The *m*-nitro-triphenylamine is lemon yellow similar to *m*-nitraniline; both differ from the *m*-nitrodiphenylamine, which is brick red. It is very soluble in nitrobenzene, benzene, ether, and ethyl acetate; moderately soluble in alcohol, insoluble in water and acids. However, it is quite soluble in glacial acetic acid and in concentrated sulfuric acid. The latter solution at first is colorless, but acquires a blue coloration in a few seconds.

Pure *o*-nitro-diphenylamine (2 g.) was phenylated in the same manner as the corresponding *m*-derivative. Here also the reaction is quantitative. The crude product, 2.6 g., melted at 96°. After several recrystallizations from alcohol, the melting point rose to 98° and there remained constant. Recrystallizations from ethyl alcohol did not change the melting point. The crude yield was 95% of the theoretical.

Subst. 0.1343; CO_2, 0.3656; H_2O, 0.0609
0.2180; 18.5 cc. dry N_2 at 21° and 734 mm. (CuO).
0.1051; 9.35 cc. dry N at 21° and 725.5 mm. ($PbCrO_4$).

Calc. for $C_{18}H_{14}O_2N_2$: C, 74.46; H, 4.86; N, 9.66. Found: C, 74.27; H, 5.07; N, 9.52, 9.87.

The *o*-nitro-triphenylamine is yellow-orange in color. In large crystals it is orange-brown. Its properties are very similar to those of the already described para and meta derivatives.

CHICAGO, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

TETRAPHENYLMETHANE.

BY M. GOMBERG AND OLIVER KAMM.

Received June 10, 1917.

There are three methods known for the preparation of tetraphenylmethane. The first (I),[1] because of the small yields of the hydrocarbon, is now more of historical than of practical interest, as by means of it the possibility of the existence of tetraphenylmethane was definitely solved. By means of the second method (II),[2] the constitution of the hydrocarbon as actually tetraphenylmethane was clearly corroborated. At the same time, as a method of preparation it is decidedly more practicable than the first method notwithstanding the fact that it involves several steps with decreasing yields in each. The third method (III)[3] should, on the face of it, prove the most promising, both as regards the ease of manipulation as well as the yield and the purity of the product. Nevertheless, this anticipation has not, up till the present, become realized, the yields being hardly ever more than 5% of the calculated, and more often only about 0.5%.

[1] Gomberg, *Ber.*, 30, 2045 (1897); **36**, 1090 (1903); THIS JOURNAL, **20**, 773 (1898).

[2] Ullmann and Münzhuber, *Ber.*, 36, 408 (1903).

[3] Gomberg and Cone, *Ibid.*, **39**, 1463 (1906); Freund, *Ibid.*, **39**, 2237 (1906).

$$(C_6H_5)_3CN : NC_6H_5 \xrightarrow{\text{heat}} (C_6H_5)_3C.C_6H_5 + N_2. \qquad \text{(I)}$$

$$(C_6H_5)_3C.C_6H_4NH_2 \longrightarrow (C_6H_5)_3C.C_6H_4N_2Cl \longrightarrow (C_6H_5)_4C. \quad \text{(II)}$$

$$(C_6H_5)_3CCl + BrMgC_6H_5 \longrightarrow (C_6H_5)_3C.C_6H_5 + MgClBr. \quad \text{(III)}$$

The principal drawback is that the reaction proceeds largely along a different path, giving rise to triphenylmethyl with the consequent production of triphenylmethyl peroxide on exposure to air.

$$(C_6H_5)_3C.Cl \xrightarrow{C_6H_5MgBr} (C_6H_5)_3C \xrightarrow{O_2} [(C_6H_5)_3C]_2O_2. \qquad \text{(IV)}$$

The present communication contains the results of further attempts made with the purpose to improve this method. In view of the fact that at least some tetraphenylmethane is always produced in this reaction, the question naturally comes up, why should not the yield of this hydrocarbon be quantitative considering that the reaction is carried out under the mildest conditions, at room temperature? Two explanations suggest themselves. First, the tetraphenylmethane formed may itself be decomposed by the Grignard reagent. Second, the possibility is suggested that in this process the free radical, triphenylmethyl, may be formed first (IV), and from it the tetraphenylmethane only slowly according to the following equation (V):

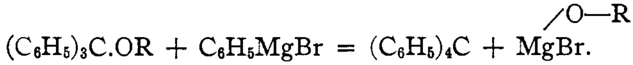
$$2(C_6H_5)_3C + 2BrMgC_6H_5 \longrightarrow 2(C_6H_5)_4C + MgBr_2 + Mg \quad \text{(V)}$$

Both of these surmises were tested by experiments. First, it was found that tetraphenylmethane is not decomposed by phenylmagnesium bromide under the conditions that are employed in method III in the preparation of that hydrocarbon, and hence the small yield of tetraphenylmethane cannot be ascribed to a reversibility, in a certain sense, of this reaction. Second, triphenylmethyl in ether solution, or in boiling benzene, treated with a solution of phenyl magnesium bromide, yielded no tetraphenylmethane. Similarly, the reaction of the same two substances at a higher temperature (150° to 200°) failed to give the expected product.

Preparation of Tetraphenylmethane from Triphenylchloromethane.—A series of experiments was then instituted with the purpose of determining more accurately to what extent the course of this reaction (III) is influenced by the nature of the solvent and the temperature. When the chloride was added directly to the Grignard reagent in ether solution, only a very small amount of the hydrocarbon was obtained together with a 50% yield of triphenylmethyl peroxide. When the experiment was repeated accompanied by the addition of benzene to the ether solution, the yield of tetraphenylmethane was increased to about five per cent. When, however, the reaction was conducted at a higher temperature and in absence of ether as a solvent, a yield of from 10 to 12% of the hydrocarbon was obtained. This improvement in yield is not the only advantage gained in using a higher temperature; in the former case the product is contaminated with a large quantity of triphenylmethyl peroxide, while in the latter an almost pure substance is obtained, as the triphenylmethyl is itself decomposed at the higher temperatures with the production of soluble products.

Tetraphenylmethane from Ethers of Triphenylcarbinol.—In the action of Grignard's reagent upon esters not only the carbonyl group enters into reaction but the alkoxyl group as well. Some evidence[1] is not lacking that this latter may be the very first step in the process, giving rise to a ketone which subsequently reacts further with more of the Grignard reagent to produce the tertiary alcohol.

We attempted to utilize this possibility for the preparation of tetraphenylmethane according to the equation VI, where R = CH_3, C_2H_5, or C_6H_5.[2]



$$(C_6H_5)_3C.OR + C_6H_5MgBr = (C_6H_5)_4C + \overset{\diagup O—R}{Mg}Br. \qquad (VI)$$

With the methyl and ethyl ethers yields of 10 to 12% of the calculated amount of the hydrocarbon were thus obtained, while with the phenyl ether as high as 20% yields are obtainable.

The requisite methyl and ethyl ethers may be prepared directly from triphenylchloromethane and the corresponding alcohol. The ease with which this reaction[3] occurs is illustrated by the following experiments: 14 g. of finely powdered triphenylchloromethane were treated with 100 cc. of absolute ethyl alcohol and the mixture shaken thoroughly for about a minute. The alcohol solution was then poured away from a trace of undissolved chloro compound and in a short time the ethyl ether of triphenylcarbinol, being less soluble than triphenylchloromethane, began to crystallize out. The yield was 12 g. By the use of sodium alcoholate a somewhat larger yield may be obtained. Although the latter procedure is more troublesome, it insures a product free from traces of acid. The preparation of the phenyl ether of triphenylcarbinol, *i. e.*, of phenoxytriphenylmethane, will be described further on in this communication.

Below are given the results of a few typical experiments with the above ethers.

Expt. (*a*).—A solution of phenyl magnesium bromide was prepared in the usual manner from 2.4 g. of magnesium and 18 g. of bromobenzene in about 30 g. of anhydrous ether. After the reaction was complete the excess of ether was distilled off by warming the mixture in an oil bath, the temperature being gradually raised until the thermometer in the bath indicated 120° to 140°. At this stage there was added, without cooling, 10 g. of the ethyl ether of triphenylcarbinol. The flask was then quickly

---

[1] Compare Stadnikoff, *J. Russ. Phys. Chem. Soc.*, **46,** 868 (1914); **47,** 1122 (1915).

[2] Stadnikoff, *Ber.*, **44,** 1159 (1911).

[3] *Ber.*, **7,** 1208 (1874); **42,** 2176; *Ann. chim.*, [6] **1,** 502; THIS JOURNAL, **25,** 1271 (1903).

connected with the condenser and its contents heated rapidly. Usually when the temperature of the outside bath reached 150° to 160° a rapid reaction took place, the liquid material in the flask foamed up, and an additional quantity of ether distilled off. The temperature was then raised to 200°. The reaction mixture at this stage consisted of a light brown solid which after cooling was treated with water and dilute acid in order to decompose the magnesium compounds, and about 100 cc. of ether added. With the exception of tetraphenylmethane all of the products formed were soluble either in the water or in the ether layer. The desired product separated gradually from the ether layer and was obtained in almost pure condition, simply by filtering and washing with ether. From the ether solution an additional quantity crystallized out after a few days. The total yield was 1.2 g., *i. e.*, 12% of the theoretical amount, and the melting point of the product before purification was 278° to 280°. Even the crude product gave no color with concentrated sulfuric acid and one recrystallization from benzene yielded a pure white crystalline product melting at 280°. Although tetraphenylmethane is quite insoluble in ether, it crystallized out slowly in the above experiment because of the impurities present in the solvent. Of the other products besides tetraphenylmethane formed in this reaction, triphenylmethane constitutes by far the largest portion. It is formed undoubtedly in virtue of the following reaction:

$$(C_6H_5)_3C.OR \xrightarrow{\text{Gr. Reag.}} (C_6H_5)_3CMgBr \xrightarrow{H_2O} (C_6H_5)_3CH. \qquad \text{(VII)}$$

Expt. (*b*).—Experiment (*a*) was repeated, using first the Grignard reagent and the ether in molecular proportions, and second, a large excess of magnesium phenyl bromide. In the first instance the yield of tetraphenylmethane was 8%; in the last it was 12%.

Expts. (*c*), (*d*) and (*e*).—The experiment as given under (*a*) was repeated in toluene solution, phenetol solution, and finally in the presence of dimethyl aniline. The yields of tetraphenylmethane were, however, not improved by these modifications.

Expt. (*f*).—The methyl ether of triphenylcarbinol was also used in the Grignard reaction, the yield of tetraphenylmethane being 12%. This indicates that there is no marked advantage in using this product in place of the ethyl ether.

Expt. (*g*).—The best yield of tetraphenylmethane was obtained from the phenyl ether of triphenylcarbinol. The details for the procedure were practically the same as those given under Expt. (*a*). The reaction in this instance took place more readily than in the experiment with the ethyl ether of triphenylcarbinol, and most of the tetraphenylmethane separated from the ether solution almost immediately. The yield was usually 20%, and in no experiment was it lower than 15%. The product even before crystallization from benzene gave no color with concentrated sulfuric acid, thus indicating the absence of triphenylmethyl peroxide.

The favorable results with the phenyl ether of triphenylcarbinol suggested the use of triphenylmethyl oxide[1] for this purpose in the expectation of still better results. But so far this has not proven to be the case.

Triphenylmethyl from Phenoxytriphenylmethane.—The ethyl ether of triphenylcarbinol is not decomposed by phenyl magnesium bromide at the boiling point of ethyl ether. The phenyl ether is, however, more reactive, and gives rise, unexpectedly, to triphenylmethyl.

$$(C_6H_5)_3C.OC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_3C. \qquad \text{(VIII)}$$

Seven g. of the phenoxy compound were added to 0.1 mol of phenyl magnesium bromide in 100 cc. of ether and the mixture heated for a short time under the reflux. The magnesium compounds were decomposed in the usual manner and air passed into the ether layer, thus causing the precipitation of triphenylmethyl peroxide. The yield was 2.5 g., 46% of the theoretically possible amount. In view of the results of this experiment it is surprising that the same products at a higher temperature produce a 20% yield of tetraphenylmethane and no peroxide; moreover, triphenylmethyl itself gives with phenyl magnesium bromide no tetraphenylmethane at all.

Phenoxytriphenylmethane and *p*-Hydroxytetraphenylmethane.—Triphenyl chloromethane, or the carbinol, may unite with phenol in two different ways.

$$(C_6H_5)_3C.Cl + HOC_6H_5 \longrightarrow (C_6H_5)_3C.OC_6H_5. \qquad \text{(IX)}$$

$$(C_6H_5)_3C.Cl(\text{or, } OH) + C_6H_5OH \longrightarrow (C_6H_5)_3C.C_6H_4OH. \qquad \text{(X)}$$

The formation of the phenoxy derivative from the chloride occurs only when the reaction medium is alkaline, *i. e.*, in presence of sodium phenolate; from the carbinol it has not as yet been prepared. But when either the chloride or the carbinol is condensed with phenol in presence of acid, *p*-hydroxytetraphenylmethane is the sole product. We have noticed, however, that, contrary to reports in the literature, condensation with phenol even in alkaline solution may give rise at times to some hydroxytetraphenylmethane.

Phenoxytriphenylmethane has been prepared by Baeyer.[2] We have prepared it by the same general method, using, however, metallic sodium instead of potassium. Triphenylchloromethane was added to sodium phenolate in dry ether and the mixture heated under reflux for 2–3 hours. The reaction mixture was shaken with water and then with dilute alkali to remove completely the excess of phenol. This treatment still left the product contaminated with a small amount (about 5%) of hydroxytetra-

---

[1] THIS JOURNAL, 35, 200 (1913).

[2] *Ber.*, 42, 2625 (1909); see also Wulfing, *Chem. Zentr.*, [1] 1896, 416.

phenylmethane, which was easily removed by the addition of a small quantity of 30% potassium hydroxide solution. The ether solution was filtered from the insoluble potassium salt, dried, and evaporated. The crude phenoxytriphenylmethane, recrystallized from alcohol, gave a pure white product melting at 102°. The yield was 90% of the calculated quantity.

p-Hydroxytetraphenylmethane has been obtained first by Baeyer and Villiger,[1] through the condensation of triphenylcarbinol with phenol in acetic, using considerable quantities of sulfuric acid as the dehydrating agent. Zincke[2] used practically the same method. The same product was also prepared by merely heating pure triphenylchloromethane and phenol together.[3] In our experience the sulfuric acid employed in this reaction functions rather as a catalyst and not as a dehydrating agent; accordingly, the amount of this acid can be greatly reduced, and it can entirely be replaced by some other acid, such as hydrochloric acid. The following experiments illustrate the striking readiness with which this tetraphenylmethane derivative is formed:

(*a*) Five grams of triphenylchloromethane were heated, with the addition of a little finely divided copper, with phenol on the water bath, and gave 5.5 g. of hydroxytetraphenylmethane. The same experiment, with the addition of benzene as a solvent, still gave 4 g. of the product.

(*b*) 2 g. of carbinol, 0.2 g. of the chloride and 2.5 g. of phenol were heated on the water bath for one hour. In spite of only the very small amount of hydrochloric acid the yield of hydroxytetraphenylmethane was none the less 2.7 g., against the theoretical quantity of 2.86 g.

(*c*) 8 g. of carbinol, 8 g. of phenol and *one drop* of concentrated sulfuric acid, heated on the water bath for 45 minutes, gave 9.3 g. of the condensation product.

(*d*) 2 g. carbinol, 2 g. phenol, 10 cc. of glacial acetic acid, and one drop sulfuric acid gave, after one hour's heating, 1.6 g. of hydroxytetraphenylmethane.

(*e*) 2 g. carbinol, 3 g. phenol, and one cc. of concentrated hydrochloric acid were heated on the water bath. The condensation product commenced to separate after 5 minutes' heating of the mixture, and after 15 minutes there was formed 2.2 g. of it.

Thus it becomes obvious that, although there is an evident hindrance of some nature when the triphenylmethyl group is to unite with a fourth phenyl group, all obstacles toward such union vanish when the fourth group carries a hydroxyl. Steric hindrance considerations, therefore, can offer no plausible explanation concerning the small yield of tetra-

---

[1] *Ber.*, **35**, 3018 (1902).

[2] *Ann.*, **363**, 288 (1908).

[3] Baeyer, *Ber.*, **42**, 2628 (1909).

phenylmethane in any of the methods that have been employed for that purpose.

It has been stated in one of the preceding paragraphs that not only phenoxytriphenylmethane but also hydroxytetraphenylmethane was obtained on some occasions when triphenylchloromethane was condensed with sodium phenolate. The formation of this second product under these conditions of experiment could not be ascribed to an intramolecular rearrangement of the first, such a rearrangement as has been assumed by Gomberg and Jickling.[1] for the formation of di-*p*-hydroxytetraphenylmethane from diphenoxydiphenylmethane through the agency of acids. Upon further examination we found that, in addition to phenoxytriphenylmethane, some hydroxytetraphenylmethane is always formed when not all the metallic sodium has gone into solution in the phenol previously to the addition of triphenylchloromethane. Under these circumstances some triphenylmethyl must be formed through the action of the metallic sodium upon triphenylchloromethane, and the triphenylmethyl unites, in its turn, with phenol.[2]

$$2(C_6H_5)_3C + C_6H_5OH = (C_6H_5)_3C.C_6H_4OH + (C_6H_5)_3CH.$$

This, we believe, offers a satisfactory explanation for the occasional formation of hydroxytetraphenylmethane in the above condensation.

Summary.

1. It has been shown that triphenylchloromethane gives, with phenyl magnesium bromide at 150–200°, yields of 10–12% of tetraphenylmethane, as compared with 3–5% that have been previously obtained at lower temperatures.

2. The methyl and ethyl ethers of triphenylcarbinol give, with phenyl magnesium bromide, yields of 10–12% of tetraphenylmethane; the phenyl ether, however, gives 20%.

3. Triphenylcarbinol and the carbinol chloride condense with phenol in the presence of very small quantities of acid and give almost quantitatively *p*-hydroxytetraphenylmethane.

[Contribution from the Chemical Laboratory of Case School of Applied Science.]

THE RELATIONS IN COMPOSITION OF THE DIFFERENT FORMS OF NATURAL BITUMENS.

By Charles F. Mabery.

Received June 22, 1917.

There has long been much discussion concerning the numerous varieties of bitumen as to their formation, composition, and their relation

---

[1] This Journal, 37, 2358 (1915).

[2] Schmidlin, *Ber.*, 45, 3180 (1912); Gomberg and Cone, *Ibid.*, 37, 2040 (1904).