

1929  
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Phenanthrene and some of its Derivatives.

(M.A.)  
Thesis for Master Degree, presented to  
Faculty of the University of Minnesota, 1903.

By

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Phenanthrene and some of its Derivatives.

Of the aromatic compounds perhaps Phenanthrene is as interesting as any although it has been studied less than some of the other compounds.

In 1873 phenanthrene was isolated from the raw anthracene material by C. Graebe; R. Fittig and Ostermayer at the same time had obtained it from destructive distillation of coal and had written an article describing the substance, although their constitutional formula was not the correct one.

Graebe's formula  $C_{14}H_{10}$  was eventually adopted by all as correct.

Fittig named the substance phenanthrene from diphenyl carboxylic acid and also to show that it was an isomeric form of anthracene.

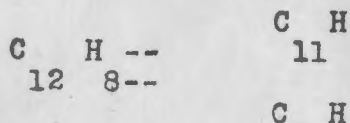
# It was because of the fact that it was possible to oxidize the phenanthrene to the phenanthriquinone and from this to diphenyl carboxylic acid  $C_{12}H_8(COOH)_2$  that Graebe found that on further heating with soda lime diphenyl was obtained.

# Graebe.

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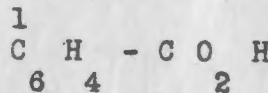
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For these reasons it was considered that phenanthrene was a diphenyl derivative which contained the group  $\text{-CH=CH-}$  thus making the analytical formula.



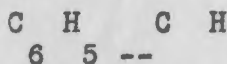
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The formation of the phenanthrene from o-ditolyl and its oxidation to diphenic acid  $\text{C}_6\text{H}_4\text{-CO}_2\text{H}$  shows

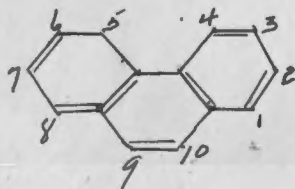


it to be a diphenyl derivative and that it contains a C-atom linked to each benzene ring; that the C-atom is joined to the corresponding one by double bond is decided

by its formation from stilbene,  $\text{C}_6\text{H}_5\text{-CH=CH-C}_6\text{H}_5$



Since diphenic acid is a di orthodiphenyl dicarboxylic acid, phenanthrene must also be di ortho derivative and possess the following constitution.



# Schultz A 196.

Thus the two C H groups form a new hexagon ring with the two carbon atoms of both benzene nuclei of the diphenyl to which they are linked , phenanthrene may thus be regarded as the condensation of three benzene rings to form one substance.

Almost at the same time and independently of the others phenanthrene was also discovered and worked upon by Hayduck.

Since this work there has been very little done with the compound until quite recently.

Max Schultz has worked on salts of the phenanthrene,, the 3-Bromphenanthriquinone.

The alkyl derivatives have been slightly studied by G. Neuhoff.

The Methoxy derivatives have been studied by A.Klein and by W. Bockow independently.

# The methoxy dibrom -5 grams (1) Methoxyphenanthrene in 5cc of chloroform .8 grams of Br dissolved in 10cc of chloroform was added to the first. The solution, which generated large quantities of H Br, was allowed to stand about a quarter of an hour then the chloroform was evaporated off.

# W. Buckow.

The methoxydibromophenanthrene remains as dirty white hard crust which is purified out of glacial acetic acid in colorless little needles which melt at 206.

# By treating the 3-methoxyphenanthrene in the same manner with 4 atoms of Br. a reddish brown oil remains which soon changes on stirring with glacial acetic acid. From the acid it crystallizes in fine needles whose melting point is 150 deg.

The phenanthroquinone has been studied perhaps more than any of the other derivatives because of the help this and further oxydation products have been in the determination of the constitutional formula and its method of formation.

Bromides have been studied by most of the workers on the subject but they seem to have come to different conclusions.

" If phenanthrene bromide is dissolved in CS to <sup>+Br</sup> saturation at the ordinary temperature and evaporated to dryness after one hour and afterward dissolved in alcohol, white wartlike groups of crystals are obtained. Their melting point was probably in the neighborhood of 110 deg. C. but was not determined accurately owing to

# A. Klein.  
" Hayduck.

the fact that the substance had a tendency to break down.

It was found that by again dissolving this new bromide in C S<sub>2</sub> adding Br and warming in reflux condenser, that another form was obtained. These crystals had a distinct melting point of 126 deg. C. and might be crystallized from hot glacial acetic acid in fine white satin like needles.

# It was also found that by dissolving phenanthrene in ether and adding bromine under conditions unfavorable to the formation of H Br that colorless four sided crystals were formed which went into solution in presence of H Br.

The tri-bromide was made by heating the di-brom already obtained with more Br in a reflux condenser for some time.

When they treated their bromide with sodium alcoholate they found that it was converted directly back to phenanthrene and there were no other products of the reaction.

The melting point of the substance does not seem to be definitely known as it is given differently in different texts. Bernthsen given it as 103 deg.C. while Richter's book says that the melting point of phenanthrene

# Fittig and Ostermayer B-1872.

is 99 deg.C.

#### Experimental Part.

Phenanthrene is a white solid which crystallizes in beautiful flakes. It has a decided but not unpleasant odor which resembles naphthalene quite closely but is more aromatic. It has a beautiful violet fluorescence when in solution or in very thin layers.

It has a sharp melting point of 99 deg. C.

Phenanthrene is very slightly soluble in water, quite soluble in both methyl and ethyl alcohol and very soluble in ether, chloroform, acetone, toluol, xylene, carbon bisulphide and glacial acetic acid.

#### Work on the Bromide.

When 5 grams of phenanthrene are dissolved in about 30 cc of absolute ethyl ether packed in freezing mixture and 15 grams of Br (6 mol) are added there is a yellow needle like precipitate which begins to form almost immediately. If left standing for about fifteen minutes and then filtered and washed with a small amount of ether.

The bromide is slightly soluble in ether and alce-

hol, very soluble in chloroform, acetone and carbon bisulphide. It has a melting point when fresh of 91 deg. C. but if it stands in moist air for a time the melting point falls and the substance loses its crystalline form to a certain extent, due to decomposition of the bromide to the monobromide which melts at 63 deg.C.

If the precipitate is left in the solution of ether and bromide it slowly goes into solution due to the excess of hydrobromic acid and forms a distinct layer at the bottom of the flask which bears a very close resemblance to bromine for which it may easily be mistaken.

If the bromine is added to an uncooled solution of phenanthrene and ether there is very little precipitate formed. At first the reaction is meagre and all the bromine is absorbed by the ether but as more is added a gummy substance forms on the sides of the enclosing vessel which on shaking in the shaking machine changes to a fine yellow powder in a heavy red liquid. This crystalline mass on further shaking goes into solution as above.

If the liquids be allowed to stand undisturbed for several days it is found that the ether gradually dis -



solves the layer of heavier liquid. Upon evaporation enormous amounts of H Br first pass off with the ether, upon complete evaporation of ether there is left a sticky mass of mixed bromides which can be redissolved in chloroform and recrystallized by the evaporation of the solvent. The mass obtained is partly crystalline, partly gummy; the latter being the mono bromide.

The second bromide decomposes quite readily in air passing over to the mono bromide.

A bromine determination made in closed tube gave the following results using .235 grams material.

Calculated for C    H    Br  
                   14   8    2

	Theoretical	Found
C	-----	-----
H	-----	-----
Br	47.61%	50.92%

This shows there was a mixture of the di brome and tri brome phenanthrene since the per cent Br in the di brome is 47.61% and that of the tri brom is 57.83%.

#### Ethoxy-dibromphenanthrene.

The bromide prepared by the method given was placed in a flask about 1 gram being used with about 40 cc of

absolute ethyl alcohol and added one gram of pure sodium wire. The mixture was allowed to stand on the low temperature water bath for about two hours and at the temperature of the room for two days. The substance at that time had undergone complete change. Instead of the pale yellow bromide there was a very fine brilliant red crystalline substance. This was filtered off and washed with absolute alcohol and dried over calcium chloride.

On examination it was found that the substance was a homogeneous mass crystallizing in the tri clinic system.

The substance darkens a little from 175 deg. to 190 deg.C. but does not become liquid below the temperature of boiling sulphuric acid.

The substance is insoluble in both hot and cold water, almost so in both methyl and ethyl alcohol and ether, sparingly soluble in petroleum ether, carbon bisulphide, chloroform, acetone, toluole, xylene and acetic acid.

An analysis of the compound shows that it is ethoxy-di brom phenanthrene.

Calculated for C<sub>14</sub> H<sub>7</sub> Br<sub>2</sub> O C<sub>2</sub> H<sub>5</sub>

Theoretical	Found	
	1.	2.
C 50.52%	50.03%	49.74%
H 3.16%	2.03%	2.81%
Br 42.11%	43.64%	43.64%
O 4.21%	4.30%	4.31%

### Methoxy Di brom Phenanthrene.

When the phenanthrene bromide is placed in absolute methyl alcohol and metallic sodium wire is added there appears at first to be no reaction but on a water bath of low temperature there is a change in the substance.

The color changes to a yellowish green and the substance becomes more gummy and has a tendency to stick to the flask in lumps.

The substance should be filtered and washed with absolute alcohol. If dissolved in ether there is a very sticky mass left on evaporation of ether. If this be treated with absolute alcohol and be worked with glass rod a fine greenish yellow precipitate is left. It is found to be as well if the ether solution be evaporated almost to dryness and the alcohol be added at

once the precipitate is of much better texture to handle. The reaction is entirely analogous to the one with the ethyl alcoholate--methoxy-di brom phenanthrene being formed.

The substance when evaporating has a peculiar not unpleasant odor.

When alcohol is used to precipitate the sale after nearly evaporating to dryness with the ether, the compound appears as a beautiful white crystalline mass under the microscope. On standing in air the crystals if watched with a good lens may be seen to give up their alcohol of crystallization and become first a gum and then a powder.

As the melting point is 152 deg.C. it seems probable <sup>207°</sup> that this is the compound made by A. Klein by another method and which has already been described.