XVI.—*The Action of Chromium Oxychloride on Nitrobenzene.*

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ACCORDING to Étard (*Ann. Chim. Phys.* [5], **22**, 218), chromium oxychloride attacks nitrobenzene with the formation of a brown, amorphous solid, $\text{C}_6\text{H}_3(\text{NO}_2)(\text{CrO}_2\text{Cl})_2$, which, when treated with water, yields chromium chloride and "nitroquinone;" the latter is said to crystallise from hot water, in which it is readily soluble, in shining, yellowish-brown crystals which melt at 232° , and sublime on further

heating in brilliant, yellow plates. The same observer states that from nitrotoluene (a mixture of the isomerides), when similarly treated with chromium oxychloride, he obtained "nitrotoluquinone" in the form of yellowish-brown leaves melting at 237° , and with properties resembling those of "nitroquinone." Von Richter, however, showed (*Ber.*, **19**, 1060) that the substance formed by the action of chromium oxychloride on nitrotoluene at about 160° is not a quinone, but is in reality paranitrobenzoic acid; whilst from nitrobenzene he obtained no analogous compound. The action of chromium oxychloride, dissolved in glacial acetic acid, on nitrobenzene was investigated by Carstanjen (*J. pr. Chem.* [N.F.], **2**, 51), who obtained a small quantity of white crystals, which, from preliminary tests, appeared to be trichloronitrobenzoic acid, together with some substance of such exceeding volatility that all attempts to isolate it were unsuccessful. Its vapour was intensely irritating to the eyes, and if a drop of an ethereal solution was allowed to fall on the skin, it caused painful smarting.

Etard's process is the only one by which nitroquinone is said to have been prepared, and it will be seen from what is quoted above that contradictory results have been obtained by other observers. We have, therefore, re-examined the action of chromium oxychloride on nitrobenzene under various conditions in the hope of settling the question one way or another.

Our first experiments were carried out in the way described by Étard, that is, nitrobenzene (carefully purified and dried) was heated to about 160° by means of an oil-bath, and chromium oxychloride was added drop by drop from a tap-funnel. The proportions used were about 1 mol. of nitrobenzene to 2 mols. of the oxychloride, the former being in slight excess. No change was observed until a small quantity of the oxychloride had been added, and then a sudden and very violet action took place, the whole contents of the flask being thrown out in one experiment, and the flask itself broken by the force of the explosion in another. The experiments were repeated under altered conditions, chromium oxychloride being gradually added to nitrobenzene heated to temperatures ranging from 80° to 140° , but the result was always the same, though sometimes we observed the presence of traces of the volatile irritating substance described by Carstanjen.

In the next place, nitrobenzene (1 mol.) and chromium oxychloride (2 mols.) were carefully mixed at the ordinary temperature and left to stand in a flask placed in a vessel of cold water. After some time a sudden and violent action took place, and the flask was broken.

We failed altogether to obtain any "nitroquinone" by any of the experiments described, though they were many times repeated. The

only products, besides the volatile substance occasionally formed, were very small quantities of a brown powder, which, on treatment with water, yielded amorphous substances which could not be crystallised, and the analyses of which gave no concordant results.

Another method was therefore adopted. A 50 per cent. solution of chromium oxychloride in pure, dry chloroform was gradually added to a similar solution of nitrobenzene in a flask attached to a reflux condenser. A slow action began, and was accelerated by heating the flask on a water-bath. Fumes of hydrogen chloride were given off and a dark-brown powder slowly separated, though, even after several hours' heating, the reaction was not quite completed. After the precipitate had settled down, the chloroform was poured off, and the precipitate was washed with dry chloroform, quickly transferred to stoppered tubes, and dried at 100°. The brown powder attracts moisture with great avidity, and decomposes almost at once when exposed to the air; it also seems to retain traces of chromium compounds. Analysis gave the following results:—

1.3145 gram substance gave 0.5960 gram Cr_2O_3 and 1.0355 gram AgCl .

	Calculated for $\text{C}_6\text{H}_3(\text{NO}_2)(\text{CrO}_2\text{Cl})_2$.	Found.
Cr	29.10 per cent.	31.02 per cent.
Cl	19.66 „	19.47 „

It will be observed that the percentage of chromium found is higher than that demanded by theory, but, as already stated, it is difficult to free the substance entirely from traces of chromium compounds precipitated with it. When thrown into cold water, the compound is decomposed with evolution of much heat and apparently with escape of a gas (possibly oxygen). Chromium chloride and chromic acid are found in solution, while an almost colourless, heavy liquid sinks to the bottom of the flask. This liquid was separated, washed repeatedly, first with dilute caustic soda and then with water, and dried. It was found to boil at 205°, and analysis showed conclusively that it was nothing but *nitrobenzene*. It is difficult to explain this result, but it seems possible that nitroquinone is formed on treating the solid compound with water, but that it at once decomposes with regeneration of nitrobenzene. Various attempts were made to obtain the nitroquinone presumably formed, but without success.

The results of the experiments briefly described above lead us to doubt the existence of Étard's "nitroquinone," but part of our work affords a possible explanation of his statements. In one set of experiments we used a quantity of nitrobenzene, sold as pure, without taking the precaution of specially purifying it. When chromium

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oxychloride was added to an excess of this nitrobenzene heated to about 160° , the addition of each drop caused a violent reaction; quantities of hydrogen chloride were evolved, and finally an almost solid mass was formed in the flask. This was washed repeatedly with dry carbon bisulphide, which removed a considerable quantity of unaltered nitrobenzene, while a brown powder was left undissolved. When thrown into water, this compound was decomposed with evolution of heat, and a green solution was obtained. This was heated to boiling, and excess of sodium carbonate added to precipitate the chromium. The clear, yellow filtrate was evaporated to small bulk and acidified with hydrochloric acid. On cooling, a solid crystallised out in the form of pale-yellow leaves with a pearly lustre, which melt at 238° . When heated cautiously, the substance sublimes in brilliant, almost colourless needles. On analysis the following results were obtained:—

0.2546 gram substance gave 0.0726 gram H_2O ($= 0.00806$ gram H)
and 0.4660 gram CO_2 ($= 0.1276$ gram C.).
0.44 gram substance gave 30.8 c.c. N at 14° and 750 mm.

	Calculated for $C_6H_4(NO_2) \cdot COOH$.	Found.
C.....	50.29 per cent.	50.11 per cent
H.....	2.99 ,,	3.16 ,,
N.....	8.38 ,,	8.50 ,,
O.....	38.34 ,,	—

This result was confirmed by an analysis of the silver salt, which was found to contain 38.99 per cent. Ag, theory demanding 39.05 per cent. The substance was therefore *paranitrobenzoic acid*.

A brown chromium compound, similar to that just described, was obtained, but in much larger quantity, when a 50 per cent. solution of chromium oxychloride in chloroform or carbon bisulphide was heated with a similar solution of the impure nitrobenzene, hydrogen chloride being evolved. In this case, however, when the chromium compound was decomposed with water, nitrobenzene was obtained as well as paranitrobenzoic acid, and in proportionally large quantity. On examining the so-called pure nitrobenzene used in these experiments, we found it to contain a considerable amount of nitrotoluene, and it is evident that the paranitrobenzoic acid was produced by the action of chromium oxychloride upon this, and not from the nitrobenzene. Incidentally, therefore, we have confirmed von Richter's results, and perhaps we may venture to make the suggestion that Etard's "nitroquinone" was really paranitrobenzoic acid, produced by using nitrobenzene containing some nitrotoluene.

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