UPON THE PREPARATION OF ARTIFICIAL INDIGO AND SOME OF ITS DERIVATIVES.

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It will be needless for me to tell you what indigo is, as you have probably all come across it, and know whence it is derived.

I will therefore only give you a graphic description of how this interesting body can be made synthetically; and in giving you this description, I can do no better than quote Baeyer's wonderful experiments :

Baeyer says : "The first thing I attempted to do was to remove the oxygen in isatine, and it will be remembered how this was accomplished, in 1865 and 1866, by the conversion of isatine into dioxindole, oxindole, and indole."

It was then tried to find an easier method for the production of indole, as Baeyer considered it to be the basis of the indigo group.

In 1868 Baeyer obtained it directly. by treating indigo with zinc dust ; and in 1869 he produced it synthetically from nitrocinnamic acid and its reduction product.

The following quotation may help to explain Baeyer's reasoning more thoroughly :

"If it is desired to make indole synthetically, it becomes necessary to introduce into benzol a diatomic carbon chain and a nitrogen atom, and then to connect the one with the other. The properties hereby necessitated will be found realized in nitrocinnamic acid, which has been deprived of carbonic acid, and the oxygen of the nitro group ; and, in fact, as we have already found, nitrocinnamic acid on being fused with potash produces indole."

Shortly after this, Kekule informed us that he had produced in a similar way isatine, from orthonitrophenylacetic acid. Baeyer and Suida then examined this compound more closely, and came to the conclusion that dioxindole and oxindole could be nothing else than the anhydrides of orthoamido-amygdalic acid and orthoamido-phenyl acetic acid. A synthetical examination soon after followed, and showed that oxindole by oxidation is converted into isatine ; which, however, was shortly afterwards produced by Claisen and Shadwell, by a new and convenient synthetical method.

In 1870, Baeyer and Emmerlin converted this isatine into indigo, and thus solved the problem he had so long been working at ; but, as the materials used (phosphorous trichloride, phosphorous, and acetyl chloride) were quite complicated, he strove to find a more simple method for accomplishing this end, and finally came to the

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*Read at the January Conversazione.

conclusion that it would be better to first treat the isatine with phosphorous pentachloride, and then phosphorus, or some other reducing agent.

It was then tried to produce, in the same way, indole from oxindole ; and, in fact, a body answering to the formula of a dichlorindole was obtained.

Without taking up any more of your time with the history of Baeyer's discoveries, I will now describe some of the products which may be converted into indigo blue.

ORTHONITROCINNAMAC ACID.

This acid may be easily prepared, according to Beilstein and Kullberg's process, and likewise the separation of the ortho from the paranitro compound by means of ether.

This acid bears a simple relation to indigo, as may be seen from the following formulœ :

Nitrocinnamic Acid. Indigo.

$$C_9 H_7 NO_4 = C_8 H_5 NO + CO_2 + H_2O$$

ORTHONITRODIBROMCINNAMIC ACID.

This acid is produced by treating the nitro compound with bromine under exclusion of sunlight.

The bromine compound crystallizes in short colorless needles, which melt at 180° C., under decomposition and formation of a small amount of indigo.

This body was found to have the formula $C_9 H_7 (Br_2) NO_4 =$ orthonitrodibromcinnamic acid.

This body is soluble in caustic alkalies, without decomposition ; which, however, by heat is converted into orthonitropropiolic acid, and then into isatine. By heating an aqueous solution of the above acid with carbonate of soda, a small amount of crystallized indigo blue is the result.

ORTHONITROPHENYLPROPIOLIC ACID.

$$C_9 H_5 NO_4$$

The bearing of orthonitrodibromcinnamic acid with alkalies differs considerably from the non-nitrated compound, inasmuch as HBr may readily be removed from the former, whereas from the latter it can only be removed by the energetic action of alcoholic potash to form propiolic acid. The propiolic acid is prepared usually from an aqueous solution of the dibrominated compound by treating with an excess of caustic soda solution.

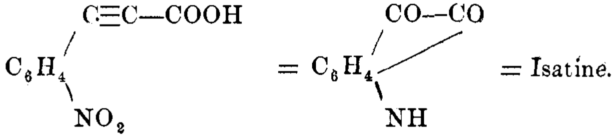
The compound is then thrown down by means of an acid, and dried. The orthonitrophenylpropiolic acid so obtained appears as little colorless needles, melting at 155—160° C. with sudden decomposition.

Orthonitrophenylacetylen.

This compound may be obtained from orthonitrophenylpropiolic acid, by boiling with water in an ascending cooler. It crystallizes from alcohol, in colorless needles, and melts at 81–82° C.

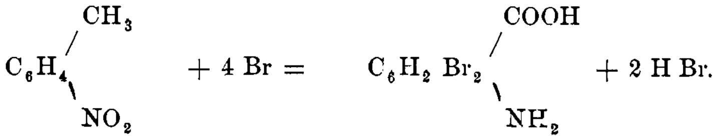
Formation of Isatine from Orthonitrophenylpropiolic Acid.

Isatine may be obtained in abundance by boiling a solution of orthonitrophenylpropiolic acid with alkalies. The reaction that takes place here may be explained as follows :



$$C_6H_4\begin{array}{l}\diagup C\equiv C-COOH\\ \diagdown NO_2\end{array} = C_6H_4\begin{array}{l}\diagup CO-CO\\ \diagdown NH\end{array} = \text{Isatine.}$$

In other words, CO_2 is split off; at the same time a reduction of the NO_2 group, and oxidation of the side chain takes place. This reaction is similar to the reaction which takes place when bromine is allowed to act on orthonitrotoluol, viz :



$$C_6H_4\begin{array}{l}\diagup CH_3\\ \diagdown NO_2\end{array} + 4\,Br = C_6H_2\,Br_2\begin{array}{l}\diagup COOH\\ \diagdown NH_2\end{array} + 2\,H\,Br.$$

Formation of Indigo from Orthonitrophenylpropiolic Acid.

If a very dilute alkaline solution of the acid be heated to boiling, and a small piece of grape sugar is added thereto, the liquid first turns blue, and then follows a copious precipitation of small blue needles, with coppery red lustre. These needles are perfectly pure indigo-blue. The yield so obtained is about 40% of the propiolic acid used.

The formation of indigo-blue in this case takes place as follows :

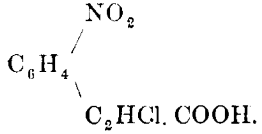
First the alkali, acting on propiolic acid, splits off CO_2, forming isatine, which, however, on being treated with a reducing agent as grape sugar, loses an atom of oxygen and forms indigo-blue, viz :

$$C_9H_5(NO_2)\,O_2 = \underset{\text{(Indigo.)}}{C_8H_5NO_2} + CO_2$$

$$C_9H_5(NO_2)\,O_2 = C_8H_5NO + O + CO_2$$

ORTHONITROPHENYLCHLORLACTIC ACID.

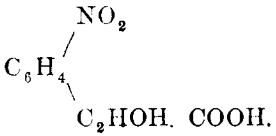
This acid may be easily prepared by passing a current of chlorine into an alkaline solution of orthonitrocinnamic acid. The mixture so produced is composed of orthonitrochlorstyrol, and orthonitrophenylchlorlactic acid, from which the latter may be separated by acidifying the mixture and then extracting the orthonitrophenylchlorlactic acid with ether. This compound appears as a white crystalline mass, and having a melting point of 119°—120° C. Its formula may be represented by



$$C_6H_4\left\langle\begin{array}{l}NO_2\\ C_2HCl.\ COOH.\end{array}\right.$$

This compound on being treated with reducing agents, such as sodium amalgam, or sulphate of iron in an alkaline solution, forms indole.

ORTHONITROPHENYLOXACRYLIC ACID.



$$C_6H_4\left\langle\begin{array}{l}NO_2\\ C_2HOH.\ COOH.\end{array}\right.$$

This compound may easily be produced from orthonitrophenylchlorlactic acid, by treating with alcoholic potash. It crystallizes from hot water, in flat needles.

If heated slowly to 110° C. it melts, giving off CO_2, and forming a dark blue mass, which, on being treated with alcohol, dissolves with a brown color, in which small crystals of indigo-blue remain suspended.

Indigo-blue may also be derived from the above by heating its solution with phenol, but the yield of coloring matter so obtained is quite small.

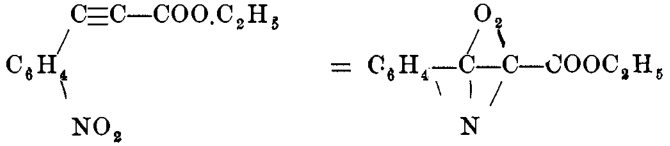
The reaction taking place here may best be explained as follows:

$$C_9H_7NO_5=C_8H_5NO+CO_2+H_2O+O.$$

The ease with which orthonitrophenylpropiolic acid is converted into indigo-blue, with such mild re-agents as grape sugar, appeared very strange to Baeyer, and in the following I will detail the experiments he made to arrive at a clear understanding of the above mentioned re-action.

By treating orthonitrophenylpropiolic acid with strong H_2SO_4, at the ordinary temperature, its isomer isatogenic acid ether is obtained, which crystallizes in yellow needles and melts at 115° C.

The formation of this compound may be explained by the following re-action :



A solution of nitrophenylpropiolic acid in H_2SO_4, on being treated with reducing agents, forms a new blue dye-stuff, called indoine. Indoine is very similar to indigo blue but differs from it in that it dissolves in strong H_2SO_4 with a blue color, which, on being heated, only forms a sulpho acid with great difficulty.

INDOXYLIC ACID ETHER.

This body is produced by the action of reducing agents, on isatogenic acid ether. It appears in the shape of thick prisms, and melts at 120—121°C.

It has the formula $C_{10}H_{11}NO_3$.

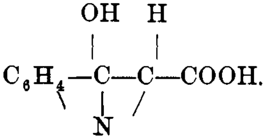
This compound on being rapidly heated forms a little indigo-blue; but if heated to 100°C. with strong H_2SO_4 it passes over into indigo sulpho acid almost quantitatively.

On being fused with caustic soda, at a temperature of 180°, it forms indoxylic acid, which melts at 160°C.

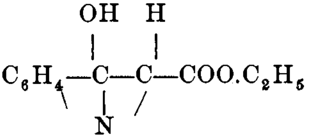
Ethyl indoxylic acid and nitrotrosoethylindoxylic acid have likewise been produced, but, I will not attempt to describe their formation.

The following formulæ will best represent the compounds just enumerated.

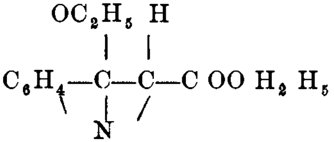
Indoxylic acid.



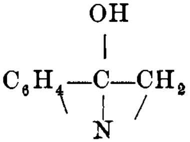
Indoxylic acid ether.



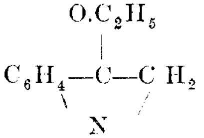
Ethylinolxylic acid ether.



Indoxyl.

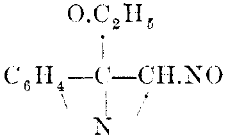


Ethyl indoxyl.



$$\begin{array}{c} O.C_2H_5 \\ | \\ C_6H_4—C—C\,H_2 \\ N \end{array}$$

Nitrosoethyl indoxyl.



$$\begin{array}{c} O.C_2H_5 \\ | \\ C_6H_4—C—CH.NO \\ N \end{array}$$

Indoxylic acid on being heated as high as its melting point with $H_2\,S\,O_4$, gives off CO_2; and passes over into indoxyl.

If indoxyl be dissolved in dilute KOH. and exposed to the air, indigo-blue is formed, which falls out as a blue precipitate.

A mixture of indoxyl and orthonitrophenylpropiolic acid, on being treated with $H_2\,SO_4$ forms indoine.

Indoxyl and nitrophenylpropiolic acid on being treated with $Na_2\,CO_3$ are immediately converted into indigo-blue.

A mixture of indoxyl and isatine in alcoholic solution, on being treated with $Na_2\,CO_3$ forms indirubine, which appears as brownish-red needles, with metallic lustre.

Thus far we have only considered the formation of indigo-blue from a theoretical point of view, and I will now try to describe the way it is made upon a large scale, or, rather, the manner in which it may be produced, and fixed in, or upon the fibre of materials at the same time.

The formation of indigo-blue within the fibre of materials to be printed, depends upon the facility with which orthonitrophenyl propiolic acid is converted into indigo-blue, by the action of reducing agents.

The reducing agents more commonly used are grape sugar, and especially the xanthates of soda or potash.

In other words, to print a pretty blue upon calico, the orthonitrophenylpropiolic acid is mixed up with a starch thickening, and xanthate of soda, and borax, and then printed in the usual way upon the calico. This is allowed to dry, and then heated to 100°C. for a certain length of time, which process develops the color within the fibre.