

It was further moved that the thanks of the Society be tendered to the Ehret Brewing Co., the Mutual Gas Light Co., the Equitable Gas Light Co., the Brin Oxygen Co., the De La Vergne Refrigerating Co., the Chemical Manufacturers of New York and to all others from whom the Society has received courtesies. Seconded and carried.

The retiring president, Prof. Barker, expressed his sense of the pleasing relations that had marked his term of office and congratulated the Society upon the election of his successor.

A motion to adjourn was then made and seconded, and the fourth general meeting was adjourned.

DURAND WOODMAN,  
Recording Secretary.

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## ON DISULPHOTETRAPHENYLENE.

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BY C. E. LINEBURGER.

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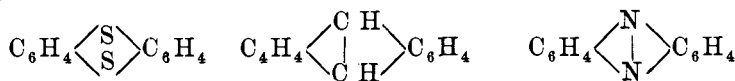
Since the work of Stenhouse<sup>1</sup> and Graebe<sup>2</sup> on Disulphodiphenylene and its derivatives, no one, so far as I know, has taken up the investigation of the subject, except Friedel and Crafts, who have effected the synthesis of the compound by means of the reaction of the sulphur chloride on benzene in the presence of aluminium chloride. These chemists have not studied the substance further. Still the constitution of the compound seems to be such as to lend itself easily to synthesis, and now that it can be so easily prepared by means of the Friedel-Crafts reaction, nothing prevents its further study. I have therefore tried to carry out some of the reactions of which disulphodiphenylene seemed capable.

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(1) Liebig's Ann., **140**, 284 and **156**, 332.

(2) Liebig's Ann., **174**, 177; **179**, 178, and **180**, 234.

From one point of view, the constitution of disulphodiphenylene much resembles that of anthracene and phenazine:



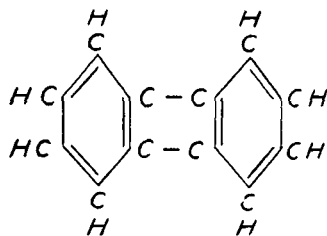
Disulphodiphenylene.

Anthracene.

Phenazine.

It was thought possible to pass, by means of suitable reactions, from one compound to another. I first tried to replace the sulphur atoms in disulphodiphenylene, by the imide group NH. I heated a pure disulphodiphenylene with alcohol saturated with ammonia, in sealed tubes, for more than twenty-four hours at 280°. If the temperature ran higher than 280°, the tubes invariably burst. No reaction, however, took place below 280°, the disulphodiphenylene forming long, finely formed crystals on cooling. The fact that above 280° the tubes burst, no matter whether filled with large or small quantities of substance, indicates that a reaction must have taken place with great violence. As it was impossible to control this reaction, I let dry ammonia act upon boiling disulphodiphenylene. I passed a rapid stream of ammonia into a quantity of disulphodiphenylene which was kept boiling vigorously for several hours. However, not a trace of sulphuretted hydrogen could be found in the ammonia that passed off. The disulphodiphenylene was, indeed, much blackened and gave off a foul odor, but I have found that by prolonged boiling this change always takes place. Disulphodiphenylene decomposes slowly on being distilled; a little black resin always remains in the retort. At any rate, the reaction, if reaction there was, between ammonia and disulphodiphenylene did not take place in the way sought for.

Attempts were then made to form diphenylene by the removal



of the sulphur and the union of the carbon atoms. As disulphodiphenylene distils unchanged over freshly reduced copper, it was necessary, in order to bring about a reaction, to pass the vapor of the compound over copper heated to intense redness. Even then a portion of the substance remained unchanged. The stability of the molecules is truly remarkable.

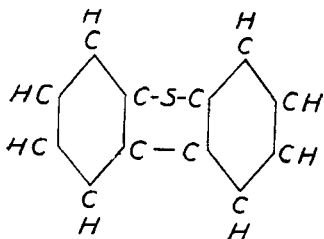
The details of the experiment are as follows: About 10 grms of disulphodiphenylene are put in the bottom of a hard glass tube about twenty mm. in diameter and fifty cm. long, and above this is a plug of asbestos. The rest of the tube is filled in with freshly reduced copper coarsely powdered. The open end of the tube is luted into a flask of about the capacity of a litre in the side of which a small hole is made by means of the blow pipe, so that the gases and uncondensed vapors may escape freely. The tube is now laid in a small combustion furnace, placed in a slanting position. The copper is first heated as hot as possible, and then the disulphodiphenylene *slowly* distilled over it. Quite a decomposition takes place with evolution of ill-smelling fumes. Care must be taken that the orifice in the flask does not become stopped up as the internal pressure will force the lute or blow open the hot tube. A dark colored distillate collects in the flask, where it solidifies on cooling. When all the substance has been distilled over the copper, the flask is disconnected and its contents treated with strong alcohol. After the insoluble resin is filtered off, the filtrate is set aside to crystallize. In a few days a crystalline crust separates out along the sides of the dish. This seems to contain alcohol of crystallization, for, on heating the air-dried substance alcohol is given off. After melting the crystalline crusts to divide off the alcohol, therefore, I dissolved the melt in benzene, in which it is very soluble. On evaporation, irregularly shaped masses of white crystals separated out which did not melt at all well. Evidently we have to do here with a mixture. In experimenting, I found that by sublimation I was able to obtain the greater part of the compound in long white needles. The sublimation takes place at quite a low temperature and the crystals obtained melt very well at 101°. As sublimation proved a much better means of purification than crystallization, I made use of it throughout.

An analysis of the sublimate carried out in a bayonet tube with a mixture of copper oxide and lead chromate gave the following results:

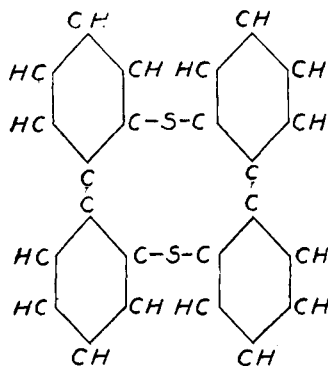
	I.	II.	Calc. for $C_{12}H_8S$ .
C .....	77.88	77.97	78.25
H .....	4.35	4.45	4.35

The substance therefore contains sulphur and is not diphenylene.

One would infer from the analysis that it was simply diphenylene sulphide formed by the removal of an atom of sulphur from the disulphodiphenylene and consequent union of the two bonds thus set free. But its properties differ greatly from those of diphenylene sulphide. Diphenylene sulphide melts at  $94^{\circ}$  (Stenhouse),  $97^{\circ}$  (Graebe), and boils at  $332^{\circ}$ – $333^{\circ}$ . The substance in



question melts at  $101^{\circ}$  and boils at  $414^{\circ}$ , under a pressure of 753 mm. of mercury. The former crystallizes in long needles from strong alcohol; the latter separates out as an indefinite crystalline crust from its alcoholic solution. Also, in their behavior towards oxidizing agents, the two substances differ markedly. By the action of potassium dichromate and dilute sulphuric acid on diphenylene sulphide, diphenylene sulphone  $C_{12}H_8SO_2$ , is formed. The new compound is hardly attacked by the oxidizing mixture, even though heated with it for several hours. These facts establish definitely that the substance obtained, although possessing the same percentage composition, is not diphenylene sulphide. From facts of which I will speak further on I am led to give the substance a formula isomeric with that of diphenylene sulphide having this constitution. I will call the compound then, from its mode of formation, disulphotetraphenylene.



Disulphotetraphenylene possesses an uncommon stability. All the methods used for estimating the sulphur were inadequate. This fact is in a certain way so noteworthy that I will describe cursorily the experiments carried out for the purpose of determining the sulphur. .1372 grms. of the substance were heated with fuming nitric acid in a sealed tube for six days at  $300$ – $350^{\circ}$ . The tube was of thick glass, such as used by

Berthelot in his experiments on reduction by means of hydriodic acid. Disulphotetraphenylene dissolves easily in cold fuming nitric acid, an oxidation product or a nitro derivative being probably formed. This is so stable, however, that it was not at all destroyed on heating. On opening the tube little pressure was manifest, and on diluting the contents with water, a white organic precipitate was thrown down.

.3024 grms. were placed in a hard glass tube containing potassium nitrate and sodium carbonate, the whole being arranged as recommended by Volhard<sup>3</sup>. But even though the vapor of the substance had to pass through a column nearly 20 cm. long of the fused alkalis kept at an intense heat, the combustion was not perfect, and vapors containing sulphur escaped from the tube.

A combustion tube about a yard long was filled about two-thirds full of dry sodium carbonate; then came a porcelain boat containing the compound, and after the boat a spiral of platinum wire., While a rapid stream of oxygen was passed through the tube, and while the platinum spiral was kept at a high heat, the substance was *slowly* distilled over upon the sodium carbonate. But even though the salt was heated intensely some of the substance passed over unchanged and condensed in the cooler portion of the tube in white needles melting at 101°. However, although I was unable to make a determination of the sulphur in the compound there is no doubt but that it has the composition given above. Being formed in a reducing medium, it would be impossible for oxygen to be present.

Another fact that renders the above constitution very probable is that the two sulphur atoms in disulphodiphenylene are not attached to the molecule with the same force. One may be removed quite easily and by a rather unexpected agent. Disulphodiphenylene dissolves in fuming nitric acid with evolution of reddish fumes even at 0°. If water be added to the solution, a white precipitate is thrown down, which is nothing but diphenylene sulphone. If barium chloride be added to the filtrate from this precipitate, barium sulphate is formed, that is, the filtrate contains

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<sup>3</sup> Liebig's Annalen, 190, 1.

sulphuric acid. The reaction may be interpreted in two ways:

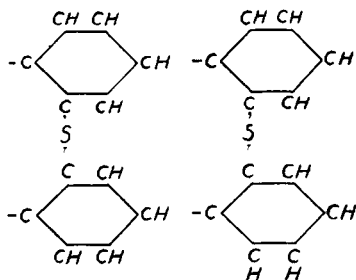
*First.*—The nitric acid removes at once an atom of sulphur from the disulphodiphenylene, and oxidizes it to sulphuric acid, while the bonds of carbon left free unite with each other and the second atom of sulphur is oxidized to the sulphone group.

*Second.*—The nitric acid oxidizes immediately the disulphodiphenylene to diphenylene disulphone, which, by further action of the acid, is decomposed into diphenylene sulphone and sulphur dioxide, the latter product being then oxidized to sulphuric acid.

These two interpretations really amount to the same thing. In both cases it is a removal of sulphur from the molecule with union of the bonds thus set free and the oxidation of the remaining sulphur atom. It is rather strange that such a reaction should be brought about by such a reagent as fuming nitric acid; but, at any rate, this explains well the formation of disulphotetraphenylene. The heated copper is able to remove the loosely bound sulphur atom, but the other atom succeeds in escaping its action. The residues of molecules thus formed seem to prefer to unite two by two, giving disulphotetraphenylene.

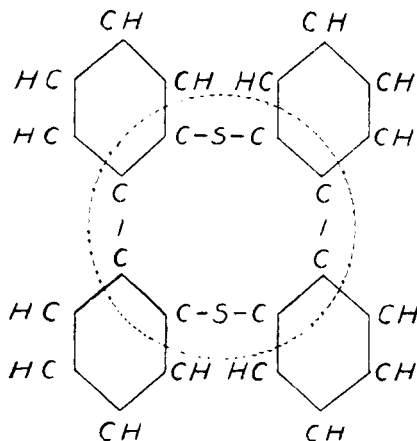
The question arises why, in the reaction of nitric acid on disulphodiphenylene, disulphotetraphenylene or an oxidation product of the same is not formed. The question is a

difficult one to answer. The conditions of the two experiments differ widely. In the one case, we have to do with a strong oxidizing agent at a low temperature, in the other with a powerful reducing agent at a high temperature. This may be the reason that the product of the two reactions are so different. It is, indeed, a little strained to assume that union between free carbon bonds takes place in adjacent molecules rather than in the same molecule. But the fact is that in the reaction of heated copper on disulphodiphenylene, but little, if any, diphenylene sulphide is formed while a comparatively large amount of a



substance with the same percentage composition, but widely different properties, is formed.

Disulphotetraphenylene possesses a ring-like structure, the ring consisting of eight carbon and two sulphur atoms.



A noteworthy fact about this ring is its remarkable stability towards heat. I have not yet obtained a sufficient quantity to make a thorough study of the action of the halogens and oxidizing and reducing agents on it. It is not by any means the only product obtained in the reaction. A quite large quantity of a resin is also obtained. Disulphotetraphenylene is, however, the only compound that I have been able to obtain in a state of purity. I am engaged in preparing a larger amount of the compound in order to carry out a thorough investigation, the results of which I hope to be able to communicate in the near future.

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This work was done in the laboratory of Professor Friedel in Paris.