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

TRIPHENYLMETHYL. XXXIII. QUINOIDATION IN THE TRIARYLMETHYLS[1]

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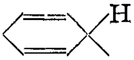
It has recently been shown by Gomberg and Sullivan[2] that when a solution of tetraphenyl-di-β-naphthylethane is diluted, or when the temperature of the solution is raised, the increase in color intensity is ever so much less than the increase in the dissociation of this hexa-arylethane into the corresponding free radical, diphenyl-β-naphthylmethyl. Thus, the results obtained from physico chemical measurements confirmed the hypothesis that color formation in the triarylmethyls must be ascribed not merely to the presence of a trivalent carbon atom but rather to the quinoidation of the free radical, $R_3C \rightleftharpoons R_2C=$  ; the quinonoid tautomer represents the colored substance.

In this paper we now present further evidence, of strictly chemical nature, in support of the existence of the quinonoid tautomer.

Discussion of Results

We have made a detailed investigation of the following three triarylcarbinol chlorides, each of these compounds containing a nuclear bromine atom in the *para* position to the methane carbon atom: *p*-bromotriphenylcarbinol chloride, which had previously been studied to some extent,[3] *p*-bromodiphenyl-1-naphthylcarbinol chloride, and diphenyl-4-bromo-1-naphthylcarbinol chloride.

These compounds were studied, first, with respect to the colored free radicals which they yield and, second, with regard to the colored carbinol sulfates which may be formed from them. There can be little doubt that the selective absorption, exhibited by the latter as well as that shown by the former substances, must be ascribed to similar causes.

Free Radicals.—When *p*-bromotriphenylcarbinol chloride, for example, is treated with molecular silver the latter removes not only the carbinol chlorine but also a portion of the nuclear bromine. These reactions, however, are distinct from one another and proceed with different velocities.

The initial reaction with the metal (removal of the carbinol chlorine) is a perfectly normal one. By the use of quite a large excess of very finely

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[1] The material here presented is from the thesis submitted by F. F. Blicke to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, **1921**.

[2] Gomberg and Sullivan, This Journal, **44,** 1810 (1922).

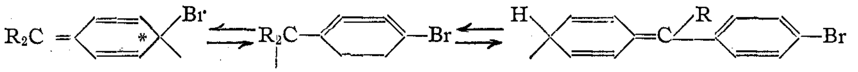
[3] (a) Gomberg and Cone, *Ber.*, **39,** 3279 (1906). (b) Cone and Long, This Journal, **28,** 519 (1906).

divided silver we found that it was possible to remove the chlorine from each of the 3 carbinol chlorides by allowing the substances to react for 20 minutes; only a trace of nuclear bromine was removed during this time. We did not succeed in isolating the resulting free radicals in a crystalline state, but their actual existence in their respective solutions was proved by the fact that oxygen was absorbed quantitatively in accordance with the equation, $(BrC_6H_4)R_2C- + O_2 = (BrC_6H_4)R_2C-O-O-CR_2(C_6H_4Br)$; the resulting peroxides were isolated and analyzed. Iodine was absorbed by the solutions of the radicals, and the iodides of the general type, R_3CI, were produced.

It is now obvious that the removal of the nuclear bromine by the silver must occur subsequently to the removal of the carbinol chlorine; that is, the bromine is removed, not from the bromotriarylcarbinol chlorides themselves, but from the free radicals which have resulted from the initial action of the silver on the carbinol chlorides.

Such a mobility of bromine in the phenyl nucleus is especially remarkable in view of the fact that not even a trace of bromine is removed by silver from such compounds as $R_2(BrC_6H_4)C-X$, where X represents H, OH, OC_2H_5 or other similar groups. It is only when the valence, which is otherwise attached to X, becomes free that the bromine in the phenyl nucleus becomes labile toward metallic silver.

No rational explanation can be advanced for such a marked change in the stability of the nuclear bromine if the structure I is accepted for the radical *p*-bromotriphenylmethyl. However, if the existence of a dynamic equilibrium between a benzenoid and some quinonoid structure such as II, is assumed we then have a plausible explanation for the lability of the bromine. It is evident that the carbon atom C*, in II, must have different properties from those which it possessed when it was part of a benzenoid nucleus; it should now function, to some extent, as though it were an aliphatic rather than an aromatic carbon atom and the bromine which is attached to it should, therefore, be removable by silver.



II I III

The problem, however, assumes greater complexity when the mobility of nuclear halogen in the brominated free radicals is studied quantitatively. It had been previously found[4] that even under the most favorable conditions only $^1/_2$ of the total amount of nuclear bromine is removed from *p*-bromotriphenylcarbinol chloride. We have now established a similar behavior for the other two *p*-brominated carbinol chlorides previously mentioned; presumably this phenomenon is characteristic for all triarylmethyls that contain a bromine atom in the *para* position to the methane

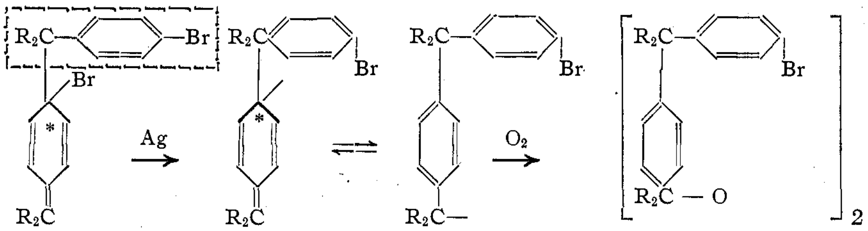
[4] Ref. 3a, p. 3294.

carbon atom. It seems to us that without the aid of the quinonoid hypothesis it would be impossible to explain why only a fraction, and moreover, a very definite fraction of the total bromine is removed from the bromotriarylmethyls.

When a radical of the type under discussion is produced, the following factors must be taken into consideration: in addition to the dynamic equilibrium, existing between the unimolecular forms I, II and III, there is undoubtedly a state of equilibrium operating between these unimolecular and various bimolecular forms; there is no valid reason for assuming that the ordinary hexa-arylethane is the only bimolecular form possible. On the contrary, it is only rational to assume that union, with the formation of a bimolecular radical, may take place between I and I, or between any two of the unimolecular tautomers, 6 forms of R_6C_2 being possible.

Now it is evident that a bimolecular form, resulting from the union of I and I, III and III or I and III would not contain mobile bromine atoms; in a combination of II and II both bromine atoms would be equally labile and, therefore, both would be removable by silver. It is only when combination has taken place between I and II or II and III that one of the two bromine atoms in the resulting compound is linked to a quinonoid nucleus and is, therefore, labile while the second bromine remains attached to a true benzenoid ring. Consequently, if either one of these latter two bimolecular forms is present, in the complex system of tautomers which may result when a *p*-bromotriarylmethyl is formed, it then becomes possible to account for the very remarkable fact that $^1/_2$, and no more than $^1/_2$, of the total bromine is removed by the molecular silver.

If it is assumed, for example, that the principal component in solution, with respect to reactivity toward molecular silver, is IV (that is, I + II) the result of the interaction with silver would be as follows:



IV V VI VII

Removal of the labile bromine, by metal, from IV leads to the formation of V which contains a trivalent carbon atom in the nucleus, thus making this compound analogous to II; since II is in tautomeric equilibrium with I, in a similar way V must be in equilibrium with VI. The latter substance (VI) may be designated as a free radical of "the second order," $R_3C–C_6H_4–CR_2$, while I represents a free radical of "the first order," R_3C.

When a mole of *p*-bromotriphenylcarbinol chloride, in solution, is converted into the radical of the first order, the solution, in accordance with the equation previously given, should absorb an amount of oxygen in agreement with the following ratio; 1 mole of oxygen for each 2 moles of the brominated triarylcarbinol chloride. When, however, prolonged reaction with the metal has resulted in the formation of the radical of the second order (VI), then only $^1/_2$ of that amount of oxygen which has been required by Radical I is necessary for the formation of the peroxide (VII) which corresponds to Radical VI.

Experiments have conclusively established the validity of this assumption. It was found that when chlorine alone was removed from the triarylcarbinol chloride the subsequent absorption of oxygen was, as anticipated, 1 mole of oxygen for 2 moles of R_3C–Cl; but when, in addition to the chlorine, the full $^1/_2$ of the nuclear bromine was eliminated the subsequent absorption of oxygen was found to be only $^1/_2$ mole for 2 moles of R_3C–Cl. Finally, when only a part of the total possible $^1/_2$ gram atom of bromine was removed, the amount of oxygen absorbed was also a corresponding fraction between 1 mole and $^1/_2$ mole.

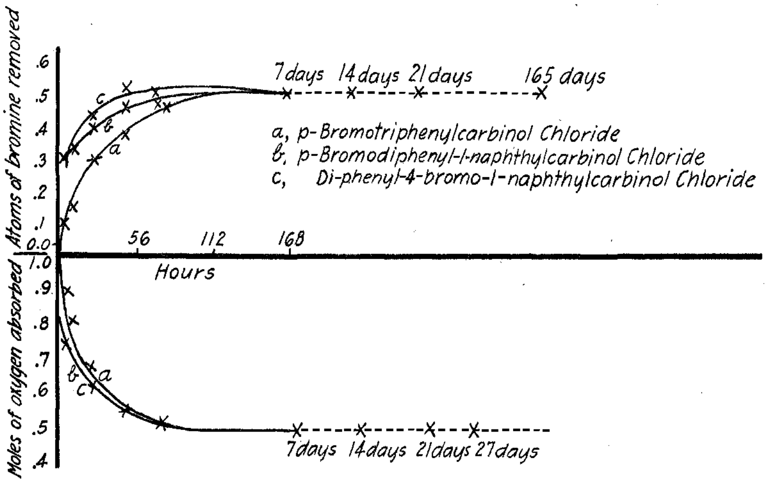


Fig. 1.—The relation between increase of nuclear bromine removed and the corresponding decrease of the amount of oxygen absorbed by the radicals

The curves of Fig. 1, which have been constructed from data in Tables I, II and III given in the experimental part of this paper, show the concordance between these two phenomena; increase in the quantity of nuclear bromine removed is paralleled by a decrease in the amount of oxygen which the reaction product was capable of absorbing.

In further confirmation of the above hypothesis concerning the mechanism of the reaction, we have isolated the peroxides, corresponding to the radicals of the second order, in the case of each of the 3 *p*-bromotriarylmethylcarbinol chlorides. All our attempts to isolate the free radicals themselves in crystalline condition proved unsuccessful; these radicals appear to be extremely sensitive to various influences, and upon concentration of their respective solutions they were either polymerized or decomposed into inert substances.

Another phenomenon, namely, a change in color, indicates a change of the free radical of the first order into the radical of the second order. With the elimination of chlorine from *p*-bromodiphenyl-1-naphthylcarbinol chloride there was formed a blue-violet solution, resembling an aqueous solution of potassium permanganate; upon the removal of nuclear bromine the color gradually changed into an intense blue.

It seems to us that the results we have obtained leave no alternative to the conclusion that the *p*-bromotriarylmethyls exist, not only in a benzenoid state but also in a quinonoid modification; union of the two types gives rise to a bimolecular combination, the constitution of which is tautomeric with the ordinary, bimolecular hexa-arylethane.

If the phenomenon of quinoidation is accepted for the *p*-bromotriarylmethyls, must it not be equally operative in the case of other, halogen-free radicals of the triarylmethyl type?

Salt-like Derivatives.—In discussing the salt-like derivatives of the triarylcarbinols it must be remembered that only combinations between the carbinols and certain acids produce colored compounds; with hydrochloric and hydrobromic acids, colorless chlorides and bromides are produced;[5] combinations with the organic acids, studied so far, are devoid of color. On the other hand, the carbinol sulfates, sulfites, nitrates, perchlorates and phosphates all possess color, some of these derivatives being as intensely colored as the triphenylmethane dyes themselves.

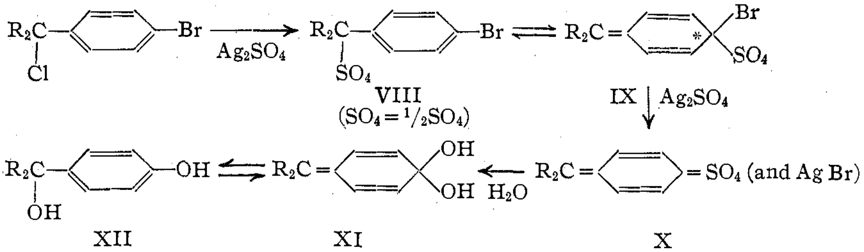
It has been shown that the nuclear halogen is not removed from the colorless, salt-like derivatives, even to the slightest extent, by contact with silver salts. However, in the case of the *colored*, *para*-halogenated triarylcarbinol derivatives, such as the sulfates, the halogen in the aromatic nucleus is readily removed by silver sulfate. Here, again, the mobility of the nuclear halogen finds its best explanation in the assumption of a quinonoid chromophore in the molecule.

Silver sulfate removes 1 atom of chlorine and, subsequently, 1 whole atom of bromine from 1 molecule of *p*-bromotriphenylcarbinol chloride.[6] The mechanism of this reaction can be formulated as follows: first, the carbinol chlorine is removed, resulting in the formation of the colorless carbinol sulfate (VIII); this tautomerizes instantly into the colored sulfate (IX). The bromine, being now attached to a carbon atom (C*),

[5] Hantzsch, *Ber.*, **54,** 2577 (1921).

[6] Gomberg, *ibid.*, **40,** 1852 (1907).

essentially aliphatic in nature, becomes reactive toward silver sulfate, and there results a colored, *para*-quinonoid sulfate (X).



This interpretation of the experimental results according to the quinonoid hypothesis was, at one time, challenged by v. Baeyer[7] who stated that the formation of silver bromide did not necessarily indicate that the compound X had been formed; according to him the silver halide might have been produced during a disruption of the triarylmethyl nucleus. We have now been able to prove, in a very decisive manner, that v. Baeyer's criticism is not valid. We have shown that in the case of each of the 3 bromocarbinol sulfates the bromine is actually removed by the silver sulfate, approximately 1 whole atom of bromine from each R_3C-X. Moreover, the reaction mixture, on hydrolysis, yields the corresponding *p*-hydroxytriarylcarbinol XI and XII, and this has been identified in both the benzenoid and the quinonoid state. It is, therefore, evident that, both subsequent as well as prior to the removal of the *para* bromine, the triarylmethyl nucleus remains intact.

Thus, just as in the case of the colored triarylmethyls, the mobility of nuclear halogen in the colored salts also is logically explained by the assumption of a quinonoid constitution. The inference is fully justified that the colored triarylcarbinol sulfates, in general, regardless of whether or not they contain nuclear halogen, must be quinonoid.

Experimental Part

Preparation of Materials

para-Bromotriphenylcarbinol Chloride

The Carbinol, $(BrC_6H_4)(C_6H_5)_2C—OH$.—This carbinol was prepared by the action of phenylmagnesium bromide on *p*-bromobenzophenone[3a] and also by the interaction of phenylmagnesium bromide and the methyl ester of *p*-bromobenzoic acid.[3b]

Since the resulting crude carbinol was an oil and consequently difficult to purify, it was converted by means of hydrogen chloride into the corresponding crystalline chloride. From the pure chloride the carbinol was readily obtained by the following process. Three g. of the chloride, 8 cc. of acetone, 1.2 cc. of dimethyl aniline and 2 cc. of water were refluxed for $^1/_2$ hour. The acetone was removed on a steam-bath and the viscous residue was freed from dimethylaniline hydrochloride by washing with water. When the product was stirred with a small amount of carbon disulfide the material quickly be-

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[7] Baeyer, *Ber.*, **40,** 3085 (1907).

came crystalline. After recrystallization from glacial acetic acid the carbinol was found to melt at 102–103°; this temperature is 30° higher than that recorded in the literature. Recrystallization from other solvents such as petroleum ether did not change the melting point. The compound dissolves very readily in benzene, in ether, in acetone and in carbon disulfide; with concd. sulfuric acid an orange-red solution is formed.

The Chloride.—The pure carbinol was dissolved in the smallest possible amount of absolute ether and the solution was then saturated with hydrogen chloride. The carbinol chloride soon precipitated; after several hours, the chloride was collected and then thoroughly dried over soda lime and sulfuric acid in a vacuum desiccator. The chloride melted at 112-114°, as recorded in the literature.

para-Bromodiphenyl-1-naphthylcarbinol Chloride

The Carbinol, $(BrC_6H_4)(C_6H_5)(C_{10}H_7)C—OH$.—A solution of 1-naphthylmagnesium bromide was prepared from 4.0 g. of magnesium turnings, which had been etched with a small amount of iodine, 125 cc. of absolute ether and 25 cc. of 1-naphthyl bromide. Forty g. of *p*-bromobenzophenone, dissolved in 50 cc. of warm benzene, was added to this solution and the mixture was then heated for 5 hours in a bath. When the magnesium addition product settled out it was collected on a filter, thoroughly washed with benzene and then decomposed with ice and a small amount of acid in the usual manner. The carbinol was then obtained at once quite pure. When the magnesium addition product failed to precipitate, the reaction mixture, after treatment with ice and acid, was distilled with steam in order to remove the solvent and any unchanged ketone. The crude carbinol was then recrystallized from carbon disulfide. The yield, based on the ketone, was 80%. The carbinol melts at 132–133°. It dissolves readily in ether, benzene and warm alcohol and is colored an intense green by concd. sulfuric or perchloric acid.

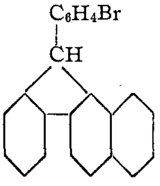
Analysis. Calc. for $C_{23}H_{17}OBr$: Br, 20.55. Found: 20.72.

The Chloride.—A warm, concentrated solution of the carbinol in benzene was saturated with hydrogen chloride. After 36 hours most of the chloride had precipitated. The hydrochloric acid, produced from the water formed during the reaction and the excess of hydrogen chloride, was removed by means of a pipet and the carbinol chloride was quickly filtered on a Büchner funnel. The material was washed several times with absolute ether and finally suspended in ether to remove the last traces of acid. After 24 hours the chloride was filtered and dried in a vacuum desiccator over sulfuric acid and soda lime; m. p., 182–183°.

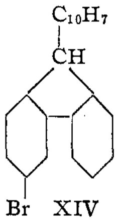
The carbinol chloride combines with the chlorides of such metals as zinc, tin, iron, mercury and aluminum, forming intensely colored, green addition products.

Analyses. Calc. for $C_{23}H_{16}ClBr$: C, 67.75; H, 3.93; Cl, 8.70; Br, 19.62. Found: C, 67.53; H, 4.02; Cl, 8.84; Br, 19.83.

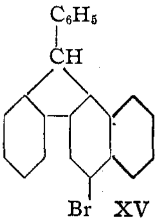
***p*-Bromophenyl-chrysofluorene.**—The carbinol, as well as the corresponding chloride, when heated with glacial acetic and concd. sulfuric acids, loses 1 molecule of water or 1 molecule of hydrogen chloride and is converted into a fluorene.



XIII

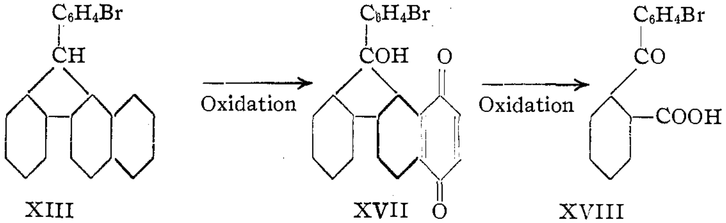


XIV



XV

That the latter has Constitution XIII, rather than XIV or XV, was proved by carrying out the reactions indicated below.



Fifty cc. of boiling glacial acetic acid was mixed with 10 g. of the carbinol and the mixture was heated until the carbinol had completely dissolved. Two cc. of concd. sulfuric acid was then added and the solution was vigorously stirred; the latter became deep green and the fluorene precipitated almost instantly. After the mixture had cooled, water was added and the material was filtered and washed; yield, 6.1 g. The compound, recrystallized from xylene, melts at 233–235°. The fluorene is only slightly soluble in the ordinary organic solvents and is not colored by concd. sulfuric acid.

Analysis. Calc. for $C_{23}H_{15}Br$: Br, 21.54. Found: 21.60.

A mixture of 1.9 g. of fluorene, 50 cc. of glacial acetic acid and 12 g. of sodium dichromate was refluxed for $2^1/_2$ hours, and then poured into 200 cc. of hot water, whereupon 0.9 g. of a yellow substance, the quinone XVII, was precipitated. The material was filtered and from the filtrate there was deposited, after 36 hours, 0.2 g. of the colorless, crystalline 4′-bromobenzoyl-2-benzoic acid (XVIII) which melted at 167–168°. The melting point given in the literature[8] is 169°.

The crystalline quinone, after several recrystallizations from glacial acetic acid, melted at 172–173°. It was found to be quite soluble in benzene, acetone or carbon disulfide; it dissolved in concd. sulfuric acid with the formation of a blood-red solution.

Analyses. Calc. for $C_{23}H_{13}O_3Br$: C, 66.19; H, 3.14; Br, 19.17. Found: C, 66.22; H, 3.21; Br, 19.02.

In conformity with its constitution as a quinone, the compound liberates iodine when treated with a mixture of potassium iodide, alcohol and hydrochloric acid.[9]

That the quinone is an intermediate product in the oxidation of the fluorene to the benzoyl-benzoic acid is proved by the fact that oxidation converts it almost quantitatively into the above-mentioned acid. To a boiling solution of 0.3 g. of the yellow material in 30 cc. of glacial acetic acid 1 g. of chromic anhydride was added during the course of an hour. The reaction mixture was then poured into 50 cc. of water and the mixture filtered. The filtrate was partly neutralized with sodium hydroxide and then extracted a number of times with ether. The ether extracts yielded 0.17 g. of the crystalline bromobenzoyl-benzoic acid.

Diphenyl-4-bromo-1-naphthylcarbinol Chloride

4-Bromo-1-cyanonaphthalene.—This substance, required for the preparation of the carbinol, was prepared as follows: 1-aminonaphthalene was acetylated[10] and the resulting 1-acetylaminonaphthalene was brominated.[11] The 4-bromo-1-acetylaminonaphthalene thus prepared was boiled with alcohol and hydrochloric acid and thereby hy-

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[8] Ger. pat., 148,110.

[9] Valeur, *Compt. rend.*, **129**, 522 (1899).

[10] Weyl, "Methoden der Organischen Chemie," Verlag G. Thieme, Leipzig, **1911**, II, 1273.

[11] Rother, *Ber.*, **4**, 850 (1871).

drolyzed into 4-bromo-1-aminonaphthalene. Upon recrystallization from gasoline this substance was obtained in the form of colorless crystals which melt at 102°.[12]

Twenty-two g. of the bromo-amine was added to glacial acetic acid which contained hydrogen chloride somewhat in excess of that required theoretically to convert the amine into the hydrochloride; the amine hydrochloride settled, with the liberation of heat, in the form of a paste. The latter was thoroughly stirred and the warm mixture then cooled to 15°. Eighteen cc. of amyl nitrite was added, all in one portion, the mixture being vigorously stirred and the temperature kept below 25°. After a short time all of the material had dissolved and only a very small amount of nitrogen was evolved. The clear acetic acid solution of the diazonium chloride was poured, a little at a time, with constant stirring, into 300 cc. of absolute ether which had previously been cooled to 0°. The diazonium chloride separated as an oil which quickly solidified to a light yellow, crystalline product. The liquid was decanted, the precipitate washed with cold ether and then filtered and quickly air-dried. The diazonium salt, which weighed about 20 g., was dissolved at once in 400 cc. of ice water.

The conversion of the dissolved material into the cyanide was effected by adding it slowly, well below the surface, to a clear solution of cuprous cyanide, prepared from 75 g. of copper sulfate in 300 cc. of water and 81 g. of potassium cyanide in 180 cc. of water. During this addition, carried out in a 3-neck, 2-liter round-bottom flask, the mixture was vigorously stirred mechanically and the temperature held at 80°. After all of the diazonium solution had been added the stirring was continued for $^1/_2$ hour. When the mixture had cooled the liquid was decanted from the brown, crystalline material and the latter was then washed with water and dried. The cyanide was extracted from the crude reaction product with glacial acetic acid, the extracts were concentrated and the cyanide was precipitated by the addition of water. The yield was 18 g., or 80%. It was found unnecessary to purify the cyanide further in order to convert it into the corresponding carboxylic acid. The pure cyanide is soluble in benzene and in warm alcohol, and melts at 102–103°.

4-Bromo-1-naphthalenecarboxylic Acid.—The crude cyanide was refluxed for 12 hours with a mixture consisting of equal parts of water, glacial acetic acid and concd. sulfuric acid. The reaction mixture was then poured into water and the acid was separated from unchanged cyanide by extraction of the precipitated material with dil. sodium carbonate solution. The clear, alkaline solution was then acidified with hydrochloric acid and the bromonaphthoic acid obtained in the form of colorless crystals. The acid is soluble in alcohol and acetic acid; m. p.,[13] 217–220°.

Analyses. Calc. for $C_{11}H_7O_2Br$: C, 52.61; H, 2.81; Br, 31.85. Found: C, 52.46; H, 2.80; Br, 31.19.

Ethyl Ester of 4-Bromo-1-naphthalenecarboxylic Acid.—Fifty g. of the acid was dissolved in 600 cc. of absolute alcohol and the solution then partly saturated with hydrogen chloride; the mixture was refluxed for 16 hours. After removal of about $^2/_3$ of the alcohol under reduced pressure the residue was poured into 3.5 liters of ice water; the resulting oil soon solidified. The ester was washed with dilute aqueous sodium carbonate and then air-dried. Since it is extremely soluble in the usual organic solvents the ester could not be recrystallized; it was purified by dissolving it in low-boiling petroleum ether, filtering and then allowing the solvent to evaporate spontaneously. The yield was 56 g., or 90%; m. p., 42–43°.

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[12] Morawski and Gläser, *Monatsh.*, **9**, 293 (1888).

[13] This compound has been recorded in the literature, since the completion of this work, by Mayer and Sieglitz, *Ber.*, **55**, 1841 (1922). The method used by these investigators is not, however, a preparative one. The melting point is given as 212°.

Diphenyl-4-bromo-1-naphthyl Carbinol, $(C_6H_5)_2(BrC_{10}H_6)C—OH$.—A solution of phenylmagnesium bromide was prepared from 10.2 g. of magnesium turnings, 45 cc. of bromobenzene and 100 cc. of ether. The ether was removed under diminished pressure and 35 cc. of dry toluene was then poured on the sirupy phenylmagnesium bromide; 15 g. of the ethyl 4-bromo-1-naphthalate dissolved in 50 cc. of dry toluene was added and the mixture gently refluxed for 4 hours. The reaction mixture was decomposed, the toluene layer separated and the toluene removed by steam distillation. The solid, slightly yellow carbinol thus obtained was dissolved in alcohol-free ether and converted directly into the carbinol chloride as described below. The yield of crude carbinol, based on the ester, was 60%.

The pure carbinol was obtained from the carbinol chloride by refluxing, for 45 minutes, a mixture of 8.2 g. of the pure chloride, 2.6 g. of dimethyl aniline, 50 cc. of acetone and 8 cc. of water. The reaction mixture was then freed from acetone and dimethylaniline hydrochloride. The carbinol was recrystallized from ether with the addition of a small amount of petroleum ether. It was obtained in the form of colorless crystals; m. p., 130°.

Analyses. Calc. for $C_{23}H_{17}OBr$: C, 70.95; H, 4.40; Br, 20.55. Found: C, 71.14; H, 4.37; Br, 19.71.

The Chloride.—A concentrated solution of the carbinol in absolute ether was saturated with hydrogen chloride, whereupon the carbinol chloride began to precipitate. After 24 hours the liquid was decanted from the crystals, the latter transferred to a Büchner funnel, washed with a small amount of absolute ether and then dried in a vacuum desiccator over sulfuric acid and soda lime. The chloride was further purified by recrystallization from benzene with the addition of an equal volume of low-boiling petroleum ether; m. p., 160–161°; it dissolves in concd. sulfuric acid, forming a deep green solution.

Analysis. Hydrolyzable Cl, Calc.: 8.7%. Found: 8.4%.

Reaction between Molecular Silver and the Carbinol Chlorides

The Radicals from *p*-Bromotriphenylcarbinol Chloride.—A number of tubes, each containing 1.000 g. of pure carbinol chloride, 3.0 g. of 20-mesh, molecular silver and 30 cc. of xylene, were rotated at room temperature for various periods of time.

A second series of tubes was prepared, identical with those described above with the exception that bromobenzene was used as a solvent instead of xylene, the latter having been used because of its comparatively low vapor pressure. After rotation for a definite period of time a tube from the first series was opened and the amount of silver halides was determined; a tube from the second series, rotated for an equal period of time, was placed in an apparatus designed for the measurement of absorbed oxygen.[14]

As the following table shows, the radical of the first order was formed quantitatively, after rotation for 20 minutes, and the solution of the radical absorbed approximately the calculated amount of oxygen. Upon further reaction of the silver the nuclear bromine was slowly removed with the gradual formation of the radical of the second order; the amount of oxygen, which the tubes were then capable of absorbing, gradually

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[14] Gomberg and Schoepfle, THIS JOURNAL, **39**, 1661 (1917).

decreased until a fairly constant value—$^1/_2$ of the amount found for the first radical—was obtained.

TABLE I

REMOVAL OF CARBINOL CHLORINE AND NUCLEAR BROMINE BY SILVER AND ESTIMATION OF CAPACITY OF THE RESULTING RADICALS FOR ABSORBING OXYGEN

Calculated absorption for Radical of the First Order, 31.2 cc.; for Radical of the Second Order, 15.6 cc.

Time rotated Hours	Halogen removed Atoms		Observed absorption of oxygen. Cc., N. T. P.	Time rotated Hours	Halogen removed Atoms		Observed absorption of oxygen. Cc., N. T. P.
	Cl	Br			Cl	Br	
$^1/_3$	0.97	0.01	33.2	48	1.01	0.36	17.2
1	0.96	0.01	31.8	72	1.00	0.46	15.0
4	0.98	0.08	27.8	1 week	0.98	0.48	16.0
12	0.96	0.12	24.6	2 weeks	1.05	0.48	15.4
24	0.98	0.27	20.6	3 weeks	1.01	0.51	14.8

***p*-Bromotriphenylmethyl Peroxide,** $[(C_6H_4Br)(C_6H_5)_2C]_2O_2$.—After the reaction mixture had rotated for 20 minutes, in absolute ether as a solvent and with exposure to the air, the peroxide was formed. It melted at 167° and was identical with the peroxide which is formed by the simultaneous action of silver and air on a solution of the carbinol chloride.[15]

The Carbinol Iodide.—A mixture of 1.000 g. of the carbinol chloride, 2.6 g. of silver and 30 cc. of benzene was rotated for 20 minutes. The mixture was then filtered, in an atmosphere of carbon dioxide, and titrated with a 0.1 *N* benzene solution of iodine. An equilibrium was established when 64% of the theoretical amount of iodine necessary to form the carbinol iodide had been added. A similar equilibrium has been found in the case of other triarylcarbinol iodides. That *p*-bromotriphenylcarbinol iodide had actually been formed was proved by the conversion of the reaction product into the chloride. Dry silver chloride was added and the mixture was shaken for several hours; *p*-bromotriphenylcarbinol chloride was isolated from the solution. $R_3C—I + AgCl \rightleftharpoons R_3C—Cl + AgI$.

Although a number of attempts were made to isolate the radical of the first and that of the second order in a crystalline state none of the experiments led to the desired result. Both radicals seemed to be characterized by great solubility in all solvents except low-boiling petroleum ether; from the latter solvent, however, products were obtained that absorbed oxygen to only a small extent.

The Radicals from *p*-Bromodiphenyl-1-naphthylcarbinol Chloride.—In this set of experiments absolute ether was used as a solvent instead of

TABLE II

REMOVAL OF CARBINOL CHLORINE AND NUCLEAR BROMINE BY SILVER, AND ESTIMATION OF THE CAPACITY OF THE RESULTING RADICALS FOR ABSORBING OXYGEN

Calculated absorption for Radical of the First Order, 27.4 cc.; for Radical of the Second Order, 13.7 cc.

Time rotated Hours	Halogen removed Atoms		Observed absorption of oxygen Cc., N. T. P.	Time rotated Hours	Halogen removed Atoms		Observed absorption of oxygen Cc., N. T. P.
	Cl	Br			Cl	Br	
$^1/_3$	0.97	0.04	25.8	24	1.00	0.39	16.4
$^1/_2$	1.03	0.03	26.5	48	0.98	0.45	..
1	0.96	0.12	24.5	72	0.96	0.48	13.2
$1^1/_2$	0.95	0.18	..	27 days	0.97	0.46	12.8
4	0.95	0.28	20.0	165 days	1.10	0.52	..
12	1.08	0.31	..				

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[15] Gomberg, *Ber.*, **37**, 1635 (1904).

xylene and the tubes containing carbinol chloride, silver and solvent were treated as previously described.

The radical of the first order formed a deep violet solution, while that of the second order was an indigo color.

Peroxide of the Radical of the First Order; *p*-Bromodiphenyl-1-naphthylmethyl Peroxide, $[(Br_6CH_4)(C_6H_5)(C_{10}H_7)C]_2O_2$.—The deep violet solution of the radical, obtained by rotating 1.00 g. of the carbinol chloride, 3 g. of 20 mesh silver and absolute ether for 20 minutes, was quickly decolorized upon exposure to air. The yields of peroxide from two experiments were 0.87 g. and 0.84 g., or 91% and 88%, respectively. The peroxide, which is crystalline, is only slightly soluble in organic solvents and is colored deep green by concd. sulfuric acid. It melts with decomposition at 146°.

Analyses. Calc. for $C_{46}H_{32}O_2Br_2$: C, 71.15; H, 3.93; Br, 20.60. Found: C, 71.32; H, 4.02; Br, 19.77.

Peroxide of the Radical of the Second Order, $[(BrC_6H_4)(C_{10}H_7)(C_6H_5)C—C_6H_4—C(C_6H_5)(C_{10}H_7)]_2O_2$.—For the preparation of this substance a tube containing 1.00 g. of the carbinol chloride, 3 g. of 40-mesh silver and dry carbon disulfide was rotated for 60 hours. Upon exposure of the indigo-colored solution to the air it turned red and finally orange and, after the solvent had evaporated spontaneously, a yellow, resinous material remained. For purification, the peroxide was redissolved in a small amount of carbon disulfide and precipitated by the addition of a small amount of low-boiling petroleum ether; in this way a cream-colored, flocculent substance was obtained. It was found impossible to obtain the compound in crystalline condition. The peroxide, when heated, undergoes a gradual decomposition which begins at about 120°. It dissolves in carbon tetrachloride and benzene and is insoluble in alcohol, acetone or ethyl acetate.

Analysis.[16] Calc. $C_{92}H_{64}O_2Br_2$: C, 81.16; H, 4.74. Found: C, 80.96; H, 5.92.

Attempts to Isolate the Radicals.—The intensely colored solution, known to contain only the free radical of the first order, was siphoned into the apparatus designed for use in the isolation of free radicals.[17] The solvent was removed at a low temperature under reduced pressure, and a gummy, indigo-blue residue was obtained. No spontaneous production of crystals could be obtained from a saturated solution of the radical; precipitating reagents likewise yielded only amorphous material. A solution of the amorphous substance absorbed a small amount of oxygen but complete decolorization did not take place.

Similar negative results were obtained in our attempts to isolate the radical of the second order.

The Radicals from Diphenyl-4-bromo-1-naphthylcarbinol Chloride.—A number of tubes, each containing 1.000 g. of the carbinol chloride, silver and solvent, were treated as previously described. In the tubes, used for the measurement of absorbed oxygen, bromobenzene was used, as before, for a solvent; for the silver halide determinations the carbinol chloride was dissolved in absolute ether.

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[16] The analytical results for bromine, obtained by the Carius method, were somewhat lower than those demanded by the above formula.

[17] Gomberg and Cone, *Ber.*, **37,** 2033 (1904). Ref. 14, p. 1659.

TABLE III

REMOVAL OF CARBINOL CHLORINE AND NUCLEAR BROMINE BY SILVER AND ESTIMATION OF THE CAPACITY OF THE RESULTING RADICALS FOR ABSORBING OXYGEN

Calculated absorption for Radical of the First Order, 27.4 cc.; for Radical of the Second Order, 13.7 cc.

Time rotated Hours	Halogen removed Atoms Cl	Br	Observed absorption of oxygen Cc., N. T. P.	Time rotated Hours	Halogen removed Atoms Cl	Br	Observed absorption of oxygen Cc., N. T. P.
$^1/_3$	0.93	0.00	25.6	12	1.01	0.35	. .
$^1/_2$	1.00	0.00	25.9	24	1.06	0.41	16.5
1	1.09	0.11	24.3	48	1.06	0.51	14.0
2	1.00	0.18	. .	72	0.99	0.48	14.2
4	1.08	0.27	20.5	27 days	0.98	0.49	14.0

Peroxide of the Radical of the First Order, $[(C_6H_5)_2(BrC_{10}H_6)C]_2O_2$.—The ether solution of the radical was brown-red with a tinge of green. Exposure of the solution to the air resulted in an instant decolorization, accompanied by peroxide formation. The yield of peroxide obtained from 1 g. of the carbinol chloride was 0.82 g. or 86%. The peroxide is insoluble in cold benzene and when heated darkens at about 148° and melts with decomposition at 153–154°.

Analysis. Calc. for $C_{46}H_{32}O_2Br_2$: Br, 20.60. Found: 20.13

Peroxide of the Radical of the Second Order, $[(BrC_{10}H_7)(C_6H_5)_2C—C_{10}H_6—C(C_6H_5)_2]_2O_2$.—The violet solution of the radical, obtained by rotating an ether solution of the carbinol chloride with silver for 48 hours, was decolorized at once upon exposure to air. The corresponding peroxide, which is quite soluble in ether, was precipitated to only a small extent; the bulk of the peroxide was obtained by allowing the solvent to evaporate spontaneously. This substance is a cream-colored, amorphous material and the color is changed to deep green by conc. sulfuric acid. In order to purify the substance for analysis it was dissolved in absolute ether and precipitated by the addition of low-boiling petroleum ether.

Analyses. Calc. for $C_{92}H_{64}O_2Br_2$: C, 81.16; H, 4.74. Found: C, 80.81; H, 5.25.

When heated, the compound turned black at about 135° and gradually melted with decomposition.

Reaction between Silver Salts and the Carbinol Chlorides

***p*-Bromo-triphenylcarbinol Chloride and Silver Sulfate.**—A number of sealed tubes, each containing 1.000 g. of the carbinol chloride, 3 g. of finely divided, thoroughly dried silver sulfate and 25 cc. of dry, acid-free nitrobenzene were prepared. Upon mixing the components a red solution was instantly formed. The tubes were rotated continuously, for a number of days, at a temperature of 50°.

After a definite period of reaction a tube was opened, the nitrobenzene solution filtered from the silver salts, and the amount of silver chloride and bromide in the latter was then estimated. The results of the silver halide analyses indicated to what extent the quinonoid sulfate (X) had been formed.

The highly colored, nitrobenzene solution was shaken with small amounts of 3% sodium hydroxide solution until the red color, due to the presence of the sulfate, had disappeared. Upon careful acidification of the alkaline extracts with acetic acid *p*-hydroxytriphenylcarbinol was obtained. The latter, after recrystallization from acetic acid, was isolated in the quinonoid modification.[18]

For further identification the colored carbinol was converted into the colorless, benzenoid form which was found to melt at 158–159°, as reported in the literature.

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[18] Gomberg, THIS JOURNAL, **35**, 1036 (1913).

Finally, the benzyl derivative, prepared from the carbinol, was found to be identical with the benzyl compound previously described.[19]

In one experiment an analysis of the silver halides showed that, in addition to all of the carbinol chlorine, 74% of the nuclear bromine had been removed; the yield of *p*-hydroxytriphenylcarbinol obtained in this instance was 70%.

It was found inadvisable to allow the reaction between the silver and the brominated carbinol chloride to proceed to completion. When the mixture was rotated long enough to remove all of the nuclear bromine, a red, alkali-soluble oil resulted; this consisted, in part, of decomposition products of the sulfate; *p*-hydroxytriphenylcarbinol could not be isolated from the mixture. This latter fact is not surprising since even the pure, crystalline *p*-hydroxytriphenylcarbinol, in the quinonoid modification, decomposes through auto-oxidation when kept for some time in a stoppered bottle.

_p_-Bromodiphenyl-1-naphthylcarbinol Chloride and Silver Sulfate.—A mixture of 1.000 g. of the carbinol chloride, 3 g. of silver sulfate and 15 cc. of nitrobenzene was rotated, at 50°, for 3 days. The red-brown solution was then filtered and the nitrobenzene removed by distillation with steam. The red residue was dried, dissolved in a small amount of benzene and precipitated by the addition of petroleum ether. The precipitate was washed with low-boiling petroleum ether and finally recrystallized from alcohol. The yellow crystals which were obtained melted at 168–170°. This compound proved to be phenyl-1-naphthylquino-methane,[20] $(C_6H_5)(C_{10}H_7):C:C_6H_4:O$.

Diphenyl-4-bromo-1-naphthylcarbinol Chloride and Silver Sulfate.—Upon mixing 1.000 g. of the carbinol chloride, 3 g. of silver sulfate and 15 cc. of nitrobenzene a very deep green solution was instantly obtained. After rotation for 65 hours, at 50°, the solution had turned deep violet in color. The mixture was filtered and the solvent was removed by distillation with steam. The deep red, solid residue was shaken for 12 hours with a solution of 1.5 g. of sodium hydroxide in 50 cc. of 50% alcohol. After filtration the filtrate was acidified with acetic acid. The precipitated material was extracted with chloroform and the latter was then allowed to evaporate spontaneously. Upon treatment of the resulting residue with a small amount of acetic acid an orange-yellow, crystalline material was obtained. This compound melted at 178–179° and was *p*-naphthofuchsone, $(C_6H_5)_2:C:C_{10}H_6:O$. When mixed with material prepared according to the literature,[21] the mixture melted at 179°.

In other series of experiments *p*-bromotriphenylcarbinol chloride in nitrobenzene solution was mixed with other silver salts, such as silver sulfite and silver nitrate. In each case intensely colored solutions resulted. Using silver sulfite a 68% yield of *p*-hydroxytriphenylcarbinol was obtained, thus proving that a quinonoid sulfite, entirely analogous to the sulfate, was formed as an intermediate product.

When silver nitrate was used, in the hope of obtaining a solution of the quinonoid nitrate, spontaneous decomposition of the resulting product took place, and only picric acid could be isolated.

This investigation was made with the assistance of The National Aniline and Chemical Company Fellowship. We wish to acknowledge our appreciation of the generous aid which has been given us.

Summary

1. *p* - Bromodiphenyl - 1 - naphthylcarbinol, diphenyl - 4 - bromo - 1 - naphthylcarbinol and the corresponding chlorides have been synthesized and described.

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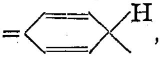
[19] Gomberg and Buchler, THIS JOURNAL, **45**, 211 (1923).

[20] Gomberg and Lang, *ibid.*, **42**, 1882 (1920).

[21] Gomberg and Sullivan, *ibid.*, **42**, 1867 (1920).

p-Bromophenyl-chrysofluorene has been prepared and its constitution proved.

2. It has been shown that prolonged reaction between *p*-bromotriarylcarbinol chlorides and excess of molecular silver, at ordinary temperature, results, in the first stage, in the removal of 1 atom of chlorine (carbinol chlorine); in the second stage, in the additional removal of $^1/_2$, and only $^1/_2$, of an atom of bromine (nuclear bromine). A formulation of the reaction has been given in this paper which explains not only the mobility of the nuclear bromine, but also gives a rational explanation of the removal of exactly $^1/_2$ of an atom, but no more, of the ring halogen. The explanation is based on the idea that the free radicals exist in 2 tautomeric modifications, benzenoid and quinonoid. According to this hypothesis, during the first stage of the reaction the radical of the "first order," $R_3C \rightleftharpoons$ $R_2C=$ , results; during the second stage, a radical of the "second order," $R_3C{-}C_6H_4{-}\underset{|}{C}R_2$, is produced.

3. It was shown that the absorption of oxygen by the compound, formed by the removal of the carbinol chlorine alone, is equal in amount to that calculated for a free radical R_3C-. Furthermore, it has been demonstrated that the substance which results from the elimination of both the carbinol chlorine and $^1/_2$ of an atom of bromine absorbs only $^1/_2$ of the above quantity of oxygen, that is a quantity of oxygen demanded by the more complex radical of the "second order."

The peroxides corresponding to the two types of radicals have been isolated and analyzed.

4. Prolonged reaction between any of the 3 carbinol chlorides and silver sulfate results, likewise, in the removal of both carbinol and nuclear halogen. In this instance 1 atom, and not $^1/_2$ of an atom, of ring halogen was eliminated from 1 molecule of the triarylcarbinol chloride. This fact, also, is in complete harmony with the assumption that the bromine is a part of a quinonoid nucleus.

5. The general conclusion is that in the colored triarylmethyls, as well as in the colored, salt-like derivatives of the triarylcarbinols, color and quinoidation are concomitant phenomena.

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