XCV.—*The Action of Nitrogen Tetroxide on Ortho- and Para-nitrobenzylic Alcohols.*

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IN the previous communication, the action of nitrogen tetroxide on benzylic alcohol has been described and, up to a certain point, elucidated.

As this action suggested a possible method for preparing other benzaldehydes and especially the ortho- and para-nitrobenzaldehydes, we have directed our attention to this subject.

The results of the first experiments were exceedingly promising. One gram each of ortho- and para-nitrobenzylic alcohols were added to a slight excess of nitrogen tetroxide dissolved in chloroform. The successive changes observed in the case of benzylic alcohol reappeared in both cases. On standing in stoppered vessels for 3 days, the liquid

had become deep green, and a small quantity of colourless crystals had separated. In each case, the chloroform and oxides of nitrogen were evaporated off on the water bath and a solid, crystalline crust remained behind. In the case of the paranitro-compound, 0.96 gram of product melting at 97—100° was obtained from 1 gram of the alcohol. The substance, after one crystallisation from water, melted at 105° and gave the phenylhydrazone melting at 155°.

In the case of the orthonitro-compound, which was treated in a similar manner, 0.94 gram of product (m. p. 41°) was obtained. It had a brown colour, but was readily purified by a single crystallisation from water. The addition of a dilute solution of phenylhydrazine acetate yielded the crystalline hydrazone melting at 153° and with acetone and dilute caustic soda, a copious precipitate of indigo-blue was formed.

The yield of aldehyde in both cases is practically theoretical. As in the case of benzylic alcohol, the aldehydes are also formed with nitrogen trioxide, but the action is slower and the yield very much smaller than with benzylic alcohol. Thus from one gram of the alcohols and a slight excess of nitrogen trioxide dissolved in chloroform, 0.45 gram of the hydrazone was obtained in each case after the action had been allowed to proceed from 2 to 3 days. It seems, in fact, not improbable, in view of the extreme difficulty of preparing the trioxide free from tetroxide, that it is the tetroxide alone which reacts on these two alcohols.

The final products of the action of nitrogen tetroxide on the alcohols are therefore the aldehyde, water, and nitrogen trioxide. Now as nitrogen trioxide readily forms the tetroxide by contact with air, it occurred to us that the latter might react catalytically, as in the sulphuric acid process. The result has not only confirmed our anticipation, but has done so in a very striking manner.

The reaction is best observed in the case of orthonitrobenzylic alcohol.

In our first experiment, 1 gram of the alcohol was powdered and introduced into a stoppered bottle of about 600 c.c. capacity and spread in a thin layer over the bottom of the vessel. A stream of nitrogen tetroxide was conducted for a moment into the bottle, which was then stoppered. It was easy to see that a reaction was in progress, as the solid became moist and at some points liquid. This is due to the formation of the nitrosate and water. The bottle was placed on one side for 2 days, after which time the contents had again become solid, but the crystalline form and general appearance of the substance had undergone a change. Yet the bottle contained red fumes, which appeared to have only slightly diminished in quantity. The product was removed and dried. It melted at 38—41°. By con-

verting a weighed quantity into the phenylhydrazone, it was found to consist of 75.7 per cent. of the aldehyde.*

In order to follow the reaction more closely, a larger quantity of orthonitrobenzyl alcohol was taken, and the amount of nitrogen tetroxide at the beginning and end of the experiment was carefully ascertained.

The experiment was performed in a bell-jar standing upon a ground glass plate. Into the neck of the bell-jar a doubly-bored cork was inserted. Through these two holes two tubes passed, one reaching to the bottom of the bell-jar and the other ending below the cork. The outside ends of the two tubes were sealed off. The cork on the inside was thickly paraffined, to protect it from the nitrogen oxide vapours. A tier of large watch glasses, each containing from 1 to 2 grams of the alcohol spread out in a thin layer, was placed upon the ground glass plate, and along with them a small tube containing a weighed quantity of nitrogen tetroxide, the closed end of which was broken off, just before covering the whole with the bell-jar, which was made to fit tightly on the glass plate by means of vaseline. Ten grams of the alcohol were used, but instead of the equivalent of nitrogen tetroxide (6 grams), only 1.72 gram was taken. The bell-jar was left in the dark for 48 hours, during which time the substance had become liquid and solidified again, the vessel remaining filled with brown vapours of the tetroxide. The closed ends of the two tubes were now opened and a current of dry air aspirated through the bell-jar, the nitrogen tetroxide being dried and then collected in two weighed potash apparatuses. The operation was continued for 12 hours, and the increase in weight amounted to 0.45 gram. The product, a weighed quantity of which was converted into the hydrazone, contained 74 per cent. of aldehyde, and melted at 43—45°. Although our point is fully proved by this experiment, we expected to obtain a larger quantity of residual tetroxide at the end of the reaction. The loss of tetroxide is to be accounted for by the fact that, as water is formed in the experiment, some of the tetroxide is decomposed, yielding nitric acid, which was plainly evident from the drops of acid liquid which condensed upon and trickled down the sides of the bell-jar.

* This method of estimating orthonitrobenzaldehyde is sufficiently accurate for practical purposes. Two specimens of the pure and *colourless* orthonitro-compound melting at $44\frac{1}{2}$ — $45\frac{1}{2}$ ° were analysed in this way and yielded a weight of the phenylhydrazone corresponding to 98.2 and 97.5 per cent. respectively of the aldehyde.