The above work was done in this laboratory during the year 1908–09. The research on the octanes will be continued and the brief comparison of the first eight given in this paper will be extended from time to time as each new series is completed.

I am deeply indebted to the C. M. Warren Fund for Research for much of the material used in this study.

CAMBRIDGE, MASS.

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

ON TRIPHENYLMETHYL.

[TWENTIETH PAPER.]

BY M. GOMBERG AND D. D. VAN SLYKE.[1]

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CONTENTS: 1. Introduction. 2. Synthesis of Materials. 3. Action of Molecular Silver on Ortho- and Para-halogenated Derivatives of Triphenylcarbinol Chloride. 4. Action of Silver Chloride on Orthobrominated Derivatives of Triphenylcarbinol Chloride in Sulphur Dioxide. 5. Action of Silver Sulfate on Ortho- and Para-halogenated Derivatives of Triphenylcarbinol Chloride; Inhibitive Effect of Sulfuric Acid upon the Action of Silver Sulfate; Structure of the Sulfates. 6. Summary.

1. Introduction.

In previous papers bearing on the constitution of triphenylmethyl and its many analogs the following facts of importance, among others, were brought out: (1) The triarylmethyls are capable of existing in two modifications—the colored and the colorless;[2] the colored form is not limited to the solid phase alone, but as has been shown by J. Schmidlin,[3] the two modifications exist in equilibrium with each other even when in solution. (2) In the colored modification one phenyl group has become apparently changed in its function, for in it the para position is extremely reactive and mobil, in strong contrast to the great stability of the three phenyl nuclei in triphenylmethane itself.[4] (3) A similarly striking change in the functions of one phenyl nucleus, simultaneously with the production of color and of salt-like properties in the compound itself, has been shown to take place when the colorless triphenycarbinol halides are dissolved in sulfur dioxide, or when the triphenylcarbinols—always colorless—are changed to the corresponding carbinol sulfates, always colored.[5]

The theoretical explanation which has been advanced in order to account for these newly acquired functions in the phenyl nucleus consists in attrib-

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[1] This investigation was presented by Mr. Van Slyke to the Graduate School of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

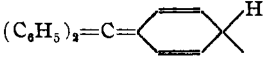
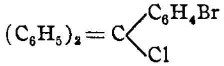
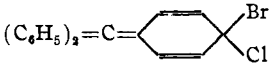
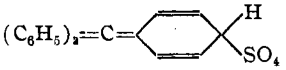
[2] *Ber.*, 34, 2729 (1901); 35, 2406 (1902); 37, 2036 (1904); 40, 1881 (1907).

[3] *Ibid.*, 41, 2471 (1908).

[4] *Ibid.*, 39, 3274 (1906).

[5] *Ibid.*, 40, 1847 (1907); 42, 406 (1909).

uting to that nucleus a tautomeric change from the benzoid to the para-quinoid state. With such a change the para-carbon atom would become in its character more like that in aliphatic than in aromatic compounds. Such an explanation accounts satisfactorily for the tremendous difference as regards the stability of the bromine in the para-brominated triphenylcarbinol halides according to whether we deal with the colorless solutions of the latter in benzene, chloroform, ether, etc., or with the colored solutions of the same compound in liquid sulfur dioxide. The following formulas illustrate the view-point.

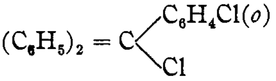
	Benzenoid.	Quinoid.
Triphenylmethyl........................	$[(C_6H_5)_3C]_n$	
p-Bromotriphenylcarbinol chloride	 $(C_6H_5)_2 = C\begin{smallmatrix}C_6H_4Br \\ Cl\end{smallmatrix}$	
Triphenylcarbinol sulfate..............	....	

The hypothesis as regards the existence of the two tautomeric forms of the triphenylmethane compounds has been since extended to the study of the xanthone and thioxanthone[1] derivatives. It was shown that there exists the closest analogy between these two classes of compounds on the one hand and the corresponding triphenylmethane compounds on the other, only that the former are far more prone towards tautomerization than the latter. It was further shown that the tautomeric colored salts obtainable from the xanthones and the thioxanthones must be considered, not as *oxonium* salts, but as *quinocarbonium* salts, just like their parent substances, the corresponding triphenylmethane derivatives.

The question now arises: Does ortho-quinoidation occur simultaneously with, or instead of, the para-quinoidation in the above mentioned instances of tautomerization. If it does, then the halogen placed in the ortho position should appear fully as reactive as it was found to be in the para position in the tautomerized products. On the other hand, if the ortho-halogen be found wholly inert then the conclusion appears justified as regards the non-occurrence of the ortho-quinoidation. This paper presents the results obtained in the attempt to answer the above question. The relative influence of chlorine and bromine in inducing tautomerization has also been studied, and there are also appended some further data in regard to the formation and behavior of the much-discussed triarylcarbinol sulfates.

2. Synthesis of Materials.

o-Chlorotriphenylcarbinol Chloride,



$(C_6H_5)_2 = C\begin{smallmatrix}C_6H_4Cl(o) \\ Cl\end{smallmatrix}$

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[1] Gomberg and Cone, *Ann.*, 370, 142 (1909); 376, 183 (1910).

o-Chlorotriphenylcarbinol, $(C_6H_5)_2C_6H_4Cl.C.OH$.—This product was synthesized by the action of ortho-chlorobenzoic ester on magnesium bromobenzene.

The ester was prepared from ortho-toluidine. The latter was diazotized according to Erdmann,[1] forming ortho-chlorotoluene. From the chlorotoluene, ortho-chlorobenzoic acid was prepared by oxidation with potassium permanganate.[2] For esterification, 1 molecule of dry sodium ortho-chlorobenzoate was heated for two hours at 160° with 1.1 molecules of dimethyl sulfate. The sodium methyl sulfate formed was dissolved in water, and the ester extracted with ether, dried over sodium sulfate, and distilled. The fraction boiling at 228–236° was equal to 80 per cent. of the theoretical amount.

For the Grignard reaction 4.1 g. (1 mol.) of magnesium were dissolved in an ethereal solution of 30 g. (1.1 mol.) of bromobenzene, and 12.5 g. (0.4 mol.) of ester added in ethereal solution. After two hours' boiling, the magnesium compound was decomposed with ice and hydrochloric acid. The ethereal extract was freed from bromobenzene by steaming, and the residue taken up in hot ligroin, boiled over charcoal and calcium chloride, then concentrated and allowed to crystallize. 11.8 g. of white carbinol were obtained melting at 91°. The pure recrystallized product melts at 95°.

Calculated for $C_{19}H_{15}Cl.O$:	C, 77.40; H, 5.13
Found:	C, 77.48; H, 5.60

o-Chlorotriphenylcarbinol Chloride.—11.8 g. of carbinol were dissolved in benzene, and the solution over calcium chloride saturated with hydrochloric acid. After standing some hours, the solution was concentrated, and on cooling 10 g. of white crystallin carbinol chloride, melting at 134–135°, crystallized. Melting point of pure product, 136°.

Calculated for $C_{19}H_{14}Cl_2$:	Hydrolyzable Cl, 11.33
Found:	Hydrolyzable Cl, 11.16.

o-Chlorotriphenylethoxymethane, $ClC_6H_4(C_6H_5)_2C.OC_2H_5$. — To a solution of 0.2 gram of sodium in absolute alcohol 2.3 g. carbinol chloride were added, and the solution boiled with reflux condenser for an hour. The sodium chloride was filtered out, and the solution concentrated. The product failed to crystallize in a freezing mixture or on standing for some time. After several weeks, crystallization occurred spontaneously, and 1.4 g. of a white product were obtained, melting at 77°. Easily soluble in ether, ligroin, alcohol, and benzene.

Calculated for $C_{21}H_{19}ClO$:	C, 78.12; H, 5.94.
Found:	C, 78.13; H, 6.13.

o-Chlorotriphenylanilidomethane, $ClC_6H_4(C_6H_5)_2C.NHC_6H_5$. — 3 g. car-

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[1] *Ann.*, **272**, 145 (1893).

[2] *Ibid.*, **276**, 55 (1893).

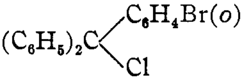
binol chloride were dissolved in about 20 cc. benzene and 2.2 g. redistilled aniline added. The anilide is not very soluble in benzene and it separated partially from solution along with the precipitated aniline hydrochloride. The anilide was extracted from the precipitate with hot benzene, and the benzene solution concentrated at room temperature. The product was obtained in 90 per cent. yield in the form of large, white crystals melting at 121°.

Calculated for $C_{25}H_{20}ClN$: N, 3.80.
Found: N, 4.11.

Unsymmetrical o-Chlorotetraphenylethane, $(ClC_6H_4)(C_6H_5)_2C — CH_2C_6H_5$.—This compound was prepared by the method of Gomberg and Cone.[1] 3 g. of carbinol chloride in dry benzene solution were added to an ethereal solution of twice the theoretical amount of benzyl-magnesium chloride. The condensation product separated out at once. The mixture was heated one-half hour on the water bath, then decomposed with dilute hydrochloric acid and ice. The ethereal extract, dried and concentrated, gave a product melting at 165°. Recrystallization from ligroin raised the melting point only to 165.5°. The product is most readily soluble in benzene, easily soluble in ether and warm ligroin, somewhat less so in alcohol.

Calculated for $C_{26}H_{21}Cl$: C, 84.64; H, 5.74.
Found: C, 84.66; H, 6.08.

o-Bromotriphenylcarbinol Chloride,



$$(C_6H_5)_2C\begin{matrix} \diagup C_6H_4Br(o) \\ \diagdown Cl \end{matrix}$$

This was prepared by the action of ortho-bromobenzoic ester on magnesium bromobenzene.

The ortho-bromobenzoic acid was prepared by diazotizing anthranilic acid in dilute sulfuric, and siphoning the diazonium solution into a mechanically agitated cuprous bromide suspension.[2] This gave us better yields (82 per cent. of the calculated) than diazotizing in the presence of cuprous bromide. A single recrystallization from water gave a pure product, melting at 150°.

The methyl ester was obtained by heating the dry sodium salt with methyl sulfate at 160° for two and a half hours, and isolating as in the case of the ortho-chlor ester. The yield was 87 per cent. of ester boiling at 245°–250°.

For synthesis of the carbinol chloride the ester was dissolved in absolute ether and added to a slight excess of phenyl magnesium bromide. After several hours' boiling, the product, which had separated as a gum, was decomposed with ice and dilute hydrochloric acid, and the resulting oily carbinol steamed to free it from bromobenzene. The carbinol was

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[1] *Ber.*, 39, 1461 (1906).

[2] Graebe, *Ann.*, 276, 57 (1893).

then dissolved in benzene, the solution boiled over charcoal and calcium chloride, and after filtration, saturated with dry hydrochloric acid in presence of fresh calcium chloride. On driving off the benzene and recrystallizing from ligroin, the carbinol chloride was obtained, the yield being 54 per cent. of the calculated.

Calculated for $C_{19}H_{14}BrCl$: Hydrolyzable Cl, 9.92.
Found: Hydrolyzable Cl, 9.82.

o-Bromotriphenylcarbinol, $(BrC_6H_4)(C_6H_5)_2C.OH$. — 2 g. of carbinol chloride were boiled in acetic acid solution. The carbinol was then precipitated by the addition of water, and taken up with ether. The ethereal extract was shaken with fresh portions of water until all the acetic acid was washed away. Concentration of the dried ethereal solution yielded 1.2 g. of pure white crystals. Recrystallized from ligroin the carbinol melts at 104°. It is easily soluble in benzene and ethe1, somewhat less so in alcohol and petroleum ether.

Calculated for $C_{19}H_{15}BrO$: Br, 23.58.
Found: Br, 23.18.

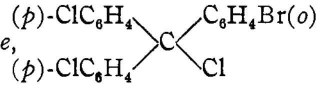
o-Bromotriphenylanilidomethane, $(BrC_6H_4)(C_6H_5)_2C.NHC_6H_5$. — 1.2 g. of aniline were added to 2 g. of carbinol chloride in benzene solution. After standing for two days, the solution was filtered from aniline hydrochloride, and concentrated by evaporation at room temperature. The product separated in pure white crystals, which were washed with ligroin, and dried *in vacuo*. Yield quantitative, 2.3 g. The anilide melts at 126°, is fairly soluble in hot petroleum ether and alcohol, slightly in cold; easily soluble in benzene.

Calculated for $C_{25}H_{20}BrN$: N, 3.38.
Found: N, 3.63.

Unsymmetrical o-Bromotetraphenylethane, $(BrC_6H_4)(C_6H_5)_2C.CH_2C_6H_5$.— 2 g. of carbinol chloride dissolved in absolute ether were added to twice the theoretical amount of magnesium benzyl chloride. The mixture was boiled an hour, then decomposed with ice and dilute hydrochloric acid. The ethereal extract was concentrated and steamed, then taken up in petroleum ether, and dried over calcium chloride. From the concentrated solution the product separated in crystals, melting at 153°.

o-Bromotriphenylethoxymethane, $(BrC_6H_4)(C_6H_5)_2C.OC_2H_5$.—2 g. of carbinol chloride were dissolved in absolute alcohol, and added to an alcoholic solution of a slight excess of sodium. The mixture was boiled for an hour, then cooled and diluted with water. The ethoxy compound was extracted with ether, the ethereal solution dried and concentrated. The product refused to crystallize from ether or ligroin, but finally was obtained from alcohol in pure white crystals after several weeks' standing. Melting point 69–70°.

o-Bromodi-p-chlorotriphenylcarbinol Chloride,



$((p)\text{-}ClC_6H_4)_2C(C_6H_4Br(o))Cl$

—The product was prepared by the action of *p*-chloromagnesiumiodobenzene on ortho-bromobenzoic ester. The *p*-chloroiodobenzene required for the synthesis was prepared by diazotizing *p*-chloroaniline.[1]

1.1 molecules of magnesium were dissolved in an ethereal solution of one molecule of *p*-chloroiodobenzene and 0.9 molecule of ortho-bromobenzoic methyl ester added. After five hours' boiling the solution was decomposed as usual, and the dark, impure carbinol steamed, and then boiled in benzene solution with calcium chloride and charcoal. The filtered benzene solution was saturated with dry hydrochloric acid and, after several hours' standing over calcium chloride, concentrated *in vacuo.* Hot ligroin was added to the residue, and the entire mass crystallized while still warm. Like other derivatives of *o*-bromodi-*p*-chlorotriphenylmethane, it showed exceptional crystallizability. A 74 per cent. yield was obtained. The recrystallized product melted at 165°. The carbinol chloride is difficultly soluble in ligroin, soluble in chloroform and ether, very soluble in benzene.

Calculated for $C_{19}H_{12}Cl_3Br$: Hydrolyzable Cl, 8.31.
Found: Hydrolyzable Cl, 8.20.

o-Bromodi-p-chlorotriphenylcarbinol, $(BrC_6H_4)(ClC_6H_4)_2C.OH$.—3.4 g. of carbinol chloride were dissolved in 20 cc. of glacial acetic acid and boiled. The solution of the carbinol was poured into 200 cc. of water and the precipitated suspension extracted with ether. The extract was washed free of acid, dried over calcium chloride and concentrated. 2.6 g. of crystalline white carbinol was obtained, melting at 107°. The melting point was not changed by recrystallization from alcohol and ligroin successively. The substance is easily soluble in benzene and ether, fairly soluble in alcohol and ligroin.

Calculated for $C_{19}H_{13}Cl_2BrO$: Cl_2, 17.38; Br, 19.59.
Found: Cl_2, 17.44; Br, 18.80.

o-Bromodi-p-chlorotriphenylethoxymethane, $(BrC_6H_4)(C_6H_4Cl)_2C.OC_2H_5$.—2 g. carbinol chloride were dissolved in absolute alcohol and added to a solution of 0.14 g. (1.2 molecules) sodium in absolute alcohol. The solution was boiled for an hour, cooled, and poured into water. The suspended ethoxy compound was extracted with ether, the extract dried over sodium sulfate, and concentrated. 1 g. of ethoxy compound crystallized on cooling. Recrystallized twice from ligroin it melted at 108°. The product is readily soluble in benzene, ether and ligroin, less so in alcohol.

The ethoxy compound, peculiarly, melts at practically the same tem-

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[1] Gomberg and Cone, *Ber.*, 39, 3281 (1906).

perature as the carbinol, although both were recrystallized until their melting points became constant. A mixture of the two, however, began to soften at 86°, and melted at 93°, showing conclusively their non-identity, which was confirmed by analysis.

Calculated for $C_{21}H_{17}Cl_2BrO$: Cl_2, 16.27; Br, 18.33.
Found: Cl_2, 16.59; Br, 18.02.

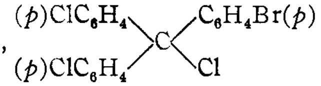
o-Bromodi-p-chlorotriphenylanilidomethane, $(BrC_6H_4)(C_6H_4Cl)_2—C—NHC_6H_5$.—To 2 g. carbinol chloride in 20 cc. benzene solution was added 20 per cent. excess of aniline (1.1 g.) and the solution allowed to stand for a day. The anilide is unusually insoluble, and a considerable portion precipitated with the aniline hydrochloride. The latter was extracted with hot benzene and the extract united with the main solution. On concentrating at room temperature the anilide was obtained in almost quantitative yield, 2.0 g. It is difficultly soluble in all the usual solvents except hot benzene. When heated it turns green at 211° and melts to a dark liquid at 212°.

Calculated for $C_{25}H_{18}Cl_2BrN$: N, 2.90.
Found: N, 2.94.

Unsymmetrical o-bromodi-p-chlorotetraphenylethane, $(BrC_6H_4)(C_6H_4Cl)_2C—CH_2C_6H_5$.—This was obtained by the same method as described for the other unsymmetrical tetraphenylethanes. Recrystallized from alcohol it melts at 162°. The substance is readily soluble in benzene, less so in ether and ligroin, and is fairly insoluble in alcohol, from which it can be recrystallized almost quantitatively.

Calculated for $C_{26}H_{19}Cl_2Br$: Cl_2, 14.71; Br, 16.59.
Found: Cl_2, 14.78; Br, 16.19.

p-Bromodi-p-chlorotriphenylcarbinol Chloride,



—This product was made from the corresponding carbinol, which was prepared by the Grignard reaction. 2.29 g. magnesium were dissolved in an ethereal solution of 24.4 g. (1.1 molecules) of *p*-chloroiodobenzene. To the solution was added 10.1 g. (1 molecule) of *p*-bromobenzoic methyl ester, and the mixture boiled six hours. It was decomposed as usual, and the product, after steaming off the excess of *p*-chloroiodobenzene, taken up in ether and boiled under reflux condenser with calcium chloride and charcoal. The colorless carbinol crystallized from the concentrated solution, and was washed with ligroin. The product recrystallized twice from petroleum ether melts at 106°. Yield, 12 g. which is 65 per cent. of the calculated amount.

Calculated for $C_{19}H_{13}Cl_2BrO$: Cl_2, 17.38; Br, 19.59.
Found: Cl_2, 17.68; Br, 19.05.

The carbinol chloride obtained by the action of hydrochloric acid on the above carbinol and melting at 122° has already been described by Gomberg.[1]

p-Bromodi-p-chlorotriphenylethoxymethane, $(BrC_6H_4)(C_6H_4Cl)_2C.OC_2H_5$.—The ethoxy compound was prepared similarly to the corresponding *o*-bromo derivative as described above. Recrystallized from ether the substance melts at 188°. The substance is soluble in benzene, moderately soluble in ether, comparatively insoluble in alcohol.

Calculated for $C_{21}H_{17}Cl_2BrO$:	Cl_2, 16.27;	Br, 18.33.
Found:	Cl_2, 16.65;	Br, 18.07.

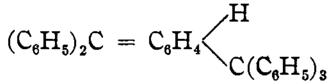
p - Bromodi - p - chlorotriphenylanilidomethane, $(BrC_6H_4)(C_6H_4Cl)_2C.NHC_6H_5$.—This anilide was obtained similarly to the above-described anilides. Recrystallized from a mixture of benzene and petroleum ether, the product on heating turns green at 178° and melts at 182°. It is soluble in benzene, fairly soluble in ether, insoluble in alcohol and ligroin.

Calculated for $C_{25}H_{18}Cl_2BrN$:	N, 2.90.
Found:	N, 2.92.

The synthesis of the di- and of the tri-ortho-chlorotriphenylcarbinol chlorides was attempted by the Grignard reaction but the reaction, when it took place at all, furnished such unsatisfactory yields of the desired products that the preparation of these compounds was given up for the present.

3. Action of Molecular Silver on ortho- and para-Halogenated Derivatives of Triphenylcarbinol Chloride.

When para-halogenated derivatives of triphenylcarbinol chloride in benzene solution are shaken with an excess of molecular silver, not only the carbinol chlorine is removed, but part of the para-nuclear halogen as well, indicating the quinoid nature of the triphenylmethyl analogs in the brilliantly colored solutions. Approximately one-half of an atom of para-halogen was removed when one such atom was present, three-fourths when there were two para-halogens, seven-eighths when there were three. Gomberg[2] explained this by the hypothesis that the reaction products successively couple together as they are formed, with elimination of an atom of para-halogen from each complex at each coupling, on the assumption that in solution triphenylmethyl exists partially in the quinol state as suggested by Jacobson,



$(C_6H_5)_2C = C_6H_4\left\langle\begin{matrix} H \\ C(C_6H_5)_3 \end{matrix}\right.$

The theoretical amount of para-halogen removable in this manner should be one-half, three-fourths, or seven-eighths of an atom for each original molecule of carbinol chloride, according as the latter possesses one, two, or three atoms respectively of para-halogen. The requirements of the

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[1] *Ber.*, 40, 1863 (1907).

[2] *Ibid.*, 40, 1886 (1906).

theory were thus found to harmonize in a remarkably close way with the results obtained.

The present experiments were undertaken in order to obtain experimental data from derivatives containing both para-bromine and para-chlorine in the same molecule, and to ascertain from ortho-halogenated derivatives whether evidence could be obtained of ortho-quinoid formation. 0.3 to 0.5 g. portions of the carbinol chlorides tabulated below were sealed with benzene and 1.5 to 2.5 g. portions of molecular silver; the tubes were then shaken at room temperature for several months and their contents analyzed.

TABLE I.—ACTION OF MOLECULAR SILVER ON ORTHO- AND PARA-HALOGENATED DERIVATIVES OF TRIPHENYLCARBINOL CHLORIDE.

No.	Carbinol chloride.	Days shaken with silver.	Carbinol chlorine.		Ring chlorine.			Ring bromine.			Total ring halogen. Atoms.
					Found.		Per cent calculated. 1 atom.	Found.		Per cent. calculated. 1 atom.	
			Found. Per cent.	Calculated. Per cent.	Per cent.	Atoms.		Per cen.	Atoms.		
1	*o*-chloro	106	11.15	11.34	0.00	0.00	11.34	..	...	...	0.00
2	*o*-bromo	222	8.98	9.92	..	...	...	0.00	0.00	22.37	0.00
3	*o*-bromodi-*p*-chloro	206	8.31	8.31	5.90	0.711	8.31	0.00	0.00	18.75	0.711
4	*o*-bromodi-*p*-chloro	206	8.31	8.31	6.05	0.728	8.31	0.00	0.00	18.75	0.728
5	*p*-bromodi-*p*-chloro	198	8.31	8.31	3.31	0.398	8.31	5.74	0.307	18.75	0.706
6	*p*-chlorodi-*p*-bromo	157	7.53	7.53	2.17	0.288	7.53	9.22	0.542	16.98	0.830
7	*p*-chlorodi-*p*-bromo	157	7.53	7.53	2.17	0.288	7.53	9.76	0.575	16.98	0.863

The conclusions afforded by the above results may be summarized as follows:

1. The results of numbers 1, 2, 3, and 4 show that no trace of ortho-halogen was removed in any case. There is no indication of the formation of ortho-quinoid nuclei.

2. The total amounts of para-halogen removed, as related to the number of para-halogen atoms present, agree (except No. 5, which is too low, probably from experimental error) with those of Gomberg and Cone mentioned above, and substantiate strongly the explanation given for the reaction and based upon successive coupling of the products.

3. Bromine in the para-position is somewhat more reactive towards molecular silver than is chlorine. A larger portion of a bromine atom is removed in Nos. 6 and 7 than of chlorine in No. 5; also of bromine in No. 5 than of chlorine in Nos. 6 and 7.

Comparative Influence of Halogen in Ortho and Para-positions upon Color caused by the Action of Molecular Silver upon Halogenated Triphenylcarbinol Chlorides.—The solutions contained 0.3 to 0.5 g. carbinol chloride dissolved in 12–15 cc. benzene and sealed in tubes with the molecular silver, free from all traces of air. The derivatives are arranged in pairs differing, except in the last, only in the position of the halogen atoms, so that the comparative effect of halogen in the ortho and para positions is clearly brought out.

TABLE II.

Substance.	Color caused by action of silver.
Triphenylcarbinol chloride	Deep yellow
Mono-*p*-chlorotriphenylcarbinol chloride	Light red
Mono-*o*-chlorotriphenylcarbinol chlordie	Deep red
Mono-*p*-bromotriphenylcarbinol chloride	Brown-red
Mono-*o*-bromotriphenylcarbinol chloride	Deep red Tinge purple
Mono-*p*-bromodi-*p*-chlorotriphenylcarbinol chloride	Orange
Mono-*o*-bromodi-*p*-chlorotriphenylcarbinol chloride	Deep purple
Di-*p*-bromotriphenylcarbinol chloride	Orange
Di-*o*-chlorotriphenylcarbinol chloride	Deep violet
Mono-*p*-chlorodi-*p*-bromotriphenylcarbinol chloride	Orange

The greater influence of the ortho-halogen substitutents in deepening the color is apparent, especially in the di- and tri-halogenated compounds. The para derivatives give colors varying from orange to red, the ortho from red to purple and violet. The similarity in the greater influence of ortho substituents in the analogs of triphenylmethyl and in the malachite green derivatives as observed by Noelting[1] indicates a similar structural cause of color.

4. Action of Silver Chloride on ortho-Brominated Derivatives of Triphenylcarbinol Chloride.

When tri-*p*-bromotriphenylcarbinol chloride is dissolved in sulfur dioxide and shaken with silver chloride the three bromine atoms are successively replaced by chlorine. The carbinol chloride in solution is at least partially in the quinoid form, an equilibrium existing, when part of the bromine has been replaced, between molecules containing brominated nuclei in the quinoid state and those in which a chlorinated nucleus is the quinoid one. The silver chloride reacts with the former, the disturbance of the equilibrium resulting in the shifting of the quinoidation to fresh bromine-containing nuclei as those formerly brominated become chlorinated. The replacement of bromine by chlorine consequently continues until it is complete, whether one, two, or three para-bromine atoms are present at the start. In the following diagram is shown the mechanism covering the replacement of the first two bromine atoms only, assuming, as we may, an equilibrium between products (3) and (4), and also between products (6) and (7).

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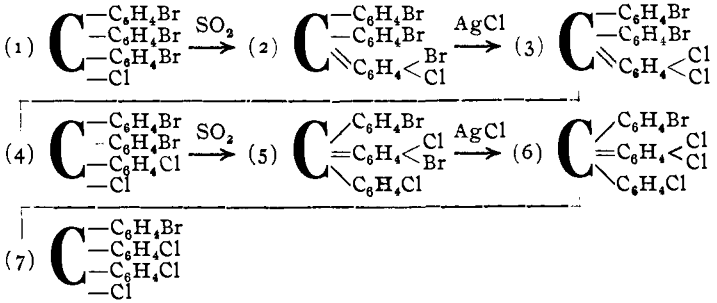
[1] *Ber.*, 39, 2041 (1906).

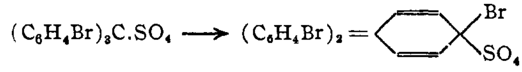


As will be shown by experiments with the sulfates described below, (p. 542) para-bromine exerts a stronger influence than chlorine in directing the quinoidation towards the nucleus in which it is situated. Even when there are two para-chlorine atoms to one bromine the quinoidation takes place almost entirely in the brominated nucleus.

We have now tested the ability of sulfur dioxide to induce ortho as well as para quinoidation. 0.3 g. portions of ortho-bromo- and ortho-bromodi-*p*-chlorotriphenylcarbinol chloride were sealed in bomb tubes with sulfur dioxide and 0.6 g. portions of silver chloride. The tubes were shaken one month at 20° and one month at 50°. *No silver bromide was formed in either case.* The tautomerization resulting from the influence of the solvent on a carbinol chloride cannot apparently be influenced by ortho-halogen, even bromine, to form ortho-quinoid nuclei.

5. Action of Silver Sulfate on ortho- and para-Halogenated Derivatives of Triphenylcarbinol Chloride.

The first action of silver sulfate on para-brominated triphenylcarbinol chloride is to remove the aliphatic chlorine attached to the central carbon atom, with formation of intensely colored neutral sulfates of the triphenylmethyl radicle. The second step in the reaction is the removal of one—and no more—para-bromine atom from each triphenylmethyl radicle. This removal can only be explained on the assumption that the sulfates undergo tautomerization at the moment of their formation and consequently have a quinoid nucleus as represented below, because the halogen in benzoid rings is absolutely inert towards silver salts.



The experiments tabulated below were undertaken in order to ascertain the comparative influence of chlorine and bromine in directing the quinoidation to or from the rings in which the halogens are substituted, and further to test the possibility of ortho-quinoid formation. The silver sulfate (1.5 to 2.5 g.), carbinol chloride (0.3 to 0.5 g.), and methyl sulfate as a solvent were sealed in a tube and shaken mechanically in a thermostat at 50°. The different carbinol chlorides are designated by the positions of their ring halogens.

TABLE III.—ACTION OF SILVER SULFATE ON CARBINOL CHLORIDES IN METHYL SULFATE.

			Carbinol chlorine removed.		Ring chlorine removed.		Ring bromine removed.	
No.	Carbinol chloride.	Days. shaken.	Calculated.	Found.	Calculated.	Found.	Calculated.	Found.
1	Mono-*o*-chloro-	7	11.32	10.84	11.32	0.00	...	...
2	Mono-*o*-bromo-	3	9.92	9.82	...	..	22.37	0.00
3	" "	11	9.92	9.65	...	..	22.37	0.00
4	*o*-Bromodi-*p*-chloro-	$^2/_3$	8.31	8.31	8.31	7.72	18.75	0.00
5	" "	$3^1/_2$	8.31	8.31	8.31	8.17	18.75	0.00
6	" "	5	8.31	8.31	8.31	8.28	18.75	0.00
7	" "	10	8.31	8.31	8.31	8.24	18.75	0.00
8	" "	13	8.31	8.31	8.31	8.35	18.75	0.00
9	*p*-Bromodi-*p*-chloro-	9	8.31	8.31	8.31	0.25	18.75	16.03
10	" "	11	8.31	8.31	8.31	0.80	18.75	15.92
11	" "	19	8.31	8.31	8.31	0.00	18.75	16.46
12	" "	26	8.31	8.31	8.31	0.77	18.75	15.34
13	*p*-Chlorodi-*p*-bromo-	6	7.53	7.53	7.53	0.04	16.98	16.83
14	" "	14	7.53	7.53	7.53	0.10	16.98	16.89

The solutions all became deep red at once upon shaking with silver sulfate, the substances containing ortho-halogen giving a deeper color, almost black, than those with only para-halogen. The "ring chlorine" was estimated by subtracting the theoretical carbinol chlorine from the total. The bromine was estimated, as usual, by igniting the mixed halides in chlorine gas.

From the data presented we may draw the following conclusions:

1. When bromine and chlorine occupy para-positions in different nuclei of the same substance, the bromine is removed in preference to the chlorine. When one bromine and two chlorine atoms occupy the para-positions (Nos. 9–12) not more than a tenth of an atom of ring-chlorine is removed, while nearly nine-tenths of the single atom of bromine is taken out. When there are two para-bromines to one para-chlorine (Nos. 13–14) an atom of bromine is taken out quantitatively, the amount of chlorine in excess of the carbinol atom being scarcely above the limit of error. In each case, however, the total amount of ring-halogen taken out by the silver sulfate never exceeds one atom. The para-bromine atom consequently influences the quinoid transformation, occurring when a sulfate is formed, strongly towards the nucleus which contains the bromine.

2. No ortho-quinoid rings are formed in the colored sulfates. Even when an ortho-bromine atom is the only halogen in the three nuclei (Nos. 2 and 3), in which case it would presumably exert a strong influ-

ence towards the formation of an ortho-quinoid ring, if such were possible, not the slightest trace of bromine is removed. When in addition to the ortho-bromine in one nucleus there are para-chlorines in the other two (Nos. 4–8), one atom of para-chlorine is removed quantitatively, showing that in the ortho position bromine completely loses its influence to direct the quinoidation towards its own nucleus.

A series of experiments was also carried out with sulfur dioxide instead of methyl sulfate as a solvent. The results obtained agree with the preceding, in showing that one para-halogen atom is removed from the colored neutral sulfate but that ortho-halogen is untouched.

Inhibitive effect of sulfuric acid upon removal of para-halogen from colored sulfates by silver sulfate.

It was found, in the case of the *p*-bromodi-*p*-chloro- and *o*-bromodi-*p*-chloro-sulfates, as by Gomberg in the cases of the *p*-bromo-and tri-*p*-bromo-sulfates, that the presence of slight amounts of free sulfuric acid in the methyl sulfate reaction mixture protects the para-halogen from removal by silver sulfate.

In the experiments tabulated below 0.3 g. portions of carbinol chloride with 1.5 g. portions of silver sulfate were weighed into test tubes, 10 cc. of methyl sulfate and the indicated amount of sulfuric acid then added, and the tube at once sealed and placed on the shaker at 50°. The results of Table IV were obtained after nineteen days' shaking.

TABLE IV.—INHIBITIVE EFFECT OF SULFURIC ACID ON REMOVAL OF PARA-BROMINE BY SILVER SULFATE FROM *p*-BROMODI-*p*-CHLOROTRIPHENYLCARBINOL SULFATE.

No.	Molecules sulfuric added per 1 mol. carbinol chloride.	Per cent. bromine removed.	Calculated 1 atom of bromine.
1	0	16.46	18.75
2	$^1/_2$	10.77	18.75
3	1	1.32	18.75
4	2	0.13	18.75

From the *o*-bromodi-*p*-chlorocarbinol chloride an atom of para-chlorine is quickly and quantitatively removed in the absence of sulfuric acid. But here again in the presence of acid, the action of silver sulfate is greatly hindered. The effect of time of reaction as well as that of the amount of acid was studied in this case.

TABLE V.—EFFECT OF AMOUNT OF SULFURIC ACID AND DURATION OF REACTION ON AMOUNT OF PARA-CHLORINE REMOVED BY SILVER SULFATE FROM *o*-BROMODI-*p*-CHLOROTRIPHENYLCARBINOL SULFATE.

Molecules sulfuric acid added per 1 mol. carbinol chloride.	Percentage of para-chlorine removed.			Calculated. 1 atom.
	16 hrs.	3½ days.	10 days.	
0	7.72	8.17	8.24	8.31
$^1/_2$	7.36	7.21	7.72	8.31
1	5.24	6.40	7.08	8.31
2	1.13	2.72	3.30	8.31

It is apparent that there is no simple ratio between the amount of sulfuric acid added and the amount of para-halogen protected. But it is equally apparent that the inhibitive effect of sulfuric acid is much smaller in case of chlorine than in case of bromine in the para position.

Tri-p-halogen Acid Sulfates.

Baeyer[1] obtained by the action of concentrated sulfuric acid upon an excess of carbinol in solution brown crystallin sulfates of tri-*p*-chloro- and tri-*p*-iodo-triphenylcarbinol. The sulfates showed a green metallic luster, and were of the constitution $(R_3C)SO_4H.H_2SO_4$. Gomberg[2] prepared similar sulfates of tri-*p*-chloro- and tri-*p*-bromocarbinol, using methyl sulfate instead of chloral as a solvent, the methyl sulfate having the marked advantage of being a solvent for sulfuric acid. Prepared with methyl sulfate, the products were found to contain not one molecule of excess sulfuric acid, as Baeyer's results indicated, but from $1^1/_2$ to 2 molecules.

The ortho-bromodi-*p*-chlorosulfate could not be brought to crystallize, but the *p*-bromodi-*p*-chlorocarbinol gave by Gomberg's method a beautifully crystallin sulfate with green metallic luster, the yield being about 80 per cent. of the calculated amount. If the sulfuric acid solution in methyl sulfate was added to a cold benzene methyl sulfate solution of the carbinol, the carbinol sulfate usually separated quickly in fine crystals, while if the solution was warm, crystallization occurred slowly, with formation of large, compact crystals, in form suggestive of cubical salt crystals. The analyses gave compositions similar to those of Gomberg's polysulfates, the percentage of (SO_4) varying from that corresponding to $(R_3C)SO_4H.1^1/_2H_2SO_4$ to that corresponding to $(R_3C)SO_4H.2H_2SO_4$. Either the substance is a mixture of the sulfates containing, respectively, one and a half and two extra molecules of sulfuric acid, or, as seems more probable, it contains two extra molecules of sulfuric acid, the analysis falling low because of the readiness with which the sulfate hydrolyzes, even by short contact with air.

The polysulfate containing three molecules of sulfuric acid, from *p*-bromodi-*p*-chlorotriphenylcarbinol, was dissolved in both methyl sulfate and sulfur dioxide, and both solutions shaken two months at 50° with silver sulfate. The residue from the methyl sulfate tube gave too slight an amount of silver halide for estimation, although it could be qualitatively determined. That from the sulfur dioxide gave an amount of silver halide corresponding only to 0.37 per cent. of bromine.

It is clear from the above results that these acid sulfates, unlike the normal sulfates, do not give up their para-halogen on treatment with

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[1] *Ber.*, 38, 1162 (1905).

[2] *Ibid.*, 40, 1853 (1907).

silver sulfate, although every precaution has been taken to insure against the possible reverse tautomerization to the benzenoid form during the treatment with the silver salt. Similar negative results with the acid sulfates, obtained by Baeyer previously in point of time to the positive results on the normal sulfates as described by one of us, led Baeyer to the conclusion that these, and also all the other similarly colored salts are not quinoid in constitution. Baeyer's conclusion based, as it is, on evidence of negative nature only, does not seem to us warranted. Certainly it is not warranted as regards the colored carbinol chlorides or the normal sulfates, the quinoid nature of which has been inferred from results of strictly positive character.

We have shown that the normal sulfates, like the colored carbinol chlorides, contain a labil para-halogen and consequently, like the latter, must be quinoid. It has been further shown that in these very same sulfates the para-halogen becomes partially protected against the action of silver salt by the presence of free sulfuric acid, and the protection becomes almost complete when the relative concentration of the free acid is equal to two molecules. The action of the free acid upon the normal sulfates consists primarily, no doubt, in the formation of acid sulfates. Does the acid at the same time induce the tautomerization of the active quinoid to the non-reactive benzenoid form, and this without change of color? Such an inference as regards the action of sulfuric acid is entirely contrary to what we know of the action of hydrochloric acid. Gomberg and Cone[1] have demonstrated that certain normal, colorless carbinol chlorides of this series are converted by excess of hydrochloric acid into acid chlorides which are colored and are quinoid. It does not seem reasonable to assume that sulfuric acid would act in the very opposit direction from that in which hydrochloric acid acts. Consequently the non-reactivity of the para-halogen in the acid sulfates must find its explanation in some hypothesis which would still admit of a structural analogy between the normal and the acid sulfates.

Some years ago, soon after the publication of Baeyer's negative results with the acid sulfate, Stieglitz and Barnard[2] have made the suggestion that the non-activity of these acid sulfates can still be reconciled with their having a quinoid constitution, if we assign to them the constitution I as "chloronium" or "bromonium" salts.

$$\underset{\text{I.}}{(BrC_6H_4)_2C:C_6H_4:Br.OSO_3H} \qquad \underset{\text{II.}}{(C_6H_5)_2C:C_6H_4:H.OSO_3H.}$$

Baeyer criticized this interpretation because on the basis of this view, in the salts obtainable from carbinols which contain in place of the para-halogen some other group, that group, or even the para-hydrogen itself

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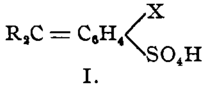
[1] *Ann.*, 370, 142 (1909).

[2] THIS JOURNAL, 27, 1016 (1905).

must likewise become basic and trivalent (Formula II).[1] We believe, however, that the kernel of Stieglitz and Barnard's view is none the less correct. So modified as to meet Baeyer's criticism, that interpretation furnishes a most satisfactory and plausible explanation of the entire behavior of these salts.

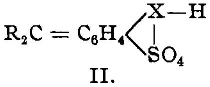
Structure of the Sulfates.

The normal sulfates must be considered as quinoid and on that basis can have only one possible constitution as given on page 541. The partial protection of the para-halogen in the mono-acid and the complete protection in the poly-acid sulfates is most rationally explained by assuming a structural connection between the para quinoid halogen and the combined acid radicles. The structure of the mono-acid sulfates may be represented as I or II, and that of the poly-acid sulfates as III, where x = halogen.



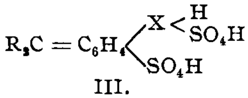
$R_2C = C_6H_4{<}\begin{matrix}X\\ SO_4H\end{matrix}$

I.



$R_2C = C_6H_4{<}\begin{matrix}X-H\\ |\\ SO_4\end{matrix}$

II.



$R_2C = C_6H_4{<}\begin{matrix}X{<}\begin{matrix}H\\ SO_4H\end{matrix}\\ SO_4H\end{matrix}$

III.

The halogen thus assumes in II the trivalent condition, as in chlorites bromites, and in iodonium compounds, and in III perhaps even a higher valence, as in chlorates and bromates. The halogen, having become trivalent, has changed its properties, and is no more capable of precipitation by silver than the chlorine in the chlorate or in some of the complex inorganic double salts of Werner that contain non-ionizable halogen. Such halogen we will term, after the iodonium compounds, bromonium or chloronium.

For the polysulfates only the bromonium or the chloronium formula III applies. It expresses the chromatic nature of these substances as well as the complete protection of the para-halogen from the action of the silver salts. For the nono-acid sulfates, present results indicate that both I and II apply, I being in considerable evidence when the para-halogen is chlorine, II almost the exclusive form when the para-halogen is bromine; *i. e.*, bromine shows much greater tendency to assume the bromonium form than does chlorine to assume the chloronium. This relative tendency of the two halogens is in harmony with our knowledge as regards the basicity of iodine in the iodonium compounds. The probability that para-chlorinated mono-acid sulfates are largly of form I follows from the fact that the greater part of their halogen appears unprotected. Table V (p. 543) shows that the addition of one molecule of sulfuric acid to the normal sulfates—a little more than sufficient to form the mono-acid sulfate—does not protect the greater part of the para-chlorine. This seems still more evident when one compares Table V with Table

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[1] *Ber.*, 40, 3083 (1907).

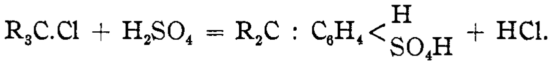
IV. The latter shows that a molecule of acid under the same conditions almost completely protects the para-halogen when the latter is bromine. Gomberg's results with mono-*p*-bromo- and tri-*p*-bromocarbinol chlorides are similar.

The following experiments show more definitly the inertness of parabromine in a para-brominated *mono*-acid sulfate. One molecule of sulfuric acid, just enough to form the mono-acid sulfate, was dissolved in methyl sulfate as a solvent with one molecule of mono-*p*-bromotriphenylcarbinol chloride, and the liberated hydrochloric acid driven off with dry carbon dioxide, until the carbinol chlorine was almost quantitatively removed. The carbinol chloride was thus changed to acid sulfate, R_3CSO_4H. To the solution of the organic sulfate was now added an excess of silver sulfate and the mixture sealed off and shaken for thirty days at 50°. 0.036 atom of chlorine was obtained, corresponding nearly to the slight amount of carbinol chlorine not driven off by the previous treatment with sulfuric acid, but no bromine whatever could be detected. In a similar experiment with the *p*-bromodi-*p*-chlorotriphenylcarbinol chloride less than 0.1 atom of bromine was freed. It is, therefore, apparent that all the para-bromine in mono-acid sulfates is protected, a fact which is explainable on the basis of structure, the para-brominated mono-acid sulfates having almost entirely the bromonium structure II.

The Action of Sulfuric Acid upon Triphenylcarbinol Chlorides.

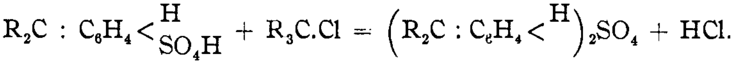
In order to gain some idea as to the avidity with which the sulfuric acid is held in the bromonium salts the following set of experiments was carried out. Exactly one molecule of sulfuric acid was allowed to act upon two molecules of various triarylcarbinol halides. In case of the simple triphenylcarbinol chloride the reaction may be expected to proceed in these two steps:

(*a*)



$$R_3C.Cl + H_2SO_4 = R_2C : C_6H_4 < \genfrac{}{}{0pt}{}{H}{SO_4H} + HCl.$$

(*b*)



$$R_2C : C_6H_4 < \genfrac{}{}{0pt}{}{H}{SO_4H} + R_3C.Cl = \left(R_2C : C_6H_4 < {}^{H}\right)_2SO_4 + HCl.$$

But in case of para-halogenated carbinol halides the presumption is that reaction (*b*) will be almost entirely absent, because of the salt-like nature of the chloronium or the bromonium sulfates which have resulted in reaction (*a*). In other words, on the basis of this structure, parahalogenated carbinol halides can yield only one mol. of hydrochloric acid, while the non-halogenated carbinol halides can yield under identical conditions twice as much hydrochloric acid.

The method of experiment adopted to determin the amount of carbinol chloride reacting with sulfuric acid was to determin the amount of hydrochloric acid freed in this reaction. The carbinol halide (2 mols.)

and sulfuric acid (1 mol.) were dissolved in carefully purified methyl sulfate, the solution was gently heated to 40–50°, and the liberated hydrochloric acid was driven out by a stream of dry carbon dioxide, the gas passing through a standard silver nitrate solution. Preliminary experiments with definit amounts of hydrochloric acid dissolved in methyl sulfate proved the method to be reliable.

The results of these experiments point unmistakably to a very marked difference in the behavior of the acid sulfate of non-halogenated carbinols on the one hand and those containing para-halogen on the other. With triphenylcarbinol chloride treated as above outlined, 1 mol. of sulfuric acid liberates readily the first mol. of hydrochloric acid (equation *a*) and somewhat more slowly the second (equation *b*), the whole process being completed in less than two days. But with para-bromo- and with di-*p*-bromotriphenylcarbinol halides, even on seven days' continuous treatment, no more than 1.3 mol. of hydrochloric acid was liberated, a result harmonizing well with the bromonium structure of the acid sulfate, wherein the acid is held in combination by the halogen.

6. Summary.

1. A number of new halogenated derivatives of triphenylmethane have been synthesized.

2. When the halogenated carbinol chlorides were treated with molecular silver, forming halogenated analogs of triphenylmethyl, the solutions obtained with ortho-halogenated derivatives were distinguished for depth and brilliancy of color.

3. When derivatives of triphenylcarbinol chloride containing para-halogen in two or three nuclei were dissolved in benzene and the solution shaken for three or more months with molecular silver, it was observed that: (*a*) a portion of each atom of such para-halogen was removed; (*b*) the total amount of para-halogen removed corresponded to about three-fourths atom when two para-halogen atoms were present, seven-eighths when three were present. Theses results substantiate the views of Gomberg concerning the quinoid structure of triphenylmethyl and its halogenated analogs in their colored solutions.

4. The conclusion of Gomberg, drawn from results obtained with normal *p*-bromo- and tri-*p*-bromotriphenylmethyl sulfates, that the colored triphenylmethyl sulfates have quinoid structure, is substantiated by further experimental evidence: One para halogen atom, and only one, becomes unstable, and can be readily removed by further action of the silver.

5. When one or two nuclei contain bromine, the other nucleus or nuclei chlorine, in the para position, the quinoidation of the sulfate in methyl sulfate solution takes place almost entirely in the brominated nuclei.

6. The para-halogen in the mono- and in poly-acid sulfates, unlike

that in the neutral sulfates, cannot be removed by the action of silver sulfate. The protection of the halogen by the sulfuric acid is explained on the ground that in the acid sulfates the sulfuric acid is combined directly with the para-halogen of the quinoid nucleus. The explanation is supported by data resulting from observation both of the inhibitive effect of sulfuric acid upon the reaction between para-halogenated carbinol chlorides and silver sulfate, and of the nature of the reaction between sulfuric acid and carbinol chlorides alone.

7. No evidence of the formation to the slightest degree of the ortho-quinoid nuclei could be obtained by experiments with ortho-brominated derivatives, either with the neutral sulfates by means of silver sulfate, or with the carbinol chlorides in sulfur dioxide solution on treatment with silver chloride, or in the triphenylmethyl analogs on treatment with molecular silver. Apparently only para-quinoid rings are formed.

ANN ARBOR, MICH.

[FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

THE SULFUR REQUIREMENTS OF FARM CROPS IN RELATION TO THE SOIL AND AIR SUPPLY.[1]

BY E. B. HART AND W. H. PETERSON.

Received January 2, 1911.

Preliminary to a special investigation on the relation of the form and supply of sulfur in feeds to wool production, it was necessary to determine the total sulfur in a number of our common crop materials. The results secured led to a further consideration of the question of the adequacy of the natural sources of supply of this element for continuous crop production and the data relating to that problem are presented in this paper.

It is generally recognized to-day by agricultural chemists that the amount of sulfur in plant materials, as determined in the ash, is in most cases entirely too low; that in the process of ashing, sulfur is lost and the residual amount found in the ash may represent but a fraction of that originally present in the plant tissue. Such losses of sulfur by ignition have been the subject for study by a number of investigators. Contributions to this phase of the question have been made by Berthelot,[2] Barlow,[3] Fraps,[4] Goss,[5] Beistle,[6] Sherman,[7] and others. The work of

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[1] Published with permission of the Director of the Wisconsin Experiment Station, University of Wisconsin.

[2] *Compt. rend.*, 128, 17.

[3] THIS JOURNAL, 26, 341 (1904).

[4] Reports of N. C. Experiment Station, 1901–1903.

[5] New Mexico Experiment Station, *Bull.*, 44.

[6] THIS JOURNAL, 24, 1903.

[7] *Ibid.*, 24, 1100.