—From 1-phenyl-2-thio-4-piperonalhydantoin[1] by reduction with sodium amalgam. The yield was about 70 per cent. of the calculated. It is difficultly soluble in alcohol and separates from hot solutions in straw-colored needles, which melt at 172–173° to a clear oil. It was dried for analysis at 100°. Analysis (Kjeldahl):

Calculated for $C_{17}H_{14}O_3N_2S$: N, 8.59; found, 8.57.

NEW HAVEN, CONN.

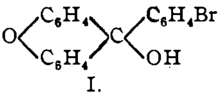
[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONDENSATION OF *p*-DIBROMOBENZENE WITH XANTHONE; A CONTRIBUTION TO THE KNOWLEDGE OF QUINOCARBONIUM SALTS.

L. H. CONE AND C. J. WEST.

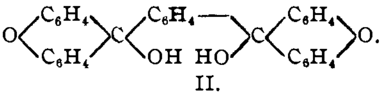
Received July 20, 1911.

Gomberg and Cone[2] found that by the action of xanthone upon the products resulting from dibromobenzene and magnesium two xanthenols resulted. One (I) is *p*-bromophenylxanthenol; the second (II), which they did not investigate, is *p*-phenylenedixanthenol.



$$O\left<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right>C\left<\begin{matrix}C_6H_4Br\\OH\end{matrix}\right.$$

I.

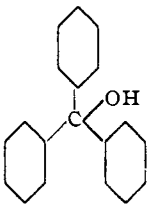


$$O\left<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right>C\left<\begin{matrix}C_6H_4—\\OH\quad HO\end{matrix}\right>C\left<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right>O.$$

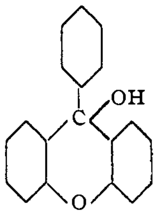
II.

This observation confirms that made by Houben,[3] who first showed that in the Barbier-Grignard reaction either one or both of the bromine atoms of *p*-dibromobenzene may react with magnesium. We have found that the reaction may be thrown largely in favor of the mono- or di-xanthenol compound, depending upon the amount of magnesium (and correspondingly of xanthone) used.

It has been shown[4] that there is a close analogy between triphenylcarbinol (III) on the one hand and phenylxanthenol (IV) on the other,



III.



IV.

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[1] Wheeler and Brautlecht, *Loc. cit.*

[2] *Ann.*, **370**, 178 (1909).

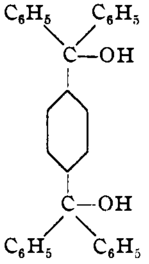
[3] *Ber.*, **33**, 3796 (1905).

[4] Gomberg and Cone, *Ann.*, **370**, 142 (1909); *Ibid.*, **376**, 183 (1910); see also Gomberg and West, THIS JOURNAL, **33**, 1211 (1911).

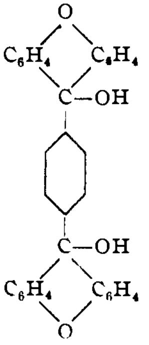
which differ only by the presence of the bridge oxygen in the latter. The general reactions of the triphenylmethane series have proven to be, with some modifications, the general reactions of the phenylxanthenol series. The increased reactivity of the xanthenols has been attributed to the bridge oxygen in the pyrone ring.

p-Phenylenedixanthenol is the simplest member of a new series of xanthenols containing, as it does, two xanthenol residues. From its constitution we would expect it to react as simple phenylxanthenol,[1] except that there would be two reactive xanthenol nuclei. Such is the case. For example, with hydrochloric acid, it yields a colored di-acid chloride, containing in all 4 atoms of chlorine; from this there may be prepared a colorless normal di-chloride, which reacts with two molecules of a metallic halide, etc.

A striking example of the influence of the bridge oxygen upon the reactions of these compounds is brought to light by a comparison of the behavior of the tetraphenylene-*p*-xylyleneglycol of Thiele[2] (V) and *p*-phenylenedixanthenol (VI), which differ in the same way as triphenylcarbinol and phenylxanthenol. The above-mentioned glycol gives, with hydrobromic acid in acetic acid solution, a colorless bromide (VII),[3] which, with metallic silver or copper, yields a quinoid orange colored hydrocarbon, tetraphenyl-*p*-xylylene[4] (VIII), which is not at all an analog of triphenylmethyl. The reaction may be represented as follows:



V.



VI.

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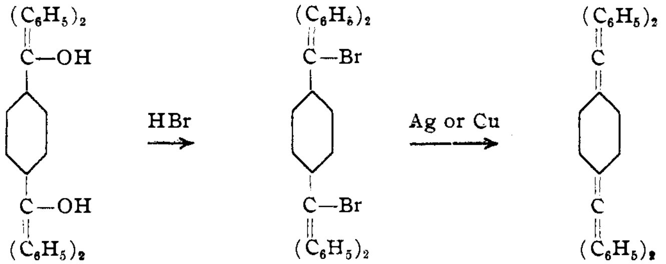
[1] *Ann.*, **370**, 153 (1909).

[2] Thiele and Balhorn, *Ber.*, 37, 1463 (1904). Ullmann and Schlaepfer, *Ber.*, 37, 2001 (1904).

[3] Ullmann and Schlaepfer (*loc. cit.*) have prepared the colorless chloride also by the action of dry hydrochloric acid gas upon the glycol in benzene solution.

[4] Staudinger, *Ber.*, 41, 1355 (1908), and Chichibabin, *Ber.*, 41, 2770 (1908), have also prepared this hydrocarbon.

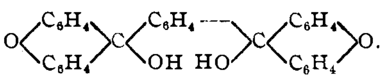


V. VII. VIII.

The *p*-phenylenedixanthenol, on the other hand, gives with hydrochloric acid a colored dihydrochloride, from which a colorless simple chloride may be prepared. Molecular silver removes the chlorine from this chloride, forming an unsaturated hydrocarbon, which is a true isolog of triphenylmethyl. With hydrobromic acid this xanthenol gives a colored dihydrobromide. Every attempt to prepare a colorless bromide by driving off the extra molecules of hydrobromic acid from this hydrobromide has thus far proved unavailing. A colored compound was always obtained. This is in direct contrast to simple phenyl xanthenol and, in fact, nearly all of its analogs, which readily yield colorless bromides. This deviation is probably due to the presence of two bridge oxygens in the molecule.

Experimental Part.

I. p-Phenylenedixanthenol,



$$O{<}^{C_6H_4}_{C_6H_4}{>}C{<}^{C_6H_4\,---}_{OH\quad HO}{>}C{<}^{C_6H_4}_{C_6H_4}{>}O.$$

—Three grams of magnesium are dissolved in an ethereal solution of 20 grams of *p*-dibromobenzene and 10 grams of finely pulverized xanthone (or dissolved in 50 cc. of boiling benzene) are gradually added to the solution. The reaction product separates out as a yellow powder soon after all the xanthone is added. After heating the mixture an hour on the water bath it is decomposed as usual. To separate the two xanthenols the following method was used:[1] The dry, crude xanthenol mixture as it comes from the Barbier-Grignard reaction is dissolved in benzene, a few cc. of acetyl chloride added, and hydrochloric acid gas passed into the solution. When the first bubble of gas strikes the solution, a bright red powder begins to separate on the walls of the flask. After the gas has been passed through the solution a few minutes, the red powder is filtered out, and the gas again passed into the solution. If more of the red powder is formed, the process is repeated until finally the solution remains a clear, pure yellow. The red powder is the hydrochloride of *p*-phenylenedixanthenol, while the solution contains the hydrochloride

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[1] Gomberg and Cone, *Ann.*, 370, 179 (1909).

of *p*-bromophenylxanthenol. The hydrochloride of *p*-phenylenedixanthenol thus obtained is hydrolyzed by boiling with ether and dilute sodium hydroxide, the ether solution dried, and evaporated to dryness. The carbinol is taken up in benzene, and the hydrochloride again precipitated, to free from any of the monoxanthenol compounds which might have been carried down at first. After hydrolyzing, the xanthenol is recrystallized from benzene and petroleum ether. Colorless crystals, melting at 176–177°, to a clear, colorless liquid. Soluble in benzene, ether, acetone, acetic ester, acetic acid, slightly soluble in alcohol, very slightly so in petroleum ether.

Calculated for $C_{32}H_{22}O_4$: C, 81.67; H, 4.71. Found: C, 81.60; H, 4.90.

Molecular weight determinations:

(1) Freezing point method, using benzene as a solvent:

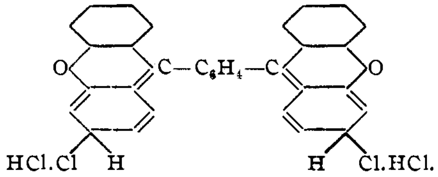
	s. Grams.	S. Grams.	*d*.	Mol. wt.
I	0.0800	12.155	0.072	457.1
II	0.1799	12.155	0.165	446.3
III	0.2802	12.155	0.255	452.0

(2) Boiling point method, using the same solvent:

	s. Grams.	S. Grams.	*r*.	Mol. wt.
I	0.2306	15.252	0.0927	446.1
II	0.7072	15.252	0.2924	434.0

Calculated molecular weight of $C_{32}H_{22}O_4$: 470.18.

p-Phenylenediquinoxanthenol-chloride hydrochloride,



The hydrochloride is best prepared by passing dry hydrochloric acid gas over a dry, fairly dilute benzene solution of the xanthenol containing a little acetyl chloride. It separates as a bright red, finely crystallin powder. The crystallin hydrochloride is filtered and dried in a stream of dry air and finally in dry hydrochloric acid gas. The excess of hydrochloric acid is then removed by dry air (two or three minutes) and the substance analyzed.

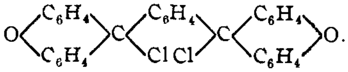
Calculated for $C_{32}H_{20}O_2Cl_2(HCl)_2$: Cl_4, 24.45. Found: Cl, 24.33.

The substance loses hydrochloric acid slowly, as a sample which had stood over night in a desiccator showed a loss of about three per cent.

If dry air is passed through a suspension of the hydrochloride in dry benzene two molecules of hydrochloric acid are gradually given off, but if the benzene is heated to boiling the evolution of hydrochloric acid is much more rapid. When exactly two molecules are removed a clear, colorless solution of the chloride remains. The amount of acid driven off was estimated by passing the air through a solution of silver nitrate.

Calculated for $C_{32}H_{20}O_2Cl_2(HCl)_2$: 2HCl, 12.59. Found: HCl, 12.48.

p-Phenylenedixanthenol Chloride,



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

—The chloride may be prepared by concentrating the colorless benzene solution obtained as above and adding petroleum ether. It separates as colorless crystals, which, however, gradually turn pink when exposed to moist air. In the absence of moisture they may be kept indefinitly with little change. The chloride begins to darken at 210° and melts at 259–260° to a dark brown liquid.

Calculated for $C_{32}H_{20}O_2Cl_2$: Cl_2, 14.00. Found: Cl, 14.05.

Action of Molecular Silver on the Colorless Chloride.—A sample of the chloride was dissolved in benzene and sealed with molecular silver. At once the surface of the silver showed a red coloration and the solution became reddish yellow. After shaking for three days, the solution had a purplish fluorescence in reflected light, while by transmitted light a thin layer appeared a reddish yellow color. The solution was decanted from the mixture of silver and silver chloride and filtered. On exposure to the air the solution rapidly lost its color, due to the oxidation by the air of the unsaturated colored analog of triphenylmethyl. We were not able, however, to isolate a definitly crystallin peroxide from this solution. Other similar cases have been noted, *e. g.*, phenyldinaphtoxanthenol[1] from which a crystallin peroxide could not be obtained.

The presence of a peroxide in our case was shown as follows: The brown residue, resulting from the spontaneous evaporation of the benzene solution of the peroxide, was hydrolyzed by dissolving in 90 per cent. sulfuric acid and allowing to stand over night. The reaction product was decomposed with ice water and the carbinol extracted with ether. It was identified by the melting point and characteristic reactions. This has been shown to be a general reaction for the peroxides.[2]

Ferric Chloride Double Salt.—This may be prepared from a solution of the colorless chloride in acetic ester and the theoretical amount of ferric chloride dissolved in the same solvent.[3] Or, it can be prepared by dissolving the xanthenol in glacial acetic acid, saturating the solution with hydrochloric acid gas, and then adding a solution of ferric chloride in

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[1] Gomberg and Cone, *Ann.*, 370, 168 (1909).

[2] Gomberg, This Journal, 22, 765 (1900); *Ber.*, 33, 3157 (1900); Gomberg and Cone, *Ber.*, 37, 3542 (1904); see also Staudinger, *Ber.*, 44, 1630 (1911).

[3] Naumann, *Ber.*, 43, 314 (1910) says that "Eisen-chlorür" is soluble but that "Eisen-chlorid" is insoluble in acetic ester. The latter must be a misprint.

acetic acid. It precipitates immediately from acetic ester as fine orange-red crystals which show no signs of decomposition at 250°.

Calculated for $C_{32}H_{20}O_2Cl_2(FeCl_3)_2$: Fe_2, 13.43; Cl_8, 34.12. Found: Fe, 13.30; Cl, 33.90.

Zinc Chloride Double Salt.—This was prepared as above, from the colorless chloride in acetic ester or from the hydrochloride in glacial acetic acid and zinc chloride in the same solvent. A little darker red in color than the corresponding iron salt.

Calculated for $C_{32}H_{20}O_2Cl_2(ZnCl_2)_2$: Zn_2, 16.77; Cl_6, 27.29. Found: Zn, 16.59; Cl, 27.15.

The *stannic chloride double salt* was prepared from solutions of the colorless chloride in benzene and stannic chloride in the same solvent. It separates at once as finely divided orange crystals, which form a rather difficult precipitate to filter and dry.

Calculated for $C_{32}H_{20}O_2Cl_2(SnCl_4)$: Cl_{10}, 38.18. Found: Cl, 38.00.

The *mercuric chloride double salt* is obtained by dissolving the carbinol in acetic ester, forming the colorless chloride with acetyl chloride and then treating with a solution of mercuric chloride in the same solvent. At the first drop of the chloride a red precipitate began to appear. The chloride was added until no further precipitate was formed. It was allowed to stand about an hour, and then filtered and dried as usual. Dull red crystals, which hydrolyzed rather slowly even in a normal sodium hydroxide solution, and which were quite stable in the presence of water.

Calculated for $C_{32}H_{20}O_2Cl_2(HgCl_2)_2$: Cl_6, 20.09. Found: Cl, 20.17.

Perbromide of the Chloride.—The perbromide may be prepared by adding a benzene solution (or a carbon disulfide solution) of bromine to a benzene solution of the colorless chloride. It separates immediately, as finely divided, yellow crystals; these were allowed to stand an hour and then were filtered out of contact with moisture and dried with dry air.

Calculated for $C_{32}H_{20}O_2Cl_2.Br_4$: Cl_2, 8.58; "perbromine" Br_4,3 8.67. Found: Cl, 8.30; "perbromine," 38.31, 38.77.

Periodide of the Chloride.—This is prepared in the same way as the perbromide. It appears as a dark brown, nearly black powder, which is quite stable. Filtered and dried as usual.

Calculated for $C_{32}H_{20}O_2Cl_2.I_4$: Cl_2, 6.98; "periodine" I_4, 50.08. Found: Cl, 7.33; "periodine," 49.70, 49.69.

The Perchlorate.—A solution of the xanthenol in about equal parts of benzene and acetone is treated with a little more than the theoretical amount of 70 per cent. perchloric acid dissolved in acetone. The perchlorate separates almost immediately as fine reddish yellow crystals, which were filtered after standing over night. It is hydrolyzed slowly by cold water, more rapidly by boiling water. The liberated perchloric acid is titrated with sodium hydroxide. It does not melt at 290°.

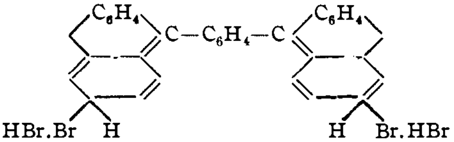
Calculated for $C_{32}H_{20}O_2(ClO_4)_2$: $2ClO_4$, 31.32. Found: ClO_4, 31.45.

The Acid Sulfate.—One-half gram of the carbinol was dissolved in 50 cc. of absolute ether and to this a little more than the theoretical amount of sulfuric acid in the same solvent was added. At once a powder-like substance was formed, which became crystallin upon standing over night. Filtered and dried as usual. Slowly hydrolyzed with water, more rapidly with sodium hydroxide.

Calculated for $C_{32}H_{20}O_2(HSO_4)_2$: $2HSO_4$, 30.45. Found: HSO_4, 31.33.

All of the above derivatives are characterized by their great insolubility in all the ordinary solvents, and their high melting points. Not one of them begins to melt at the boiling point of sulfuric acid. They would probably decompose, if heated to a temperature between 300° and 350°.

p-Phenylenediquinoxanthenol-bromide hydrobromide,



—If acetyl bromide is added to a solution of the xanthenol in dry benzene, the first drop causes a yellow turbidity and more produces a reddish brown precipitate. Hydrobromic acid passed over the surface of this solution causes the precipitation of the dibromide as reddish brown crystals. These are filtered in a stream of dry air and finally dried in an atmosphere of dry hydrobromic acid gas.

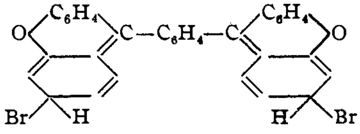
Calculated for $C_{32}H_{20}O_2Br_2(HBr)_2$: Br_4, 42.18. Found: Br, 41.22.

The hydrobromic acid is slowly given off, as after standing over night in a closed weighing bottle in a desiccator the substance had lost about 4 per cent. of hydrobromic acid.

A sample of the freshly prepared and carefully dried hydrobromide was suspended in dry xylene and a current of dry air passed through it. Hydrobromic acid was slowly given off at room temperature; the temperature was gradually raised to 80–90°, and after two hours was finally held at 110–120° for an hour. During that time two molecules of hydrobromic acid had been given off.

Calculated for $C_{32}H_{20}O_2Br_2(HBr)_2$: 2HBr, 21.35; found, 21.30.

p-Phenylenediquinoxanthenol bromide,



(?)

—After removing the hydrobromic acid from the acid bromide, as described above, there remained a red solid, insoluble in xylene. This is the simple bromide, which, unlike most halogen derivatives thus far obtained, has resisted all attempts to prepare it in the colorless form.

The red bromide is insoluble in benzene, toluene, xylene, very slightly soluble in nitrobenzene, chloroform, and glacial acetic acid.

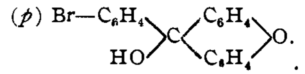
Calculated for $C_{32}H_{20}O_2Br_2$: Br_2, 26.82; found, 26.38.

If acetyl bromide is added to a solution of the xanthenol in benzene, an orange-yellow to reddish brown precipitate is formed. At the same time some hydrobromic acid is generated, due to the moisture of the solution and the air. Dry air is passed through the solution, which is heated to 80–90°, to remove the acid. The same insoluble red powder results as above. The benzene is colorless and gives no reaction with molecular silver, showing that no bromide has gone into solution. The same bromide is formed with solutions of the xanthenol in acetic ester, ether, chloroform, and to some extent in nitrobenzene and acetic acid when acetyl bromide is added.

If dry hydrobromic acid be passed into a solution of the xanthenol in glacial acetic acid the light red solution becomes a dark red, and small red crystals soon begin to appear. These are washed and dried as usual. They appear to be a mixture of the bromide and hydrobromide. This behavior is quite different from that described by Thiele for his glycol.

A small amount of a zinc bromide double salt was obtained by boiling the red bromide with chloroform, filtering hot, and adding a solution of zinc bromide in acetic ester. Red crystals. Because of the insolubility of the bromide not enough was obtained from this for analysis. A preparation in nitrobenzene gave no better results.

II. p-Bromphenylxanthenol,



$$\begin{array}{r}(p)\ \mathrm{Br{-}C_6H_4} \\ \mathrm{HO}\end{array}\!\!>\!\mathrm{C}\!<\!\!\begin{array}{l}\mathrm{C_6H_4} \\ \mathrm{C_6H_4}\end{array}\!\!>\!\mathrm{O}.$$

—Inasmuch as a large quantity of this compound resulted as a by-product from the above work, we have prepared the following derivatives of it, in addition to those already described by Gomberg and Cone.[1] They have given the method of preparation and the properties of the xanthenol, the acid chloride, the colorless chloride, the peroxide and the perchlorate.

The Ferric Chloride Double Salt.—One-half gram of the xanthenol is suspended in 15–20 cc. of glacial acetic acid and hydrochloric acid gas passed in until solution results. An acetic acid solution of ferric chloride is added, when the double salt precipitates at once as slender yellow needles, completely filling the liquid. After standing about an hour they had become orange-yellow and more compact. The double salt is also obtained from the components in acetic ester. Readily soluble in acetone, difficultly so in acetic ester and acetic acid. Melting point, 218°.

Calculated for $C_{19}H_{12}BrOCl.FeCl_3$: Cl_4, 26.57. Found: Cl, 26.69.

The *zinc chloride double salt* may be prepared in the same way as the iron salt. It does not separate as readily from acetic acid, but does

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[1] *Ann.*, **370**, 178 (1909).

so, however, after standing over night at room temperature. Large, shimmering, dark orange plates, melting at about 235° (not sharply).

Calculated for $C_{19}H_{12}BrOCl.ZnCl_2$: Cl_3, 20.95. Found: Cl, 20.97.

The stannic chloride double salt was prepared from benzene solutions of the colorless chloride and stannic chloride. A benzene solution of the hydrochloride may also be used. It appears at once upon mixing the components as dark yellow crystals. When allowed to stand, the benzene above the crystals becomes a deep red. The salt begins to soften at 155°, and melts at about 185° (not sharply).

Calculated for $C_{19}H_{12}BrOCl.SnCl_4$: Cl_5, 28.05. Found: Cl, 28.78.

The mercuric chloride double salt may be prepared from the components in acetic ester. The first drop causes the orange double salt to appear. Filtered and dried as usual. Light orange-yellow crystals which, when heated to 160°, turn a bright yellow, begin to soften at 250°, and melt to a dark red liquid at 257°.

Calculated for $C_{19}H_{12}BrOCl.HgCl_2$: Cl_3, 16.16. Found: Cl, 16.03.

The perbromide of the chloride appears slowly as fine, glistening, light orange needles from a solution of the components in carbon disulfide. Begins to melt at 190° and is completely melted at 201–202°, at which temperature bromine is evolved.

Calculated for $C_{19}H_{12}BrOCl.Br_2$: Br_2, 30.08. Found: Br, 29.80.

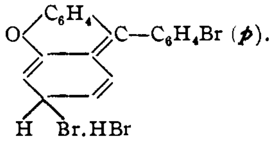
The Periodide of the Chloride.—The chloride in a mixture of benzene and carbon disulfide is treated with a solution of iodine in carbon disulfide. From the dark colored solution the iodide gradually appears in dark purple shining needles, which begin to soften at 180°, and melt at 188°.

Calculated for $C_{19}H_{12}BrOCl.I_2$: I_2, 40.59. Found: I, 40.00.

The Acid Sulfate.—A saturated solution of the xanthenol in absolute ether is treated with sulfuric acid, likewise dissolved in ether, until no further precipitation occurs. At first a yellow powder appeared, but as more acid is added this changes to a light red oil, which separated and formed a layer on the sides of the flask. This slowly became crystallin, forming rosets or large plates. The crystals are filtered and washed with careful exclusion of moisture, since they are extremely hygroscopic and are very easily decomposed by water. The large plates are brown in transmitted light and have a green metallic luster in reflected light. They melt at 77–78°.

Calculated for $C_{19}H_{12}BrO.HSO_4.H_2SO_4$: $2SO_4$, 36.18. Found: SO_4, 35.82.

p-Bromophenylquinoxanthenol-bromide Hydrobromide,



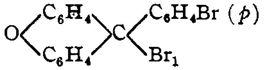
Upon adding acetyl bromide to a solution of the xanthenol in dry benzene, a slight red coloration occurs, due to a little hydrobromic acid; when dry hydrobromic acid gas is now passed over the solution, oily red drops are formed, which soon become crystallin. If a hot solution of the xanthenol is used the hydrobromide remains in solution but appears as soon as the solution is cooled under the water tap. The solution is saturated with the acid, and after adding a little petroleum ether, is allowed to stand a few hours. Filtered in the absence of moisture and finally dried in dry hydrobromic acid gas. Dark orange-red crystals, which are very hygroscopic.

Calculated for $C_{19}H_{12}BrOBr.HBr$: Br_2, 32.11. Found: Br, 31.89

A molecule of hydrobromic acid can easily be driven off by passing dry air through a suspension of the acid bromide in dry benzene, at a temperature of 60–70°. The resulting solution is clear, but has a slight yellow color.

Calculated for $C_{19}H_{12}BrOBr.HBr$: HBr, 16.29. Found: HBr, 15.99.

p-Bromophenylxanthenol bromide,



$$O\left\langle\begin{array}{l}C_6H_4\\C_6H_4\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_4Br\ (p)\\Br_1\end{array}\right.$$

The practically colorless solution obtained as above described is concentrated and petroleum ether added. The colorless bromide is obtained in crystallin form. It is very easily affected by moisture of the air, so that it becomes coated with a red layer of the hydrobromide immediately upon exposure to the air.

Calculated for $C_{19}H_{12}BrOBr$: Br, 15.49. Found: Br, 15.60.

The zinc bromide double salt is prepared from an acetic ester solution of its components, or from an acetic acid solution of the hydrobromide and zinc bromide. Bright red crystals, melting at 250° to a dark red liquid.

Calculated for $C_{19}H_{12}BrOBr.ZnBr_2$: Br_3, 37.40. Found: Br, 37.45.

The mercuric bromide double salt may be prepared from an acetic ester solution of the components. Yellow crystals, melting at 247–248° to a dark red liquid.

Calculated for $C_{19}H_{12}BrOBr.HgBr_2$: Br_3, 34.45. Found: Br, 34.00.

The bromide perbromide is obtained as orange crystals from a solution of the components in benzene or carbon disulfide. It separates at first as an oil, which soon became crystallin. Begins to soften at 185°, and melts at 188°.

Calculated for $C_{19}H_{12}BrOBr.Br_2$: Br_3, 41.64; Br_2, 27.76. Found: Br, 41.40; Br, 27.60.

The bromide periodide precipitates as a dark red oil when the components in benzene are mixed. This very soon becomes crystallin. A deeper purple than the corresponding chlorine compound, but has the same shining crystallin surfaces. Melts at 211–212° to a dark purple liquid.

Calculated for $C_{10}H_{12}BrOBr.I_2$: I_2, 37.89. Found: I, 37.50.

In conclusion we wish to thank Prof. M. Gomberg, of this laboratory, for his kindly interest and many helpful suggestions during the progress of this investigation.

ANN ARBOR, MICH.

NEW BOOKS.

Essentials of Volumetric Analysis. BY HENRY W. SCHIMPF. Second Edition, rewritten and enlarged. New York: John Wiley & Sons. London: Chapman & Hall. pp. 358. Price, $1.50.

The first edition of this book was primarily intended for the use of students of pharmacy. This edition will appeal to a wider circle of readers and is a marked improvement. The treatment follows in the main the lines laid down by Mohr. Analyses are classed as by Neutralization, Precipitation, Oxidation and Reduction. Then follows a second part on the estimation of alkaloids; assaying of vegetable drugs; phenol; fats; sugars; formaldehyde. After this we have a third part on a few gasometric analyses, and an appendix in which indicators are described.

EDWARD HART.

A Research on the Pines of Australia. By RICHARD T. BAKER, F.L.S., and HENRY G. SMITH, F.C.S. Published by Government of the State of New South Wales.

A magnificently printed volume of the Technical Education Series, No. 16, has appeared under the above title by Richard T. Baker, economic botanist and curator of the Technological Museum of Sydney, and Henry G. Smith, assistant curator and economic chemist. The volume is a record of pioneer work done by the authors on a number of species of the pine family indigenous to that country. No less than thirteen genera and thirty-nine species were studied, some of them for the first time.

The larger part of the volume is devoted to structural, botanical and chemical work with numerous photographs and colored plates. The chemical work follows the botanical descriptions and is, for the most part, a simple chemical examination of the oils, terpenes and resins, including the sp. gr., optical rotation, refractive index and the saponification and iodine values, when possible. Some attention has also been given to the lumbering industries.

The following general plan of work was observed under each species:

1. A field knowledge of the trees.
2. Morphology of fruit, leaves, inflorescence and their functions.
3. The anatomy of the organs.
4. Anatomy, nature and character of the timber and bark.