

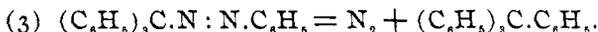
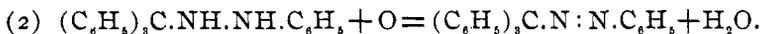
heat. The ammeter gives the total current absorbed, and the voltmeter the electromotive force at the arc. With this simple arrangement, copper and brass are easily melted, as well as iron and steel. As to the adjustment of the carbons, it is only necessary to feed the upper one down a fraction of an inch every two or three minutes. Should rheostats not be at hand, a bank of thirty-two C. P. lamps arranged in multiple and joined in with the furnace, answer the purpose for smaller fusions, and for metals possessing lower melting-points. By using ten 32 C. P. lamps in parallel, a good arc may be maintained, sufficient for small reductions, etc. Should three of these "flower-pot" furnaces be placed in series, the principle of the large furnace will obviously be brought into play, if some means is devised for controlling the upper carbons simultaneously.

### ON TETRAPHENYLMETHANE.<sup>1</sup>

BY M. GOMBERG.

Received August 29, 1898.

ABOUT a year ago<sup>2</sup> I reported a method by which small quantities of tetraphenylmethane were obtained, a substance which it had been proved impossible to prepare by the usual reactions.<sup>1</sup> The method consisted in oxidizing triphenylmethanehydrazobenzene to the corresponding azo-compound, and heating the latter to 110°-120° C. The reactions can be summarized by the following equations:



Unfortunately, the yield was very small, and even then the substance could be obtained only with difficulty.

The work has since been subjected to a revision, but with no better results in so far as the yield of tetraphenylmethane is concerned.

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

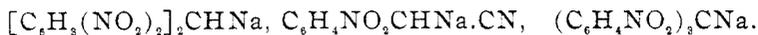
<sup>2</sup> *Ber. d. chem. Ges.*, 30, 2043, 1897.

<sup>3</sup> Haemilian, 1874: *Ber. d. chem. Ges.*, 7, 1209; Friedel and Crafts: *Compt. rend.*, 1877, 153; *Ann. chim. phys.*, 1884, 1, 497; E. and O. Fischer, 1878: *Ann. Chem. (Liebig)*, 194, 254; Magati, 1879: *Ber. d. chem. Ges.*, 12, 1468; Schwartz, 1881: *Ber. d. chem. Ges.*, 14, 1523; Waga, 1894: *Ann. Chem. (Liebig)*, 282, 330; Weisse, 1895: *Ber. d. chem. Ges.*, 28, 1537.

The method of oxidizing the hydrazo- to the azo-body has been greatly improved, and was found to be of general application for the preparation of azo-derivatives of this class.<sup>1</sup>

A mere elementary analysis is not sufficient to establish the composition of tetraphenylmethane, as the percentage of carbon and hydrogen is almost the same as that in triphenylmethane, and in other phenylated methane and ethane derivatives. A redetermination of the *molecular weight* seemed therefore very desirable, inasmuch as only about one-tenth gram of the substance was at my disposal for the first determination. The amount employed this time was again small, about 0.124 gram. It was nearly all recovered, and used for the preparation of a nitro-compound, furnishing, *quantitatively*, a tetranitro-derivative.

It has been shown by V. v. Richter<sup>2</sup> that the accumulation of nitro-groups in phenylmethanes imparts to these compounds sufficient negative character, so that they form salts with caustic potash, and especially with sodium ethylate. These salts are intensely colored, usually dark violet. They are formed by the replacement of sodium for the methane-hydrogen, giving, for example,



This reaction with triphenylmethane is exceedingly characteristic,—a fragment of a crystal of trinitrotriphenylmethane dissolves in sodium ethylate with a fine violet color.<sup>3</sup> The nitro-derivative, however, obtained from tetraphenylmethane, does not give any colored salts with caustic alkali or with sodium ethylate, even on heating. This is strong corroborative evidence of the constitution of tetraphenylmethane, showing that all the four hydrogen atoms in methane must have been replaced.

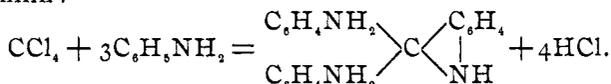
When the nitro-compound is treated with acetic acid and zinc dust, it shows the characteristic fuchsin reaction. Three to four milligrams suffice for this test. Lack of material prevented from fully identifying the dye as pararosanilin, since all this work, including the molecular weight determination, was performed on about two-tenths gram of tetraphenylmethane. An alcoholic

<sup>1</sup> See next paper : This Journal, 20. 780.

<sup>2</sup> *Ber. d. chem. Ges.*, 21, 2470, 2475, 1888.

<sup>3</sup> Trinitrotriphenylcarbinol gives the same reaction on warming.

solution of the dye gave the same absorption spectrum as *para*-rosanilin, prepared under exactly similar conditions directly from triphenylmethane. The formation of a rosanilin dye, involving, as it does, a splitting off of a *p*-amidophenyl group, is not so very surprising, when we consider the great tendency for the formation of such dyes under the most varied conditions. The historic reaction of Hofmann,<sup>1</sup> which led to the discovery of the rosanilin group, may be cited in this connection. By the action of anilin upon carbon tetrachloride, he obtained not the expected tetraamidotetraphenylmethane,  $(C_6H_4NH_2)_4C$ , but *p*-rosanilin :



The formation of the *para*-rosanilin or a rosanilin-like dye, from the tetranitrotetraphenylmethane shows, that at least three nitrogen groups are in *para* position to the central carbon atom. And it is quite probable that the fourth nitro-group also occupies the *para* position.

#### EXPERIMENTAL PART.

*Triphenylmethaneazobenzene*,  $(C_6H_5)_3C.N:N.C_6H_5$ .—The hydrazo-derivative was obtained by the action of phenylhydrazine upon triphenylbrommethane, in an ethereal solution, with a yield of seventy to eighty per cent. of the theoretical quantity. It has been stated before,<sup>2</sup> that of all oxidizing agents tried, amyl nitrite gave the best results in oxidizing the hydrazo to the azo-body. But even with amyl nitrite the oxidation sometimes goes too far, especially if larger quantities are worked with at one time. In such cases a considerable amount is oxidized to triphenylcarbinol, and a portion is entirely decomposed. It was now found that the substitution of nitrous acid gas for amyl nitrite gives much better results. The hydrazo-compound is dissolved in ether, and nitrous acid gas is passed in, until the solution turns milky and shows signs of boiling. The solution is allowed to stand about half an hour. On concentrating, the azo-derivative separates in large, bright yellow crystals, melting at  $110^\circ-112^\circ C$ . The yield is very satisfactory.

<sup>1</sup> *Compt. rend.*, 47, 492.

<sup>2</sup> *Ber. d. chem. Ges.*, 30, 2045, 1897.

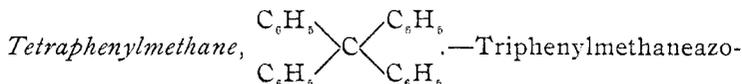
Seventeen grams of the hydrazo-body furnished by this method 14.5 grams of the azo-compound.

*Action of Bromine.*—When bromine is added to a solution of the azo-compound in chloroform, a heavy dark oil separates, which, after standing for some time, changes to a crystalline perbromide on stirring. The addition of a little petroleum ether hastens greatly the crystallization. The crystals obtained in this way were filtered, washed with a little chloroform and petroleum ether, and rapidly dried *in vacuo*. The inner portion, showing no decomposition by loss of bromine, was analyzed. The “perbromine” was estimated by suspending weighed samples of the perbromide in a solution of potassium iodide in water, and titrating the iodine with a standard solution of sodium thiosulphate.

	Calculated for (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CB <sub>2</sub> Br <sub>3</sub> .	Found.
Perbromine.....	55.33	54.85

When the perbromide is exposed to the air, it loses bromine, and leaves a white powder, which consists for the most part of triphenylbrommethane. On boiling the perbromide with alcohol, triphenylcarbinol was obtained (melting-point 158° C.)

The existence of such a perbromide is made quite probable by the existence of an analogous periodide.<sup>1</sup> Indeed, triphenylbrommethane itself, treated in a chloroform solution with bromine, gives also a crystalline perbromide, with similar properties and of the same composition as the perbromide described. This reaction is to be further studied.



benzene behaves in many respects like a true mixed fatty-aromatic azo-body. Thus, when heated to its melting-point, it decomposes with evolution of nitrogen, the amount of gas given off being quantitative.<sup>2</sup> The decomposition this time has been carried out as follows: About ten grams of pure clean sand, which had been thoroughly washed with benzene, was placed in a small flask and heated in an oil-bath to 110°–120° C. Fifteen grams of the finely powdered azo-compound was then gradually

<sup>1</sup> This Journal, 20, 790.

*er. d. chem. Ges.*, 30, 2045, 1897.

added, a little at a time, with constant stirring. When no further evolution of gas could be noticed, the mass was extracted with hot benzene, filtered, and the solution concentrated on the water-bath. The residue consisted of a very thick, dark mass. This was divided into two portions. To one portion a very little benzene was added, and the sirupy mixture was allowed to stand until crystallization set in, in about four or five days. The small crop of crystals was separated from the mother-liquid by filtration on a pump and washed on a porous plate with a little petroleum ether. It was then recrystallized several times from small quantities of hot benzene, until absolutely white and of a constant melting-point. The yield of the pure substance was a little over two-tenths gram. The molecular weight determination was made with this material. The mother liquor, after several weeks' standing, furnished another crop of the tetraphenylmethane, which, when purified, will probably amount to about one-tenth gram.

The second portion of the original dark mass, as obtained from the decomposition of the azo-compound, was subjected to distillation *in vacuo*, at fifteen to eighteen mm. The temperature of the metal-bath was allowed to go up to 320° C. The distillate, which amounted to about one-half of the quantity taken, presented a dark-yellow viscous mass. On standing, a small quantity of triphenylmethane crystallized out. The rest, as well as the residue in the distilling flask, could not be brought to crystallization. No diphenyl or diphenylmethane could be detected.

*Molecular Weight.*—As naphthalene had given very good results in the first determination, the same solvent was chosen again for the cryoscopic method. It has the advantage when small quantities of the substance are at one's disposal, because of its high constant. Trials with triphenylmethane had shown that the naphthalene was pure, and that very good results could be obtained with this solvent.

Solvent : Benzene.

$$\text{Formula : } \frac{69 \times p}{d} = m.$$

$p$  = per cent. of substance in solvent.

$d$  = depression.

Tetraphenylmethane,  $m = 320$ .

Solvent. Gram.	Substance. Gram.	$\rho$ .	$d$ . °C.	$n$ .
9.427	0.1239	1.314	0.285	318

The tetraphenylmethane as now obtained has been found to agree in all properties with the substance previously reported. It is insoluble in ether, chloroform, petroleum ether, glacial acetic acid. Fairly soluble in hot benzene, but very little in the cold. It crystallizes from benzene in white, glistening needles. The melting-point, determined this time in a closed dish and with a normal thermometer, was found to be  $272^{\circ}$  C. instead of  $267.5^{\circ}$  C., as given before.

*Recovery of the Tetraphenylmethane.*—Nearly all the quantity employed in the determination of the molecular weight was recovered. The naphthalene was placed in a crystallizing dish and sublimed off at the lowest possible temperature. The residue was boiled out first with a little petroleum ether, and then thoroughly washed with ether. The white silky residue showed the correct melting-point of tetraphenylmethane, and amounted to 0.1075 gram.

#### TETRANITROTETRAPHENYLMETHANE, $(C_6H_4NO_2)_4C$ .

The quantity of tetraphenylmethane recovered from naphthalene after the determination of the molecular weight, was nitrated. The nitration was done according to the method employed by E. and O. Fischer<sup>1</sup> for the preparation of *para*-trinitrotriphenylmethane. The hydrocarbon was added in small quantities to two cc. of nitric acid (sp. gr. 1.50), cooled in ice-water. The substance dissolved very readily. The bright yellow solution was allowed to stand about fifteen minutes. On the addition of water the nitro-compound separated in white minute crystals, without the slightest trace of any oily, sticky by-products, as is always the case when triphenylmethane is nitrated. The crystalline precipitate was separated by means of a pump, thoroughly washed with water, alcohol, and finally with a little ligroïn, and dried *in vacuo* over sulphuric acid. The yield was 0.166 gram, while theoretically 0.107 gram of tetraphenylmethane should yield 0.1669 gram of the tetranitro-derivative.

The substance was analyzed with the following results :  
0.1417 gram gave 14.8 cc. nitrogen at  $24^{\circ}$  and 737 mm.

<sup>1</sup> *Ann. Chem.* (Liebig), 194, 254.

	Calculated for (C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>4</sub> C.	Found.
N .....	11.20	11.68

The nitro-derivative, as already mentioned, consisted of minute, white, needle-like crystals. It is insoluble in ether, petroleum ether, alcohol; insoluble in cold glacial acetic acid, and only slightly when heated. It is somewhat soluble in hot benzene and hot chloroform, from either of which solvents it can be obtained in a nice crystalline form. It begins to darken at about 268° C., and melts at 275° C.

Unlike the trinitrotriphenylmethane, or the trinitrotriphenylcarbinol, it does not dissolve in sodium ethylate, nor does it give any coloration with it even on heating. The non-formation of colored alkali salts, as well as the high melting-point, show the absence of any nitrotriphenylmethane.

The nitration of the hydrocarbon has been repeated several times on small quantities, five to ten milligrams, of the original tetraphenylmethane, which had not been employed for the determination of the molecular weight, but the results were in every respect identical with those described above.

*Reduction to a Rosanilin Dye.*—About five milligrams of the nitro-compound were dissolved in boiling glacial acetic acid, and zinc dust gradually added in small quantities. On the first addition of the zinc the solution turned a bright red, and the reduction to a colorless base required considerable zinc dust and boiling. The solution was diluted with water, filtered from the excess of zinc dust, treated with excess of ammonia, and the precipitated colorless leuco-base was filtered and washed. The base was then gently ignited with a few drops of concentrated hydrochloric acid on a platinum foil, according to the method of E. and O. Fischer<sup>1</sup> for triphenylmethane. The characteristic fuchsin color so developed could not be distinguished at any stage from that produced by the reduction-product of *p*-trinitrotriphenylmethane. The two were reduced in about the same quantities and under the same conditions. The two dyes were dissolved in about the same amount of alcohol, and when examined spectroscopically, gave about the same absorption bands.

Lack of material prevented me from establishing the identity of the dye.

<sup>1</sup> *Ann. Chem.* (Liebig), 194, 273.

The subject will be continued, and it is hoped that perhaps larger quantities of tetraphenylmethane will be obtained by the action of triphenyliodomethane upon mercury-diphenyl.

ANN ARBOR, MICHIGAN.

## HYDRAZO- AND AZO-DERIVATIVES OF TRIPHENYL-METHANE.<sup>1</sup>

BY M. GOMBERG AND A. CAMPBELL.

Received August 29, 1898.

ONE of us has recently<sup>2</sup> described a method by which small quantities of tetraphenylmethane were obtained. The method involved the synthesis of triphenylmethaneazobenzene, which was obtained by the oxidation of the corresponding hydrazo-derivative. The azo-body, on being heated to 110°-120° C., loses nitrogen, and furnishes, among other products, tetraphenylmethane.

The present work was undertaken with the hope of obtaining substitution derivatives of tetraphenylmethane, by subjecting substituted azo-compounds of triphenylmethane to the same treatment as the simple azo-compound itself. For the present, we shall only give a description of the hydrazo- and azo-bodies, which have been prepared by us in connection with this work.

The number of mixed azo-bodies, *i. e.*, those containing an aliphatic and an aromatic radical, is quite limited. A few have been prepared by E. Fischer and Ehrhard,<sup>3</sup> and Tafel<sup>4</sup> by the oxidation of the corresponding hydrazo-derivatives. The principal method of preparation is, however, by combining aromatic diazo-salts with aliphatic compounds. This reaction, first worked out by V. Meyer<sup>5</sup> on nitroethane, has since been extended to a large number of such aliphatic compounds, as contain a (CH<sub>2</sub>)-group linked to some negative groups. Nitro-compounds, malonic ester, aceto-acetic ester, etc., give such bodies. The constitution of all these so-called azo-bodies has, however, recently been called into question by the work of Japp

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

<sup>2</sup> *Ber. d. chem. Ges.*, 30, 2043; *This Journal*, 20, 773.

<sup>3</sup> *Ann. Chem. (Liebig)*, 199, 328, 1879; *Ber. d. chem. Ges.*, 29, 793, 1896.

<sup>4</sup> *Ber. d. chem. Ges.*, 18, 1742, 1885.

<sup>5</sup> *Ber. d. chem. Ges.*, 8, 751, 1875; 18, 1742, 1885.