	First crop.	Second crop.	Third crop.	Calculated for $(C_6H_5)_3C.Cl.$
I	12.35	12.74	12.69	12.75
III	12.45	12.48	12.49	12.75
IV	12.62	12.60	12.56	12.75

The product obtained by this method may, therefore, be considered quite pure. For further purification it can be recrystallized from benzene alone, or better by precipitating it from a concentrated solution in benzene by means of dry ether. By this method large quantities of pure triphenylchlormethane can be more easily obtained than by the old method[1],—by treating triphenylcarbinol with phosphorus pentachloride.

In conclusion I wish to express my thanks to Messrs. A. G. Marion, H. W. Emerson, and F. L. Woods for their kind assistance in carrying out some of the experimental work.

UNIVERSITY OF MICHIGAN,
CHEMICAL LABORATORY.

AN INSTANCE OF TRIVALENT CARBON: TRIPHENYL-METHYL.

BY M. GOMBERG.

[PRELIMINARY PAPER.]

SOME time ago[2] I published a method of preparing tetraphenylmethane. The yield was rather small and I was obliged to study the solubilities, composition, molecular weight, and the nitro derivative on about 0.5 gram of the hydrocarbon. The stereochemical interest attached to this compound has induced me to take up the subject once more, in the hope of obtaining larger yields. I have, therefore, gone over most of the methods which have been tried by others for the preparation of tetraphenylmethane. My results, while differing in detail from those published by others, agree in the main,—the hydrocarbon could not be obtained by the usual reactions. One of the main proofs advanced by me for the constitution of tetraphenylmethane was that it furnished a tetranitro derivative which gave no colored salts with alcoholic potash, while most of the less phenylated methanes do respond to this test. To prove whether

---

[1] Hemilian : *Ber. d. chem. Ges.*, **7**, 1207.

[2] *Ber. d. chem. Ges.*, **30**, 2043 ; This Journal, **20**, 773.

this reaction could safely be relied upon I decided to pre-
pare hexaphenylethane, $(C_6H_5)_3C—C(C_6H_5)_3$. This hydrocar-
bon should by nitration give a hexanitro body with no hydrogen
attached to the ethane carbon atoms.   Consequently it also
should give no colored salts with sodium ethylate or alcoholic
potash.

Accordingly, triphenylbrommethane in benzene was treated
with metallic sodium, but without success.   The chloro com-
pound gave no better results.   Molecular silver was substituted
for sodium.   After several hours' boiling a white crystalline body
began to separate, and on filtering the hot benzene solution a
considerable amount of the same substance separated on cooling.
It was recrystallized from benzene, gave a constant melting-
point, 185° C., and contained no halogen.   In its high melting-
point and in its only slight solubility in the usual organic solvents
it resembled closely tetraphenylmethane, and this new body was
taken for hexaphenylethane.   An elementary analysis gave,
however, the following results :

	Calculated for $(C_6H_5)_6C_2$.	Found.
Carbon	93.83	87.93
Hydrogen	6.17	6.04

The low per cent. of carbon found was rather surprising.   It
was explained on the assumption that this was, perhaps, an instance
of a hydrocarbon which is not easily burnt.   The next com-
bustion was, therefore, carried on in an atmosphere of oxygen from
the very beginning.   The substance was mixed in the tube with
copper oxide ; a very high heat was applied towards the end of
the combustion.   The results were as follows :

Carbon	87.74
Hydrogen	6.46

An entirely new lot of the material was then prepared.   Ten
grams of triphenylchlormethane and 10 grams of silver gave,
after several hours' boiling, 4 grams of the same hydrocarbon.
This was recrystallized twice from benzene and twice from chloro-
form.   It was perfectly free from halogen, was snow-white, and
melted at 185°–186° C.   The combustion was again made in an
atmosphere of oxygen, lead chromate being used instead of cop-
per oxide.

Carbon ································· 87.77
Hydrogen ······························ 6.23

The next analysis was made in a bayonet tube, the tube being filled with fine copper oxide for about four-fifths of its length, to insure combustion of any methane gas which would perhaps otherwise escape. The combustion was carried on slowly, and a very high heat was used towards the end.

Carbon ································· 88.23
Hydrogen ······························ 6.34

Several new lots of the same substance were made both from the triphenylbrommethane and triphenylchlormethane, and purified by successive recrystallization from benzene, chloroform, acetic ether, and carbon disulphide. They all gave the same results, entirely concordant with each other. Combustions were then made in a porcelain tube, applying the direct heat of the furnace ; also by the moist method with chromic acid in concentrated sulphuric acid,[1] but with no better result. I therefore came to the conclusion that the body under consideration was not a simple hydrocarbon, but an oxygen derivative. The oxygen could come from either of two sources : first, the molecular silver may have contained some oxide of the metal ; second, the atmospheric oxygen may act upon the hydrocarbon.

As only the molecular silver, and not the finely powdered crystalline metal appeared to act in this case, a very pure sample of the former was prepared. The moist silver, as obtained by reduction of the chloride with zinc, was digested for a day with dilute sulphuric acid. It was then thoroughly washed by decantation, digested for several hours with ammonium hydroxide, again washed with water, then with alcohol, absolute alcohol, ether, and finally with benzene. This sample of silver gave, however, results not differing from those previously obtained. To make it more certain that the oxygen did not come from the silver, I substituted other metals for it. Mercury and zinc were found to act equally well, if not better, and the yield of the oxygen compound obtained by either of these two metals was even greater than in the case of silver. Another great advantage in the use of zinc and mercury is that the reaction takes place at *ordinary temperature*. Mercury is especially well suited for a

[1] Fritzsche : *Ann. Chem.* (Liebig). **294**, 79.

lecture experiment showing this reaction. If a benzene solution of triphenylchlormethane or triphenylbrommethane be shaken in a test-tube for a few minutes with some metallic mercury and the solution rapidly filtered, the separation of the insoluble oxygen compound in the filtrate will soon begin, due to the absorption of atmospheric oxygen.

I next proved that it is really the oxygen from the atmosphere which oxidizes the hydrocarbon. By working in an atmosphere of carbon dioxide no such insoluble compound is produced, even on weeks' and months' treatment of the halogen bodies with silver, mercury, or zinc in benzene. After a long series of experiments I settled upon zinc as the best reagent with which to carry on this reaction. Ordinary granulated zinc, zinc strips, zinc dust,—all act upon the halogen compounds. In all further experiments what is known as *powdered zinc*, freed from zinc dust by sifting, has been employed. In this form the metal can readily be obtained free from the oxide, is easily handled, has a large surface exposure, and presents no difficulties in filtering from the benzene solution. Triphenylchlormethane[1] has been used altogether instead of the bromine compound.

The successful preparation of the unsaturated hydrocarbon requires the *absolute* exclusion of oxygen from the apparatus. Corks are to be avoided. and even rubber stoppers, exposed to the action of benzene vapors, become after a while porous. I have constructed for this work an apparatus by means of which the reaction can be carried on for several weeks, and months, if necessary. The zinc, benzene, and triphenylchlormethane are first digested for any length of time desired at ordinary temperature; the solution is then filtered into a distilling flask and the zinc washed with fresh portions of benzene. The combined liquids are distilled under diminished pressure at 30° C., and the solid crystalline residue containing the unsaturated hydrocarbon can be examined as to its solubility in different solvents, or treated in any manner desired. The apparatus is so arranged that all these steps are carried on in an atmosphere of dry carbon dioxide. Only ground-glass joints are used. The description of the apparatus is reserved for a future paper.

[1] For the preparation of this see the preceding paper.

I. THE HALOGEN IS TAKEN OUT BY THE ZINC QUANTITATIVELY.

The zinc removes the halogen from triphenylchlormethane quantitatively at ordinary temperature. The zinc chloride separates as a thick dark yellow sirup, probably forming a compound with benzene similar to the one produced by aluminum chloride. This is of very great advantage, because by this means fresh, clean surfaces of the metal are continually exposed for further action. For this reason the reaction is very slow, and soon stops altogether when carbon tetrachloride is substituted for benzene. With 20 grams of triphenylchlormethane, 150 grams of benzene, and 25 grams of zinc the reaction is completed in about five to six days. After removing the benzene solution and washing the residue thoroughly with benzene, the zinc chloride was dissolved in water and the chlorine estimated in the usual way.

|	Triphenyl-chlormethane taken. Grams.	Number of days of digestion.	Chlorine as $ZnCl_2$.	Calculated.
I	5	12	12.61	12.75
II	20	5	12.25	12.75
III	20	20	12.41	12.75

II. THE UNSATURATED HYDROCARBON.

The clear filtered solution containing the unsaturated hydrocarbon is concentrated under diminished pressure at a temperature of $30°-35°$ C., a slow stream of carbon dioxide being used to prevent bumping. When all the benzene has been distilled off, a strong stream of the gas is allowed to bubble through the thick yellow sirup, while the temperature is raised to about $40°$ C. On cooling, the whole residue solidifies to a crystalline cake, which does not melt even at $60°$ C. Even after several weeks' standing it redissolves readily in benzene with the exception of some of the oxygen compound whose formation is due to unavoidable leakage of the stop-cocks. The hydrocarbon is quite soluble in chloroform, less so in carbon tetrachloride, and is quite readily dissolved by carbon disulphide. If a concentrated solution of it is allowed to stand for three or four weeks, some large transparent crystals are formed. An attempt was made to remove these and wash with petroleum ether, but before the operation was finished enough oxygen was absorbed to form the

insoluble derivative. I hope to be able to isolate the hydrocarbon itself in a pure state.

The body is extremely unsaturated. A solution of it in benzene or in carbon disulphide absorbs oxygen with great avidity and gives an insoluble oxygen compound. It absorbs chlorine, bromine, and iodine. It does not unite with carbon monoxide.[1]

III. DI-TRIPHENYLMETHYLPEROXIDE,

$$(C_6H_5)_3C—O—O—C(C_6H_5)_3.$$
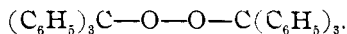
The crystalline compound which is formed by the action of the atmospheric oxygen upon a solution of the unsaturated hydrocarbon, is the peroxide of triphenylmethyl. It is best prepared by passing air or oxygen through a solution of the hydrocarbon in benzene. Twenty grams of the halogen compound give about 12 grams of the peroxide. The elementary composition fully agrees with that required by the formula :

	Calculated for $(C_6H_5)_6C_2O_2$.	I.	II.	Found. III.	IV.	V.
Carbon	88.03	87.93	87.74	87.77	88.22	87.60
Hydrogen	5.79	6.04	6.46	6.23	6.34	6.09

This body is characterized by extreme insolubility. It is only with difficulty dissolved by hot benzene, toluene, and then not without some decomposition. It can be recrystallized from chloroform. It is insoluble in ether, alcohol, and water. It is best recrystallized from carbon disulphide, 1 gram dissolving in about 150 cc. of the hot solvent. I have obtained by the use of this solvent remarkably beautiful and regular crystals, six-sided hexagons, of a very high refractive index. The peroxide melts at 185°-186° C. (uncorr.)

It is quite stable on exposure to air but decomposes gradually when a solution of it is heated. For this reason solvents of low boiling-point are to be preferred.

Formation by Means of Sodium Peroxide.—On heating triphenylchlormethane in benzene with commercial barium peroxide for several days a small amount of the triphenylperoxide was obtained. On repeating the experiment with a purified sample of barium peroxide the result could not be duplicated. I have resorted to the use of sodium peroxide, and with this

[1] Compare Nef : *Ann. Chem.* (Liebig). **270,** 267.

reagent I never failed to get the peroxide. A 10 per cent. solution of sodium peroxide is made by dissolving the latter in ice-water. Three to four grams of triphenylchlormethane in just enough benzene to make a clear solution are added, and a stream of air, free from carbon dioxide, is passed through the cold mixture until all the benzene is evaporated. The air keeps the two liquids in constant motion and fresh quantities are continually exposed to action. The solution is now filtered and washed. The unchanged chloro compound and the carbinol are removed by ether and the insoluble residue is boiled up with a large amount of carbon disulphide. The filtered solution gives, on concentration, a small amount of the characteristic crystals of the peroxide. This method was repeated several times, with and without the use of benzene, and has invariably given from 5 to 10 per cent. of the calculated amount of the peroxide. The larger portion of the chloride is changed to the carbinol, as it always does when left in contact with water, especially in presence of alkalies. The peroxide so obtained was identical with the one previously described. An analysis gave the following figures :

	Calculated for $(C_6H_5)_6C_2O_2$.	Found.
Carbon	88.03	87.55
Hydrogen	5.79	6.00

That the formation of the peroxide is really due to the presence of sodium peroxide, and does not result from the oxidation of the chloride or the carbinol by atmospheric oxygen, is shown by the following experiment : Three grams of the chloride dissolved in 10 cc. of benzene, were added to 100 cc. of a 10 per cent. solution of sodium hydroxide, and air was passed through the flask exactly in the same way as when sodium peroxide was used. On working up the product not a trace of triphenylmethyl-peroxide was found.

Molecular Weight.—Attempts to get an exact determination of the molecular weight have not proved as successful as desired. The peroxide is only slightly soluble in the usual organic solvents, and, therefore, only a slight elevation of the boiling-point could be expected, from 0.003°-0.150° C. I have found no liquid or low-melting solvent which could be used for the freezing-point

method. In using the boiling-point method it was found necessary to select as low-boiling a solvent as possible, since the peroxide suffers gradual decomposition at higher temperatures. Carbon disulphide was tried first. As the solubility of the peroxide in this solvent is only about 1 gram in 150 cc., the maximum rise of temperature could not be expected to be above 0.040° C. I therefore constructed an apparatus similar to the one described by Jones.[1] From 100–200 grams of the solvent could then be employed for a single determination. By this means the influence of the absolute error due to the weighings, vaporization of the solvent, etc., is greatly reduced. The apparatus proved very reliable, and the solvents employed could be kept boiling for an hour with a variation of temperature not exceeding 0.002° C. Tested on triphenylmethane the apparatus gave a molecular weight of 252 (244 calculated) when 1.2862 grams of the substance and 113 grams of the solvent were employed. The rise of temperature was to 0.107° C.

SOLVENT : CARBON DISULPHIDE. K = 2370.

Carbon disulphide. Grams.	Peroxide. Gram.	Rise in boiling-point.	Calculated rise for $m = 515$.	Molecular weight.
121.7	0.7300	0.035	0.028	406

The temperature remained constant for about fifteen to twenty minutes; after that it gradually began to rise, about 0.001 every ten minutes. The experiment was interrupted when 0.045 was reached. The solution was yellowish, showing slight decomposition of the peroxide.

SOLVENT : BENZENE. K = 2770.

Benzene. Grams.	Peroxide. Grams.	Rise in boiling-point.	Calculated rise for $m = 518$.	Molecular weight.
66	0.853	0.09	0.070	448

This temperature remained constant for about ten minutes, after that the rise was gradual until in an hour it reached 0.185° C. The solution was then quite yellow.

Ethylene dibromide was also tried, but as this boils still higher, there was even more rapid decomposition. The results in the main agree with those obtained when benzene was used.

The only conclusion that can be safely drawn from these results is that we have here a substance of very high molecular

[1] *Am. Chem. J.*, **19.** 581.

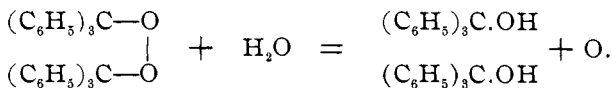weight, above 400 at least. The formula for the peroxide would require 518.

Conversion of the Peroxide into the Carbinol.—The peroxide dissolves in cold concentrated sulphuric acid with considerable evolution of heat, giving a yellow solution which soon turns dark, and finally almost black. The sulphuric acid does not induce any explosion as is the case with most organic peroxides. On diluting the acid with water the triphenylcarbinol is precipitated out as a dark flocculent precipitate.

2.85 grams of the pure peroxide were dissolved in 25 cc. of sulphuric acid and allowed to stand over night. The solution was then poured upon ice and the precipitate separated by filtration. It was dissolved in ether, and the dark ethereal solution was repeatedly shaken with dilute sodium hydroxide until the ether was only of a pale yellow color. The dried ethereal solution was then concentrated to a small bulk and rhigolene added. Crystals of triphenylcarbinol separated and were almost pure, melting at $159°-160°$ C. The yield was 1.948 grams, which represents 70 per cent. of the peroxide taken. The mother-liquid, on concentration, gave additional 0.215 gram, and 0.050 gram was obtained from the third crop, making a total of almost 80 per cent. The remaining 20 per cent. were probably oxidized by the oxygen evolved or perhaps sulphonated, as the sodium hydroxide removes all the dark color from the ethereal solution. An analysis gave the following results :

0.2910 gram substance gave 0.9330 gram carbon dioxide and 0.1654 gram water.

	Calculated for $(C_6H_5)_3C.OH.$	Found.
Carbon	87.69	87.44
Hydrogen	6.15	6.31

The reaction may therefore be represented by the following equation :

$$\begin{matrix} (C_6H_5)_3C{-}O \\ | \\ (C_6H_5)_3C{-}O \end{matrix} + H_2O = \begin{matrix} (C_6H_5)_3C.OH \\ \\ (C_6H_5)_3C.OH \end{matrix} + O.$$

Di-trinitrotriphenylmethylperoxide, $(C_6H_4NO_2)_3C-O-O-C(C_6H_4NO_2)_3.$—Brodie,[1] Vanino,[2] and Nef[3] have shown that the

[1] *Ann. Chem.* (Liebig). Suppl. III. 209.
[2] *Ber. d. chem. Ges.*, **30**, 2004 ; **33**. 1045.
[3] *Ann. Chem.* (Liebig). **298**, 287.

superoxides of acid radicals can be nitrated with fuming nitric acid. The peroxide here described shares the same property. It forms very readily a hexanitro compound. One gram of the peroxide gave 1.375 grams of the pure nitro body, while theory requires 1.555 grams. The nitro compound is insoluble in the usual organic solvents. One gram refuses to dissolve completely in 500 cc. of boiling glacial acetic acid. It is best recrystallized by dissolving it in nitrobenzene at 120°–130° C., and precipitating with petroleum ether.

	Calculated for $C_{38}H_{24}N_6O_{14}$.	I.	Found. II.
Carbon·············	57.87	57.55	....
Hydrogen·········	3.05	3.34	....
Nitrogen··········	10.65	11.03	10.94

IV. TRIPHENYLIODOMETHANE,
$(C_6H_5)_3C.I.$

The unsaturated hydrocarbon, which is formed when the halogen is removed from triphenylchlormethane, unites not only with oxygen, but also instantly with chlorine, bromine, and iodine. The reaction with chlorine and bromine is, however, not one of mere addition. The hydrocarbon is so reactive that even at —10° C. chlorine and bromine act both by addition and substitution. When the hydrocarbon, entirely freed from benzene, is dissolved in carbon tetrachloride there is always some hydrochloric and hydrobromic acid produced on the addition of the halogen. Triphenylchlormethane and triphenylbrommethane are among the products but it is not easy to separate the substitution halogen-compounds formed at the same time. This reaction will be further studied.

Iodine is absorbed by the hydrocarbon as readily as the other two halogens. When a solution of the hydrocarbon in carbon disulphide is treated at 0° C. with a solution of iodine in the same solvent, the latter is instantly decolorized. The end-reaction is quite sharp. In one instance, working with a product from 20 grams of triphenylchlormethane, 6 grams of iodine were absorbed, which is equivalent to 12 grams of $(C_6H_5)_3C$— ; in another case, where 25 grams of the chloro compound were employed, the absorption amounted to 8 grams of iodine. The isolation of the iodo compound requires considerable precautions, as it is a very

unstable body. I have found it best to work in an atmosphere of dry carbon dioxide, but am not as yet prepared to say whether it is the oxygen or the moisture of the air that affects it most. Probably it is the latter. The solution of the iodo compound was filtered to remove a slight amount of a periodide[1] and the peroxide. To the clear carbon disulphide solution rhigolene was added and the mixture cooled in ice. After some crystals had separated the liquid was transferred to another flask and cooled again, when more crystallized out. This last crop was recrystallized by dissolving it in carbon disulphide and precipitating with rhigolene. The crystals were of a pale yellow color, the same in appearance as the chloro compound when the latter is similarly precipitated. The crystals were washed several times with rhigolene and dried rapidly *in vacuo*.

The iodine was estimated by treating a weighed sample of the compound in dilute alcohol with ammonia and zinc dust. The hot alcoholic solution was filtered, the zinc washed thoroughly with hot alcohol, and then with water. The alcohol washings were concentrated, filtered, and the residue was exhausted with water. The insoluble portion was purified with ether, and was identified as triphenylcarbinol. It melted at 153° C., probably due to the presence of some triphenylmethane. On recrystallizing twice from alcohol the melting-point was raised to 157°–159° C. The yield of the carbinol was 0.383 gram, while the calculated quantity for the 0.602 gram of triphenyliodomethane was 0.422 gram.

0.602 gram substance gave 0.3704 gram AgI.

	Calculated for $(C_6H_5)_3C.I.$	Found.
Iodine	34.29	33.23

The iodide turns dark very readily and loses iodine. It is very unstable. It melts approximately at 135° C., with decomposition. Water, especially in the presence of alkalies, converts it into triphenylcarbinol, a reaction similar to that with the corresponding chloro and bromo compounds. Alcohol, however, behaves in this case differently. On boiling with alcohol large quantities of iodine are set free and the body is reduced by the

[1] For a periodide of triphenylbrommethane, see this Journal, **20**, 790.

alcohol to triphenylmethane, while in the case of triphenylchlor-methane and triphenylbrommethane the ethyl ether,

$$(C_6H_5)_3C.OC_2H_5.^1$$
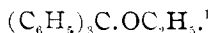
is formed. The triphenylmethane was freed from a small amount of the unreduced ether by fractional crystallization from alcohol, and was identified by its characteristic crystals containing benzene of crystallization and melting at $77°$ C. On exposure to air the benzene of crystallization was lost and the crystals melted at $92°$ C.

V. TRIPHENYLMETHYL,
$$(C_6H_5)_3 \equiv C.$$
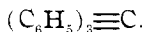
The experimental evidence presented above forces me to the conclusion that we have to deal here with a free radical, tri-phenylmethyl, $(C_6H_5)_3 \equiv C$. On this assumption alone do the results described above become intelligible and receive an adequate explanation. The action of zinc results, as it seems to me, in the mere abstraction of the halogen, leaving the free radical,

$$(C_6H_5)_3C.Cl + zn = (C_6H_5)_3C + znCl.$$

The radical so formed is apparently stable, for it can be kept both in solution and in the dry crystalline state for weeks. The radical refuses to unite with another one of its kind, and thus forms a distinct exception to all similar reactions. It might be said that, perhaps, it does polymerize to hexaphenylethane, $(C_6H_5)_3C—C(C_6H_5)_3$. but this hydrocarbon is so unstable that mere exposure to air is sufficient to break it down. Such an assumption seems to me less tenable than that of a free radical. Hexaphenylethane must, according to all our present notions of valence, be a saturated compound. Yet the hydrocarbon under consideration is decidedly unsaturated. We know of no better positive test for unsaturation in hydrocarbons than the absorption of halogens. Perhaps chlorine and bromine would in this case attack and decompose hexaphenylethane, if that be the hydrocarbon; but, certainly. a dilute solution of iodine. at $0°$ C., would scarcely do that. It seems to me rather that hexaphenyl-ethane, once formed, would prove quite a stable compound. This may be justly inferred from analogous reactions, where a

<hr/>

[1] Hemilian : *Ber. d. chem. Ges.*, **7**, 1203.

fourth heavy radical has been successfully introduced into the methane,—as is the case with triphenylthiophylmethane, $(C_6H_5)_3.C.C_4H_4S$,[1] tetraphenylmethane, $(C_6H_5)_3C.C_6H_5$,[2] triphenvl-acetic acid,[3] etc.   It is a phenomenon parallel to that expressed by V. Meyer's esterification law of diortho substituted aromatic acids : It is very difficult to introduce an alkyl into the carboxyl of such acids by the *usual method* of esterification, but once intro-duced, it is just as difficult to remove it again.

On the assumption of the existence of triphenylmethyl itself, as such, all the reactions of the unsaturated body become clear. Oxygen adds itself, a whole molecule, and gives the peroxide :

$$(C_6H_5)_3{\equiv}C \atop (C_6H_5)_3{\equiv}C \quad + \quad {O \atop \| \atop O} \quad = \quad {(C_6H_5)_3{\equiv}C-O \atop | \atop (C_6H_5)_3{\equiv}C-O}.$$
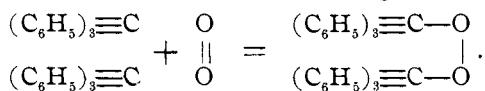
The addition of a molecule of oxygen is entirely in accord with the recent studies of M. Traube, van 't Hoff, Engler, Manchot, Bach, Baeyer and Villiger, and Nef.   This case forms an excellent illustration of Engler's[4] theory that " autoxidation" results first of all in the formation cf superoxides.   The action of halogens upon the unsaturated body is primarily that of addition.   Thus iodine gives triphenyliodomethane :

$$(C_6H_5)_3{\equiv}C \atop (C_6H_5)_3{\equiv}C \quad + \quad {I \atop | \atop I} \quad = \quad {(C_6H_5)_3{\equiv}C-I \atop (C_6H_5)_3{\equiv}C-I}.$$
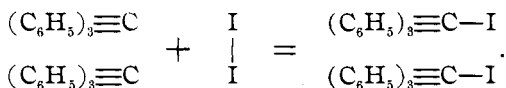
That the unsaturated hydrocarbon is not the result of some complicated reaction between triphenylchlormethane, benzene, and the nascent zinc chloride formed during the experiment, is proved by the following : 5 grams of the halogen compound were dissolved in 100 cc. of carbon disulphide and shaken at intervals with 100 grams of metallic mercury for two days.   The clear fil-tered solution on exposure to air furnished 3.8 grams of tri-phenylmethyl peroxide.   Five grams of triphenylchlormethane, treated with zinc and benzene for four days, gave 3.1 grams of the peroxide.

The existence of triphenylmethyl implies, of course, the exist-ence of *trivalent carbon*, at least in this particular instance.   The

[1] Weisse : *Ber. d. chem. Ges.,* **28,** 1538.

[2] Gomberg : *Ibid.,* **30,** 2043.

[3] E. and O. Fischer : *Ann. Chem.* (Liebig). **194,** 260 : Heyl and V. Meyer : *Ber. d. chem. Ges.,* **28,** 2782.

[4] *Ber. d. chem. Ges.,* **30,** 1669 : **33.** 1090. 1097.

conception of such a trivalent carbon in this instance is entirely distinct from that which is ascribed to it by some in benzene, or even in ethylene, where there are always *two* adjoining carbon atoms acting as trivalent.   The unsaturation in such cases has always been indicated by a '' double linking.''   In triphenyl-methyl there is *only one carbon atom* that is unsaturated.   The existence of such a body means that when three valences of carbon are taken up by three phenyl groups it is difficult, or perhaps even impossible, to introduce as a fourth group such a complicated radical as $(C_6H_5)_3C$—.   Only simpler groups, chlorine, bromine, iodine, oxygen, etc., may still combine with such a carbon atom.   Whether this be due to the negative character of the three phenyl groups, or whether it is caused by the fact that these groups take up so much space around the carbon atom as to hinder the introduction of another complicated group, is a question of an entirely different nature and need not be discussed here.   There are, however, numerous reactions which go to show that there is a limit to the number of complicated groups which can ordinarily be linked to one and the same carbon atom.   A few of these reactions may be mentioned.

Hemilian,[1] Friedel and Crafts,[2] E. and O. Fischer,[3] Magati,[4] Schwartz,[5] V. Meyer,[6] Weisse,[7] Waga,[8] and Meisel,[9] have all attempted to prepare tetraphenylmethane, but in all cases tri-phenylmethane resulted.   Even such comparatively simple compounds as $(C_6H_5)_3C.C_2H_5$,[10] or $(C_6H_5)_3C.CH_3$,[11] could not be obtained by reactions from which, *a priori*, we should certainly expect the formation of such bodies.   The disinclination of carbon to hold more than three complicated groups is well illustrated by the results of Anschütz's[12] extended researches on tetra-phenylethane.   A large number of methods which ought to give the unsymmetrical derivative, $(C_6H_5)_3C.CH_2(C_6H_5)$, always

[1] *Ber. d. chem. Ges.*, **7**. 1209.
[2] *Ann. chim. phys.*, 1884. I. 497.
[3] *Ann. Chem.* (Liebig). **194**, 254.
[4] *Ber. d. chem. Ges.*, **12**. 1468.
[5] *Ibid.*, **14**, 1523.
[6] *Ibid.*, **28**, 2792.
[7] *Ibid.*, **28**, 1538; **29**, 1402.
[8] *Ann. Chem.* (Liebig). **282**, 330.
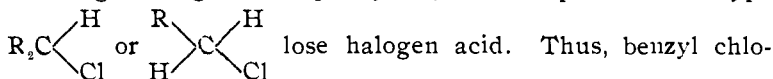[9] *Ber. d. chem. Ges.*, **32**, 2422.
[10] E. and O. Fischer: *Ann. Chem.* (Liebig). **194**, 259.
[11] Biltz : *Ibid.*, **296**, 253.
[12] *Ibid.*, **235**, 203.

give the symmetrical one, $(C_6H_5)_2CH.CH(C_6H_5)_2$. And lastly, the abnormal behavior of tetraphenylethylene towards bromine, as found by Biltz,[1] shows again the same point. Bromine will substitute in, but not add itself to, tetraphenylethylene, although we have here an unsaturated linking, $(C_6H_5)_2C : C(C_6H_5)_2$. These and a number of other facts show conclusively that with three valences of carbon taken up by such complicated or large groups as phenyl, the fourth valence can ordinarily be linked to atoms or groups of simple construction only. Now, as a result of the removal of halogen from triphenylchlormethane in benzene by zinc, or in carbon disulphide by mercury, the fourth valence of the methane carbon is bound either to take up the complicated group $(C_6H_5)_3C—$, and polymerize, or remain as such, with carbon as trivalent. Apparently the latter is what happens.

In conclusion, it may be mentioned that the action of metals upon triphenylhalogenmethane has been tried before. Elbs[2] acted upon triphenylbrommethane with sodium, magnesium, and copper. Anschütz[3] employed sodium upon a mixture of triphenylbrommethane and benzyl chloride. The action of metals upon the di- and monophenylhalogen methanes has also been extensively studied. While diphenyldichlormethane loses all its halogen and gives tetraphenylethylene, compounds of the type

$$R_2C\begin{smallmatrix}H\\ \diagup\\ \diagdown\\ Cl\end{smallmatrix} \quad \text{or} \quad \begin{smallmatrix}R\\ \diagdown\\ \diagup\\ H\end{smallmatrix}C\begin{smallmatrix}H\\ \diagup\\ \diagdown\\ Cl\end{smallmatrix}$$

lose halogen acid. Thus, benzyl chloride, when treated with zinc,[4] zinc-copper couple,[5] gives polymers and reduction-products of phenylmethylene. Recently Nef[6] has used aluminum chloride upon benzyl bromide in the hope of splitting off hydrobromic acid and thus obtaining the free radical phenylmethylene, $(C_6H_5)CH$. The formation of the latter as an intermediate product was made quite probable, but the isolation of it proved impossible, owing to a rapid polymerization.

This work will be continued and I wish to reserve the field for myself.

UNIVERSITY OF MICHIGAN.
CHEMICAL LABORATORY.
August. 1900.

[1] Ann. Chem. (Liebig). **296**, 231.
[2] Ber. d. chem. Ges., **17**, 700.
[3] Ann. Chem. (Liebig). **235**, 226.
[4] Zinke : Ibid., **159**. 1368.
[5] Gladstone and Tribe : J. Chem. Soc., **45**, 154; **47**, 448.
[6] Ann. Chem. (Liebig). **298**, 248.