PAPERS READ BEFORE THE CHEMICAL SOCIETY.

X.—*Transformation of Aurin into Rosaniline.*

By R. S. DALE, B.A., and C. SCHORLEMMER, F.R.S.

In our paper on aurin (this Journal, 1873, 434) we shortly mentioned a red colouring matter called peonin or red aurin, which is formed by the action of ammonia on aurin. This compound contains nitrogen, and yields, when heated with solid caustic potash a distillate containing aniline. When red aurin is heated with alcoholic ammonia for several days to 150°, the red colour of the solution disappears, and a yellow liquid is obtained, which on the addition of water deposits a white crystalline precipitate. This body possesses all the characteristic properties of rosaniline; it dissolves in acetic acid with a splendid crimson colour, and yields with strong hydrochloric acid a dark yellow solution, which on the addition of water becomes red. It dyes wool and silk the same shade, and under exactly the same conditions as pure magenta does, and fixes on cotton mordanted with antimony tannate like this colour. The formation of this colouring matter from aurin is explained by the equation—

According to Hofmann, however, rosaniline has the composition $\text{C}_{20}\text{H}_{19}\text{N}_3$, and Caro and Wanklyn converted it (1866), by means of the diazo-reaction, into rosolic acid, which, as Caro and Graebe have shown (1873), has the formula $\text{C}_{20}\text{H}_{16}\text{O}_3$, while aurin has undoubtedly the formula $\text{C}_{20}\text{H}_{14}\text{O}_3$. A careful investigation of our base and its salts will clear up these points; we will only here remark that, in analyses of organic colouring matters, the percentage of hydrogen is often found too high. An example of this kind is offered by Schunck's classical research on alizarin, which he carefully analysed, and found that the results agree best with the formula $\text{C}_{14}\text{H}_{10}\text{O}_4$, instead of $\text{C}_{14}\text{H}_8\text{O}_4$.

In comparing the absorption-spectrum of the hydrochloride of our base with that of pure rosaniline hydrochloride, we found them quite identical.

We have transformed our rosaniline, not only into Hofmann's violet and aniline-blue, but also into aniline-green, obtaining at the same time the violet, which is always produced in the formation of the green.

When aurin is heated with alcoholic ammonia for several days to 150° , the rosaniline which is first formed is converted into *leucaniline*. This is readily explained: the alcohol in presence of an alkali acts as a reducing agent. But from that one might conclude that a similar action took place in the formation of rosaniline from aurin, thus—

But this is not the case, inasmuch as rosaniline is readily formed by heating aurin with aqueous ammonia to 120° for 20 hours. If the temperature be raised to 180 — 200° , other colourless bodies are formed besides, resembling those which Liebermann obtained by heating rosaniline with water.

We believe that rosolic acid and aurin are identical. One of us, who first investigated the action of nitrous acid on rosaniline, and patented the new colour thus formed, in conjunction with Paraf, examined it after our investigation of aurin, and found that on purifying the crude product by ammonia in the same way as we purified crude aurin, a crystalline ammonia compound is obtained, which after decomposition with an acid and crystallisation from alcohol or acetic acid, yielded crystals which could not be distinguished from aurin. He made a few analyses, which showed that it contained the same amount of carbon as aurin, but the percentage of hydrogen was always found too high. He did not continue this research when he became aware that Caro and Gräbe were engaged in an investigation of the same subject. These two chemists state, in their paper on rosolic acid, that they found it more difficult than they expected to prepare an aurin having exactly the composition $\text{C}_{20}\text{H}_{14}\text{O}_3$, and that they frequently obtained a compound having the formula $\text{C}_{40}\text{H}_{28}\text{O}_7$, but as chief product substances containing still more oxygen were formed. We never found the least difficulty in obtaining pure aurin, which since our last paper we have prepared repeatedly by heating a mixture of sulphuric acid and pure phenol on a water-bath, and adding the oxalic acid only gradually, always waiting until the evolution of gas ceased, and not using sufficient to attack all the phenol.

Zulkowsky has lately published a paper on "The Constituents of Corallin" (*Deut. Chem. Ges. Ber.*, x, 460), in which he says that crude corallin (aurin) contains so large a quantity of a pale red resinous body, that it is difficult to understand how it could hitherto have been overlooked. The existence of this body, which in the pure state is perfectly colourless, has been known to us since the commencement of our researches, and we then stated that commercial aurin was a mixture of several bodies. Besides the white resin, it also contains a dark red colouring matter, which is not only much more soluble in alcohol than aurin, but also increases the solubility of the latter, which can be

obtained pure only by a number of re-crystallisations. None of these bodies is formed by preparing aurin according to the method which we have just described, and its formation from phenol and oxalic acid, as well as that from phenol and salicyl-aldehyde, lead to the formula $C_{20}H_{14}O_3$.