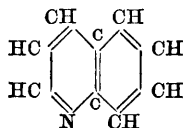


LXIV.—*An Additional Evidence, by Analysis of the Quinoline Molecule, that this Base belongs to the Aromatic Series of Organic Substances.*

By WATSON SMITH and G. W. DAVIS.

MERZ, in conjunction with Ruoff, Moe, Zetter (*Inaug. Disserts.*), and other pupils of his, showed that on exhaustive perchlorination, all members of the aromatic series break up so as to yield perchlorobenzene, unaccompanied or accompanied with perchlorinated paraffin groups according to circumstances. An exception occurs in the case of diphenyl, which forms perchlorodiphenyl, and this body refused to disintegrate on further chlorination. The formation of perchlorodiphenyl was found to be of very rare occurrence. Of course in many cases the formation and separation of perchlorobenzene made it possible to predict what the perchlorinated members of the paraffin group formed at the same time in the general disintegration of the aromatic molecule must be. Thus light was obtained and thrown upon the constitution of several aromatic compounds, besides which a remarkable confirmation of the truth lying at the root of Kekulé's benzene-ring hypothesis was obtained.

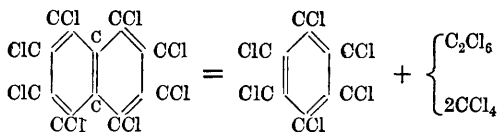
If quinoline has the constitution now generally assigned to it—



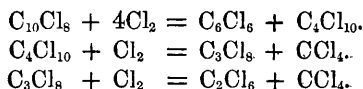
(and this has been made clear to a considerable extent by the several researches of Dewar, Baeyer, Königs, and Skraup), then by an exhaustive perchlorination according to the method of V. Merz, it might be expected that in the disintegration following, that portion of

the compound nucleus containing nitrogen would prove least stable as being most complex, and would consequently give way, yielding perchlorethane, perchloromethane, and nitrogen, whilst the other portion would yield perchlorobenzene.

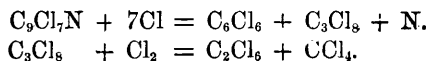
It will now be interesting to examine what the actual experience of Merz and Ruoff was in their perchlorination of naphthalene. They found that on repeated treatment in sealed tubes with antimony pentachloride at gradually increased temperatures, finally at 350° to about 400° C., naphthalene first changes to perchloronaphthalene, becomes disintegrated gradually and yields perchlorobenzene, perchlorethane, and perchlormethane,



This reaction, as regards the appearance both of perchlor-methane and -ethane, is better interpreted by assuming, as Graebe proposes, the presence in the naphthalene molecule of the group  $(\text{C}_4\text{H}_4)''$ , which becomes split off from the chlorinated benzene-ring as the first step of disintegration, and by the action of the chlorine is converted into perchlorbutane, which then immediately after its formation (as Krafft and Merz (*Ber.*, 1875, 1300) have actually shown in the case of perchlorbutane) at the high temperature, is first broken up into perchlorpropane and perchlormethane, and the former later on into perchlorethane and perchlormethane, thus :—



In our experiments then we might expect to realise the following, possibly :—



Perchloronaphthalene has of course been prepared and studied by Berthelot and Jungfleisch (*Ann. Chim. Phys.* [4], 15, 331); perchlorquinoline has, so far as we are aware, not been prepared as yet.

We took 1·7 grams of chemically pure quinoline, and placed it in a strong tube of hard glass, together with ten times its weight of antimony pentachloride, slowly and cautiously added. The tube was well sealed up and heated to 170°, then to 280°, to 320°, and finally to 400° about, each for a space of five hours, leaving the contents to cool, and

opening the tube after each heating, to allow hydrochloric acid gas and nitrogen to escape. Dry chlorine gas was then passed into the brown mass for about 20 minutes, and the tube, after re-sealing, was again heated at the above intervals as before. The chlorinating and heating were repeated till on opening the tube no more hydrogen chloride was evolved. The contents of the tube were now quite black from separation of carbon, but the mass was also crystalline. This black mass was now washed out with strong hydrochloric acid into a beaker and washed by decantation several times with strong hydrochloric acid and afterwards with a strong tartaric acid solution, till a portion of the filtrate from the mass gave no longer a precipitate of antimony sulphide with  $\text{H}_2\text{S}$ . The residue, dried and a portion submitted to sublimation, yielded vapours having the characteristic camphor-like odour of perchlorethane, which condensed to small white needles having a melting point of  $210^\circ$ . Now the melting point of perchlorethane is  $183^\circ$ : hence probably this first crop was contaminated with some perchlorobenzene which melts at  $220$ — $223^\circ$ . This crop first obtained was submitted to a careful re-sublimation, when a melting point in the crop now obtained was exactly  $182^\circ$ , the correct melting point of perchlorethane. After the perchlorethane was all sublimed and expelled from the black mass, the temperature was further raised, when, after some time long white needle-shaped crystals formed themselves on the surface of the dark mass in the sublimation apparatus. A quantity of these needles was carefully collected, and it was observed, on heating a portion of them, that the vapour possessed only an extremely faint odour, unlike that of the perchlorethane; in fact the vapour might be described as odourless. The melting point of these crystals was  $223^\circ$ , which is the correct melting point of perchlorobenzene.

Quinoline is a substance which is exhaustively perchlorinated with the greatest difficulty, and in future experiments we should recommend a 10-hours' heating at each successive temperature already mentioned. The opening of the sealed tubes is by no means unattended with danger, and, for the sake of safety, we should recommend that after heating and leaving it to cool, the tube should be opened by just allowing the drawn-out point to project from the oven, and then to let the flame of a lamp play upon it.

No perchlormethane could be detected, and this was probably owing to the volatility of the substance, by virtue of which it would be carried off in the violent rushes of gas ensuing on opening the tube from time to time. The danger of the operation of opening the tube indeed prevented any observations of the nature of gaseous bodies generated during the process from being made.

It may now just be pointed out how our experience just described

coincides with that of Dewar, who in 1877 obtained quinolinic acid (this Journal, 1881, p. 1044) ( $C_6H_4(NH_2).CH_2.CO.COOH$ ) by the oxidation of quinoline, this acid on distilling with soda-lime yielding aniline ( $C_6H_5.NH_2$ ). Dewar thus by an oxidation process obtains analytically proof of the aromatic nature of quinoline, actually getting the benzene-nucleus with the still adherent nitrogen, now in the form of an amido-group. We have succeeded in obtaining analytically by a chlorination process the perchlorinated benzene-nucleus ( $C_6Cl_6$ ), together with half the remainder of the residue containing the nitrogen-atom, also as a perchlorinated group, viz., as perchlorethane ( $C_2Cl_6$ ).

Writing quinoline as  $\overbrace{C_6H_4.N : C_2H_2 : CH_2}$ , we have obtained by chlorination the following groups.....  $\underbrace{C_6Cl_6}$      $\underbrace{C_2Cl_6}$     as perchlorinated products, whereas—

Dewar obtained ....  $C_6H_5.NH_2$  (aniline) as the result of an oxidation process, followed by a distillation of the product with soda-lime.

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