ON THE FORMATION OF ANTHRAQUINONE UNDER PECULIAR CONDITIONS.

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Both the indophenin reaction, formerly used as a test for benzol[1], and the phenanthraquinone reaction of Laubenheimer[2], effected with toluol, have been shown by Victor Meyer[3] to be due, *not* to benzol and toluol, but to thiophene and methylthiophene respectively. The first suggestion of an experiment looking towards the isolation of thiophene was the fact that some benzol, obtained by distillation of benzoïc acid[4] with lime, did *not* show the indophenin reaction[5]. This reaction consists in treating coal tar benzol with isatin and concentrated sulphuric acid, when deep blue indophenin $C_{12}H_7NOS$ results.

But benzol and toluol, after proper treatment with concentrated sulphuric acid, will not show the indophenin or the phenanthraquinone reaction respectively[6].

This latter reaction, also called the Laubenheimer reaction, was described by its discoverer in 1875 (*loc. cit.*) as follows :

"A few drops of toluol are added to a dilute solution of " phenanthraquinone in glacial acetic acid. The mixture is " cooled continually and drops of concentrated sulphuric acid are " allowed to run into it. After a few minutes water is added. " A coloring substance is precipitated, which, on shaking with " ether, dissolves with a beautiful purple tint."

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[1] A. von Baeyer, Ber. **12**, 1311 ; **16**, 1477 ; **18**, 2637.

[2] Ber. **8**, 224.

[3] Die Thiophengruppe ; Vieweg, 1888.

[4] From urine, from resin or from toluol.

[5] V. Meyer, (*loc. cit.*) pp. 1 *et seq.*

[6] Ber. **17**, 1338.

The indophenin reaction is caused by the presence of thiophene (C_4H_4S) which exists in all coal tar benzol, while correspondingly, the Laubenheimer reaction is occasioned by α-methylthiophene, called α-thiotolene, $C_4H_3S\ CH_3$, contained in all coal tar toluol. The pure thiophene and thiotolene show the two described reactions most distinctly.

The analysis of the coloring matter prepared from phenanthraquinone, α-thiotolene and conc. sulphuric acid, shows approximately the formula, $C_{19}H_{12}OS$, so that V. Meyer[1] writes the following equation for the formation of this body, which is precipitated in the shape of indigo blue flocks :

$$C_{14}H_8O_2 + C_5H_6S = C_{19}H_{12}OS + H_2O.$$

It is a dark blue powder which, on pressure, assumes a copper lustre. It is easily soluble in alcohol, benzol, chloroform and carbon disulphide, but insoluble in water. Heated alone, it does not show any characteristic behavior.

A remarkable result was shown, however, on combustion of the substance with lead chromate. At a comparatively low heat a *yellow vapor* was formed, which sublimed in the colder part of the tube (outside of the combustion furnace), in the shape of large golden yellow needles. These were free from sulphur, did *not* give the phenanthraquinone reaction, showed on resublimation the melting point of 274° C. and exhibited every other property of *anthraquinone.* The characteristic reaction of Claus [2] for anthraquinone was also obtained and finally the body was transformed into *alizarine.*

The phenanthraquinone that was used for the preparation of the above mentioned coloring substance had been newly prepared

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[1] Die Thiophengruppe, p. 40.

[2] Mix 1 mg. anthraquinone with some sodium amalgam, add absolute ether (free from alcohol) and shake. On now adding a few drops of water a red coloration ensues, which disappears again on shaking, in consequence of the admission of air. On adding absolute alcohol to the mixture of anthraquinone and sodium amalgam a green coloration sets in, disappearing on agitation with air. Both colors reappear on standing. (Claus, Ber. **10**, 927.)

from its pure bisulphite compound and did *not* contain any anthraquinone.

V. Meyer[1] says: "It will be difficult to find an explanation for this peculiar pyrogenous reaction. It seems almost as if the methyl group of the thiotolene has to do with this formation of anthraquinone. The fact that the green coloring substance obtained from *thiophene,*[2] and phenanthraquinone under the same treatment did *not* lead to anthraquinone, favor this assumption.

In the following pages I offer an explanation of this peculiar formation of anthraquinone, and I shall also propose some experiments which will decide whether my theory is right or not. A careful study of V. Meyer's work on thiophene and its derivatives and an extended acquaintance with the behavior of aromatic compounds, particularly of those formed by condensation from the fatty series, lead me to regard this explanation as highly probable.

Before considering the main object of this paper, it may be well to glance briefly at the mode of preparation and the constitutional formula of thiophene, also to mention some of its properties. V. Meyer,[3] Volhard and Erdmann,[4] Paal,[5] also Paal and Tafel,[6] Tiemann and Haarmann,[7] have contributed methods for the synthesis of thiophene. According to these researches[8] many substances which contain the group;  $\begin{array}{ccc} C & — & C \\ | & & | \\ CO & & OC \end{array}$ as for instance, succinic acid, pyro-tartaric acid, acetonyl-acetone, laevulinic acid,

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[1] Die Thiophengruppe, page 41.

[2] See pp. 30 and 43 of this paper.

[3] Ber. **16**, 2176.

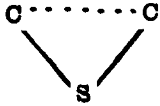
[4] Ib. **18**, 454.

[5] Ib. **18**, 367 and 2251.

[6] Ib. **18**, 456 and 688.

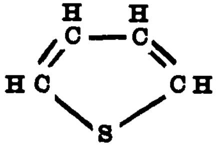
[7] Ib. **19**, 1257.

[8] V. Meyer, die Thiophengruppe, p. 249.

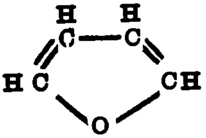
etc., when treated with phosphorus trisulphide,[1] yield thiophenes, a complex group  being formed from the two CO groups. The best synthetical preparation of thiophene, one of practical value, is that of Volhard and Erdmann (*loc. cit.*), published in 1884. It consists in the treatment of sodium succinate with a *double* quantity of phosphorus trisulphide. This method, which has since been improved, yields fifty per cent. of the theoretical quantity. Thiophene thus prepared is sold at 130 marks per kilo.

V. Meyer[2] gives a discussion of the structural formula of thiophene, which leads him to compare it to *furfurane* and *pyrrol.*

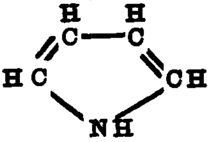
Thiophene :



Furfurane :



Pyrrol :



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[1] Which is *not* to be considered a real chemical combination, but a fused mixture of the components in the proportion of P_2 to S_3.

In order to understand this formation, we must assume that five molecules of sodium succinate would be acted upon by a mixture of

P_8S_{10} (very nearly $4P_2S_3$).

Because *one* molecule of sodium succinate would have to lose O_4 and Na_2, while one atom of sulphur would take the place of these.

The reaction could then most simply be expressed :

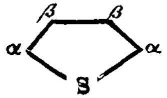
$$5\left(\begin{array}{l}CH_2 \text{ --- } COO\,Na \\ | \\ CH_2 \text{ --- } COO\,Na\end{array}\right) + P_8S_{10} = 5C_4H_4S + 4P_2O_5 + 5Na_2S.$$

The molecular weight of sodium succinate and of P_2S_3 are very nearly the same, being as 162 to 158.

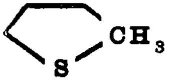
Since phosphoric anhydride cannot easily be supposed to exist under these conditions along with either sodium succinate or sodium sulphide, a more complicated reaction will take place, leading to sulphur compounds higher than thiophene. To avoid this may be the reason for the practical prescription of using 2½ times the amount of P_8 S_{10} indicated by the equation. L. H. F.

[2] Die Thiophengruppe, p. 30, *et seq.*

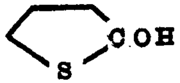
To facilitate the study of the substituted thiophenes, he uses the abbreviated formulæ :



Thus the methyl thiophene above mentioned as *α-methylthiophene* or *α-thiotolene*, has the constitution :



while the corresponding thiophenaldehyde, which will be referred to later, would be :



The properties of thiophene are the following : It is a colorless, clear liquid, boiling at 84° C. (Benzol boils at 80.5° C.) It has a feeble and not very characteristic odor. It is not miscible with water. It does *not* solidify in a mixture of ice and salt. Concentrated sulphuric acid dissolves it in the cold with dark brown coloration ; later the mixture evolves hydrogen sulphide, then sulphur dioxide, finally the mass thickens, and when water is added a thick, gray, amorphous precipitate is formed, which is insoluble in all liquids. The reaction between thiophene, isatin and conc. sulphuric acid, forming by condensation, according to A. v. Baeyer (*loc. cit.*), the beautifully blue dyestuff indophenin, is the most delicate reaction, indicating the presence of the smallest traces of thiophene. According to A. v. Baeyer, the reaction takes place thus :

$$[C_8H_5NO_2 + C_4H_4S] - H_2O = \overset{\textit{Indophenin.}}{C_{12}H_7NOS.}$$

Thiophene and phenanthraquinone show the Laubenheimer reaction, when *ether* is replaced by *chloroform*, the dye formed dissolving in the latter with deep emerald green color.[1]

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[1] V. Meyer, die Thiophengruppe, pp. 24 and 25. See also pp. 28 and 43. of *this* paper.

Thiophene is not attacked when distilled over metallic sodium. In physiological action it differs from benzol.[1]

Approaching now the main object of our discussion, which is, to explain the formation of anthraquinone from the dye $C_{19}H_{12}OS$,[2] when this latter is heated with lead chromate, we find, *a priori*, three possible cases of decomposition.

I.—The anthraquinone is exclusively formed out of the phenanthraquinone residue, by rearrangement of the atoms within the molecule and oxidation.

II.—Both, the phenanthraquinone residue *and* the thiotolene residue participate in building up anthraquinone.

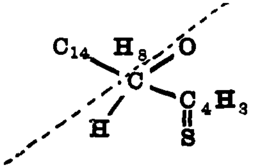
III.—The *thiotolene residue only* is transformed into anthraquinone, being at first and intermediately oxidized to thiophene aldehyde.

I shall only consider the third case, which also implies the formation of anthraquinone out of *α-methylthiophene*.

The following two equations express the supposed formation :

1. $[3C_5H_6S] + [6O]$ minus $[CO_2 + 3H_2S + 2H_2O] =$ $C_{14}H_8O_2$. Anthraquinone
2. $[3C_5H_4OS]$ minus $[COS + 2H_2S] = C_{14}H_8O_2$.

In constructing these two equations I have, of course, recognized the fact that we do not find a *whole* molecule of methylthiophene in the blue dye obtained from phenanthraquinone plus methylthiophene minus water, but probably the residue C_5H_4S very closely linked to one oxygen atom, which binds the carbon of the methyl group to the phenanthraquinone, while a second valency of this same carbon atom is directly linked to the phenanthraquinone residue, according to the following formula :



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[1] Die Thiophengruppe, p. 26 ; and A. Heffter, Archiv für die gesammte Physiologie, **39**, 420.

[2] From α-thiotolene, phenanthraquinone and conc. sulphuric acid.

The splitting off of thiophene aldehyde is then indicated by the dotted line.

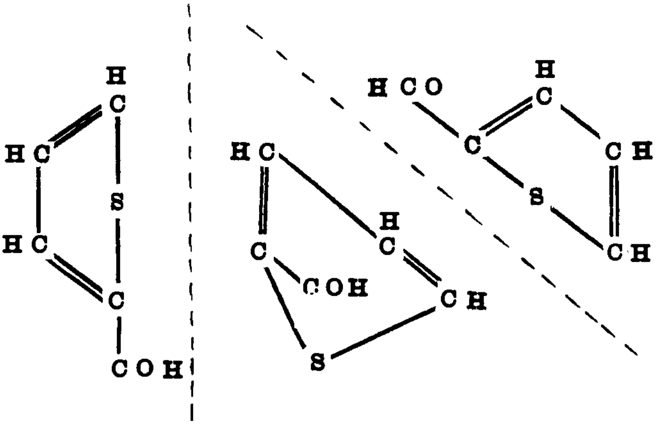
Further, it will be snown how anthraquinone may be formed from thiophenaldehyde, transitorily existing in our reaction as the formula indicates. I will only point out here, that *simultaneously* with such a formation, the phenanthrene residue $C_{14}H_8$ also might suffer a rearrangement of its nucleus and then be oxidized by the lead chromate to anthraquinone, so that a formation of this latter might take place according to case III. and case I. together.

But the main interest being attached to case III., since it shows the possibility of a transition from a thiophene derivative to an anthracene derivative, I will consider it exclusively.

Let us then look at the inner mechanism, as indicated by equation 2.

To this end I arrange on the paper the formulæ[1] of three thiophenaldehyde molecules in such a manner that the supposed formation of anthraquinone may be more easily foreseen.

FIG. 1



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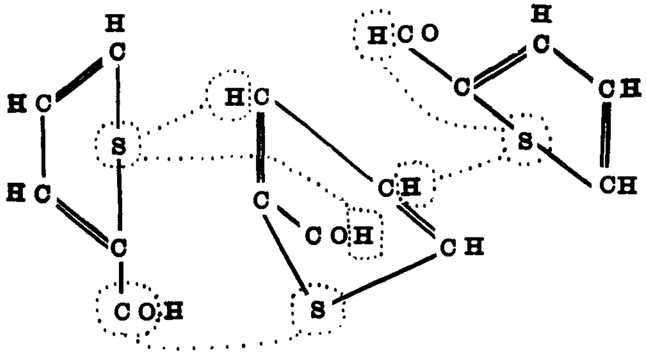
[1] *Ladenburg*, Theorie der aromatischen Verbindungen (Vieweg, 1876), page 23, says: In modern chemistry the formula of a substance is an expression which gives not only an account of the composition and the true molecular weight of that substance, but which *also* indicates a definite view of the manner in which the atoms, forming that molecule, are linked together.

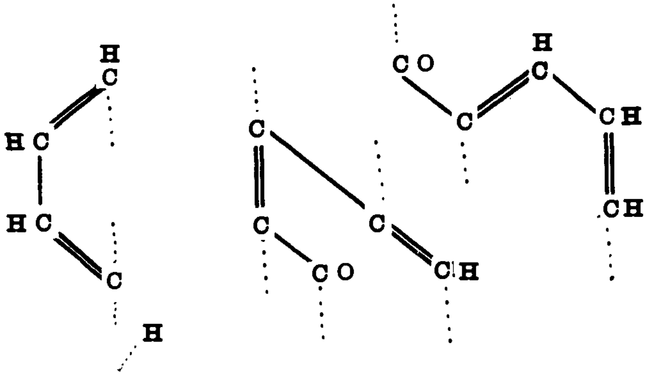
We may now remove from these three molecules of thiophenaldehyde, two of hydrogen sulphide and one molecule of carbon oxysulphide in the following manner .

FIG. 2



The remaining residues, in which the unsaturated valencies are indicated by dotted lines, would then face each other thus :

FIG. 3



Now in order to do justice, in a manner, to Kekulé's repeatedly expressed demand [1] ("in imagining the construction of such for-

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[1] See page 35 of this paper, foot note.

" mulæ, care should be taken to unite as far as possible those carbon " atoms with each other, which *together* have furnished the ele- " ments for the eliminated compounds,") we may mutually saturate the free valencies as indicated in Fig. 3, in the manner shown in Fig. 4. Maintaining the sequence of numbers of the carbon atoms, this Fig. 4, as will be easily seen, is a *phenanthraquinone,* as shown in Fig. 5. It is not necessary at this point to give a correct picture of anthraquinone, this will be done later. I restrict myself here to showing merely that a similar ring can easily be formed out of thiophenaldehyde. The forms which would correspond to equation 1, are quite

FIG. 4

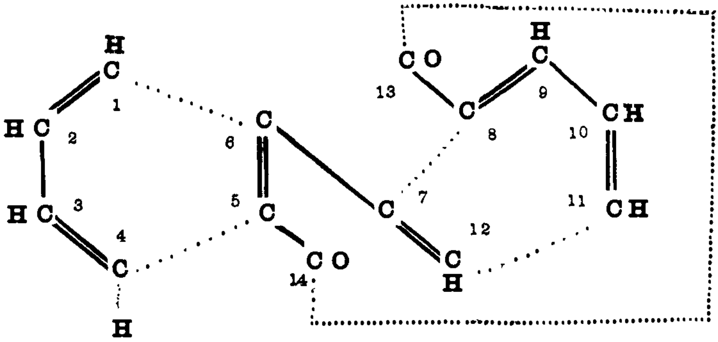
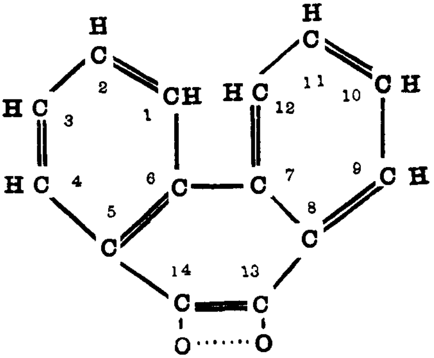


FIG. 5



analogous to the ones given just now, only we have to start from methylthiophene under oxidizing conditions. In relation to the arbitrary abstraction of H_2S and of COS, we must not forget that we work in the presence of lead and of available oxygen, and that I only assume, that the *elements* which can form those two compounds are taken away, so as to form finally water, carbon dioxide and lead sulphate.

The decisive experiment which I propose, is to conduct thiophenaldehyde (or methylthiophene) over fused lead or lead oxide, at a gentle heat, perhaps also over mercuric oxide, and only if that experiment should not produce anthraquinone, to take lead chromate.

But here I must suggest an important consideration.

Intermediate products have always been of great weight in the study of the formation of aromatic nuclei. I merely instance phorone and mesityloxide in the formation of mesitylene from acetone, as one example.[1] I have thought, that it might lead more easily to the point, if the possibility of formation of intermediate products were considered also in this case. One such product for example, could be formed from *two* molecules of thiophenaldehyde, from which the elements of one mol. H^2S and of one mol. COS would be eliminated. Fig. 6 indicates, in a

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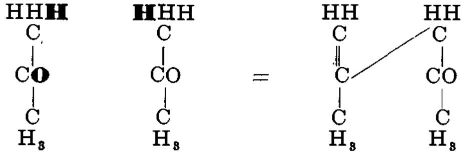
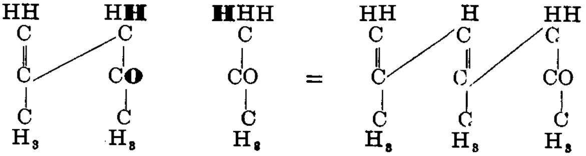
[1] Two mols. of acetone minus one mol. of water = $\frac{\text{Mesityloxide}}{C_6H_{10}O}$

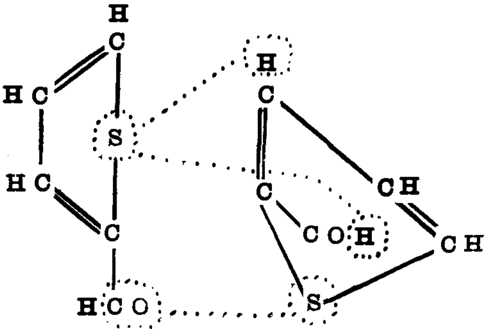


One mol. of mesityloxide plus one mol. of acetone minus one mol. of water = $\frac{\text{Phorone}}{C_9H_{14}O}$ (see also Kekulé, Ber. 2, 368).



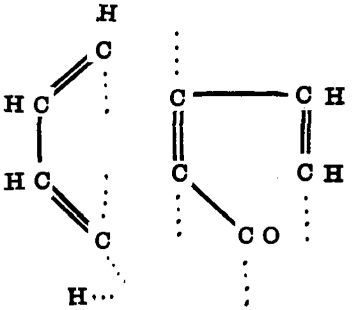
manner perfectly analogous to that of Fig. 2 how this elimination might be supposed to take effect.

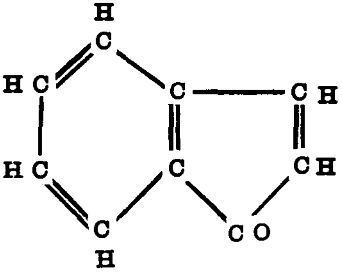
FIG. 6



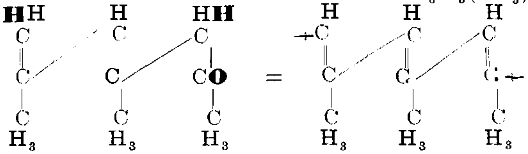
The remaining residues are shown in Fig. 7 with the free valencies indicated by dotted lines, while in Fig. 8 those valencies are mutually saturated :

FIG. 7 FIG. 8





One mol. of Phorone minus one mol. of water = $\overset{\text{Mesitylene}}{C_6H_3(CH_3)_3}$

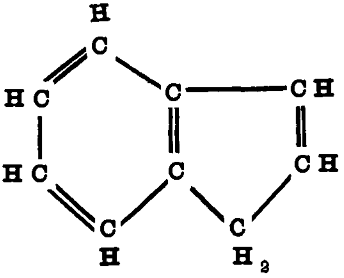


[*Note.*—In the last three equations (footnotes pp. 35 and 36) symbols in faced type show atoms eliminated. The daggers mark the two carbon atoms joined to one another by a single bond.]

Such an intermediate body would be of the highest interest. As a comparison for it we may look to the also hypothetical

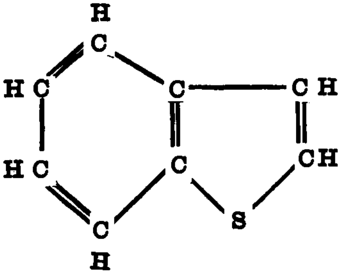
FIG. 9

indonaphthene: [1]



We might call this new hypothetical substance *ketonaphthene*, indicating the presence of a ketonic group (CO). There are two other compounds which are very properly drawn into this comparison, the one is the hypothetical *thionaphthene* of V. Meyer:[2]

FIG. 11



the other, a substance prepared by A. W. Hofmann [3] (called by V.

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[1] Derivatives of these hypothetical bodies have been prepared; see W. Roser, Ber. **20**, 1574; also **16**, 926; 1041; 2261; **18**, 190; further, A. v. Baeyer and W. H. Perkin, Jr., Ber. **17**, 125; see likewise Perkin, Ber. **16**, 208, 1787, 2136.

[2] Thiophengruppe, p. 252.

[3] Ber. **13**, 224.

Meyer a quinoline of the thiophene series, and by Hofmann,[1]—who places it parallel with the thiophene group, and who has prepared quite a number of derivatives—*methenylamidophenylmercaptan*) which has this constitution :

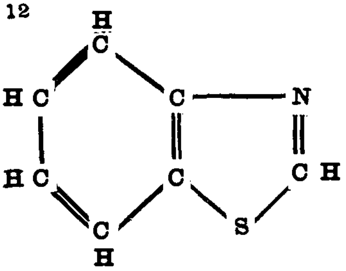

FIG. 12

Also the *cumarone*[2] and derivatives of the same, as, for instance *Hantzsch's*[3] oxymethyl cumarone: may be men-

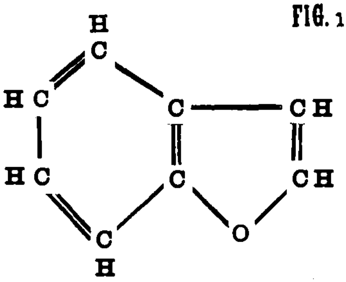

FIG. 13

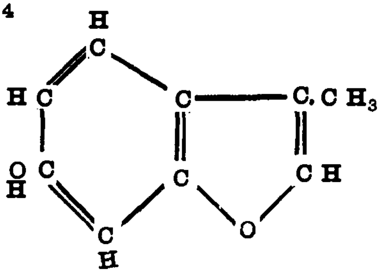

FIG. 14

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[1] Ber., **12**, 1127; **13**, 9; **12**, 1128; **19**, 1811; **20**, 1790; **20**, 2257; **12**, 1129, etc., etc.

[2] Beilstein, Handbuch d. org. Chemie, 1888, v. **3**, 442.

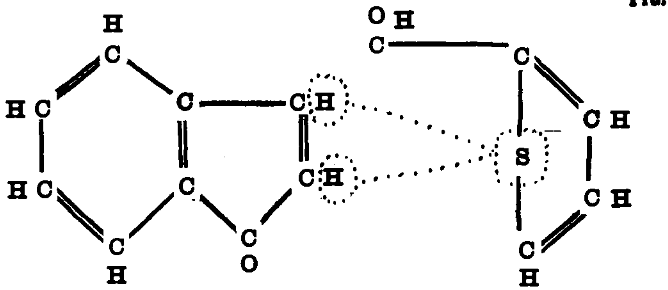
[3] Ber. **19**, 2929.

tioned here[1]. Altogether the existence of the intermediate product, to which our investigation has brought us, and which I have proposed to call *ketonaphthene*, can be looked upon as possible. Such a substance may yet be prepared, and when prepared it will not stand alone.

It is now but one step to show how, by way of this intermediate product, anthraquinone may be finally produced from thiophenaldehyde.

Let us suppose that the so formed ketonaphthene is acted upon (under the given conditions) by one mol. of thiophenaldehyde and that the elements of one mol. of H_2S are expelled in consequence. We would, on the same principle as in former diagrams, arrive at the three formulæ :

FIG. 16



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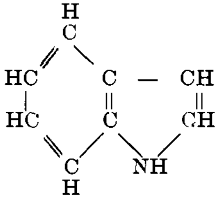
[1] Of course also the indol:



and

the hydrindonaphthene:

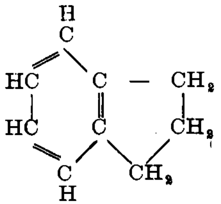


FIG. 16

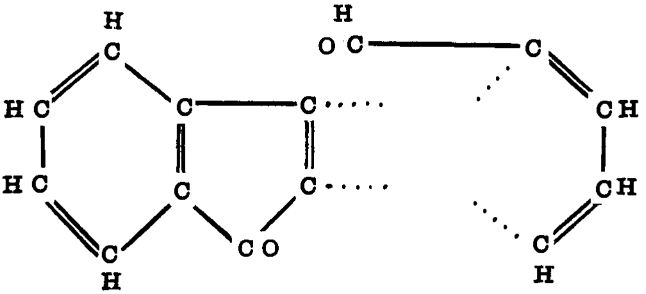
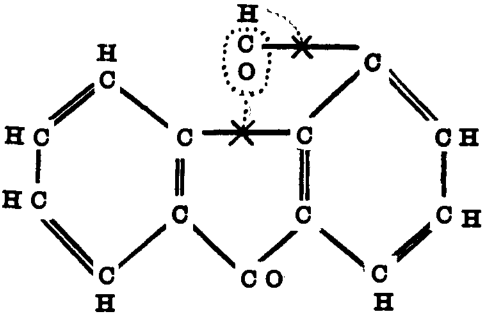


FIG. 17



[1] In order to understand how this construction can lead to anthraquinone we have to suppose that the two crossed valencies are ruptured, that consequently the hydrogen atom of the aldehydic group (COH) is more closely attracted by that carbon atom to which this group was linked, and that the two carbonyl groups

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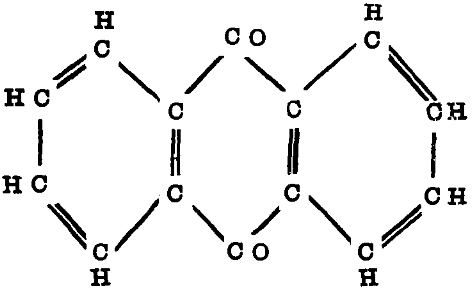
[1] This Fig. 17 would represent a substance which we might call benzophenealdehyde, an unknown compound isomeric with anthraquinone, etc. But such ketone-aldehydes seem to be incapable of existence in the free state. So, for example, the aceto-acetic aldehyde, $CH_3 - CO - CH_2 - COH$, in reference to which see, Ber., **21**, 1144.

(CO) enter into a union, peculiar to quinones. We thus arrive at

FIG. 18

anthraquinone :



But much simpler yet we shall obtain this same figure of anthraquinone if we assume that this is formed from two mols. of *ketonaphthene* :

$$2C_9H_6O \text{ minus } C_4H_4 = C_{14}H_8O_2.$$

This formation would be quite analogous to that of naphthalene from two mols. of benzol, or of anthracene from napthalene.

The following formulæ demonstrate the supposed condensation :

FIG. 19

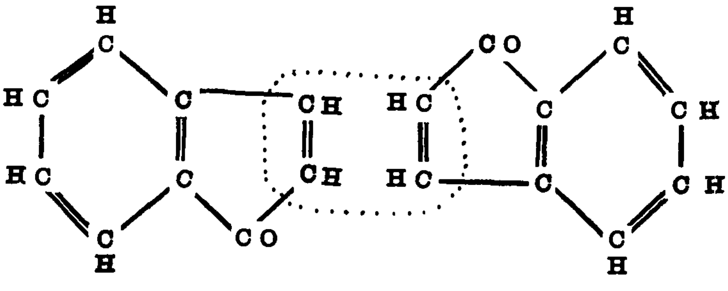
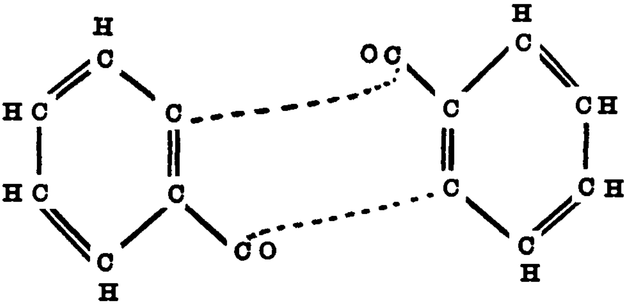


FIG. 20



Here then at least it is not required to rearrange any bonds, which was necessary in the condensation of ketonaphthene plus thiophenaldehyde to form anthraquinone.

I have supposed in the above that the blue dye formed from phenanthraquinone, methylthiophene and conc. H_2SO_4 under elimination of water, permits the splitting off of thiophenaldehyde, which on its part can be supposed to form anthraquinone in two ways, as just demonstrated. An experiment should be performed, under carefully devised conditions, by means of which thiophenaldehyde would really be obtained from that blue dye. This would be a good support for the theory which I have developed and would also be a highly interesting case of oxidation of methylthiophene by means of phenanthraquinone to thiophenaldehyde. The preparation of this latter substance is not now an easy matter. Starting from thiophene, according to V. Meyer[1], acetothienone[2] has first to be prepared by means of acetylchloride and aluminium chloride. From acetothienone the thienylglyoxylic acid[3] is formed by means of oxidation in an alkaline permanganate solution; finally the thienylglyoxylic acid is subjected, in portions of five grammes, to destructive distillation in a current of carbon dioxide, when thiophenaldehyde results. This substance (which

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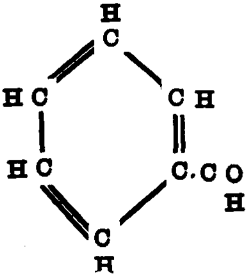
[1] Die Thiophengruppe, pp. 155; 219 and 220; 151.

[2] $C_4H_3S - CO - CH_3$.

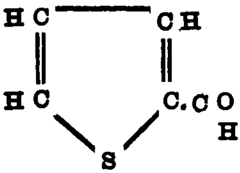
[3] $C_4H_3S - CO - COOH$ [the glyoxylic acid being $HCO - COOH$; or, $(OH)_2\,HC - COOH$.]

resembles benzaldehyde more closely than it does furfurol, even in possessing its odor) might, if the proposed experiment should prove a success, be prepared therefore in a simpler way.

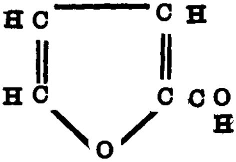
Benzaldehyde.



Thiophenaldehyde.



Furfurol.



Finally I will state that, in the explanation offered above for the formation of anthraquinone from thiophenaldehyde, I have taken into full account the fact (also mentioned here[1]) that *no* anthraquinone results from the treatment with lead chromate of the green coloring substance resulting from thiophene, phenanthraquinone and conc. H_2SO_4 ; that, therefore, as V. Meyer, expressly remarks, (*loc. cit.*), it seems to be the methyl group of methylthiophene, which promotes the formation of anthraquinone. The experiments by means of which I hope to sustain this theory will be performed soon, and I shall report on the same as early as possible.

College of the City of New York,
February 7, 1890.

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[1] See pages 28 and 30 of this paper.