

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

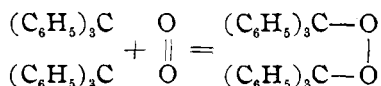
ON TRIVALENT CARBON.

(FOURTH PAPER.)

BY M. GOMBERG.

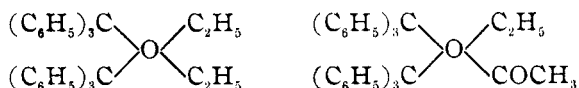
Received April 9, 1902.

It was shown in previous papers upon this subject that by the action of various metals upon triphenylchloromethane an extremely unsaturated hydrocarbon is produced, to which was assigned the constitution of triphenylmethyl, $(C_6H_5)_3C$. The hydrocarbon was found to unite very readily not only with atmospheric oxygen and with iodine, but also with a number of oxygen compounds, such as ethyl ether, acetic ester, etc. The simple oxygen compound was shown to possess the constitution of a peroxide, being formed by the direct addition of a molecule of oxygen to the unsaturated hydrocarbon:



This peroxide is a beautifully crystalline stable body, only very slightly soluble in the usual organic solvents, and shows none of the unsaturated properties of the original hydrocarbon. The ether and ester compounds, on the contrary, still possess the unsatura-

tion to the same extent as the hydrocarbon itself. Their solutions, when exposed to air, absorb oxygen almost as readily as triphenylmethyl itself, and also give the above-mentioned peroxide. The composition of these compounds was found to be 2 molecules of triphenylmethyl to 1 molecule of the ether or the ester. The theory was tentatively advanced¹ that the constitution of these bodies could best be explained by assuming the existence of tetravalent oxygen:



Experiments have since shown that this reaction of the hydrocarbon towards ethers and esters is quite general. Analogous compounds are formed with methylpropyl ether, ethylpropyl ether, methylbenzyl ether; with methyl acetate and other esters. Experimental data in favor of the existence of tetravalent oxygen were, at the time when the above formulas were proposed, very few. The principal support in favor of such a view was to be found in the physico-chemical studies of Brühl,² in the work of Collie and Tickle³ upon the oxonium bases of dimethylpyron, and in the azoxonium bodies of Kehrmann.⁴ Since the publication of my last paper, several important contributions in regard to the existence of tetravalent oxygen have been published. We should be quite justified at present, in the light of the recent work of Baeyer and Villiger,⁵ Werner,⁶ Walden,⁷ Büllow and Sicherer,⁸ and Kehrmann⁹ to consider the existence of tetravalent oxygen as entirely probable, and to employ this probability as a support of the view as to the constitution of the ether and ester compounds of triphenylmethyl. Still, even at present, it seems best to adhere to the original plan: to place the constitution of triphenylmethyl itself upon an experimental basis first; after that we can employ this extremely unsaturated body for a further study of the valency of oxygen, and perhaps that of other elements.

¹ This Journal, **23**, 501.

² *Ber. d. chem. Ges.*, **28**, 2847, etc.

³ *J. Chem. Soc.*, **75**, 710.

⁴ *Ber. d. chem. Ges.*, **32**, 2610; **34**, 1623.

⁵ *Ibid.*, **34**, 2679, 3612.

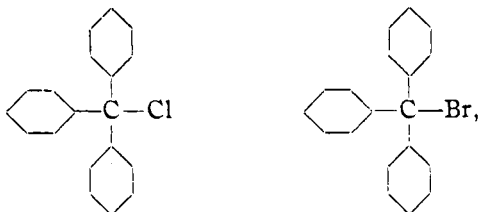
⁶ *Ibid.*, **34**, 3390.

⁷ *Ibid.*, **34**, 4185.

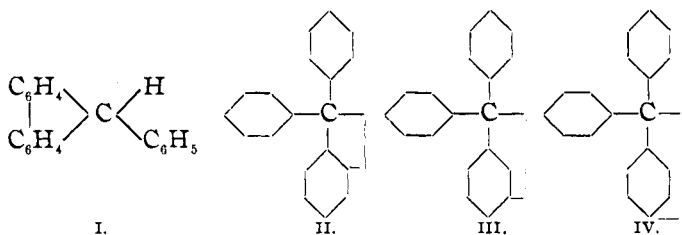
⁸ *Ibid.*, **34**, 3916.

⁹ *Ibid.*, **35**, 341, 343.

That the constitution of triphenylchloromethane and triphenylbrommethane is really as shown below,



there can be no doubt, as was again shown quite recently by Kehrmann.¹ It is well known that metals may act upon halogen compounds in either of the two ways: (1) the halogen alone may be removed, and then 2 radicals unite into 1 molecule; (2) the metal may induce the splitting off of a halogen acid, and thus give rise to an unsaturated body. If metals affect triphenylchloromethane in such a way as to cause the removal of hydrochloric acid then the constitution of the resulting body may be expressed by one of the following four formulas:



A substance possessing constitution I has been prepared some time ago by Hemilian,² and also by E. and O. Fischer,³ by the action of heat (250° C.) upon triphenylchloromethane. It is a stable, saturated hydrocarbon, and is different in every respect from the "triphenylmethyl" described by myself. Formulas II, III, and IV⁴ give no adequate explanation why the hydrocarbon should be so very unstable and unsaturated. Because of these considerations I expressed myself as follows⁵: "Should it be proved at some future time that the action of metals upon triphenylchloromethane results, after all, in the elimination of hydrochloric acid, the behavior of the hydrocarbon will best be explained by the constitution

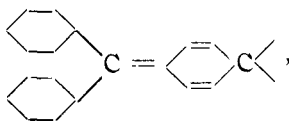
¹ *Ber. d. chem. Ges.*, **34**, 3818.

² *Ibid.*, **7**, 1208.

³ *Ann. Chem. (Liebig)*, **194**, 259.

⁴ Norris: *Am. Chem. J.*, **25**, 122.

⁵ *Am. Chem. J.*, **25**, 333.



involving the existence of bivalent carbon". Kehrman,¹ in a recent paper, seems to give preference to this constitution, without, however, advancing any new experimental proofs.

It has, however, been assumed by me all along that metals in this instance do not split off hydrochloric acid, but only the chlorine, giving as a result the free radical, triphenylmethyl, $(C_6H_5)_3C$. One of the reasons for this assumption was the fact that by the action of iodine upon the unsaturated hydrocarbon a body of the composition $(C_6H_5)_3CI$ was obtained. As the yield was very small, only a few qualitative tests were made, and little could be said with certainty as to the mechanism of its formation. The reaction has now been studied in detail, and it will be shown that if certain conditions are observed it is possible to obtain triphenyliodomethane almost *quantitatively*. The iodocompound is an extremely unstable body, and the isolation of it in the dry state is attended with great difficulties. It was therefore prepared in most instances only in solution in some organic solvent, and the solution was at once used up for the experiments. I have made a comparative study of the reactions of triphenylchloromethane and triphenylbrommethane on one hand, and triphenyliodomethane on the other, with the result that the latter was found to be absolutely identical in its chemical behavior with the former two. The following reactions were studied: 1. Amount of iodine taken up by the hydrocarbon; 2. Reaction of the iodocompound with ammonia; 3. Reaction with substituted amines; 4. Formation of perhalides; 5. Empirical composition of the iodocompound; 6. Formation of double salts with the halide salts of metals.

I. TITRATION WITH IODINE.

Preparation of the Hydrocarbon.—The triphenylmethyl was prepared in the following way: 20 grams of triphenylchloromethane are dissolved in thoroughly dried benzene, and about .10 grams of zinc in the form of turnings or sticks are added to the solution. All the air in the flask must be completely displaced by

¹ *Ber. d. chem. Ges.*, **34**, 3515.

dry carbon dioxide. The solution at once turns yellow, and the metal soon becomes coated with a number of small droplets of a dark viscous mass. This syrupy material is a compound, in the nature of a double salt, of triphenylchloromethane with the zinc chloride which has been formed in the reaction. In five to fifteen days, depending upon the amount of the surface of zinc exposed, the reaction is completed. About 15 grams of the chlorocompound are reduced to the triphenylmethyl, while about 5 grams combine with the zinc chloride, forming a compound which is insoluble in benzene and which is therefore no further attacked by the metal. The benzene solution of triphenylmethyl is siphoned off from the zinc and the precipitated double salt, and is concentrated to a small bulk under diminished pressure. All the air must be rigorously excluded throughout the whole operation. If now to the very concentrated benzene solution acetic ester be added the ester compound will separate in a very short time in transparent, colorless crystals. By the addition of ethyl ether instead of the ester, the corresponding ether combination may be similarly obtained. If, however, acetone is added then one of the following two things will happen: If the solution still contains about 15 cc. of benzene then the triphenylmethyl will separate in combination with benzene, although the latter has become diluted with a large quantity of acetone; but if care has been taken to drive off all, or nearly all, the benzene before the acetone is added then the pure triphenylmethyl is obtained as a colorless, granulated precipitate. This tendency on the part of the hydrocarbon to enter into combination with benzene has been noticed in other instances, when solvents other than acetone are added to a concentrated benzene solution of the triphenylmethyl. It is peculiar that the combination of the hydrocarbon with benzene is in the same proportions as in the case of the ether and ester compounds: 2 molecules of the triphenylmethyl to 1 of the solvent.

A sample of the benzene compound obtained by the addition of acetone as described above, furnished on analysis the following results:

0.379 gram substance gave 1.2930 gram CO_2 and 0.2250 gram H_2O .

	Calculated for $2(\text{C}_6\text{H}_5)_3\text{C} + \text{C}_6\text{H}_6$.	Found.
Carbon	93.56	93.00
Hydrogen.....	6.44	6.59

A portion, 1.622 grams, was heated for some time in a stream of carbon dioxide at 80°-90° C., and the loss amounted to 0.2100 gram.

	Calculated for $2(\text{C}_6\text{H}_5)_3\text{C} + \text{C}_6\text{H}_6$.	Found.
Loss, as benzene....	13.83	12.94

The escaping vapors were condensed in a freezing-mixture and were identified as benzene by the melting-point, the characteristic odor, and the smoky flame. In another instance, a combustion of the condensed liquid was made and the results proved beyond doubt that it was benzene.

For the preparation of the pure triphenylmethyl in all subsequent work the benzene solution of the hydrocarbon was evaporated to dryness and the dry crystalline residue was heated for an hour in a vacuum at 60°-80° C. To the residue warm acetone was added and the mixture was kept at a temperature of boiling acetone for one-half hour. On cooling, the crystalline mass was filtered, washed several times with acetone, and dried in a stream of carbon dioxide.

1.4600 grams were heated for two hours at 80° C., then for three hours at 90° C., and the loss amounted only to 0.0005 gram.

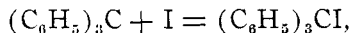
0.3307 gram substance gave 1.1310 gram CO_2 and 0.1851 gram H_2O .

	Calculated for $(\text{C}_6\text{H}_5)_3\text{C}$.	Found.
Carbon	93.74	93.28
Hydrogen.....	6.26	6.22

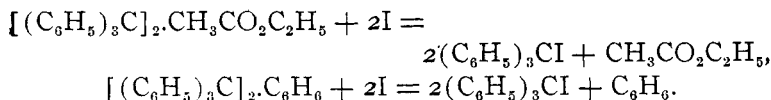
Triphenylmethyl when dry is a fairly stable substance. It may be exposed to air for a short time without danger of oxidation. It is white when freshly prepared, but soon turns pale yellow. It is soluble in benzene, carbon disulphide, only slightly soluble in acetone, and hardly at all in petroleum ether. While colorless itself, the solutions of triphenylmethyl are always yellow, no matter what solvent be employed. This phenomenon will be studied more fully later. The solutions of the hydrocarbon when exposed to air instantly become covered on the surface with a crystalline crust of the peroxide; in a short time the whole of the triphenylmethyl is converted into the oxidized product, and the supernatant liquid becomes colorless.

Titration.—Triphenylmethyl absorbs not only oxygen but also iodine. When a solution of the latter is added to that of the

former the iodine is absorbed instantly, the solution remaining pale yellow till nearly the end of the reaction. Many attempts have been made to make this a basis of a quantitative method for the estimation of the hydrocarbon, but owing to the instability of the triphenyliodomethane, only approximately quantitative results could be obtained. It will be seen from the reaction,



that the hydrocarbon requires 52.17 per cent. of its own weight of iodine for complete saturation. Similarly, when the acetic ester or the benzene compound are used for the titration it ought to proceed according to the equations



Accordingly, the ester compound should take up 44.2 per cent., and the benzene derivative 45 per cent. of iodine respectively for their complete saturation. The method of procedure was as follows: The substance to be titrated was placed in a flask from which all the air had been displaced by carbon dioxide. The substance was then either dissolved or just covered with a solvent, such as benzene, carbon disulphide, or petroleum ether, and a standard solution of iodine, from tenth-normal to half-normal, also in one of the above-mentioned solvents, was gradually added to the hydrocarbon. At the beginning, the halogen is taken up at once, the solution remaining pale yellow. After about 75-80 per cent. of the theoretical amount of the halogen has been added the absorption becomes noticeably slower and the solution grows darker in color; any further addition of halogen above 80-85 per cent. only tends to deepen the color. A large number of experiments were made in order to determine the cause why the reaction does not proceed smoothly to the end. Of the several explanations which have been thought of in this connection the following may be mentioned here as appearing, for the present, the most plausible: The triphenyliodomethane which is formed during titration is an exceedingly unstable body; when in solution it rapidly breaks down, being quite readily affected by light, and completely decomposed by atmospheric oxygen. When, in titration, about four-fifths of the triphenylmethyl is converted into the halogen derivative an equilibrium is apparently established; beyond this point any further

formation of the iodocompound will be checked by a corresponding decomposition with liberation of iodine.

The study of this halogen compound involves a great many difficulties, and anything like quantitative results can only be obtained by observing the strictest precautions, especially in regard to the exclusion of oxygen from the apparatus. In the following table is given a summary of the results obtained in this part of the work. The amounts of iodine indicated are those added until the pale yellow solution of the hydrocarbon just began to turn darker in color.

Substance employed.	Solvent.	Amount of substance. Grams.	Quantity of iodine taken up. Grams.	Per cent. of iodine taken up.	Per cent. of iodine required by theory.	Per cent. absorbed as compared with the theoretical amount.
Acetic ester compound } Acetic ester compound } Acetic ester compound }	Benzene	5.1200	1.8132	35.41	44.20	80.10
Acetic ester compound } Acetic ester compound }	Benzene	2.9500	0.9967	33.78	44.20	76.50
Acetic ester compound }	Benzene	2.8500	1.0014	35.21	44.20	80.00
Benzene compound } Benzene compound }	Benzene	1.3640	0.4760	34.17	45.00	77.50
Benzene compound }	Carbon disulphide	2.0900	0.8252	39.00	45.00	86.70
Triphenylmethyl }	Benzene	1.7380	0.6955	40.00	52.17	76.70
Triphenylmethyl }	Benzene	2.0540	0.8620	42.00	52.17	80.40
Triphenylmethyl }	Benzene	1.5150	0.6275	41.41	52.17	79.40
Triphenylmethyl }	Carbon disulphide	1.5650	0.6874	43.92	52.17	84.10
Triphenylmethyl }	Carbon disulphide	1.7060	0.7375	42.65	52.17	81.70

The table clearly shows that under the conditions above described about four-fifths, or somewhat more, of the hydrocarbon can be titrated without difficulty. All the solutions of the triphenyliodomethane obtained as given in the above table were at once used up for further experiments to be described below. In nearly every instance there was obtained some peroxide, which points to an incomplete saturation in the titration. Results considerably nearer to quantitative were obtained later in the work,

in the preparation of triphenyliodomethane in the dry state. The triphenylmethyl was covered with petroleum ether and warmed on the water-bath. To the warm mixture a standard solution of iodine in the same solvent was slowly added. The titration has to be carried on slowly, so as to prevent the separation of the triphenyliodomethane through the addition of the cold iodine solution. The end-reaction can be recognized fairly well. 2.3700 grams of triphenylmethyl took up 1.0342 grams iodine, which represents 83.60 per cent. of the theoretical amount. In working up this solution for triphenyliodomethane there was also separated nearly 0.300 gram of a mixture of the peroxide and some other body. By deducting this from the original 2.3700 grams, we see that the amount of absorbed iodine would be equivalent to 96 per cent. of the amount required by theory. In another instance, 2.4900 grams required 1.0710 grams iodine, or 82.4 per cent. of the theoretical amount. By subtracting 0.350 gram of non-halogen product found on working up the reaction mixture, we find that the amount of iodine actually taken up represents again almost 96 per cent. of the amount required by theory for pure triphenylmethyl. Further study of this question is necessary.

2. REACTION WITH AMMONIA.

It was shown by Elbs,¹ and by Heimilian and Silberstein,² that triphenylbrommethane reacts with ammonia and gives triphenylamine. The same reaction was carried out by Nauen³ on triphenylchloromethane. I find that triphenyliodomethane reacts at *ordinary* temperature with ammonia, and the yield of the amine compound is almost quantitative.

4 grams of the acetic ester compound of triphenylmethyl were dissolved in benzene, and iodine added as described under titration. 1.4960 grams of the halogen were added. The solution was then placed in ice-water and dry ammonia was passed into the solution of the halogen compound. The separation of ammonium iodide began with the first few bubbles of the gas. The ammonium iodide was filtered off, the benzene solution concentrated to a small bulk, and to that alcohol was added. On cooling, the triphenylaminomethane crystallized almost pure, containing a small

¹ *Ber. d. chem. Ges.*, **17**, 703.

² *Ibid.*, **17**, 741.

³ *Ibid.*, **17**, 442.

amount (0.150 gram) of the triphenylmethyl peroxide. It melted at 102° C., and agreed in every respect with the amine obtained from triphenylchloromethane in a parallel experiment. The yield was 2.6 grams, which represents 85 per cent. of the quantity required by theory. The calculation of the theoretical quantity of this and of the other amines must be made, of course, not upon the basis of triphenylmethyl used in the experiment, but only upon the amount of iodine added, because this alone determines the amount of triphenyliodomethane which is available in the reaction. For analysis, the amine was recrystallized from dilute alcohol.

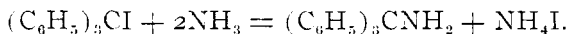
0.2090 gram substance gave 0.6762 gram carbon dioxide and 0.1186 gram water.

0.2825 gram substance gave 14.9 cc. nitrogen at 23.5° C. and 748 mm.

	Calculated for (C ₆ H ₅) ₃ C.NH ₂ .	Found.
Carbon	87.97	88.24
Hydrogen	6.63	6.31
Nitrogen	5.41	5.71

In another experiment 2.09 grams of the benzene compound of triphenylmethyl took up 0.8252 gram iodine and gave 1.995 grams of the almost pure amine, while the calculated quantity should have been 2.005 grams. One recrystallization from ether sufficed to furnish an absolutely pure product.

For further identification of the amine, the hydrochloride of it was prepared, which, on boiling with water, was converted into triphenylcarbinol, just as is the amine obtained by Elbs from triphenylbrommethane. The platinum double salts of the two amines were compared and were also found to be identical. There can be no doubt that the reaction above described takes place quantitatively according to the equation



3. REACTION WITH SUBSTITUTED AMINES.

Triphenylchloromethane and triphenylbrommethane¹ react not only with ammonia but also with substituted amines, and give the corresponding substituted triphenylaminomethanes. The iodo-compound obtained by the addition of iodine to the unsaturated hydrocarbon behaves in every way similarly. It gives the identical substituted amines. While the reaction takes place quite readily

¹ Elbs: *Loc. cit.*; Hemilian: *Loc. cit.*

and with good yield, with all the amines tried, by far the best results were obtained with para-toluidine. In this latter case the product obtained is at once pure, and the yield is as nearly quantitative as could be desired.

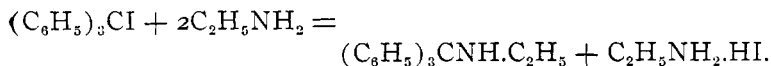
Triphenylmethylethylamine, $(C_6H_5)_3C.NH(C_2H_5)$. — 2.850 grams of the acetic ester compound of the hydrocarbon absorbed 1.001 grams of iodine. To this solution a little more than the theoretical amount of ethylamine in benzene was added. The reaction took place at once. On concentrating the filtered benzene solution of the amino-compound the latter separated as an oil which did not solidify until after several days' standing in a vacuum desiccator. The amine was dissolved in absolute ether, and precipitated as the hydrochloride by means of dry hydrochloric acid gas. In order to obtain the free base the salt was finely broken up under dilute alcoholic ammonia, filtered, washed with dilute alcohol and with water, and dried. Obtained in this way it is a white granular powder. When dissolved in any solvent it shows a great tendency to separate as an oil, which begins to crystallize only after some standing, or on introducing a crystal of the substance into the solution. When purified in this way it gives a melting-point of $75^\circ-77^\circ$ C. It behaves in every way as the simple triphenylaminomethane. It forms salts which suffer partial hydrolysis when dissolved in water, and which on boiling are completely decomposed with formation of triphenylcarbinol.

0.2995 gram substance gave 14 cc. nitrogen at 19° C. and 745 mm.

	Calculated for $(C_6H_5)_3CNH(C_2H_5)$.	Found.
Nitrogen.....	4.91	5.34

A sample of the same ethylamine compound was also prepared from pure triphenylchloromethane, and this was found to be absolutely identical with the one obtained from the iodo-compound in all its reactions, as well as in the tendency to separate from solvents in the form of an oil.

In the formation of this amine the reaction therefore proceeds as follows:



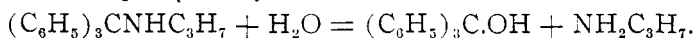
Triphenylmethylpropylamine, $(C_6H_5)_3C.NHC_3H_7$. — This body was prepared in a manner analogous to that which furnished the

ethylamine derivative. It, also, possesses the tendency to remain oily. After standing in a vacuum desiccator for some time the oil solidifies to a solid crust of crystals. These can be purified by spreading them out upon a porous plate and washing first with petroleum ether, then with a little alcohol. The substance melts at 70° C.

0.2230 gram substance gave 11.5 cc. N at 27° C. and 741 mm.

	Calculated for (C ₆ H ₅) ₃ CNHC ₃ H ₇ .	Found.
Nitrogen.....	4.65	5.06

The hydrochloride is easily formed by passing dry hydrochloric acid gas into an ethereal solution of the base. On boiling the base or the salt with dilute hydrochloric acid it decomposes, and triphenylcarbinol is produced, a reaction which is common to all the amines of triphenylmethyl,



Triphenylmethylamylamine, (C₆H₅)₃C.NH(C₅H₁₁).—Amylamine acts upon the iodine compound apparently somewhat slower than the other amines mentioned, and the reaction is best hastened by gentle heat. The substance was obtained as an oil, and all attempts to bring it to crystallization have failed. It was therefore analyzed in the form of its hydrochloride, which was prepared in the same way as the salts of the other bases here described. The oil itself was also analyzed and gave results which indicate that it was pure triphenylpropylamine.

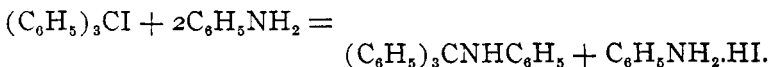
0.2300 gram substance gave 9.1 cc. N at 25° C. and 740 mm.

	Calculated for (C ₆ H ₅) ₃ CNHC ₅ H ₁₁ .	Found.
Nitrogen.....	4.20	4.29

The oil was boiled with dilute hydrochloric acid, and the triphenylcarbinol obtained was of such purity as to require no further treatment for analysis. It melted as obtained at 159° C. Consequently the oil was pure triphenylmethylamylamine.

Triphenylmethylaniline, (C₆H₅)₃C.NH(C₆H₅).—The reaction with aniline is very smooth; the resulting amine is produced in almost quantitative yield and is easily obtained pure. The experiment was repeated several times, and in no case was there noticed the formation of any other products than that of the aniline base and of some triphenylmethyl peroxide. In several instances the amount of aniline hydriodide formed in the reaction was also

determined, and was found to correspond exactly to the quantity of iodine added in the formation of the triphenyliodomethane. The yield of the aniline base, as well as that of the aniline salt, leaves no doubt that all the iodine added to the triphenylmethyl is used up in the formation of triphenyliodomethane, and that the reaction with aniline proceeds strictly according to the equation



In one experiment there was formed 14.5 grams of the crude aniline base while the amount required by theory was 16 grams. The product was divided into several portions and each purified by recrystallization from different solvents. The resulting products were all found to be identical, all melting at the same temperatures, namely at 149°-150° C. As Elbs gives the melting-point for the aniline base which he obtained from the triphenylbrommethane as 146° C., and as Hemilian gives it as 144.5° C., I prepared a sample of triphenylmethylaniline from carefully purified triphenylchloromethane, and found that it melts at 149°-150° C.

In another experiment 12 grams of the acetic ester compound of triphenylmethyl absorbed 4.3 grams iodine, and gave 9 grams of the aniline body. The latter was dissolved in ether and filtered in order to remove the small amount of triphenylmethyl peroxide mixed with the aniline base. On the addition of alcohol to the concentrated ethereal solution the triphenylmethylaniline crystallized in snow-white little prisms, possessing a melting-point of 148° C. The yield was 6.5 grams.

0.4607 gram substance gave 1.5010 grams CO₂ and 0.2697 gram H₂O.

0.4395 gram substance gave 17 cc. N at 22° C. and 729 mm.

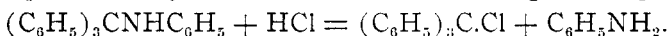
0.3115 gram substance gave 12.2 cc. N at 19° C. and 742 mm.

	Calculated for (C ₆ H ₅) ₃ C.NH.C ₆ H ₅ .	I.	Found.	II.
Carbon	89.53	89.98
Hydrogen	6.26	6.40
Nitrogen	4.18	4.25	4.25	4.27

The base obtained from the iodo-compound agreed in every respect with that made from the corresponding chlor- and brommethane. On treatment with amyl nitrite it gave the nitroso derivative which, when heated slowly, was found to melt at 156° C., as given by Elbs.¹

¹ *Ber. d. chem. Ges.*, 17, 704.

Hemilian and Silberstein¹ state that when a benzene solution of triphenylmethylaniline is treated with hydrochloric acid gas it is decomposed even by the first few bubbles according to the equation



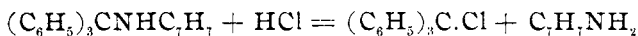
This is correct in so far as a benzene solution of the base is concerned. But, curiously enough, if the benzene is diluted with absolute ether, or better still, if ether alone is employed as a solvent, then there is hardly any decomposition,—the base separates quantitatively as the hydrochloride salt. By this means the base can be readily and completely freed from the accompanying non-basic impurities.

Triphenylmethyl-o-toluidine, $(C_6H_5)_3C.NHC_6H_4CH_3$.—On the addition of orthotoluidine to a freshly prepared solution of triphenyliodomethane the reaction takes place at once. The hydriodide of the toluidine separates readily in the form of fine silky needles. On the addition of alcohol to the concentrated benzene solution the base is precipitated as an oil, which, however, soon changes to a crystalline mass. The crystals are dissolved in chloroform and separated by filtration from a little insoluble triphenylmethyl peroxide. On the addition of alcohol to the concentrated chloroform solution the triphenylmethyltoluidine crystallizes out pure, the crystals melting at 140° C., while the absolutely pure substance should melt at 142° C. The yield is about 80 per cent. of the calculated quantity. In one experiment, the base was obtained in a very pure state by precipitating the original benzene solution by means of ether instead of with alcohol, the subsequent purification being the same as before,—from a mixture of chloroform and alcohol.

0.2318 gram substance gave 8.9 cc. at 16.5° C. and 745 mm.

	Calculated for $(C_6H_5)_3CNH(C_6H_7)$.	Found.
Nitrogen.....	4.01	4.22

The preparation of the salts of this base is accompanied with very great difficulties, as has already been noticed by Elbs. In this respect this body behaves differently from the aniline compound. Hydrochloric acid gas decomposes quantitatively not only a benzene solution, but also an ethereal solution of the toluidine body:



¹ *Ber. d. chem. Ges.*, **17**, 747.

Triphenylmethylmetatoluidine, $(C_6H_5)_3C.NH(C_6H_4CH_3)$, is formed when metatoluidine is added to a solution of triphenyliodomethane. The reaction is, however, much slower than in the formation of the above-described amines. The purification of the base cannot be done without considerable loss of material, as it is quite soluble in the usual solvents.

Triphenylmethylparatoluidine, $(C_6H_5)_3C.NH(C_6H_4CH_3)$.—Of all the amino-compounds tried, paratoluidine furnished the most satisfactory results. The product is very easily obtained pure, and the yield is fully 90 per cent. of the theory.

5.12 grams of the acetic ester compound of triphenylmethyl required for apparent saturation 1.8132 grams of iodine. 5 grams of para-toluidine in benzene were added to the solution of the iodo-compound; the reaction took place at once, at ordinary temperature. The toluidine hydriodide was removed by filtration, washed with benzene, dried, and weighed. The quantity found was 3.2 grams, while the calculated amount should have been 3.35 grams. The benzene solution was concentrated under reduced pressure, and to the residue a mixture of alcohol and ether was added. As triphenylmethyl-*p*-toluidine is only sparingly soluble in either of those two solvents it crystallized out at once pure, leaving the excess of toluidine in solution. The yield of the base was 4.55 grams, while the quantity calculated from the amount of iodine added should have been 5.003 grams; the actual yield, therefore, of the pure product was 90 per cent. of the theory. In a second experiment, 4 grams of the toluidine base were obtained, against 4.4 grams as calculated, which is equivalent to 91 per cent. of the theory.

For analysis the substance can be recrystallized from ether, or from a mixture of chloroform and alcohol. By either method it can be obtained in beautiful large transparent crystals, melting, as given by Elbs, at 177° - 178° C.

0.3138 gram substance gave 1.0329 gram CO_2 and 0.1898 gram H_2O .

0.4496 gram substance gave 15.6 cc. nitrogen at 25° C. and 735 mm.

0.4617 gram substance gave 18.6 cc. nitrogen at 26° C. and 716 mm.

	Calculated for (C ₆ H ₅) ₃ CNHC ₇ H ₇ .	Found.	
		I.	II.
Carbon	89.39	89.77
Hydrogen	6.65	6.71
Nitrogen	4.01	4.31	4.25

4. FORMATION OF PERHALIDES.

It was reported by me¹ some years ago that on the addition of iodine to a solution of triphenylbrommethane a periodide is formed. The body possessed the appearance and properties of the periodides of organic bases. The analyses led me to the conclusion at that time that the composition of the body was (C₆H₅)₃CBr.I₄. I also described² a perbromide, the composition of which was found to be (C₆H₅)₃CBr.Br₅. Nef³ reported that he got a perbromide of a composition similar to the periodide. As no figures of analysis are given by him it was to be interpreted⁴ that he had a tetrabromide, (C₆H₅)₃CBr.Br₄. In analyzing the periodide which was made from triphenyliodomethane it was found that it had the composition (C₆H₅)₃Cl.I₅. I have, therefore, decided to go over the whole work on the perhalides of triphenylmethane. It may be now considered established that there is a strict uniformity in composition in all these substances—they are all pentahalides.

Triphenylbrommethane Pentabromide, (C₆H₅)₃CBr.Br₅.—Triphenylbrommethane is dissolved in as little chloroform as possible and the calculated quantity of bromine is added. On cooling, the perbromide separates in dark orange crystals. These are rapidly filtered off, dried on a porous plate in soda-lime desiccator, and are analyzed at once. The total bromine was estimated by Carius' method; the "perbromine" was estimated by suspending weighed amounts of the perhalide in a solution of potassium iodide in water, adding some chloroform, and titrating the iodine set free by the "perbromine". Several samples were analyzed.

0.5569 gram substance gave total 0.8935 gram AgBr.

0.2712 gram substance gave 0.1548 gram perbromine.

0.3121 gram substance gave 0.1761 gram perbromine.

	Calculated for (C ₆ H ₅) ₃ CBr.Br ₅ .	Found.	
		I.	II.
Total bromide	66.42	67.23
Perbromine	55.32	55.04	56.4

¹ This Journal, 20, 790.

² *Ibid.*, 20, 1776.

³ *Ann. Chem. (Liebig)*, 308, 304.

⁴ Beilstein: Ergänzungsband II. 127.

The perbromide is very unstable, losing bromine very readily, even in a desiccator, the residue consisting of pure triphenylbromomethane. It can, however, be kept without decomposition for a considerable length of time in a tightly closed bottle.

Triphenylbrommethane Pentiodide, $(C_6H_5)_3CBrI_5$.—This can be prepared by the addition of the calculated quantity of iodine dissolved in benzene to a solution of triphenylbrommethane. The periodide separates as an oil which in a few seconds becomes crystalline. The yield is usually from 75 to 80 per cent. of the calculated quantity. The periodide is much more stable than the corresponding perbromide. It can be kept in a desiccator for days without any appreciable loss of iodine. It is only slightly soluble in benzene and in carbon disulphide, is quite soluble in ether, probably with decomposition. All the iodine can be titrated with standard thiosulphate solution in water, the bromide being at the same time converted into the carbinol.

The total halogen was estimated by reducing the perhalide in ether by means of a dilute solution of sulphurous acid in water, making the solution slightly alkaline, and then boiling the mixture for one-half hour in order to insure the complete conversion of the bromide into the carbinol. The solution of the sodium iodide and bromide is filtered from the carbinol and the total halogen estimated with silver nitrate. A large number of samples of this body were prepared under slightly varying conditions, in order to ascertain positively its composition. The best results were obtained by adding a *warm* solution of iodine to a *warm* solution of the bromide. Either benzene or carbon disulphide may be used as a solvent.

I. Sample from benzene:

- 0.6930 gram substance gave 0.4523 gram iodine.
- 0.6085 gram substance gave 0.3975 gram iodine.
- 0.7895 gram substance gave 1.1015 grams $AgBr + AgI$.

II. Sample from carbon disulphide:

- 0.5000 gram substance gave 0.3312 gram iodine.
- 0.4210 gram substance gave 0.2739 gram iodine.
- 0.4455 gram substance gave 0.2917 gram iodine.
- 0.6550 gram substance gave 0.9125 gram $AgBr + AgI$.

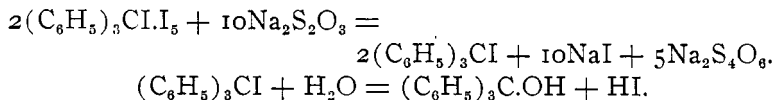
	Calculated for (C ₆ H ₅) ₃ CBr.I ₅ .	Found.				
		I.		II.		
Iodine ...	66.25	65.25	65.43	66.20	65.05	65.48
Bromine .	8.41	7.90	7.85

The periodide is of a dark blue iridescent color. It melts at 92° C. It is quite probable that triphenylbrommethane may also give rise to lower periodides. The one reported by me as the tetraiodide was described as having a melting-point of 121° C.; and I once came across a periodide, also at this time, which melted at 120° C.

That we have here a true periodide of triphenylbrommethane, and that iodine did not replace bromine, is proved by the following two facts: First, some of the periodide was heated at 70°-80° C. until all the iodine was driven off; the residue was recrystallized from petroleum ether, and the product was found to be pure triphenylbrommethane. Second, some of the periodide was dissolved in ether and the solution was shaken with molecular silver until the color of iodine had just disappeared; on concentrating the filtered ethereal solution and recrystallizing the residue, pure triphenylbrommethane was again obtained.

Triphenyliodomethane Pentiodide, (C₆H₅)₃I.I₅.—This periodide is formed just as readily, if not more so, as the one described above. Indeed, it is even liable to be formed to some extent when triphenylmethyl is being titrated with iodine, unless the latter is added slowly. The hydrocarbon, or the ester or ether derivative of it, is dissolved in benzene or in carbon disulphide, and a solution of iodine in the same solvent is added until the end-reaction of the titration is reached. The solution is now gently warmed and more iodine is slowly added, with constant stirring, until the whole of the calculated amount is introduced. The periodide separates in fine shining needles, dark blue in color, and cannot be told by its appearance from the periodide of triphenylbrommethane. It is filtered, washed with a little benzene, and dried in a vacuum desiccator. Unlike the hydrocarbon, or the normal triphenyliodomethane, the periodide is stable, and can be exposed to dry air without fear of oxidation. The yield of the pure product is from 75 to 80 per cent. of the calculated amount, one part of triphenylmethyl furnishing three times its weight of the periodide. It melts at 90° C.

The total halogen is estimated, according to the method described under the periodide of the triphenylbrommethane, by reducing with sulphurous acid and precipitating with silver nitrate. If the periodide is dissolved, or merely suspended in ether and titrated with a standard solution of sodium thiosulphate, it will be found that of the *six* atoms of iodine only *five* can be titrated. This fact is very important, because it definitely proves that of the several atoms of iodine present in the molecule there is *one* that has an entirely distinct function, and this function corresponds to that of the bromine in triphenylbrommethane. Here again the titration must therefore be represented by the following equations:



A few of the many analyses made will be given here.

0.5470 gram substance gave 0.7655 gram AgI.

0.5450 gram substance gave 0.3592 gram iodine by titration.

0.8805 gram substance gave 0.5788 gram iodine by titration.

0.4855 gram substance gave 0.6755 gram AgI.

0.7340 gram substance gave 0.4754 gram iodine by titration.

0.7700 gram substance gave 1.0650 grams AgI.

0.5680 gram substance gave 0.3651 gram iodine by titration.

	Calculated for (C ₆ H ₅) ₃ CI.I ₅ .	Found.			
		I.		II.	
Total iodine.....	75.79	75.65	75.18	75.10
Titrated iodine....	63.36	65.91	65.74	64.77	64.40

The carbinol formed in the reduction was identified by the melting-point, crystalline form, and by elementary analysis as such. Estimations of the yield of the carbinol gave results very close to those required by the equation.

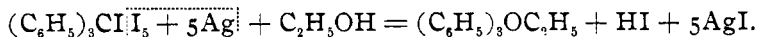
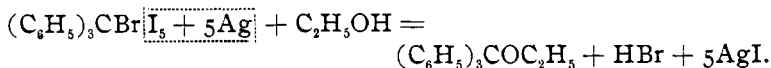
It will be noticed from the figures of analysis that in all instances the titrated iodine was a little too high. This was puzzling, especially in view of the fact that the total halogen was always a little too low. The cause of this discrepancy was finally discovered to lie in the disturbing influence of the ether which is added in the titration. When either of the periodides is titrated with thiosulphate there is produced, at the early stages of the titration, triphenylbrommethane or triphenyliodomethane, and these form a coating over the crystals of the periodide; the further

action of the thiosulphate is in this way hindered. For this reason ether or some other solvent was added to keep the reduction products in solution. Triphenylbrommethane is affected by cold water only slowly, while the iodide is rapidly hydrolyzed, giving rise to the triphenylcarbinol and hydriodic acid. It is a well-known fact that in presence of certain substances hydriodic acid is far more affected by light than when pure. Pinnow¹ recently showed that small quantities of quinine and acridine sulphate exert a very appreciable effect upon the rate of oxidation of hydriodic acid solutions in water on exposure to light. I find that ether also, greatly accelerates the oxidation. 50 cc. of a 0.5 per cent. solution of hydriodic acid, to which 15 cc. of ether were added, were exposed to ordinary diffused daylight for five minutes; almost 15 mg. of iodine were liberated in that short time. It is due, no doubt, to this influence of the ether present during the titration that high results are obtained in the case of triphenyliodo-periodide, while in the titration of the periodide of the brom-compound, ether has but little effect, as the solution remains nearly neutral till the end of the operation. Other immiscible solvents, such as chloroform, carbon disulphide, etc., also exert a marked influence upon the rate of oxidation. It seems therefore quite probable that the cause of this influence lies in the greater solubility of the iodine in the organic solvent than in water. The equilibrium being thus disturbed, more hydriodic acid will be oxidized.

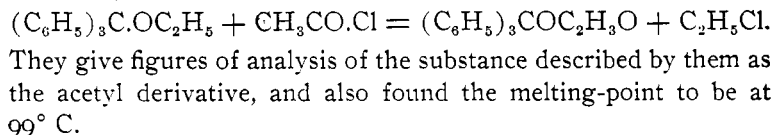
Reactions of the Two Periodides. (1) With Water.—In this respect the two periodides behave absolutely alike. It has already been mentioned that during titration with sodium thiosulphate the triphenylcarbinol is formed. The same result can be reached without the use of any reducing agent, simply by boiling the periodides with water. Reduction of the iodides with a dilute solution of sulphurous acid, as described under the estimation of the total halogen, gave especially good results, the carbinol in both instances being formed quantitatively, and requiring no further purification. The carbinol was identified by its characteristic crystalline form and its melting-point (161° - 162° C.) as well as by elementary analysis. There can be no doubt that in so far as the reaction with water is concerned the two periodides show exactly the same behavior.

¹ *Ber. d. chem. Ges.*, **34**, 2528.

(2) *Reaction with Alcohols.*—When triphenylbrom- or triphenyliodoperiodide is boiled with alcohol, and the excess of the iodine liberated in the reaction is removed by means of a solution of potassium iodide in water, the residue is triphenylmethane.¹ This formation of the hydrocarbon is not a result of the action of alcohol alone, but is caused by the hydriodic acid resulting from the interaction of the iodine and alcohol. This was established first, by a blank experiment with hydriodic acid and triphenylbrommethane; and second, by the following experiment, formed on each of the two periodides separately: The periodide was suspended in absolute alcohol, and to the solution small amounts of zinc dust were added, with constant stirring, until all the iodine was taken up by the zinc and the solution became clear. Water was now added, and the precipitated carbinol ether was freed from the alcohol and zinc iodide by filtration, and dried. The residue was recrystallized from ether and was identified as absolutely pure ethyl ether of triphenylcarbinol, $(C_6H_5)_3COC_2H_5$. No other products but the one mentioned were found. That the function of the zinc is no other than that of removing the "periodine" is quite evident from the fact that equally good results were obtained by substituting molecular silver for zinc. The action of alcohol upon the two periodides is therefore the same:



In order to more positively insure the identity of the carbinol ethers an attempt was made to convert them into the acetyl derivative. According to Allen and Kölliker² the carbinol ether reacts with acetyl chloride as follows:



The carbinol ethers obtained by me from the periodides were subjected to the action of acetyl chloride. They dissolved in acetyl chloride with an evolution of heat, but there was no ethyl chloride

¹ This Journal, 22, 768.

² Ann. Chem. (Liebig), 227, 117.

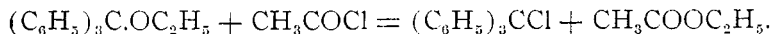
given off. On cooling, white crystals separated. These were recrystallized from petroleum ether, and the substance was obtained in snow-white, perfectly transparent prisms. The melting-point, however, was found to be not at 99° C. but at 112° C. A closer examination of the substance established the fact that it was not at all the acetyl compound, but pure triphenylchloromethane. The discrepancy between the results of Allen and K olliker and those which I have obtained are not due to the presence of some foreign substance in the carbinol ethers which were made from the periodides. A sample of the carbinol ether was made from absolutely pure triphenylchloromethane; it was recrystallized from alcohol and from petroleum ether, was absolutely free from halogen, and melted at 83° C., as given by Allen and K olliker. 3.2 grams of this ether gave on treatment with acetyl chloride 2.90 grams of perfectly pure triphenylchloromethane, while the calculated quantity should have been 2.95 grams.

0.2446 gram substance gave 0.7312 gram CO_2 and 0.1268 gram H_2O .

0.5600 gram substance gave 0.2870 gram AgCl .

	Calculated for (C_6H_5) $_3\text{C.Cl}$.	Found.
Carbon	81.84	81.52
Hydrogen.....	5.44	5.76
Chlorine	12.75	12.66

It is evident that the action of acetyl chloride proceeds as follows:



I also tested this action on the methyl and the propyl ethers of triphenylcarbinol, and found that they, too, give pure triphenylchloromethane.

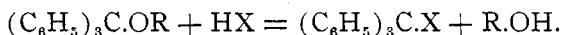
This action of acetyl chloride is entirely analogous to that of the halogen acids. Silva¹ found that hydriodic acid decomposes mixed ethers, the halogen combining with that radical which contains the smaller number of carbon atoms. Lippert² confirmed this also for hydrochloric and hydrobromic acids on a large number of primary and secondary ethers. But the tertiary ethers, as was shown recently by Mammontoff,³ behave in this respect differently. They, too, are readily decomposed by halogen acids, but

¹ *Ann chim. phys.*, [5], **7**, 429.

² *Ann. Chem.* (Liebig), **276**, 148.

³ *Jour. Russ. phys. chim. soc.*, **29**, 235.

the halogen unites with the radical which contains the larger number of carbon atoms, as was shown by Mammontoff on the ethyl and propyl ethers of triphenylcarbinol,

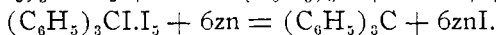
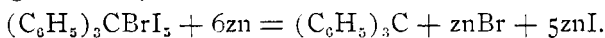


The two reagents, hydrogen halide and acetyl halide, act therefore similarly upon triphenylcarbinol ethers.

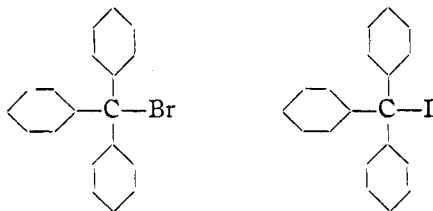
Whether the substance described by Allen and Kölliker was really the acetyl derivative or not, I cannot say. The low results which they got for hydrogen correspond better for triphenylchloromethane. An attempt will be made to prepare the acetyl derivative by some other method.

Methyl alcohol gave, with the periodides, the methyl ether of the carbinol melting at 82°C . With propyl alcohol the propyl ether was obtained.

(3). *Action of Metals.*—The action of metals upon the perhalides in neutral solvents such as ether, benzene, and acetic ester, results in the formation of the same unsaturated hydrocarbon, triphenylmethyl, which is produced when the normal halides are subjected to the same treatment. Of the different metals tried, zinc was found to give the most satisfactory results. Both periodides gave exactly the same results. The reaction is as follows:



From all that has been given in regard to the behavior of the two periodides we must conclude that the two react in every respect alike. Hence, they must not only have an analogous composition, but also a similar constitution. Consequently, the normal halides which gave rise to the perhalides must also have an analogous constitution:



5. TRIPHENYLIODOMETHANE.

In the first paper upon triphenylmethyl it was reported that tri-

phenyliodomethane was obtained. The yield of this product was, however, so small that only one analysis and a few qualitative tests were made. From 20 grams of triphenylchloromethane not more than 1 gram of the iodo-body was obtained. Although the reactions with ammonia and with the substituted amines, as well as the behavior of the periodide, showed conclusively that the substance produced by the addition of iodine to triphenylmethyl is the normal triphenyliodomethane, yet it appeared desirable to isolate the iodide itself in order to study its reactions directly. Of all the methods tried the following has given the best results: Triphenylmethyl is placed in a flask filled with dry carbon dioxide gas. A dilute solution of iodine in petroleum ether is added slowly to the hydrocarbon, the temperature of the flask being kept at about 60°-70° C. On cooling, there separates first a white crystalline substance, and later the iodide in clusters of large yellow prisms. The supernatant liquid is carefully decanted, the residue washed with petroleum ether, and dried in a stream of carbon dioxide. The crystals of the iodide can then be detached from the flask, and are at once put away in a closed bottle. I was able by this method to get 2.5 grams of the iodide from 2.3 grams of triphenylmethyl. The iodine was estimated by boiling the iodide with a dilute solution of sodium hydroxide containing a small amount of sulphurous acid, and precipitating the iodine in the filtered solution with silver nitrate.

I. 0.4620 gram substance gave 0.2982 gram AgI.

II. 0.5040 gram substance gave 0.3240 gram AgI.

	Calculated for (C ₆ H ₅) ₃ CI.	I. Found.	II.
Iodine	34.29	35.05	34.72

The iodide possesses a light yellow color, but on exposure to light it darkens rapidly. The color of the iodide can best be observed when the substance is placed under ether, as it is only sparingly soluble in that solvent. It is soluble in hot acetic ether, but only slightly in cold. It is quite soluble in benzene and in carbon disulphide. It melts at 132° C.¹

With *water* it reacts exactly in the same manner as the triphenylchlor- and brommethane, and gives the carbinol. This was so pure that it melted as obtained at 161° C.

0.3443 gram substance gave 1.1003 grams CO₂ + 0.2027 gram H₂O.

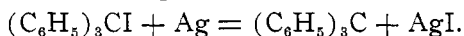
¹ In my first paper the melting-point of the iodide was given as about 135° C.

	Calculated for (C ₆ H ₅) ₃ C.OH.	Found.
Carbon	87.64	87.15
Hydrogen.....	6.21	6.53

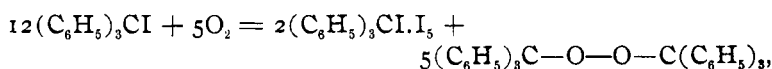
With *alcohol*, on heating, it gives triphenylmethane, which, however, is due to secondary reactions, just as is the case with the periodide. But when treated with alcohol in the cold, and better still with the addition of a little molecular silver, it gives the ether of the carbinol, just like the chloride and bromide of triphenylmethane,



With *metals* the reaction is again perfectly similar to that of triphenylchlor- and brommethane: triphenylmethyl is formed, which, on exposure to air, gives the insoluble peroxide,



When in solution, the iodo-compound decomposes readily, with liberation of some free iodine. Its reaction with *oxygen* is especially interesting. When a solution of the iodide is allowed to come in contact with air, or when oxygen is passed through the solution, iodine is liberated at once, and combines with a portion of the undecomposed iodide, forming the insoluble periodide¹; also triphenylmethyl peroxide is produced. The decomposition by oxygen is not, however, as smooth as indicated by the equation



but depends upon a number of circumstances, such as the nature of the solvent, whether the oxygen be dry or moist, etc. This susceptibility to the action of oxygen, no doubt, is one of the principal causes why previous attempts² to prepare this substance have failed.

It should be noticed that in the preparation of the iodo-compound there was also isolated a small amount of a substance which melts only a few degrees lower than the triphenylmethyl peroxide, namely at 177°-178° C., and which possesses almost exactly the same solubilities as the peroxide. There is, however, reason to

¹ The periodide comes down in exceptionally beautiful crystals, of green iridescence. Analyses point that it is more likely the tetraiodide, (C₆H₅)₃CI.I₄. Organic bases also give lower periodides when the iodine is not directly added, but formed slowly in the solution, as by the oxidation of hydriodic acid. So caffeine under these conditions gives the diiodide in contrast to the tetraiodide, which is ordinarily formed. This Journal, 18, 1.

² Jour. Russ. Phys. and Chem. Soc., 29, 238.

believe that it is not the peroxide, but a decomposition product of the iodide, because it was obtained in certain reactions in which the pure iodide was employed. The small quantity available did not suffice for a complete identification of this body.

Action of Silver Chloride.—When a solution of triphenylbromomethane in benzene is shaken for several days with silver chloride, dried at 200° C., it is completely converted into triphenylchloromethane. As the bromide can be obtained very pure this method of converting it into the chloride offers one of the best methods for getting the latter absolutely pure, when it is desired for physical constants. The conversion of the iodide into the chloride is not as smooth as that of the bromide. The reaction is necessarily slow because of the practically complete insolubility of silver chloride in benzene. The longer the time of the reaction the more of the triphenyliodomethane becomes decomposed in various other ways. The chloride of silver must be as finely divided as possible. It was prepared by precipitating it in water in the usual manner, washing the precipitate successively with alcohol, absolute ether, and benzene. It was kept under benzene until needed for the reaction. 2.5 grams of triphenyliodomethane gave about 1 gram of the crude chloride. It was necessary to recrystallize the latter several times in order to free it from the accompanying decomposition products of the iodide. Individual crystals could be picked out which possessed the crystalline form, the solubilities, and the melting-point of triphenylchloromethane.

0.4410 gram substance gave 0.1867 gram AgCl.

	Calculated for (C ₆ H ₅) ₃ C.Cl.	Found.
Chlorine	12.75	10.45

6. FORMATION OF DOUBLE SALTS.

It was already mentioned that when zinc is allowed to act upon triphenylchloromethane the zinc chloride formed in this reaction unites with a portion of the still unreduced triphenylchloromethane. This combination is a heavy oil, perfectly insoluble in benzene, only very slightly in ether, and readily in acetic ester. The compound is something in the nature of a double salt. It can also be prepared by adding a solution of zinc chloride in ether to a solution of triphenylchloromethane in any solvent. All attempts to induce the oil to crystallize have proved fruitless. This tendency

on the part of triphenylchloromethane to enter into combination with salts of metals is by no means limited to zinc chloride. A compound of this nature with aluminum chloride was described by Norris.¹ The halide salts of mercury, tin, and antimony also give such combinations. Nor is it triphenylchloromethane alone that enters with metals into these peculiar combinations. It seems to be a property apparently common to all the phenylhalogenmethanes. These compounds are quite easily formed by triphenylbrommethane, tritolylchloromethane, diphenyldichloromethane, diphenylbrommethane, and in some instances even benzotrichloride gives rise to such derivatives. There can hardly be any doubt that this forms a general reaction which is shared not only by all phenylated halogenmethanes, but will be found to belong to analogous ethane and propane derivatives. In accordance with this I find that triphenyliodomethane also gives combinations with a great many salts of metals.

Why these halogenmethanes should at all give these combinations, is a question which requires further study. We are accustomed to think that usually substances themselves basic in nature form double salts with metals. But here we have a set of bodies which are supposedly non-basic; on the contrary, they share more the properties of acyl chlorides, and yet, they behave as salts of basic radicals. It is remarkable, that all these bodies possess intense color, from yellow to dark red, irrespective of whether the metal itself is colored or not. When first formed they are oils, but on scratching or cooling, most of them change to the crystalline form. Water and alcohol decompose these salts; they can be prepared, therefore, only in such solvents as ether, benzene, carbon disulphide, etc.

Benzotrichloride gives with *antimonic chloride* an orange-red precipitate. As this is formed even in absence of benzene it cannot be due to a previous condensation of the trichloride to triphenylchloromethane.

Benzophenone Chloride, $(C_6H_5)_2C.Cl_2$, forms dark red crystalline compounds, both with antimonic chloride and with stannic chloride.

Diphenylbrommethane, $(C_6H_5)_2CHBr$, gives similar salts with

¹ *Am. Chem. J.*, 25, 54.

the above-mentioned reagents. They have not been analyzed.

The compound of *triphenylchlormethane* with *zinc chloride* could not be brought to crystallization. With *stannic chloride*, however, it is easily obtained in beautiful crystals on the addition of a benzene solution of the metal salt to one of triphenylchlormethane. The composition of this substance is identical with the one recently described by Kehrmann.¹

0.2535 gram substance gave 0.3364 gram AgCl.

	Calculated for (C ₆ H ₅) ₃ C.Cl + SnCl ₄ .	Found.
Chlorine	32.96	32.78

With *antimonic chloride*, the formation of the double salt is almost instantaneous, the precipitate consisting of fine red crystals.

0.7103 gram substance gave 0.2264 gram Sb₂S₅.

0.3261 gram substance gave 0.4785 gram AgCl.

	Calculated for (C ₆ H ₅) ₃ C.Cl + SbCl ₅ .	Found.
Antimony.....	20.84	19.12
Chlorine.....	36.94	36.30

Crystalline salts were also obtained from triphenylchlormethane and *mercuric chloride*, and from *triphenylbrommethane* and *mercuric bromide*.

Tritolylchlormethane possesses, to an unusual degree, the tendency to combine with halogen salts of metals. The number of compounds which can be so obtained, is limited only by the number of salts of metals which can be brought into solution in some inert organic solvent. The salts are all intensely colored, finely crystalline, and are easily obtained exceptionally pure. The following few were analyzed.

With *zinc chloride* in acetic ester, orange-red crystals were obtained.

0.5108 gram substance gave 0.0920 gram ZnO.

0.4283 gram substance gave 0.4038 gram AgCl.

	Calculated for (C ₆ H ₄ CH ₃) ₃ C.Cl + ZnCl ₂ .	Found.
Zinc.....	14.31	14.47
Chlorine.....	23.31	23.29

With *ferric chloride*, in dry ether, the double salt was precipitated in dark yellow, long needles.

0.3300 gram substance gave 0.7720 gram Fe₂O₃ and 0.2065 gram tritolylcarbinol.

¹ Ber. d. chem. Ges., 34, 3515.

	Calculated for (C ₆ H ₄ CH ₃) ₃ C.Cl + FeCl ₃ .	Found.
Iron.....	11.74	12.13
Carbinol.....	63.10	62.60

Mercuric chloride, in acetic ester, gives a beautiful, bright red double salt.

0.3060 gram substance gave 0.1205 gram HgS and 0.1552 gram carbinol.

	Calculated for (C ₆ H ₄ CH ₃) ₃ C.Cl.HgCl ₂ .	Found.
Mercury.....	33.84	33.88
Carbinol.....	50.86	50.82

Triphenyliodomethane shares with the halogenmethanes this peculiar property of entering into combinations with metals. It, too, gives a series of such bodies, but in many instances the formation of the double salt is accompanied by a partial oxidation of the iodo-compound. In most instances the formation of the salts was shown only in a qualitative way, leaving, however, no room for doubt that the iodide is in this respect, as in all others, entirely analogous to triphenylbrom- and triphenylchloromethane.

Stannic chloride, even in very dilute solutions, gives a dark red crystalline precipitate.

Antimonic chloride, for the most part, decomposes the iodo-compound, with liberation of iodine.

Zinc chloride and bromide give double salts which remain as oils, but with *zinc iodide* the salt becomes crystalline on scratching the oil. It is of a dark red, almost black, color.

SUMMARY.

The experimental work detailed in this paper can now be summarized as follows:

Triphenylchloromethane and triphenylbromomethane.

1. Empirical composition:

C₁₉H₁₅Cl, C₁₉H₁₅Br.

2. React with water readily and give triphenyl carbinol. With alcohol the ether is formed. With silver chloride the bromide gives triphenylchloromethane.

3. With ammonia the amine, (C₆H₅)₃CNH₂, is produced.

The iodo-compound formed on the addition of iodine to the unsaturated hydrocarbon.

1. C₁₉H₁₅I.

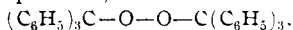
2. Reacts with water and with alcohol, and gives the same products as the bromide and the chloride. With silver chloride, triphenylchloromethane is formed.

3. Gives with ammonia the same amine, almost quantitatively.

4. React with substituted amines and give the corresponding bases $(C_6H_5)_3CNHR$.

5. The bromide gives rise to a perbromide and also to a periodide $(C_6H_5)_3CBr.Br_3; (C_6H_5)_3CBr.I_3$.

6. When acted upon by metals the chloride and the bromide give an unsaturated hydrocarbon, which, on exposure to air, forms triphenylmethyl peroxide,



7. Both unite with halides of metals, forming combinations of the nature of double salts.

4. Gives with amines also the same substituted bases; in some cases quantitatively.

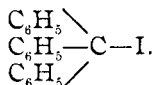
5. Forms with iodine, with about the same yield, a similar pentiodide, $(C_6H_5)_3CI.I_5$.

6. Exactly the same unsaturated hydrocarbon is produced by the action of metals upon the iodo-compound.

7. Forms similar double salts.

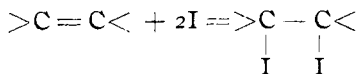
The facts described fully justify, I believe, the following conclusions:

1. The iodo-compound is triphenyliodomethane, and its constitution must be entirely analogous to that of the corresponding bromide and chloride,



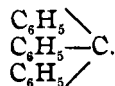
2. All the iodine added in the titration of the hydrocarbon is used up in the formation of this iodomethane; in other words, all the iodine is taken up by *one carbon atom*.

If these facts are to be interpreted in terms of the valence theory it must be admitted, that in case the hydrocarbon here described is really unsaturated, then we are dealing with a case of unsaturation which is entirely distinct in its nature from what is generally designated by this term. The unsaturation of one carbon atom in a molecule always implies a simultaneous unsaturation of another atom in the same molecule. In case of a hydrocarbon this second atom must, evidently, also be a carbon atom. We are accustomed to represent graphically such a state of unsaturation by a "double linking". In becoming saturated, as by the addition of halogens, each of the two atoms performs a similar function, each taking up one atom of halogen:



I am not aware of any exceptions to this general rule. But in the case of the unsaturated hydrocarbon under consideration *all* the

iodine, as I have shown, goes to *one* carbon atom. Hence, in the language of the valence theory, the unsaturation must be limited in this instance to one carbon atom in the molecule. The hydrocarbon must therefore, from this point of view, be represented by the constitution



The numerous facts which have been known for a long time, and which can be looked upon as supporting this view, were cited in the first paper¹ upon trivalent carbon. In a paper of recent date Thiele² expresses the opinion, that apart from the facts cited by me the existence of triphenylmethyl is no less supported by his theory of conjugated linkings and partial valencies. According to Thiele, we have here a case wherein the fourth valence of a methyl carbon atom is affected by the residual affinities of three phenyl carbon atoms. Such a neutralization of a valence of one carbon atom by three residual affinities of three other atoms is equivalent to a certain extent in its effect to what we have in Thiele's "conjugated system of double bonds", a stability not ordinarily present in unsaturated compounds. It will be noticed that this explanation involves a distribution of one valence of an atom in a certain indefinite way to several other atoms,—a theory not unlike Baeyer's "centric" theory of the constitution of benzene.

We may then arrange the derivatives of the hydrocarbon in a series, in order of increasing stability, something like this:

1. The unsaturated hydrocarbon, $(\text{C}_6\text{H}_5)_3\text{C}$.
2. Its ester and ether derivatives, obtained from 1. They, too, act as unsaturated.
3. Triphenyliodomethane, $(\text{C}_6\text{H}_5)_3\text{CI}$, can be obtained from 1 and 2.
4. Triphenylmethyl peroxide, $(\text{C}_6\text{H}_5)_3\text{COOC}(\text{C}_6\text{H}_5)_3$, is obtained from 1, 2, and 3.

We see that iodine can displace ethers and esters, and that oxygen can displace even iodine. The question comes up, is not the unsaturation of the hydrocarbon merely apparent unsaturation? Perhaps, we have here a case similar to Curtius' diazoacetic ester:

¹ This Journal, **22**, 770.

² *Ann. Chem.* (Liebig), **319**, 154.

or to Pechmann's diazomethane. Both these substances absorb iodine¹ even in dilute solutions; in fact, they can be titrated by means of this reagent, the halogen replacing quantitatively the azo group. Perhaps the unsaturated hydrocarbon here described has the composition $(C_6H_5)_3C-R$, and this group R is being simply replaced by iodine, like the azo group in the two examples mentioned. If we assume that the R has a molecular weight equal to about one-fourth of that of triphenylmethyl, then we have an explanation why the unsaturated-like hydrocarbon takes up only four-fifths of the amount of iodine calculated for triphenylmethyl.

Against this view there are, it seems to me, a number of very valid reasons. In the first place, not taking into consideration unsaturated substances like fumaric and maleic acids, which take up no iodine at all in an alcoholic solution, there are a number of unsaturated bodies, others than triphenylmethyl, which absorb only from 10 to 80 per cent. of the calculated amount of iodine. Thus, crotonic and cinnamic acids absorb only about 8 per cent., styracine about 43, and allyl alcohol 85 per cent.² In the second place, by a series of experiments with different metals and with a variety of solvents, it was established that the fourth radical, if there be any, cannot come from the solvent. Thirdly, as will be shown in a paper soon to be published, this radical cannot come from the partial decomposition of triphenylchlormethane either. Strictly quantitative experiments on samples of 20 grams of triphenylchlormethane proved that the hydrocarbon can be obtained in yields of from 85 to 90 per cent. of the calculated amount.

Taking all these facts into consideration it seems to me that the constitution of the unsaturated hydrocarbon is best represented as $(C_6H_5)_3C$.

Further study of the hydrocarbon itself as well as of its behavior towards different oxygen and nitrogen derivatives is in progress.

To Mr. M. Hanson, who assisted me in the prosecution of this work, I desire to express my thanks.

ANN ARBOR, MICHIGAN,
April, 1902.

¹ *J. prakt. Chem.*, **38**, 422; *Ber. d. chem. Ges.*, **27**, 1889.

² Lewkowitsch: "Chemical Analysis of Oils and Fats," p. 176.