solution both for calcium and oxalic acid. If either is in excess, carefully add a small quantity of the solution required to remove it. In this way a solution, free from oxalic acid and calcium, will be obtained. Filter and concentrate the filtrate first on the water bath and then for several days in an air-closet at 100°. The temperature should not go much above that point. Set the vessel containing the fused acid in a vacuum desiccator and upon standing it will gradually solidify to a snow-white, crystallin mass.

ST. LOUIS, MISSOURI.

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

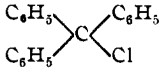
THE ACTION OF HALOGEN ACIDS UPON THE OXYARYL-XANTHENOLS.

[PRELIMINARY PAPER.]

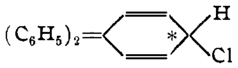
BY M. GOMBERG AND C. J. WEST.

Received May 24, 1911.

It has been demonstrated[1] that triphenylchloromethane and all its analogues exists in two tautomeric forms: the benzenoid (I) when colorless, and the quinoid (II) when colored. The quinoid compounds behave like salts. In definit solvents they obey the general laws of molecular conductivity; they possess, like all other salts, the capacity to form double salts, to yield perhalides, etc. The salt-like character of these "quinocarbonium" salts was attributed to the carbon atom C*, in so far as it was at all possible to localize upon a single atom in any complex molecule the cause of basicity and of consequent salt-formation.

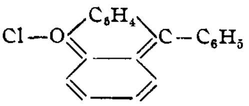


I.

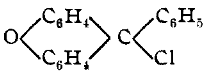


II.

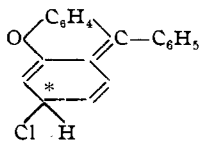
The idea of the quinocarbonium constitution was afterwards extended to the so-called "carboxonium" and "carbothionium" salts—colored compounds obtainable by the action of acids upon xanthenols and thioxanthenols, and to which the constitution (III) had been generally assigned by various investigators, without, however, any direct evidence of an experimental nature. Gomberg and Cone[2] have shown that these xanthenols yield, on proper treatment, absolutely colorless halides. These



III.



IV.



V.

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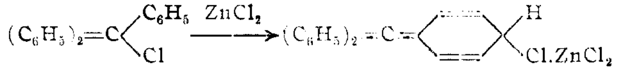
[1] Gomberg, *Ber.*, 40, 1847 (1907); 42, 406 (1909).

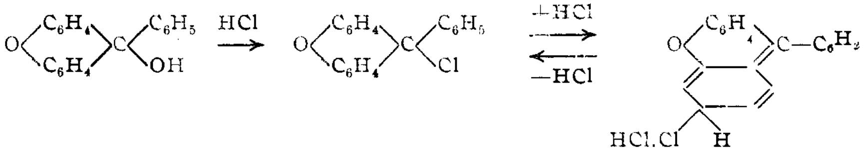
[2] *Ann.*, 370, 142 (1909); 376, 183 (1910).

halides were found in every essential characteristic to be true isologues of triphenylchloromethane, and hence the constitution (IV) was assigned to them. The same methods of study that served so well in demonstrating the quinocarbonium structure of the colored triphenylcarbinol salts were applied to the colored xanthenol compounds. The results furnished unmistakable evidence that these colored xanthenol halides are, in reality, quinocarbonium (V) and not "oxonium" salts, the constitution bearing exactly the same relation to the colorless xanthenol halides (IV) as was found to exist in the triphenylmethane series (I and II).

The triphenyl carbinol halides are readily tautomerized to the quinocarbonium salts by means of sulfur dioxide, metallic halides and, in some rare instances, by halogen acids:



The aryl-xanthenol halides (and also those of the thioxanthenols) possess a still more pronounced tendency to tautomerize, and the resulting quinoid salts are decidedly more stable than the corresponding salts of the triphenylmethane series. Halogen acids *very generally* induce this quinoidation in the xanthenol halides, and the resulting acid-salts are frequently only partially decomposed by water. Thus the action of dry hydrochloric acid upon phenylxanthenol can be represented as follows:



The bridge oxygen in the pyrone ring, as has been shown by Gomberg and Cone, possesses, therefore, the double function: first, it imparts to the xanthenol molecule a much greater tendency towards quinoidation than is possessed by the triphenylcarbinol compounds; second, it directs the quinoidation to one of the two phenyl nuclei which are linked to that of oxygen. An examination of the literature[1] shows that oxygen in any form, especially as methoxy or hydroxy groups, universally imparts to the molecule, wherein it is present, a greater tendency to tautomerize to the quinoid state than it might otherwise possess. So pronounced is this influence that polyhydroxy-para-triphenylcarbinols frequently exist only in the quinoid state, although the bridge oxygen is not present in them.

It is, therefore, quite reasonable to presume that the oxyxanthenols are likely to show, when treated with acids, a still greater tendency to tautomerize to the quinocarbonium state than the xanthenols them-

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[1] Baeyer and Villiger, *Ber.*, 35, 3019 (1902); Stobbe, *Ann.*, 370, 99 (1909); Gomberg and Cone, *Ann.*, 370, 191 (1909); 376, 211 (1910).

selves. The action of acids upon aryl-oxyxanthenols has been the subject of numerous investigations.[1] It has been generally reported that they gave rise to colored "oxonium" salts of the constitution (III). We have made a systematic study of this reaction with respect to the oxyxanthenols as an introduction to the study of the constitution of fluoran, fluorescein, hydrochinonphthalein, etc.

Our results, as far as they have gone, differ materially from those reported in the literature. We find: (1) that methoxy- and hydroxyxanthenols, except as specified below under (3), yield *colorless* carbinol chlorides, just like the other xanthenols studied; (2) that these carbinol chlorides tautomerize with extreme readiness to the quinocarbonium salts in the presence of *excess* of acid, forming acid chlorides; (3) that when one of the two phenyl nuclei in the xanthone ring contains a hydroxy group in the *para* position to the carbinol carbon atom, then the normal carbinol halides, even in the absence of excess of acid, tautomerize spontaneously to the colored quinoid state, similarly to the benzo-γ-pyronoles.[2]

In this preliminary paper we shall merely give the results as regards the composition of these colored salts. The method of preparation, the properties of the colorless carbinol halides, their various reactions, the double salts, etc., will be given in a later paper.

The Carbinol-hydrochloride of[3]	Total chlorine. Found.	Total chlorine. Calculated Cl_2.	Carbinol chloride.
Phenyl-2-methoxyxanthenol	19.56	19.76	colorless
Phenyl-3-methoxyxanthenol	19.38	19.76	colorless
Phenyl-4-methoxyxanthenol	19.53	19.76	colorless
p-Anisylxanthenol	19.78	19.76	colorless
Phenyl-2-hydroxyxanthenol[4]	20.35	20.56	colorless
Phenyl-3-hydroxyxanthenol	20.32	20.56	yellow, insoluble
Phenyl-4-hydroxyxanthenol[5]	20.41	20.56	colorless
p-Hydroxy-phenylxanthenol	20.38	20.56	colorless

ANN ARBOR, MICH.

THE ADSORPTION OF SOME SUBSTANCES BY STARCHES.

BY HOYES LLOYD.

Received May 20, 1911.

Wolff and Fernbach[6] found that some properties of starch and starch

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[1] Baeyer, *Ann.*, **372**, 97 (1910); Decker and Fellenberg, *Ann.*, **356**, 312 (1907); Kropp and Decker, *Ber.*, **42**, 578 (1909); Kehrmann and Dengler, *Ber.*, **41**, 3440 (1908); **42**, 870 (1909); Kehrmann, *Ann.*, **372**, 287 (1910); Pope and Howard, *J. Chem. Soc.*, **97**, 1023 (1910); **99**, 545 (1911).

[2] Gomberg and Cone, *Ann.*, **370**, 196 (1909).

[3] The nomenclature in this table is that given by Richter, *Lexikon* (3rd Ed.); Baeyer (*Ann.*, **372**, 98) suggests a different system.

[4] Kropp and Decker (*Ber.*, **442**, 578) describe a red chloride. Also Baeyer (*Ann.*, **372**, 104).

[5] Baeyer (*loc. cit.*) describes a red chloride.

[6] *Compt. rend.*, **140**, 1403–6.