

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE THREE NITRO-TRIPHENYLAMINES.

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(1) Theoretical Part.

Hitherto, only one mono-nitro derivative of triphenylamine has been known; it was prepared by Herz¹ in the year 1890 by the treatment of triphenylamine with nitric acid. Although this method of preparation contains no proof as to whether it is an ortho, a meta, or a para derivative, it was, nevertheless, listed in the literature as the para. For a purpose,² which will be discussed later, Piccard and Kharasch, needed the *p*-nitro-triphenylamine. Since we could not find in the literature any proof for the constitution of the compound prepared by Herz,³ nor a general method for the preparation of the nitro-triphenylamines, we tried to prepare *p*-nitro-triphenylamine by the introduction of phenyl groups into *p*-nitraniline. The substance thus produced was indeed identical with the product prepared by Herz. Against our proof, however, the objection could be raised, that a rearrangement might have taken place in the course of the reaction (heating for 30 hours at 200° in the presence of potassium carbonate). Were this last objection valid, then we could not obtain, when starting from the three mono-nitranilines, three different mono-nitro-triphenylamines. Hence we phenylated *o*- and *m*-nitraniline as well as *p*-nitraniline and obtained three isomeric mono-nitro-triphenylamines. Absolute proof is thus given that our three derivatives are, respectively, the ortho, the meta, and the para compounds.

Irma Goldberg⁴ has introduced the use of phenyl iodide for the preparation of triphenylamine and some of its substitution derivatives. She heated diphenylamine with phenyl iodide and potassium carbonate in nitrobenzene solution in the presence of some copper powder. The latter had already been used for similar condensations as a catalytic reagent. Since Kahlbaum had introduced under the name "Kupferbronze" or "Naturkupfer C," a very good preparation made by powdering metallic copper in a special manner, no one in the past, it seems, prepared the cop-

¹ *Ber.*, 23, 2537 (1890).

² For the identification of nitroso-triphenylamine.

³ When this article was ready for publication, we happened to find that Bamberger (*Ber.*, 41, 3510 (1908)) had already prepared the *p*-nitro-triphenylamine by heating together diphenylamine and *p*-iodo-nitrobenzene from which it follows that its structure is the para. This reference is not given in Richter's "Lexikon" of 1911.

⁴ Irma Goldberg, when making *o*-nitro-diphenylamine by heating in this manner *o*-nitraniline with phenyl iodide, obtained in addition to tarry by-products, a mixture consisting of unchanged *o*-nitraniline, *o*-nitro-diphenylamine, and *o*-nitro-triphenylamine. She did not, however, isolate the last substance. *Ber.*, 40, 4542 (1907).

per powder for himself. Being unable to secure at this time the German product, we tried a new chemical method for making it, and we are glad to say that it is possible to make in this country a copper powder, which is equal, if not superior, to the German standard.

(2) Experimental Part.

A. The Preparation of Catalytic Copper.—A solution of chromous chloride was prepared by the reduction of 190 g. of commercial sodium dichromate by means of an excess of pure zinc (600 g.) in the presence of 1250 cc. of concentrated hydrochloric acid. The acid was added in three portions. The reaction was vigorous, generating much heat with the evolution of much steam, acid, and hydrogen. The color changed first to a green and finally to a light blue. When the reaction had subsided and the reduction was complete, the mixture was freed from zinc by filtration through glass wool. The chromous chloride was protected from oxidation by a rapid current of carbon dioxide. The solution was now rapidly cooled.

A solution of 120 g. of crystallized copper sulfate in 700 cc. of water was prepared and, shaken well, cooled in a freezing bath until it had become filled with a mass of ice crystals. The mixture was now poured into the chromous chloride with proper stirring. The reduction is quantitative and instantaneous. The precipitated copper was washed by decantation with much water, then with absolute alcohol, then transferred to a suction filter and washed with benzene and finally with a solution of vaseline in benzene. The vaseline prevents oxidation by the air and makes the preparation quite stable. The yield is theoretical.

The copper thus prepared forms a light red powder, which is exceedingly finely divided, without any metallic luster. Rubbed between the fingers, it remains on the skin like flour.

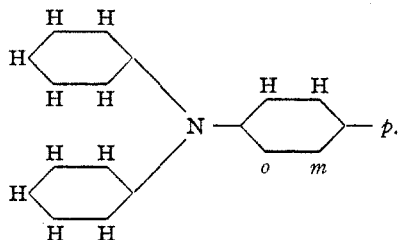
For catalytic purposes in the phenylation of aromatic amines the copper may be used alone or it may be mixed with a small amount of potassium iodide as recommended by Irma Goldberg.¹

B. The Preparation of the Three Nitro-triphenylamines.—For the preparation of a nitro-triphenylamine by phenylation, we can start directly from the respective nitraniline. First one phenyl group is introduced and the nitro-diphenylamine formed reacts then with a second molecule of phenyl iodide. In this manner we get in addition to unchanged nitraniline and nitro-diphenylamine, the nitro-triphenylamine together with a quantity of tarry by-products. As the nitro-triphenylamine has no basic properties, its isolation and purification is a disagreeable piece of work. We find that the tarry products are only formed during the first step of the reaction, they are derivatives of the nitraniline and not of the nitro-di- or the nitro-triphenylamines. For this reason it is better to make first in one way or

¹ *Ber.*, 40, 4542 (1907).

another a pure nitro-diphenylamine and then phenylate this. We have then but to isolate the nitro-triphenylamine from a nitrobenzene solution, which contains, only a very small amount of unchanged nitro-diphenylamine, if any, no nitraniline and no tar.

Nitro-triphenylamines.—



Two grams of pure *p*-nitro-diphenylamine, 5 cc. of phenyl iodide, 0.7 g. of potassium carbonate, about 0.1–0.2 g. of copper powder mixed with a little potassium iodide, were boiled together with 10 cc. of nitrobenzene under a reflux condenser for 30 hours on a sand bath. The excess of phenyl iodide and of nitrobenzene was removed by steam distillation. The mixture remaining was extracted with ether and the extract filtered. After due removal of the ether and after cooling, the residue crystallized. Any unchanged *p*-nitro-diphenylamine was completely removed by treatment with warm concentrated hydrochloric acid. The *p*-nitrotriphenylamine was recrystallized from 50% alcohol. The pure substance melted at 140° and when mixed with the product of direct nitration of triphenylamine,¹ no depression was observed. Thus, the direct nitration gives the para product. The statement that decomposition occurs at the melting point is incorrect. The crude yield (m. p. 133°) was 94% of the theoretical.

Pure *m*-nitro-diphenylamine (2 g.) was heated at boiling for 30 hours, together with 5 cc. of phenyl iodide, 0.7 g. of potassium carbonate, about 0.2 g. of copper mixed with a little potassium iodide, and 10 cc. of nitrobenzene. The mixture acquired a lighter color as the reaction went on. The excess of phenyl iodide and nitrobenzene was removed by a steam distillation. After treatment with concentrated hydrochloric acid, the crude light yellow residue was recrystallized from dilute alcohol and also from methyl alcohol. The crude product melted at 75–76° and the pure product at 78°. Recrystallization from acetic acid did not change the melting point. The crude yield was about 95% and only a few per cent. were lost during further purification.

Subst. 0.1120; CO₂, 0.3044; H₂O, 0.0500.

0.0674; CO₂, 0.1837; H₂O, 0.0307.

0.2833; 24.9 cc. dry N₂ at 22° and 726 mm.

Calc. for C₁₈H₁₄O₂N₂: C, 74.46; H, 4.86; N, 9.66. Found: C, 74.14, 74.36; H, 4.99, 5.10; N, 9.72.

¹ M. p. 139–140° according to Herz.

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; CO₂, 0.3656; H₂O, 0.0609

0.2180; 18.5 cc. dry N₂ at 21° and 734 mm. (CuO).

0.1051; 9.35 cc. dry N at 21° and 725.5 mm. (PbCrO₄).

Calc. for C₁₈H₁₄O₂N₂: 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.

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TETRAPHENYLMETHANE.

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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).