

Nitration. Part III. Nitration of Naphthalene.

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α -Nitro-naphthalene is a compound of great commercial importance as it is required in quantity for the preparation of α -naphthylamine and of α -naphthylamine sulphonic acids. Attempts have been made to study the methods of the preparation and see if the existing method of manufacture can be improved. The manufacture of this compound is described by Witt (*Chem. Ind.* 1887, 10, 25): a mixture of nitric and sulphuric acid is employed as a nitrating agent, the temperature being kept at 45—50° until towards the end when it is raised to 60°. The whole process is completed in one day. The yield is said to be about 95 per cent. of the theory. Triller (D. R. P. 100417) obtained α -nitro-naphthalene by passing an electric current through a mixture of one part of naphthalene and 50 parts of nitric acid (d 1.25) at 80°. Amongst other methods for the preparation of α -nitro-naphthalene, one by the action of NO_2 on naphthalene (Leeds, *J. Amer. Chem. Soc.*, 1980, 2, 283) may be mentioned.

The part played by sulphuric acid in nitrating mixtures has not yet been satisfactorily explained. "It is generally understood that the advantage of the addition of sulphuric acid is to absorb the water formed during nitration and thus to keep the nitric acid from being too dilute. The stronger the acid and the higher the temperature, the larger the amount of nitro-groups introduced".

(Sudborough: Bernsthen, "Organic Chemistry.") If this is true, there is no reason why mechanical absorbents of water should not equally serve the purpose, but so far as the nitration of benzene is concerned this is not the case, as in experiments that have been carried out in this laboratory in which the place of sulphuric acid has been taken by plaster of Paris and such other substances, no improvement in the nitration of benzene has been observed. But so far as the nitration of naphthalene is concerned the case has been found to be different. In this case plaster of Paris and quick-lime have been found equally effective in removing the water formed during the reaction and in giving as good a yield of nitro-naphthalene as that obtained in presence of sulphuric acid.

In addition, a number of other agents, some of them never tried before on naphthalene, have been tried with a view to ascertain their utility in nitration. The various nitrating agents used in the experiments described in this paper are given below with the yield of α -nitro-naphthalene obtained therefrom. Five g. of naphthalene were treated in each case.

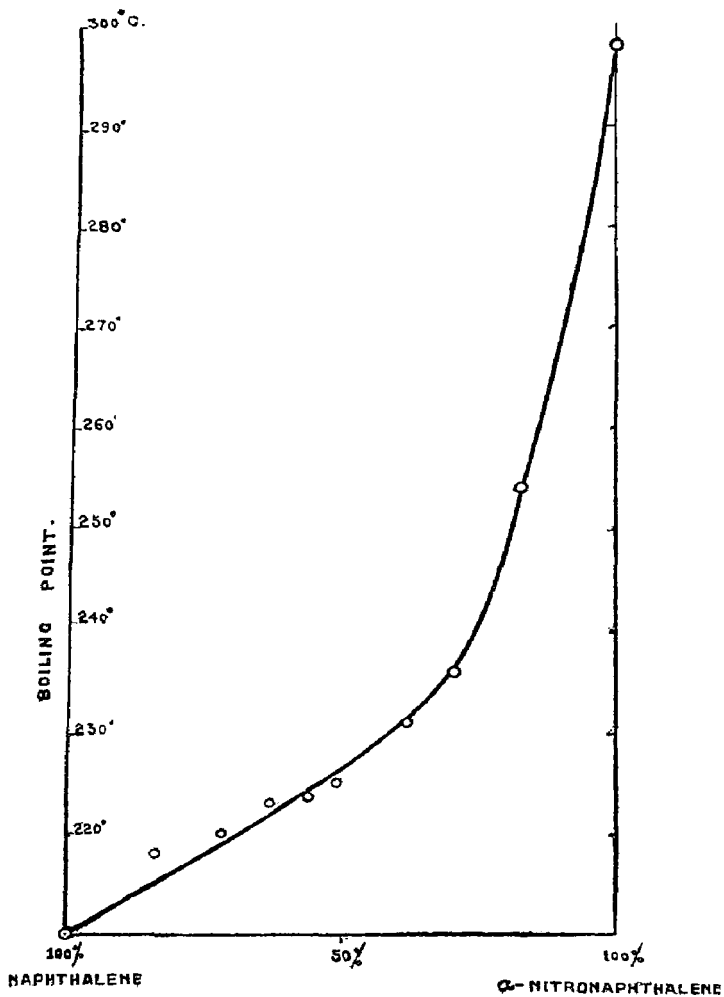
Expt.	Nitrating Agent.	Yield of α -nitronaph.	
		In grams.	In per cent.
1	Conc. HNO_3 alone	4.7	70
2	Conc. HNO_3 + Conc. H_2SO_4 (5 c.c.) ...	5.8	86
3	Conc. HNO_3 + acetic anhydride (0.5g) ...	5.2	77
4	Conc. HNO_3 + quicklime (0.5g) ...	5.8	86
5	Conc. HNO_3 + plaster of Paris (0.5g) ...	5.6	86
6	Conc. HNO_3 + P_2O_5 (0.5g) ...	5.8	86
7	Fuming HNO_3 + Nitro-sulphonic acid ...	5.4	80
8	NaNO_3 + Conc. H_2SO_4 ...	5.5	81
9	NaNO_3 + dilute H_2SO_4 ...	2.9	43
10	NO_2 ...	0.5	7
11	NO ...	0.2	3
12	N_2O_5 ...	4.2	73

It is obvious from the data given above that the same yield of α -nitro-naphthalene is obtained by using nitric acid either in presence of conc. sulphuric acid or of phosphorous pentoxide or of quick-lime or of plaster of Paris. Sodium nitrate and conc. sulphuric acid and a mixture of fuming nitric and nitro-sulphonic acids also produce good yields. It is interesting to note that neither NO nor NO_2 gives appreciable yields of nitro-naphthalene whilst N_2O_3 produces a good yield.

In certain cases a mixture of α -nitro-naphthalene and naphthalene was obtained as the final product. Here difficulty was experienced in ascertaining the proportion of the two constituents in the mixture without involving considerable loss in separation and purification. This difficulty was got over by finding out the boiling points of a mixture of α -nitro-naphthalene and naphthalene and drawing a curve therefrom. With the help of this curve it is possible to have a rough idea of the amount of the two constituents in the mixture.

EXPERIMENTAL.

Variation in the Boiling point of a Mixture of Naphthalene and α -Nitro-naphthalene :—five g. of naphthalene were placed in a dry test tube the mouth of which was closed by a loose plug of cotton wool through which passed a thermometer. The test tube was put inside an iron chimney so that the bottom was just above the surface of the wire-gauze placed at the bottom of chimney. The gauze was then heated with a steady flame and the boiling point of the substance in the test-tube was quickly and carefully noted so as to avoid loss of material by evaporation. The cotton was removed, different quantities of α -nitro-naphthalene introduced, the mouth of the test-tube quickly closed and the boiling point noted.



The experiments were repeated with 5 g. of pure α -nitro-naphthalene at the outset and determination of the points made successively when no naphthalene was present and when 1, 2, 3, 4 and 5 g. of naphthalene were successively added. The results obtained are recorded below:—

Naphthalene. (in gms.)	α -Nitro-naphthalene.	Boiling point.	Percentage of α -nitro- naphthalene.
0	5	298°	100
1	"	254°	83.3
2	"	236°	71.4
3	"	231°	62.5
4	"	227°	55.5
5	"	225°	50
5	"	225°	50
"	4	223.5°	44.5
"	3	223°	37.5
"	2	220°	28.5
"	1	218°	16.7
"	0	210°	0

The accompanying curve is drawn with the boiling points along the *Y*-axis and the percentage of the constituents along the *X*-axis.

A Mixture of Concentrated Sulphuric and Nitric Acids.—Concentrated nitric acid (*d.* 1.42; 5 c.c.) was mixed with concentrated sulphuric acid (5 c.c.) in a flask of 100 c.c. capacity. The flask was placed on a water-bath and powdered naphthalene (5 g.) was added gradually during the course of ten minutes. The mixture was well-stirred after each addition, the temperature being maintained at 40-50°. After every addition of naphthalene there was an evolution of brown fumes of nitrous gases. When the whole of the naphthalene had been added the temperature was gradually raised to 60° and maintained for half an hour. The contents were then allowed

to cool. The reddish-yellow cake was freed from the adhering liquids and crystallised from rectified spirit, m. p. 58-5°. Yield 5.8 g. of α -nitronaphthalene.

Concentrated Nitric Acid:—Naphthalene (5 g.) was added gradually to concentrated nitric acid (*d* 1.42; 5 c.c.). The subsequent operations were the same as in the preceding case. Yield of α -nitro-naphthalene was 4.7 g.

Nitric Acid in Presence of Acetic Anhydride:—Naphthalene (5 g.) was mixed thoroughly with acetic anhydride (0.5 g.) and concentrated nitric acid (5 c.c.) was added drop by drop with continuous stirring in about five minutes, the vessel being cooled from time to time to prevent rise of temperature above 50°. When the whole of the acid has been added, the mixture was warmed to 60° for half an hour, cooled, freed from the adhering acid and crystallised. Yield 5.2 g. By using 1 g. instead of 0.5 g. acetic anhydride the yield was 5.6 g.

Nitric Acid in presence of Quick-lime, of Plaster of Paris and of Phosphorus Pentoxide:—Similar experiments using (a) 1.0 and 0.5 g. of quick-lime, (b) 1.0 and 0.5 g. of plaster of Paris and (c) 1.0 and 0.5 g. of phosphorus pentoxide gave in each case 5.8 g. of α -nitro-naphthalene from 5 g. of naphthalene.

A Mixture of Fuming Nitric and Nitro-Sulphonic Acid:—This mixture contained about 50 per cent. of nitro-sulphonic acid. This mixture (5 c.c.) was taken in a flask and naphthalene (5 g.) was added at intervals in five minutes. The evolution of brown fumes was very copious. The subsequent procedure was the same as in the preceding cases. α -Nitro-naphthalene (5.4 g.) and 1:5-dinitro-naphthalene (0.2 g.) were obtained.

Sodium Nitrate and Concentrated Sulphuric Acid:—Naphthalene (5 g.) and sodium nitrate (5 g.) were placed in a round-bottomed flask and concentrated sulphuric

acid (2 c.c.) added. The flask was immersed in an oil-bath and heated gradually in an hour to 100° , adding in the mean time 3 c.c. more of sulphuric acid. The contents were thoroughly stirred. Naphthalene melted and gradually turned deep red. After being heated for 10 minutes more, the flask was allowed to cool and the solid cake washed several times with water and crystallised. Yield of α -nitro-naphthalene, 5.5 g.

Sodium Nitrite and Dilute Sulphuric Acid:—Powdered naphthalene (5 g.) was suspended in dilute sulphuric acid (50 c.c.) in a round-bottomed flask on oil-bath. Finely-powdered sodium nitrite (5 g.) was added at intervals with stirring. Brown fumes were evolved and on raising the temperature, molten naphthalene changed to a yellowish and then to a brownish colour. The reaction was more vigorous at $109-110^{\circ}$. When the whole of sodium nitrite was added the flask was heated for half an hour more and allowed to cool. The solid product crystallised from rectified spirit. Yield 2.9 g.

Nitrogen Peroxide:—This peroxide was led into the flask containing naphthalene (5 g.). The gas was passed for about 45 minutes. No action took place in the cold but when the naphthalene melted, some action took place. The flask was cooled and the product crystallised. The boiling point of the product was found to be 230° . Therefore only 0.5 g. of α -nitro-naphthalene is present.

Nitric Oxide:—This oxide was led into molten naphthalene (5 g.). Only 0.2 g. of α -nitro-naphthalene was found in the product.

Nitrous Gases:—Nitrous gases, prepared by the action of nitric acid on arsenious oxide, were led into naphthalene (5 g.) which was attacked slowly at the outset but vigorously later on when naphthalene melted by the heat evolved in the reaction. The flask was cooled to prevent too much heating. The gases were

passed for half an hour and the contents of the flask heated for another half an hour at 60° and allowed to cool. The crystalline product (4.9 g.) was found to be α -nitro-naphthalene.

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