

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY]

## THE ROLE OF MERCURIC NITRATE IN THE "CATALYZED" NITRATION OF AROMATIC SUBSTANCES. II. NITRATION OF NAPHTHALENE<sup>1</sup>

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In an earlier paper,<sup>2</sup> experiments were discussed which showed that the direct production of picric acid from benzene by the action of nitric acid in the presence of mercuric nitrate is not an oxidation catalyzed by the presence of the mercury salt. It is a series of reactions involving the formation of a dark colored intermediate compound which is later oxidized, presumably to yield the mercury salt of dinitrophenol, and this, by the further action of nitric acid, is converted into picric acid, regenerating mercuric nitrate. The reaction may be explained plausibly by supposing that its first step involves the addition of mercuric nitrate to adjacent carbon atoms of the benzene nucleus, the  $-\text{NO}_2$  group adding to one and the residue  $-\text{OHgONO}_2$  adding to the other. If now the hydrogen atoms originally resident on the carbon atoms to which the mercuric nitrate has added are supposed to be removed by oxidation, the rest of the reaction is clear.

In the case of benzene we have been able to isolate the dark colored intermediate mercury compound, but analysis of various samples has given widely discordant results for mercury.

When toluene and chlorobenzene were nitrated in the presence of mercuric nitrate,<sup>2</sup> phenolic substances were formed in which the hydroxyl group is in the *meta* position with reference to the *ortho-para*-orienting methyl and chlorine originally present in the molecule. This surprising result, also, is explained plausibly by supposing the addition of mercuric nitrate, the  $-\text{NO}_2$  group taking a position *ortho* or *para* to the methyl or chlorine, and the residue  $-\text{OHgONO}_2$  taking a position adjacent to it and, naturally, *meta* to the methyl or the chlorine.

Similarly, the nitration of naphthalene in the presence of mercuric nitrate might be expected to yield (in addition always to the products of simple nitration) nitro- $\beta$ -naphtholes, the nitro group taking its natural position on the naphthalene molecule and the hydroxyl appearing at a place adjacent to it. We find, however, that the products are nitro- $\alpha$ -

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naphtholes, and are left at the moment, therefore, without any general hypothesis in explanation of the reaction.

In the reaction with benzene, a deep color develops soon after the reagents are brought together, and a dark colored compound containing mercury precipitates from the mixture if it is diluted with water. In the reaction with naphthalene there is no deepening of color nor any other evidence of an intermediate compound, even when the reaction is carried out in the manner which gives the best yields of nitronaphthole.

Since naphthalene nitrates very easily, strong nitric acid, even in the presence of mercuric nitrate, converts it promptly into nitro derivatives and the amount of nitronaphthole which is formed is exceedingly small. The best conditions for the formation of nitronaphthole direct from naphthalene are moderately dilute acid and moderately low temperature.

In our best experiment, where one gram molecule of naphthalene was stirred at 35° for 37 hours with a liter of a solution containing 600 cc. of nitric acid (sp. gr. 1.35) and one gram molecule of mercuric nitrate, a yield of 55 g. of crude nitronaphthole was obtained. This was found to consist in large part of 2,4-dinitro- $\alpha$ -naphthole (identical with martius yellow) and was identified by mixed melting point with a known sample and by the properties of its methyl ether. It contained also a small amount of another substance which has the properties of 2-nitro- $\alpha$ -naphthole but which has not been positively identified.

While the reaction has considerable theoretical interest, it is not to be recommended as the most feasible method for the preparation of nitronaphtholes from naphthalene.

### Discussion of Experiments

The first experiments were carried out in a manner as nearly as possible like that which had been found to give satisfactory results with benzene. Five g. of mercuric oxide was dissolved in 300 cc. of nitric acid (sp. gr. 1.42) and the solution was added, small portions at a time, to 100 g. of naphthalene in a 2000cc. flask. After the first vigorous reaction had subsided, the material was heated for an hour with frequent shaking in a boiling water-bath. The spent acid containing the mercuric nitrate in solution was decanted, evaporated, fortified to its original state, and used for another nitration. The oily nitrated product, washed thrice with hot water and dried, amounted to 126 g. and had a "solidification point" of 130°. Eight runs were made, each with 100 g. of naphthalene and all with the same mercuric nitrate, the spent acid being fortified and re-fortified. The solidification point of the reaction product dropped off regularly through the series; in the eighth run it was 82°. The total product amounted to 1008 g. It was extracted with a hot solution of sodium carbonate; this was made acid with hydrochloric acid and shaken

with ether. The ether deposited about 15 g. of dark brown oily material (crude nitronaphthole) which solidified after a month's standing to a brittle powdery mass. The material remaining from the sodium carbonate extraction, worked up by fractional crystallization from alcohol, ethyl acetate, and acetone, yielded about 200 g. of  $\alpha$ -nitronaphthalene, 350 g. of 1,3-dinitronaphthalene (m. p.  $144^{\circ}$ ), and 400 g. of 1,5-dinitronaphthalene (m. p.  $213-213.5^{\circ}$ ).

From the spent acid a few grains of another substance was isolated. This melted at  $207-208^{\circ}$  with effervescence; it was readily soluble in warm water, in alcohol, and in acetone, somewhat less soluble in ethyl acetate, and insoluble in benzene. From water it yielded slightly brownish crystals, but from conc. nitric acid it came down in clear white plates. A water solution of the substance was acid to litmus, and a small crystal dropped into sodium carbonate solution liberated carbon dioxide. Calc. for nitronaphthalic acid: N, 6.63. Found: 6.87.

In later experiments more dilute acid was used and the reaction was carried out at a lower temperature. Only a few typical experiments are reported here.

Six hundred cc. of nitric acid (sp. gr. 1.35) was diluted with water to the volume of a liter, 360 g. of crystallized mercuric nitrate was dissolved in it, 128 g. of naphthalene was added, and the mass was stirred actively in a glass flask in a water-bath maintained at  $35^{\circ}$ . At the end of about 12 hours the solid material had become converted to an oil, but the oil solidified at about  $25^{\circ}$  when a sample of it was removed. The stirring was continued at a temperature of  $35^{\circ}$  until it had gone on for 25 hours altogether. The reaction mixture was extracted with benzene which removed the organic material, and the spent acid was discarded. The benzene solution was then extracted with sodium carbonate solution for the removal of the nitronaphtholes. Considerable trouble was experienced at this point as it was found that the benzene and aqueous sodium carbonate mixture showed a great tendency to emulsify. Moreover, the sodium salt of the nitronaphtholes was sparingly soluble in aqueous sodium carbonate solution (due doubtless to the "common ion effect"), and the separation of crystals of sodium salt only aggravated the tendency toward emulsification. The sodium carbonate extract, which amounted in this case to 4 liters, was heated to boiling and filtered through a wet filter for the removal of neutral organic material carried along with droplets of benzene. It was acidified with hydrochloric acid while still hot, and was set aside overnight. The precipitated crude nitronaphthole, collected on a filter and dried at  $40^{\circ}$ , was dark brown in color and weighed 23 g.

Calc. for dinitronaphthole: N, 11.97. Found: 12.2.

The crude product, therefore, consisted in large part of dinitronaphthole.

In a similar experiment with the same amounts of material and the same method of operating, the action was continued for 50 hours at  $35^{\circ}$  and the crude nitronaphthole which was obtained amounted to 36. g.

In another similar experiment the action was carried on for 37 hours, and a different method was used for working up the product. The reaction mixture was chilled and filtered. The greasy material which was left on the filter was transferred to a flask, 3% aqueous solution of sodium carbonate was added and the mixture heated to boiling. The hot aqueous extract was decanted through a filter, the residue in the flask was again extracted with hot 3% soda solution, and the process was repeated until a portion of the

extract cooled and acidified gave scarcely any turbidity. The alkaline extract, worked up as before, gave 55 g. of crude nitronaphthole. Analysis showed 10.2% of nitrogen in this material.

Other similar experiments were carried out by another operator. In two 37-hour runs with 192 g. of naphthalene he obtained respectively 75 g. and 70 g. of crude nitronaphthole.

### Identification of Products

The crude nitronaphthole was entirely soluble in alcohol; recrystallized from this solvent it yielded two pure substances, one present in relatively small quantity, yellow needles from alcohol, m. p. 128°, the other present in large amount, yellow needles and rosettes from alcohol, m. p. 138°.

The substance which constituted the principal product of the reaction was identified as 2,4-dinitro- $\alpha$ -naphthole by the fact that it melted at the same temperature as a pure sample of known identity and by the fact that a mixture of the known and the unknown also melted at this same temperature. It yielded a methyl ether, pale yellow needles from methyl alcohol, melting at 97° which is the reported melting point of 2,4-dinitro- $\alpha$ -naphthole methyl ether.

The methyl ether was prepared by the action of methyl iodide on the silver salt. It could not be prepared by the method which is frequently successful, *i. e.*, by the interaction of the sodium salt with methyl sulfate. Seven tenths g. of the nitronaphthole was dissolved in a dilute solution of sodium hydroxide, an excess of methyl sulfate was added, and the mixture was shaken vigorously for about 20 minutes. As no reaction was apparent, the mixture was then refluxed for 4 hours. On diluting the product with water, filtering it, and recrystallizing the solid from dil. alcohol, 0.6 g. of the original material was recovered unchanged. The nitronaphthole was, therefore, converted into its silver salt by precipitating a solution of the sodium salt with silver nitrate; the silver salt was washed and dried, and refluxed with a large excess of methyl iodide for 4 hours. The excess of iodide was distilled and the residue, extracted with methyl alcohol, gave the expected methyl ether.

The substance which was present in relatively small quantity melted at the reported melting point of 2-nitro- $\alpha$ -naphthole, and it was doubtless this substance. We have not been able to obtain it in quantity sufficient for positive identification. Beilstein reports that 2-nitro- $\alpha$ -naphthole is volatile with steam while 2,4-dinitro- $\alpha$ -naphthole is not. We have found that both of our substances were volatile with steam. When the product of a steam distillation was worked up by fractional crystallization from alcohol, 90% of its weight was obtained in the form of pure 2,4-dinitro- $\alpha$ -naphthole.

### Summary

When naphthalene is nitrated in the presence of mercuric nitrate, in addition to the products of simple nitration of the hydrocarbon, there are formed nitro derivatives of  $\alpha$ -naphthole. The formation of  $\alpha$ -naphthole derivatives leaves us for the time being without any general hypothesis in explanation of this type of reaction.