quino-xanthenol Chloride.—(Formula XXIV, p. 1537.) This was prepared as indicated above, by passing a stream of dry air through a suspension of the chloride hydrochloride in dry benzene for several hours at room temperature. The yellow insoluble product is filtered out, washed with low boiling petroleum ether, and dried in a vacuum for half an hour.

Calculated for $C_{19}H_{13}O_2Cl$: Cl, 11.49. Found: Cl, 11.40.

The chloride is easily soluble in chloroform, giving a pure yellow solution; in nitrobenzene, glacial acetic acid, and boiling ethylene bromide. Like other quinocarbonium salts, it is insoluble in benzene, ether, acetic ester. It appears to be soluble in absolute methyl or ethyl alcohol; there is probably some decomposition. When heated it turns red at 180°, and melts at 198–200°.

The Action of Molecular Silver on the Chloride.—Here again we have a complete analogy with the pyranoles. It has been shown that 2,4-diphenyl-7-hydroxypyranole chloride on treatment with molecular silver loses a molecule of hydrochloric acid, becoming a quinone. The quinoxanthenol chloride behaves in the same way and fluorone is formed. Apparently, molecular silver has the same effect upon these quinochlorides as an elevation of temperature, *i. e.*, it splits off a molecule of hydrochloric acid, and does not, as with the other chlorides, remove merely the halogen.

Phenyl-3-hydroxy-quinoxanthenol Bromide.—This was prepared by passing dry hydrobromic acid gas into a solution of the fluorone in benzene. It precipitates at once as orange colored needles, which were filtered and

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[1] Gomberg, Cone and Winter, *Ann.*, **370**, 199 (1909).

[2] Gomberg and Cone, *Ann.*, **376**, 213 (1910). In that paper, line 3, p. 214, should read "phenylfluorone" and not "phenyl-oxy-fluorone."

dried in a stream of dry air. The color is very similar to that of the fluorone. It melts at 238–240°. It resembles the chloride in solubilities. Alcohol decomposes it at once. It is slowly decomposed by water and dilute alkalies. The formation of the bromide hydrobromide was not noticed.

Calculated for $C_{19}H_{13}O_2Br$: Br, 22.65. Found: Br, 22.59.

The *perchlorate* may be prepared from a benzene solution of the fluorone and an acetone solution of perchloric acid and the salt precipitated with absolute ether. It separates as fine, yellow crystals, which melt at 250°.

Calculated for $C_{19}H_{13}O_2ClO_4$: ClO_4, 26.69. Found: ClO_4, 26.86.

The Sulfate.—Kehrmann[1] has used the sulfate as a method of purification of the fluorone. He prepared it from an alcoholic solution of the fluorone and 50% sulfuric acid. We have prepared it from a hot saturated solution of the fluorone in absolute ether and concentrated sulfuric acid in the same solvent. It separated as fine, golden yellow crystals. The sulfate melts at 201–202°. It is quite readily hydrolyzed by water or alcohol. Kehrmann did not analyze his compound.

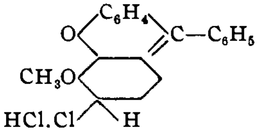
Calculated for $C_{19}H_{13}O_2HSO_4$: SO_4, 25.97. Found: SO_4, 25.80.

V. Phenyl-4-hydroxy-xanthenol Salts.

4-Methoxyxanthone was prepared according to the directions of Ullmann from *o*-chlorobenzoic acid and guaiacol. It melts at 173–174°. The following addition derivatives were prepared:

Name.	Formula.	Solvent.	Color.	M. p.
Stannic bromide	$(C_{14}H_{10}O_3)_2SnBr_4$	Benzene	Yellow	125–135°
Stannic chloride	$(C_{14}H_{10}O_3)_2SnCl_4$	Benzene	Yellow	187–188°
Mercuric chloride	$C_{14}H_{10}O_3.HgCl_2$	Acetic ester	White	204–205°
Perchlorate	$C_{14}H_{10}O_3.HClO_4$	Nitrobenzene	Yellow	160°
Hydrobromide[2]	$C_{14}H_{10}O_3.HBr$	......	Yellow	....

Phenyl-4-methoxy-quino-xanthenol Chloride Hydrochloride,



Phenyl-4-methoxy-xanthenol was prepared according to the directions of Baeyer[3] from 4-methoxy-xanthone and phenylmagnesium bromide. It may be recrystallized from ether or benzene and melts at 172°.

A solution of the xanthenol in a mixture of benzene and petroleum ether, to which a little acetyl chloride had been added, is saturated with dry hydrochloric acid gas. The hydrochloride separates as dark red needles with a purple irridescence. It is filtered and dried in a stream of

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[1] *Ann.*, **372**, 323 (1910); Dengler, Thesis, p. 22.

[2] Gomberg and Cone, *Ann.*, **376**, 233 (1910).

[3] *Ann.*, **372**, 104 (1910).

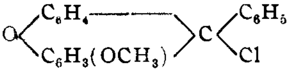
dry air. It begins to soften at 125° and melts to a red liquid at 144–145°.

Calculated for $C_{20}H_{15}O_2Cl.HCl$: Cl, 19.76. Found: Cl, 19.73.

Upon passing a stream of dry air through a suspension of the hydrochloride in dry benzene, a molecule of hydrochloric acid is driven off, leaving a clear solution, which however reddens upon exposure to the air.

Calculated for HCl, 10.16. Found: HCl, 10.10.

Phenyl-4-methoxy-xanthenol Chloride,



$$O\left\langle\begin{matrix}C_6H_4 \\ C_6H_3(OCH_3)\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5 \\ Cl\end{matrix}\right.$$

A concentrated solution of the chloride obtained as above was allowed to stand after the addition of petroleum ether. Colorless crystals separated after two days, which turned pink while washing with low boiling petroleum ether after decanting off the mother liquor. It melts at 237–238°.

Calculated for $C_{20}H_{15}O_2Cl$: Cl, 10.99. Found: Cl, 10.77.

The ferric chloride double salt, dark red, melts at 147–8°.

The mercuric chloride double salt, also dark red, melts at 205–7°.

The zinc chloride salt, red, melts at 240–41°.

Phenyl-4-methoxy-xanthenol peroxide was prepared by shaking a benzene solution of the chloride with molecular silver for twenty-four hours. A dark red fluorescent liquid was obtained, which was immediately decolorized by the air. After the evaporation of the benzene, the red mass was washed with ether until colorless. The crude peroxide was recrystallized from benzene with the addition of petroleum ether. It formed colorless crystals, which melted at 202° with decomposition.

Calculated for $C_{40}H_{30}O_6$: C, 79.18; H, 4.99. Found: C, 79.34; H, 4.86.

Phenyl-4-methoxy-quino-xanthenol Bromide Hydrobromide.—A solution of the xanthenol in dry benzene, which contains a few drops of acetyl bromide, is saturated with dry hydrobromic acid. The hydrobromic separates as dark red crystals, which must be dried in an atmosphere of hydrobromic acid. They begin to soften at 175°, but are not completely melted until 260°.

Calculated for $C_{20}H_{15}O_2Br.HBr$: Br, 35.68. Found: Br, 35.74.

When dry air is passed through a suspension of the hydrobromide in dry xylene, a molecule of hydrobromic acid is slowly given off, leaving a nearly colorless solution.

Calculated for HBr, 18.05. Found: HBr, 17.59.

The colorless bromide was not isolated, but some derivatives of it were prepared and analyzed:

Name.	Formula.	Color.	M. p.
Zinc bromide	$C_{20}H_{15}O_2Br.ZnBr_2$	Dark purple	234–235°
Mercuric bromide	$C_{20}H_{15}O_2Br.HgBr_2$	Brownish red	223°
Perbromide	$C_{20}H_{15}O_2Br.Br_2$	Reddish brown	188–189°

Phenyl-4-hydroxy-quino-xanthenol Chloride Hydrochloride.—Phenyl-4-hydroxy-xanthenol, requisit for the preparation of these salts, was prepared by treating the corresponding methoxy-compound with aluminium chloride.[1] After acidifying the alkalin solution, the product is allowed to stand a few hours, filtered, dried, and recrystallized from ether and petroleum ether. It melted at 161°. The perchlorate, dark red crystals, melts at 248–9°.

A saturated solution of the xanthenol in dry benzene was treated with a few drops of acetyl chloride, and then saturated with dry hydrochloric acid gas. The hydrochloride separates as dark red crystals. After an hour, the product was filtered and dried in an atmosphere of hydrochloric acid. It melts with decomposition at 210–211°. The hydrochloride is also obtained if an ether solution of the xanthenol is treated with hydrochloric acid gas. Baeyer, who did not analyze this salt, mistakes these crystals to be those of the chloride. Further, the same hydrochloride is obtained when either acetic acid, or concentrated hydrochloric acid, are employed as solvents.

Calculated for $C_{19}H_{13}O_2Cl.HCl$: Cl, 20.56. Found, Cl, 20.41.

Phenyl-4-hydroxyquino-xanthenol Chloride.—The hydrochloride suspended in boiling xylene, or, still better, heated in a vacuum at 130°, loses a molecule of acid and gives the monochloride. The dark red salt shows the characteristics of the quinoid salts: it is insoluble in benzene or ether, soluble in chloroform, acetic acid or nitrobenzene. It melts at 200–201°.

Calculated for $C_{19}H_{13}O_2Cl$: Cl, 11.49. Found: Cl, 11.73.

Treated with molecular silver, the chloride in nitrobenzene loses its deep purple color, changing to clear red. This is probably due to the formation of a triarylmethyl compound.

Phenyl-4-hydroxy-quino-xanthenol Bromide.—If a solution of about 1 gram of the xanthenol in 10 cc. absolute ether is treated with dry hydrobromic acid, the first trace of the gas causes the formation of a dark red precipitate. After passing the gas into the solution for two or three minutes, it is allowed to stand for an hour, during which time the bromide separates out, leaving the ether above it perfectly clear. This is filtered off and dried in an atmosphere of hydrobromic acid gas. A slight amount, about 1%, of acid is absorbed, but the excess of acid is removed if the crystallin bromide is kept in a vacuum over soda lime for an hour.

Calculated for $C_{19}H_{13}O_2Br$: Br, 22.65. Found: Br, 22.83.

The bromide may also be prepared by adding a little acetyl bromide to a solution of the xanthenol in benzene and passing in dry hydrobromic acid. The bromide is a dark, reddish purple substance, insoluble in ether,

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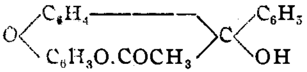
[1] Baeyer, *Ann.*, 372, 103 (1910).

benzene, etc., soluble in chloroform, nitrobenzene or boiling ethylene bromide. It melts at 261–262°.

Phenyl-4-acetoxy-xanthenol.



$$O\left\langle\begin{matrix}C_6H_4 \\ C_6H_3O.COCH_3\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5 \\ OH\end{matrix}\right.$$

The xanthenol was prepared from the corresponding hydroxy-xanthenol by boiling it with acetic anhydride and sodium acetate for half an hour. The solid resulting after the addition of water to the cooled product is recrystallized from a mixture of ether and petroleum ether. Colorless needles, forming into rosets, which melt at 127–128°. It is soluble in nearly all the usual organic solvents. The xanthenol is stable towards water, but, if allowed to stand a few days at room temperature with a dilute solution of sodium hydroxide, it is hydrolyzed to the hydroxy compound.

Calculated for $C_{21}H_{16}O_4$: C, 75.86; H, 4.85. Found: C, 75.71; H, 5.01.

The *perchlorate*, $C_{21}H_{15}O_3.ClO_4$, orange crystals, melts at 190°.

Phenyl-4-acetoxy-quino-xanthenol Chloride Hydrochloride.—The hydrochloride, as in the case of the other acetoxy-xanthenols, could not be prepared using a benzene solution. It was best prepared by passing dry hydrochloric acid gas over the solid carbinol chloride (see below) in a porcelain boat. At the first trace of acid, the colorless chloride became orange red. As more acid is absorbed the compound gradually became liquid. When no further change was noticed, the gain in weight was determined.

Calculated for HCl, 10.40. Found: Gain, 10.00.

When placed in a desiccator, hydrochloric acid is slowly given off, leaving the colorless chloride. The hydrochloride is quite rapidly decomposed by absolute ether, giving a solution of the colorless chloride. It is also decomposed by water, alcohol, and alkalies.

Phenyl-4-acetoxy-xanthenol Chloride.—The chloride was prepared from an ether solution of the xanthenol and an excess of acetyl chloride. One gram of the xanthenol and 3 cc. of acetyl chloride were used. The ether was evaporated to about half its volume, an equal amount of petroleum ether added, and the solution allowed to stand two days. The chloride had separated as two hemispherical conglomerates, which showed gray surfaces, but proved to be absolutely colorless upon being broken open. It is quite stable and does not suffer any noticeable change when exposed to the atmosphere. Upon standing, however, it gradually darkens. It begins to soften at 130°, and melts at 134–135°. It is quite soluble in all the usual organic solvents except petroleum ether.

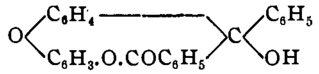
Calculated for $C_{21}H_{15}O_3Cl$: Cl, 10.10. Found: Cl, 10.00.

With metal halides, colored double salts are obtained. The ferric chloride salt, orange crystals, melts at 136–7°. The zinc chloride also orange, melts at 160–65°.

Phenyl-4-acetoxy-xanthenol peroxide was prepared in the ordinary way, by shaking a benzene solution of the chloride with molecular silver. The solution of the unsaturated compound, which is cherry red, is immediately decolorized by the air. The peroxide may be recrystallized from benzene. It forms colorless crystals, which melt at 145–146°

Calculated for $C_{42}H_{30}O_8$: C, 76.15; H, 4.72. Found: C, 76.00; H, 4.80

Phenyl-4-benzoxy-xanthenol,



$$O\left\langle\begin{array}{l}C_6H_4\text{———————}\\C_6H_3.O.COC_6H_5\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_5\\OH\end{array}\right.$$

The xanthenol was prepared by shaking an alkalin solution of the hydroxy-xanthenol with benzoyl chloride. The reaction product separates as a half solid mass, which was filtered off, washed, taken up in ether, and dried. The solution was evaporated nearly to dryness, petroleum ether added, and the oil which separates scratched until it began to crystallize. The compound does not crystallize readily; it does not show a sharp melting point, beginning to soften at 105°, and melting between 113–115°. It is readily soluble in all the organic solvents except petroleum ether. It dissolves in concentrated sulfuric acid with a red color.

The *perchlorate*, $C_{26}H_{17}O_3ClO_4$, yellow crystals, melts at 157–158°.

Phenyl-4-benzoxy-quino-xanthenol Chloride Hydrochloride.—The hydrochloride precipitates as an oil, when dry hydrochloric acid gas is passed into a solution of the xanthenol in dry petroleum ether, which contains a little acetyl chloride. It soon crystallizes, forming yellow needles. It melts with decomposition between 85–90°. It is very easily decomposed by alcohol and dilute alkalies, also by water and ether.

Calculated for $C_{26}H_{17}O_3Cl.HCl$: Cl, 15.79. Found: Cl, 15.50.

The extra molecule of hydrochloric acid is easily removed by passing air through a suspension of the hydrochloride in dry benzene, yielding a colorless solution.

Calculated for: HCl, 8.30. Found: HCl, 8.05.

Phenyl-4-benzoxy-xanthenol Chloride.—This colorless chloride was prepared by treating an ether solution of the xanthenol with an excess of acetyl chloride, and evaporating nearly to dryness in a vacuum at room temperature. The oily residue is then treated with petroleum ether and scratched until it becomes crystallin. It is very easily soluble in all organic solvents. The colorless crystals begin to soften at 108°, and melt at 111–112°.

Calculated for $C_{26}H_{17}O_3Cl$: Cl, 8.59. Found: Cl, 8.41.

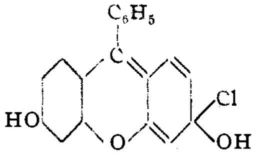
It gives orange colored salts with the chlorides of iron, zinc, etc.

VI. Phenyl-3,6-dihydroxy-xanthenol Salts.

Phenyl-3-hydroxyfluorone was prepared from resorcinol and benzotrichloride according to the method of Kehrmann and Dengler.[1] Recrystallized from nitrobenzene, or from alcohol and benzene, light red crystals; precipitated from a hot alkalin solution with dilute acetic acid, lemon yellow crystallin powder. It is quite easily soluble in alcohol, nitrobenzene or acetone; very little soluble in chloroform or ether. The pure compound gives a pure yellow solution with sulfuric acid, and not a dark brown solution as Pope and Howard report.

This fluorone is important because it is the mother substance of fluorescein. We find that it shows an analogous behavior to the other derivatives we have studied, except that the presence of the two hydroxyl groups gives to the compound a much greater tendency to tautomerize to the quinoid state.

Phenyl-3,6-dihydroxy-quino-xanthenol Chloride,



Kehrmann and Dengler obtained an orange yellow hydrochloride from an alcoholic solution of the base and concentrated hydrochloric acid, which, when dried to constant weight at 100°, was found by them to contain one atom of chlorine.[2] von Liebig describes a compound which he obtained in the same manner from resorcinbenzein, to which he ascribes the formula $C_{76}H_{50}O_{12}.4HCl$, which, however, may be, as far as the analysis is concerned, $C_{19}H_{12}O_3.HCl$, as the difference in the percentage of the chlorine in the two cases would be 0.03%. Pope and Howard describe the hydrochloride as a dark reddish brown solid, obtained from chloroform as a solvent, or by passing dry hydrochloric acid gas over the solid fluorone.

We repeated Kehrmann's experiment, using absolute alcohol, or a mixture of alcohol and benzene, and dry hydrochloric acid gas, but we find that under these conditions the chloride invariably contains one molecule of alcohol of crystallization (analyses I and II), which cannot be driven off even when the compound is dried at a moderate temperature in a stream of dry hydrochloric acid (analysis III). But when dried in a partial vacuum for two hours at a temperature of 110–130°, all the alcohol is driven off (analysis IV, loss on heating) carrying at the same time only a small amount of hydrochloric acid.

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[1] Kehrmann and Dengler, *Ber.*, **41**, 3440 (1908); **42**, 873 (1909); Dengler, Inaug. Diss., 1910, p. 25; cf. also von Liebig, *J. prakt. Chem.*, [2] **78**, 524 (1910); **85**, 97 (1912); Pope and Howard, *J. Chem. Soc.*, **97**, 1023 (1910); **99**, 545 (1911).

[2] Dengler, Diss., p. 42.

Calculated for $C_{19}H_{12}O_3.HCl.C_2H_6O$: Cl, 9.56; C_2H_6O, 12.41.
Found: Cl, 9.37, 9.10, 9.10; C_2H_6O, 11.64.

In substituting nitrobenzene for alcohol as a solvent, we obtained the salt as a voluminous, yellow crystailin precipitate. This was washed with benzene and low boiling petroleum ether, and dried in an atmosphere of hydrochloric acid. The analysis shows that when so prepared it contains a molecule of nitrobenzene of crystallization.

Calculated for $C_{19}H_{12}O_3.HCl.C_6H_5NO_2$: Cl, 7.93. Found: Cl, 8.21, 8.13, 8.22.

The pure salt itself, free from any solvent of crystallization, was obtained by two methods: First, after driving off the alcohol of crystallization at 110°, the salt was treated with dry hydrochloric acid gas until it was a pure yellow color (analysis I); second, a saturated solution of the fluorone in ether, in which it is only slightly soluble, was treated with dry hydrochloric acid. This darkened when heated to 250° but did not melt at 275° (analysis II).

Calculated for $C_{19}H_{12}O_3.HCl$: Cl, 10.93. Found: Cl, (I) 10.99, (II) 10.81.

Phenyl-3-hydroxyfluorone Hydrobromide.—This has been described by Gomberg and Cone[1] as a red compound, prepared by treating the fluorone in dry benzene with dry hydrobromic acid. It may also be prepared by treating an ether or chloroform solution of the fluorone with hydrobromic acid, when it is obtained in small quantities as lemon yellow flakes. From acetone the hydrobromide precipitates as a light brown powder.

Calculated for $C_{19}H_{12}O_3.HBr$: Br, 21.66. Found: Br, 21.30.

It is slightly soluble in acetone, chloroform, nitrobenzene and ethylene bromide. Alcohol decomposes it very quickly, water or dilute alkalies more slowly.

All attempts to make the chloride or bromide take up a second molecule of halogen acid were unsuccessful. Thus, while in the case of phenylfluorone the chloride does form an acid chloride and the bromide does not, in the case of phenyl-3-hydroxyfluorone neither the chloride nor the bromide show any tendency to combine further with halogen acids.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 210.]

THE PREPARATION AND PROPERTIES OF 5-AMINOQUINOLINE-6-CARBOXYLIC ACID AND CERTAIN RELATED COMPOUNDS.

BY MARSTON TAYLOR BOGERT AND HARRY LINN FISHER.

Received September 11. 1912.

The purpose of this investigation was to prepare an aminoquinoline carboxylic acid of anthranilic type from which, in turn, new heterocyclic systems might be derived and studied.

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[1] *Ann.*, 376, 216 (1910).