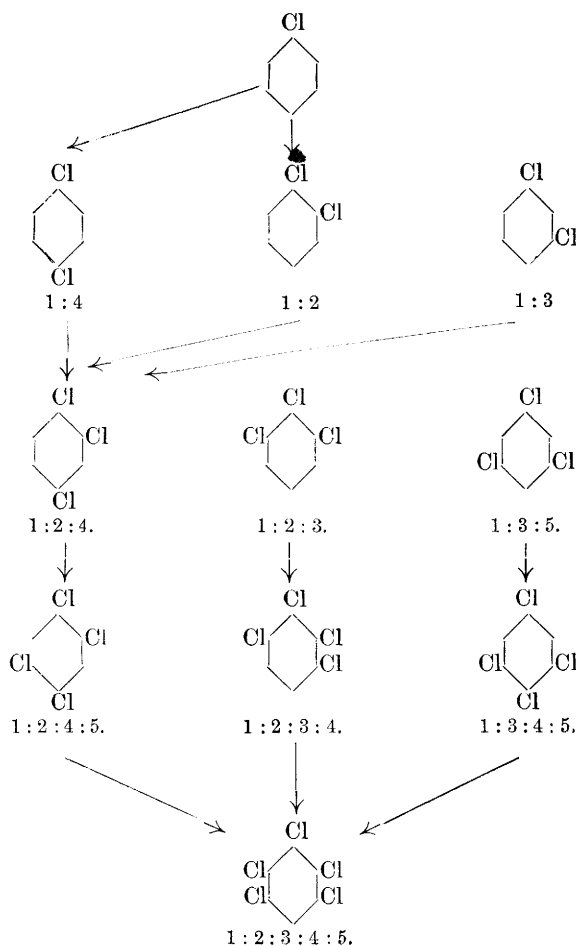


CXXXV.—*Studies in Chlorination. III. The Progressive Chlorination of Benzene in Presence of the Aluminium-Mercury Couple.*

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IN the present paper a description is given of the products obtained by the progressive chlorination of benzene. The task has been a comparatively easy one, inasmuch as the total number of possible chlorine derivatives is small (10); each step in the chlorination process, except in the case of the monochlorobenzene, has only given rise to one product; finally, the whole series of compounds is known and had already been exhaustively studied by Beilstein and Kurbatoff (*Annalen*, 1876, 182, 97; 1878, 192, 229). It was only necessary, therefore, to prepare each chlorine derivative in turn, and to study the action of chlorine upon it. The progressive chlorination of benzene is represented in the accompanying diagram.



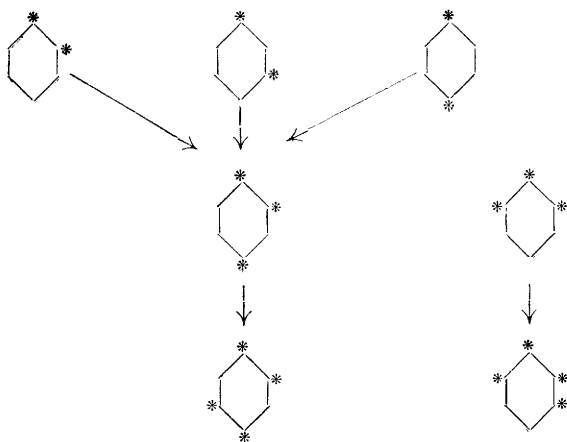
The results confirm the general rule which has been found to obtain in the case of the chlorotoluenes and the chloronitro-derivatives of benzene and toluene (Trans., 1902, 81, 1326, 1345; 1904, 85, 1276; 1905, 87, 320), and which may be expressed as follows:

The third substituent (chlorine atom or nitro-group), entering the dichloro- or chloronitro-benzenes, or the chlorotoluenes, occupies the unsymmetrical position, forming a 1:2:4-compound. The fourth substituent (Cl or NO_2) occupies position 5.

In all the adjacent (1:2:3) chloro- or chloronitro-derivatives of benzene and toluene, the fourth substituent (Cl or NO_2) is adjacent to the other three.*

* The symmetrical compounds are omitted as they can only give one product.

There is no marked exception to this rule, which, in the majority of cases, has reference to the only product of the reaction in question; in a few cases, to the main product. The general scheme embodying this rule may be represented as follows:



EXPERIMENTAL.

Chlorination of Chlorobenzene.

Fifteen grams of chlorobenzene, prepared from pure aniline, were taken, and chlorine gas passed into the liquid for some time. The vessel and contents were then weighed; 0.2 gram of the aluminium-mercury couple was added, when a vigorous reaction occurred, which was moderated by surrounding the vessel with cold water. The gas was passed until the increase in weight amounted to 4.6 grams. The product was then treated by Friedel and Crafts' method for the separation of the ortho- and para-compounds (*Ann. Chim. Phys.*, 1887, [vi], 10, 411) as follows: the liquid was immersed in a freezing mixture of ice and salt, when a portion of the para-compound solidified and was separated by filtration. The liquid was again cooled, and a further small quantity of para-compound was removed. The total amount of solid obtained in this way was 7.6 grams. It was identified as the para-compound by converting it into the nitro-derivative, which melted at 55°. To the liquid portion was then added an equal volume of fuming sulphuric acid (18 per cent. of SO_3), when the mixture became very hot. It was left for an hour, after which small pieces of ice were added, the whole being cooled by immersion in a freezing mixture. This addition of water (or ice) is necessary, as the sulphonic acid

otherwise crystallises out on cooling. A small portion of the para-compound separated, which was not removed, but was recovered in the next operation. The sulphonated product was now distilled in steam with a thermometer in the liquid. The temperature rose quickly to 115° , and a white solid condensed in the receiver, which was identified as the para-compound. At 130° the receiver was changed, and a second fraction collected at $130\text{--}230^{\circ}$. The quantity of this fraction was small, and apparently neither solid nor oil distilled. A third fraction was collected between 230° and 260° , when a considerable quantity of oil distilled. The action was very vigorous, owing to the decomposition of the *o*-dichlorobenzene-sulphonic acid into *o*-dichlorobenzene.

In addition to the solid, amounting to 0.4 gram, which distilled in the first fraction, a quantity of oil collected in the receiver which did not solidify in a freezing mixture, and was separated by filtration. This oil distilled at $195\text{--}210^{\circ}$ and amounted to 2.45 grams. It was identified as the 1:2:4-trichlorobenzene by conversion into the nitro-compound (m. p. 57°).

The third fraction, distilling at $230\text{--}260^{\circ}$, was cooled, but no solid separated. When redistilled it boiled at $174\text{--}182^{\circ}$. The greater portion, which passed over at 178° , amounted to 4.1 grams, and was identified as *o*-dichlorobenzene by conversion into the nitro-derivative (m. p. $42\text{--}43^{\circ}$). Of the 15 grams taken, 14.5 grams were recovered in the form of the para-compound (8 grams), the ortho-compound (4 grams), and trichlorobenzene (2.5 grams).

Chlorination of o-Dichlorobenzene.

The *o*-dichlorobenzene was prepared from *o*-chloronitrobenzene (Kahlbaum). Fifteen grams were taken and saturated with dry chlorine gas; 0.1 gram of the couple was added, and the reaction at once commenced. Chlorine was again passed in until the required increase in weight (3.5 grams) was attained. The dark product was shaken with a little caustic soda solution, dehydrated, and distilled. The main portion distilled at $208\text{--}218^{\circ}$ and weighed 15.5 grams. There was no unchanged *o*-dichlorobenzene, which boils at 179° . The remainder in the flask, which amounted to 2.3 grams, solidified and melted at $117\text{--}125^{\circ}$. After recrystallisation from alcohol, it melted at $136\text{--}137^{\circ}$; it was converted into a nitro-compound, which melted at $96\text{--}97^{\circ}$. It is therefore 1:2:4:5-tetrachlorobenzene, which, according to Beilstein and Kurbatoff (*loc. cit.*), melts at 138° and yields a nitro-derivative (m. p. 98°).

The main product of chlorination was nitrated with fuming

nitric acid in the cold and, after standing, poured on to ice. The solid which separated melted at 54—55°, and, after recrystallisation, the melting point rose to 57—58°. The nitro-compound was reduced to the base (m. p. 95—96°), and this substance converted into the acetyl derivative (m. p. 184—185°) and into tetrachlorobenzene (m. p. 138—139°). As the nitro-derivatives of the other two trichlorobenzenes melt respectively at 56° and 68°, there can be little doubt that the product of chlorination of *o*-dichlorobenzene consists wholly of the unsymmetrical trichloro-compound.

Chlorination of m-Dichlorobenzene.

The process was carried out as previously described. Ten grams of pure *m*-dichlorobenzene, prepared from *m*-nitroaniline (Kahlbaum), were chlorinated until an increase of 2.3 grams was obtained. The product was fractionated under 146 mm. pressure, when all but about 0.5 gram distilled at 148—155° (*m*-dichlorobenzene distils at 117—118°/154 mm.). This residue solidified, and, after recrystallisation from alcohol, melted at 139°.

The main product was converted into the nitro-derivative, which, without purification, melted at 54—59°, and after recrystallisation at 57—59°. This compound was reduced to the amino-compound melting at 96°, and finally converted into the tetrachloro-derivative (m. p. 139°). The product, as in the previous case, is wholly 1 : 2 : 4-trichlorobenzene.

Chlorination of p-Dichlorobenzene (m. p. 53°).

The chlorination was conducted at 60° so as to keep the para-compound (m. p. 53°) fused, and 15 grams of the substance were chlorinated. A portion, which was unchanged and boiled at 170—195°, was recovered on distillation; the main fraction distilled at 195—218° (nearly the whole at 210—212°); a residue of 1.6 grams remained, and proved to be the 1 : 2 : 4 : 5-tetrachloro-compound (m. p. 136—137°). The main portion was nitrated, reduced to the amino-compound, acetylated, and the amino-group replaced by chlorine. The melting points of the various products were the same as those previously obtained in the other two cases, and showed that the original chlorination product was the 1 : 2 : 4-compound. This compound is, of course, the only one which can be produced from *p*-dichlorobenzene.

Chlorination of 1 : 2 : 4-Trichlorobenzene.

The fact that the 1 : 2 : 4 : 5-tetrachlorobenzene was found to accompany the 1 : 2 : 4-trichloro-compound in the chlorination of the three dichlorobenzenes may be taken as evidence of the formation of this product from the 1 : 2 : 4-compound. Nevertheless, several experiments were made with different quantities of 1 : 2 : 4-trichlorobenzene in the manner already described to confirm this result. In each case one product only was obtained, melting at 135—136°. For example, in one experiment 5 grams of material were taken and chlorine passed in until the requisite additional weight was obtained; the product was crystallised, and melted at 135—136°. Its weight was 4.3 grams, and 0.3 gram was recovered from the mother liquors (m. p. 128—131°). This shows unmistakably that there is only one product, since the other two tetrachlorobenzenes melt respectively at 50—51° and 45—46°. The 1 : 2 : 4 : 5-compound was further converted into the nitro-derivative (m. p. 97—98°).

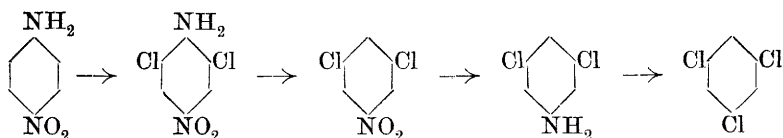
Chlorination of 1 : 2 : 3-Trichlorobenzene (m. p. 53°).

The 1 : 2 : 3-trichlorobenzene was prepared in the manner described in a paper by Cohen and Bennett (Trans., 1905, 87, 324). The amino-group from the 3 : 4 : 5-trichloroaniline was removed by diazotisation in the ordinary way. Contrary to the experience of Beilstein and Kurbatoff (*loc. cit.*), we found this to be much the simplest method of obtaining it.

As the substance is solid, it was dissolved in an equal weight of carbon tetrachloride. The use of carbon tetrachloride necessitated the use of a double tube, so arranged that any vapour of carbon tetrachloride carried over from the first tube was condensed in the second, which was immersed in a freezing mixture. The whole apparatus was weighed, and the chlorination continued until the necessary additional weight was obtained. After removing the carbon tetrachloride, the residue solidified, and melted sharply at 44—45°. It was nitrated and the crude nitro-derivative melted at 59°, which, after one crystallisation, melted at 61—62.5°, and after a second at 62—63.5°. The chlorination product was, therefore, nearly pure 1 : 2 : 3 : 4-tetrachlorobenzene, since the only other product would be the 1 : 2 : 3 : 5-compound, which melts at 50—51° and gives a nitro-derivative melting at 21—22°. The process was repeated, with the same result.

Chlorination of 1:3:5-Trichlorobenzene (m. p. 63—64°).

The compound was prepared for us by Mr. P. F. Crosland from *p*-nitroaniline, which is first converted into the dichloro-derivative, the amino-group then replaced by hydrogen, and the nitro-group reduced and replaced by chlorine.



A very pure product was obtained, melting at 63—64°. The chlorination proceeds smoothly, and, although only one tetrachloro-derivative can be formed, it was extremely difficult to obtain it with the correct melting point, the crude product melting at 45° instead of 51°. The explanation probably is that a small trace of unchanged substance is sufficient to produce a large depression in the melting point. After repeated crystallisation from methyl alcohol, a substance was eventually obtained in long, colourless needles melting at 46—49°. It is curious that the tetrachloro-compound is more soluble than the trichloro-compound, and the less fusible fraction consequently accumulates in the mother liquor. The above fraction was analysed, with a result which leaves no doubt that the compound was nearly pure 1:2:3:5-tetrachlorobenzene.

0.1609 gave 0.4250 AgCl. Cl = 65.36.

$C_6H_2Cl_3$ requires Cl = 58.68; $C_6H_2Cl_4$ requires Cl = 65.74 per cent.

In another experiment a small, less soluble fraction, melting at 79—81.5°, was isolated, which was probably impure pentachlorobenzene (m. p. 85—86°).

Chlorination of the Tetrachlorobenzenes.

Although the three tetrachlorobenzenes can only give a single product, it seemed an interesting point to attempt a comparison between the relative rates of chlorination. It appeared not improbable that the different distribution of the chlorine atoms might produce some effect, either in promoting or retarding the process.

The following observations were recorded. In the first place all three substances gave pentachlorobenzene (m. p. 86°), usually associated with more or less hexachlorobenzene. The product from the 1:2:4:5-tetrachlorobenzene melted at 83—84.5°, that from

the 1:2:3:4-compound melted at 83—85°, and that from the 1:3:4:5-isomeride at 84—85.5°.

None of the tetrachloro-compounds chlorinate as readily as the lower chlorinated products, and there is little action in the cold. The rate of chlorination, so far as it was possible to determine it by direct observation, appeared to follow the order 1:3:4:5, 1:2:3:4, and 1:2:4:5, the last isomeride being the least readily attacked. It should, however, be pointed out that the 1:2:4:5-compound is much less soluble in carbon tetrachloride than the other two, and the dilution has a considerable effect on the chlorination process. Nevertheless, as chlorination proceeds, it is possible to remove the carbon tetrachloride, and even when the normal concentration is reached the action in the last case seemed very slow.

Another point observed was the relatively large quantity of hexachlorobenzene in the product. It appears as if the pentachlorobenzene, when once formed, is rapidly chlorinated, so that it not unfrequently happened that either little change had occurred, or that the greater part of the material had passed to the final stage of chlorination.

The tetrachlorobenzenes used in the above experiments were prepared as follows:

The 1:2:4:5-compound (m. p. 138°) was obtained from the 1:2:4-trichloro-compound by nitrating, reducing, and finally diazotising. The 1:2:3:4-compound (m. p. 45°) was prepared by the chlorination of the 1:2:3-compound, and the 1:2:3:5-compound (m. p. 51°) was made from trichloroaniline by replacing the amino-group by chlorine.

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