and reverting to selenic acid. All of the methods which are described in the literature for the preparation of nitrosyl sulphuric acid have been tried with selenic acid but all others than the method described have proven fruitless in our hands.

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MONOHALOGEN DERIVATIVES OF TRIPHENYLCARBINOL CHLORIDE.

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IT WAS shown by Gomberg[1] that the monohalogen derivatives of triphenylcarbinol chloride can be prepared from benzophenone dichloride and the corresponding phenyl halide by the Friedel and Crafts reaction. The position of the halogen was assumed to be the para. This was proven in the case of the monochlor compound by preparing it from the dichloride of *p*-chlorbenzophenone and benzene. We now undertook to condense in a similar way the dichloride from *p*-brombenzophenone with benzene in order to determine the position of the bromine in the monobrom compound. Very unexpected results were obtained. They were found to be due to an abnormal reaction of phosphorus pentachloride with the *p*-brombenzophenone. Recourse was had to Grignard's reaction, using both the methyl ester of *p*-brombenzoic acid and *p*-brombenzophenone as starting materials. The monobromtriphenylcarbinol chlorides from both of these materials were identical, and were, of necessity, the para-compound. The comparison of the carbinol chloride from the benzophenone dichloride and brombenzene by the Friedel and Crafts reaction with that obtained by Grignard's reaction showed the former to be also the *p*-compound.

1. *Preparation of p-Bromtriphenylcarbinol Chloride by the Friedel and Crafts Reaction,* $(p\text{-}BrC_6H_4(C_6H_5)_2CCl)$.[1]—A mixture of an excess of brombenzene (2-3 mol.) and benzophenone dichloride (1 mol.) was treated with a small quantity of aluminum chloride and heated until the reaction started. It was usually necessary to heat the mixture to about 115°. After the reaction was well started, the temperature was allowed to drop to 80°. The reaction was maintained smoothly at this temperature for several hours by frequent additions of aluminum chloride. The reaction

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[1] Ber. 37, 1633.

mixture was decomposed with ice and hydrochloric acid. After removing the excess of brombenzene by steam distillation, the oily layer was taken up in benzene and dried over calcium chloride. The benzene solution was saturated in the presence of solid calcium chloride with dry hydrochloric acid in order to convert the carbinol to the carbinol chloride. The benzene was distilled off, the last portions under diminished pressure. The residue was taken up in petroleum ether (70–80°) and purified with animal charcoal. Transparent, prismatic crystals of melting-point 111° C. separated on standing. Yield 55 per cent. of the theoretical.

2. *Preparation by Grignard's Reaction.*—The carbinol obtained by Grignard's reaction from *p*-brombenzoic methyl ester and the magnesium compound of brombenzene was changed into the carbinol chloride by dry hydrochloric acid gas. The purified product had a melting-point of 113.5°. The same carbinol chloride was also obtained by Grignard's reaction from *p*-brombenzophenone and the magnesium compound of brombenzene. The melting-point of this product was 114°. This compound was shown to be identical with the product of the Friedel and Crafts reaction by a series of derivatives.

p-Bromtriphenylcarbinol ($p\text{-}BrC_6H_4(C_6H_5)_2COH$). — The carbinol was prepared by dissolving 3 grams of the carbinol chloride in a mixture of glacial acetic and sulphuric acids (3:1)[1] with gentle heating to remove the hydrochloric acid liberated. The acid solution was poured with stirring into a large volume of water. The carbinol separated as a white flocculent precipitate and was extracted with ether. The ethereal extract was washed with sodium carbonate and then dried over fused sodium sulphate. After distillation of the ether, the residue was taken up in petroleum ether. For several weeks the carbinol showed no tendency to separate except as an oil, but on longer standing, it crystallized. After several crystallizations it melted at 74°.

p-Bromtriphenylmethyl Peroxide ($(p\text{-}BrC_6H_4(C_6H_5)_2CO)_2$.—The peroxide was prepared from the *p*-bromtriphenylcarbinol chloride by shaking a benzene solution of the latter with a solution of sodium peroxide.[2] The residue left by evaporation of the benzene solution was washed with ether, giving a peroxide melting at

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[1] Am. Ch. J. 25, 328.

[2] Ber. 33, 3155; 37, 1630.

167°. The peroxide is slightly soluble in ether and also in petroleum ether. Small quantities of the peroxide were recrystallized from both of these solvents. Melting-point 171.5–173.5°.

The analyses by Carius' method gave 22.69 and 23.52 per cent. Br. Calculated, 23.66 per cent.

p-Bromtriphenylmethylamine (p-$BrC_6H_4(C_6H_5)_2CNH_2$).[1] — The amide was formed by passing dry ammonia into a benzene solution of the carbinol chloride, filtering out the precipitate of ammonium chloride, and taking up the residue, left by distillation of the benzene, in petroleum ether. The crystals formed melted at 108.5–109°.

p-Bromtriphenylmethylaniline (p-$BrC_6H_4(C_6H_5)_2CNHC_6H_5$).[2] — A benzene solution of one molecule of *p*-bromcarbinol chloride was treated with two and a half molecules of freshly distilled aniline. The oil, left after the removal of the aniline hydrochloride and the benzene, was taken up in ether, in which it is rather insoluble. Crystals formed on concentrating the solution. These were carefully washed with ether to remove as much as possible the excess of aniline and then crystallized from petroleum ether, melting-point 148°.

An analysis gave the following results:

Calculated for p-$BrC_6H_4(C_6H_5)_2CNHC_6H_5$: N, 3.39 per cent. Found: N, 3.63 and 3.88 per cent.

3. *Action of Phosphorus Pentachloride on p-Brombenzophenone.*— As mentioned above, unexpected results were obtained in attempting to prepare *p*-monobromtriphenylcarbinol chloride by the action of benzene on the dichloride from *p*-brombenzophenone. These were finally found to be due to the abnormal action of phosphorus pentachloride on the *p*-brombenzophenone used in making the dichloride.

p-Brombenzophenone (p-$BrC_6H_4COC_6H_5$).[3]—Kollaritz and Merz[4] obtained a monobrombenzophenone of a melting-point of 81.5° by heating benzoic acid and brombenzene with phosphorus

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[1] Ber., 35, 1827.

[2] Ibid. 35, 1829.

[3] Richter in the "Lexikon der Kohlenstoffverbindungen," Supplement II, p. 255, gives an incorrect value (172°–173°) for the melting-point of *p*-brombenzophenone, and in Vol. II, p. 1302, gives Schafer's value (81.5°) for *p*-brombenzophenone as that of the meta compound.

[4] Ber. 6, 547.

pentoxide. Schafer[1] prepared it from *p*-brombenzoyl chloride and benzene by the Friedel and Crafts reaction. It can, however, be prepared much more easily and from cheaper materials by a method used in this laboratory for the preparation of *p*-chlorbenzophenone with nearly quantitative results. To a mixture of an excess of brombenzene (2-3 mol.) and benzoyl chloride (1 mol.) heated to 115°, some aluminum chloride was added to start the reaction. The temperature was then lowered to 80° as in the preparation of *p*-bromtriphenylcarbinol chloride. The reaction was maintained at this temperature for several hours with additions of small quantities of aluminum chloride. The reaction mixture was treated with ice and hydrochloric acid. The excess of brombenzene was removed by steam distillation. The light brown oily layer solidified on cooling. It was taken up in carbon disulphide, washed with sodium carbonate to remove any benzoic acid, and then dried. The solvent was evaporated and the residue purified by distillation *in vacuo*. The brombenzophenone distilled at 210° under 19–20 mm. as a colorless liquid which solidified to a pure white solid. The smallest yield was 65 per cent. while yields of 75–80 per cent. were usually obtained. The product is rather soluble in benzene and ether, and less soluble in petroleum ether and alcohol. It crystallizes from the last two solvents as needles, melting at 81.5–82°. A sample which melted at 81.5° was prepared from *p*-brombenzoyl chloride and benzene according to Schafer.[2]

Action of Phosphorus Pentachloride.—The *p*-brombenzophenone was mixed with 1.3 times the calculated quantity of phosphorus pentachloride required for the formation of a phenone dichloride. The mixture was heated in an oil-bath at 150° for five hours. The excess of phosphorus penta- and oxychlorides was removed and the residue distilled under diminished pressure. It distilled at 212–220° under 19 mm. This dichloride, assumed at first to be the pure parabrom compound, was mixed with several molecules of benzene and condensed by aluminum chloride at 90°. The carbinol chloride obtained on working up the reaction product crystallized as prismatic crystals very similar to the expected *p*-bromtriphenylcarbinol chloride. The melting-point of these was 95.5° and could be brought up finally as high as 97.5–98°,

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[1] Ann. 264, 152.

[2] Loc. cit.

while that of *p*-bromtriphenylcarbinol chloride from Grignard's reaction was 113.5° and from benzophenone dichloride and brombenzene by the Friedel and Crafts reaction was 111°. The carbinol obtained from the product crystallized readily in contrast to the *p*-bromtriphenylcarbinol and had a melting-point of 81.5° and, after many repeated recrystallizations, of 83.5°, while the *p*-bromtriphenylcarbinol from the carbinol chloride of Grignard's reaction melted at 74° and *p*-chlortriphenylcarbinol at 85°.

Analyses of the carbinol chloride for chlorine which could be obtained by hydrolysis, gave results which were much too high for a monobromtriphenylcarbinol chloride but which were considerably nearer to what would be expected from a monochlorcarbinol chloride. A sample of carbinol (m. p. 78°) was analyzed for total halogen by the sodium carbonate method.[1] The bromine was determined by heating the silver halide in a stream of dry chlorine gas:

Weight of substance taken. Gram.	Weight of silver halide. Gram.	Loss in weight after heating with Cl_2. Gram.	Calculated.		Found.	
			Bromine in $BrR'R_2COH$. Per cent.	Chlorine in $ClR'R_2COH$. Per cent.	Br. Per cent.	Cl. Per cent.
0.3909	0.1757	0.0198	23.59	12.05	9.1	5.83

This analysis and others of the carbinol and carbinol chloride showed that the product from the Friedel and Crafts reaction was not homogeneous but was a mixture of brom- and chlortriphenylcarbinol chlorides whose separation by crystallization was impossible. A blank experiment with a mixture of pure *p*-brom- and *p*-chlortriphenylcarbinol chlorides confirmed this view. The formation of the two monohalogen-triphenylcarbinol chlorides could only be explained by the action of phosphorus pentachloride on the *p*-brombenzophenone. The dichloride obtained from the *p*-brombenzophenone was saponified with sodium carbonate. The product obtained was crystallized several times from petroleum ether and alcohol. The melting-point varied from 73–76.5°. *p*-Chlorbenzophenone melts at 77–78° and *p*-brombenzophenone at 82°. A blank experiment with a mixture of pure *p*-chlor- and *p*-brombenzophenones showed that separation by crystallization was impossible and that the melting-point did not furnish a criterion of purity. Analyses of different samples of the saponified material were made with the following results:

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[1] Classen: "Ausgewählte Methoden der Analyt. Chem.," Vol. II, p. 763.

Weight of substance. Gram.	Weight of silver halide. Gram.	Loss of weight after heating in chlorine. Gram.	Calculated. Bromine in p-$BrC_6H_4COC_6H_5$. Per cent.	Calculated. Chlorine in p-$ClC_6H_4COC_6H_5$. Per cent.	Found. Bromine. Per cent.	Found. Chlorine. Per cent.
I. 0.5583	0.3725	0.0449	30.64	16.39	14.45	8.11
II. 0.3902	0.2666	0.0303	......	......	14.11	8.21
III. 0.4255	0.2882	0.0282	......	......	11.91	9.77
IV. 0.3404	0.2412	0.0211	......	......	11.14	11.04

To see if a complete change to a chlor-compound could be effected, the treatment of the *p*-brombenzophenone with phosphorus pentachloride was repeated, using twice the theoretical quantity of pentachloride necessary for replacement of both the oxygen and bromine. The mixture was heated at 150° for ten and one-half hours. The dichloride was saponified and analyzed (see IV of preceding table).

Evidently an equilibrium is reached and to secure complete conversion of the *p*-brombenzophenone to *p*-chlorbenzophenone, long heating with a large excess of the pentachloride would be required.

The replacement of bromine in the benzene ring due to the action of the phosphorus pentachloride is very exceptional. In this connection, it may be mentioned that it has been found in this laboratory that there is very slight, if any, replacement in *p*-dibrombenzophenone. There are several examples in the literature in which there has been a replacement of halogen in the benzene nucleus but we are not aware of one exactly analogous to this case.

R. Benedikt and M. v. Schmidt,[1] by treatment of tribromresorcinol with chlorine gas, obtained a monochlordibromresorcinol. Tribromphenol in hydrochloric acid suspension gave a mixture of chlorine and bromine derivatives which they were not able to separate. O. Srpek,[2] by action of chlorine on bromtoluene, obtained an impure *p*-brombenzylbromide which seemed to have both chlorine and bromine in the nucleus as well as in the side-chain. Kastle and Beatty[3] found that benzenedichlorsulphamide splits off chlorine in the light and under those conditions could replace bromine and iodine from several compounds, *e. g.*, from dibrombenzene, tribromphenol, etc. A. Eibner,[4] in attempting

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[1] Monatsh. 4, 604.

[2] Ibid. 11, 431.

[3] Chem. Centr. 1897, p. 578; Am. Ch. J. 19, 139.

[4] Ber. 36, 1, 1229 (1903).

to prepare addition products of chlorine and brombenzene, found that bromine was replaced, especially in the light. Silberstein[1] tried to make the chloride from the nitrate of the diazonium derivatives of *s*-tribromaniline and always obtained an insoluble perbromide. The solution always contained a mixture of chlor- and brom-derivatives. A. Hantzsch[2] found that diazonium chlorides of ortho- and para-di- and poly-brombenzene derivatives in alcoholic solution suffered replacement of bromine by chlorine. R. Wegscheider[3] found that by heating *s*-tribromaniline with concentrated hydrochloric acid at 200°, *s*-trichloraniline was formed. By treating *s*-trichloraniline with concentrated hydrobromic acid under similar conditions, he formed tribromaniline. In neither case did he secure complete conversion although he used 29 molecules of the hydrobromic acid and 26.6 molecules of the hydrochloric acid. Howitz and Witte,[4] by the action of strong hydrochloric acid on certain quinoline derivatives, obtained a change of chlorine for bromine.

4. *Preparation of m-Bromtriphenylcarbinol Chloride by Grignard's Reaction.*—The saponified benzophenone from the dichloride obtained from *p*-brombenzophenone melted usually at 76-77°. This corresponds closely to that of *m*-brombenzophenone (77°). At first it was thought that possibly a shifting of position had occurred. To ascertain if this were the case, *m*-bromtriphenylcarbinol was prepared by Grignard's reaction from the ethyl ester of *m*-brombenzoic acid. The *m*-brombenzoic acid was made from *m*-aminobenzoic acid by Sandmeyer's reaction and was esterified by passing dry hydrochloric acid gas into its absolute alcoholic solution. The ester was distilled *in vacuo* and then in air at 261.2°. The *m*-bromtriphenylcarbinol from Grignard's reaction was changed to the carbinol chloride with hydrochloric acid gas. The melting-point of the carbinol chloride was 67°.

In conclusion we wish to thank Prof. M. Gomberg, of this laboratory, for his many helpful suggestions during the carrying out of this work.

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[1] J. pr. Chem. [2] 27, 114 (1883).

[2] Ber. 30, 2, p. 2334.

[3] Monatsh. 18, 329 (1897).

[4] Ber. 38, 1260 (1905).

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