

VII.—*Contributions to the History of the Naphthalene Series.*No. I. *Nitroso- $\beta$ -naphthol.*

By JOHN STENHOUSE, LL.D., F.R.S., and CHARLES E. GROVES.

FUCHS (*Deut. Chem. Ges. Ber.*, viii, 625) has shown that, as in the case of phenol, an atom of hydrogen in  $\alpha$ -naphthol can readily be directly replaced by the nitrosyl group, NO, giving rise to two isomeric nitroso- $\alpha$ -naphthols. He has also obtained a nitroso- $\beta$ -naphthol (*ibid.*, 1026) by a similar process, but on repeating the experiment we found that not only was the dirty greenish coloured precipitate containing the nitrosonaphthol very difficult to purify, but that the yield of the nitroso compound was far from satisfactory. It seemed probable, however, that the use of nitrosyl sulphate which had answered so admirably as a nitriting agent for the preparation of nitroso-orcin and nitroso-resorcin might also give better results in this instance. A preliminary trial at once showed this to be the case.

*Nitroso- $\beta$ -naphthol.*

On mixing dilute aqueous solutions of sodium  $\beta$ -naphtholate and of nitrosyl sulphate, a brilliant yellow precipitate of the nitroso compound was at once formed, but on standing, a portion of this soon rose to the surface and gradually became darker in colour, probably owing to secondary action between the nitroso-naphthol and unattacked naphthol; the portion which remained suspended in the liquid retaining its bright yellow colour. After several trials the following process was found to yield the best results: 1 part of pure  $\beta$ -naphthol was dissolved in 10 parts of boiling water by means of 1 part by measure of sodium hydrate solution of sp. gr. 1.323,\* cooled, and poured into 100 parts of water. A nitriting solution was then prepared by pouring 2 parts by weight of the 15 per cent. nitrosyl sulphate solution previously described (this Journal, 1877, vol. I, p. 545) into 200 of water, with constant stirring, and the dilute aqueous solution of sodium  $\beta$ -naphtholate above mentioned was at once added and thoroughly and intimately mixed, which when small quantities were operated on was most conveniently done by pouring the liquid from one vessel into another. After standing 12 to 20 hours, the precipitate of crude nitroso- $\beta$ -naphthol was collected on a linen filter and washed with cold water until the washings ceased to be acid. This precipitate when dried weighed rather more than the  $\beta$ -naphthol originally taken.

\* A solution of this strength contains 30 grams sodium oxide in each 100 c.c.

Fuchs purified his crude nitroso- $\beta$ -compound by dissolving it in petroleum, and concentrating by distillation. This, however, is exceedingly inconvenient, as the slight solubility of the substance in petroleum renders it necessary to use very large quantities of the latter; moreover, the product obtained in this manner is far from pure. A modification of this method, however, obviating the distillation of large quantities of petroleum, was adopted in the first instance for the partial purification of small quantities of the nitroso-compound. The crude product, after being carefully dried at the ordinary temperature, or at a very gentle heat, was agitated with 200 times its weight of light petroleum at about  $40^{\circ}\text{C}$ ., and filtered from the insoluble portion. A few drops of an alcoholic solution of ammonia was then added to the clear petroleum solution, which produced a bright green precipitate consisting of the ammonium compound of nitroso- $\beta$ -naphthol. This was collected, and the petroleum, after removal of the excess of ammonia by agitation with dilute sulphuric acid, employed again to extract the crude product. The green ammonium compound, when exposed to the air to allow the petroleum to evaporate, gradually lost part of its ammonia, becoming yellow. The remainder of the ammonia was removed by moistening it with acetic acid, and washing with water, but the nitroso-naphthol thus obtained, even after crystallisation from boiling petroleum was still impure, and had to be converted into the sodium salt and precipitated in the manner subsequently described. As Fuchs states that he obtained two isomeric derivatives from  $\alpha$ -naphthol, the nitroso- $\beta$ -naphthol was submitted to a careful fractional crystallisation from petroleum, but no evidence could be obtained of the existence of a second isomeric nitroso compound.

The attempts made to purify the crude product by crystallisation from various solvents such as alcohol, ether, benzene, carbon bisulphide, acetic acid, &c., met with but indifferent success, as did also the precipitation of the alcoholic solution by ammonia or soda. The method ultimately adopted was based on the insolubility of the barium compound, which is thrown down as a bulky green precipitate on adding a solution of barium chloride to a solution of the nitroso compound in a dilute alkali. The moist crude product mentioned above as obtained from 1 part of  $\beta$ -naphthol was suspended in 35 parts of water, that is sufficient water was added to the moist crystalline paste to make it up to 35 parts by measure; 1 part of the 30 per cent. solution of sodium hydrate diluted with 35 of water was added to this, and the mixture agitated occasionally, and filtered after standing about an hour.\*

\* In this and the subsequent operations distilled water was used, as the lime in ordinary water forms an insoluble compound with a portion of the nitroso naphthol, occasioning loss.

The clear olive-brown filtrate was then precipitated by a slight excess of a dilute solution of barium chloride,—about 1·5 parts of a cold saturated solution diluted with twice its volume of water,—and the green precipitate collected on a fine cambric filter. The reddish-brown filtrate when neutralised with an acid gave a dark-brown precipitate containing a crystalline substance: this has not been further examined as yet. The green barium compound, after being thoroughly washed, was suspended in about 35 parts of water and decomposed with hydrochloric acid in excess. The brownish-yellow, partially purified nitroso-compound was then thoroughly washed until free from barium chloride, again dissolved in dilute soda,—35 parts water and 0·5 parts, 50 per cent. solution of sodium hydrate,—filtered, precipitated as barium compound, washed, decomposed by acid, &c., as before, and the same process repeated a third time. In this way the nitroso- $\beta$ -naphthol was obtained in minute needles of a brilliant yellow colour, containing water of crystallisation. They retain their colour when dried at the ordinary temperature, but may readily be converted into the anhydrous compound by crystallisation from hot spirit (5 parts): the solution must not, however, be boiled for any length of time, as decomposition would take place. The best method of recovering the nitroso-compound dissolved in the spirituous mother-liquors is to add one-tenth of its bulk of the solution of sodium hydrate; this throws down a green precipitate consisting of the sodium compound of the nitroso- $\beta$ -naphthol. As the barium compound is bulky and very finely divided, it was found better when large quantities were to be operated on, to slightly modify the process just described. The barium compound first obtained (from 1 part of naphthol) after being decomposed with hydrochloric acid and thoroughly washed, was suspended in 15 parts of water, 0·5 parts 30 per cent. solution of sodium hydrate added, and the mixture heated in a water-bath. On filtering and adding one-tenth of its bulk of the soda solution, the sodium compound of the nitroso-naphthol, being almost insoluble even in comparatively dilute solutions of sodium hydrate, was thrown down as a green precipitate; this was collected, pressed, and decomposed by acid, the process of precipitation as sodium compound being repeated if necessary. The amount of pure nitroso- $\beta$ -naphthol obtained in this manner is rather more than half the weight of the naphthol originally taken. A full account of the method of preparation and purification of this substance has been given, as success depends in a great measure on careful attention to details.

The anhydrous substance, crystallised from hot alcohol, and dried at the ordinary temperature *in vacuo*, was submitted to analysis with the following results:—

I. .318 gram substance gave .810 gram carbonic anhydride and .119 gram water.

II. .263 gram substance gave .672 gram carbonic anhydride and .100 gram water.

III. .386 gram substance gave 27.2 cub. cent. of nitrogen at 13.5° C., and under a pressure of 751.6 mm. (corr. at 0° C.) equivalent to 25.239 cub. cent. dry nitrogen at 0° C., or .031662 gram of nitrogen :

		Theory.	I.	II.	III.	Mean.
C <sub>10</sub>	= 120	69.36	69.47	69.68	—	69.57
H <sub>7</sub>	= 7	4.05	4.16	4.22	—	4.19
N	= 14	8.09	—	—	8.20	8.20
O <sub>2</sub>	= 32	18.50	—	—	—	—
		<hr/> 173	<hr/> 100.00			

These numbers correspond to those required by the formula C<sub>10</sub>H<sub>7</sub>NO<sub>2</sub>, or C<sub>10</sub>H<sub>6</sub>(NO).OH that of nitroso-naphthol.

The hydrated nitroso-β-naphthol is of a brilliant yellow colour, and crystallises in minute needles. It is obtained in this state when any of its salts are decomposed by dilute acids, or when an alcoholic solution of the compound is poured into water. The yellow needles lose water at a gentle heat, and become brown. The anhydrous compound obtained by crystallisation from alcohol, ether, benzene, carbon bisulphide, or petroleum forms thin plates or short thick prisms of an orange-brown colour, melting at 109.5°. It is only slightly soluble in water, even when boiling, and separates almost entirely as the solution cools in long yellow needles. It dissolves very readily in carbon bisulphide, benzene, ether, acetic acid, and hot alcohol, and requires about 42 parts of alcohol at 13° for solution. It is comparatively slightly soluble in light petroleum, even when boiling.

Nitroso-β-naphthol dissolves in cold concentrated sulphuric acid with development of heat, forming a bright red solution from which the substance is precipitated unaltered on the addition of water. On strongly heating the acid solution the colour changes to brown, and the addition of water then no longer produces a precipitate, probably owing to the formation of a sulphonic acid. The nitroso-compound is decomposed when heated with concentrated nitric acid, yielding a tarry substance which dissolves on long continued boiling with the strong acid.

The compounds which nitroso-β-naphthol forms with ammonia and the alkalis are crystalline and of a bright green colour when in a finely divided state, although the masses of crystals deposited from a hot concentrated solution appear black by reflected light. The derivatives containing the metals of the alkaline earths are also of various shades of green.

*Mononitro-β-Naphthol.*

Although, as stated above, nitroso-β-naphthol when heated with concentrated nitric acid is decomposed and converted into tarry products, the action is different when it is submitted to the regulated action of the dilute acid at the ordinary temperature. The pure yellow crystalline hydrate was suspended in ten times its weight of water and mixed with an equal bulk of nitric acid of sp. gr. 1·25. It soon began to change in character, the yellow needles aggregating in flocks, whilst the odour of nitrous acid became distinctly apparent. In the course of an hour the precipitate had again become dense and non-coherent, the colour having changed to a yellowish-grey. It was at once collected, washed thoroughly with water, and treated with 50 parts of a cold very dilute solution of soda (1 part 30 per cent. sol. to 50 of water) and filtered from the insoluble residue. A slight excess of acetic acid was then added to the deep orange-coloured filtrate; and the bright yellow precipitate collected, washed, and crystallised once or twice from boiling alcohol in which it is very soluble. Dried in a vacuum and analysed, it gave the following results:—

I. ·215 gram substance gave ·499 gram carbonic anhydride and ·074 gram of water.

II. ·649 gram of substance gave 40·6 cub. cent. of nitrogen at 10·5° C., and under a barometric pressure of 770·2 mm. (corr. at 0°) equivalent to 39·134 cub. cent. dry nitrogen at 0° or ·049094 gram of nitrogen.

		Theory.	I.	II.
C <sub>10</sub>	= 120	63·49	63·30	—
H <sub>7</sub>	= 7	3·70	3·82	—
N	= 14	7·41	—	7·56
O <sub>3</sub>	= 48	25·40	—	—
	<hr/>	<hr/>		
	189	100·00		

From these results it will be seen that the new substance, as might have been expected, is a mononitro-β-naphthol formed from the corresponding nitroso-compound by the displacement of the NO group by NO<sub>2</sub>. This nitro-naphthol is precipitated from its solutions as a pale yellow crystalline powder apparently a hydrate. It crystallises from alcohol in orange-brown plates scarcely distinguishable in appearance from the nitroso-compound. It melts at 96°, and forms orange-coloured crystalline compounds with the alkalis and ammonia. It is more soluble than the nitroso-compound, but behaves very like the latter with concentrated sulphuric or nitric acids.

This nitro-β-naphthol, however, is not the only compound formed

by the action of dilute nitric acid on the nitroso derivative, as a portion of the crude product is insoluble in dilute alkaline solutions; it is crystalline, and of a pale-yellow colour. Again, if the nitroso- $\beta$ -naphthol be suspended in spirit instead of water, and then treated with dilute acid, and allowed to stand a considerable time, a greenish crystalline substance is formed almost identical in appearance with that above described. On examination, however, it was found to consist of two compounds: treatment with a dilute alkaline solution left an insoluble crystalline residue of an orange colour, whilst the addition of an acid to the filtrate threw down a pale-coloured flocculent precipitate, consisting of minute slender needles. With ammonia, the latter forms a sparingly soluble salt, crystallising in deep yellow rhomboidal plates. These substances have not been further examined as yet.

*$\beta$ -naphthaquinone.*

When the ammonium compound of nitroso- $\beta$ -naphthol was treated with hydrogen sulphide, it was reduced to an amido-compound. It was found more convenient, however, to pass hydrogen sulphide into the barium compound suspended in dilute ammonia, as the finely-divided precipitate was more readily and completely attacked than the crystalline ammonium salt; 2 parts of pure nitroso- $\beta$ -naphthol were dissolved in a mixture of about 100 parts of water, with 2 of the soda solution, filtered and precipitated with barium chloride in slight excess. The precipitate, after being collected and washed, was suspended in 140 parts of water; 3 parts of ammonia solution (S.G. 0.880) were added, and hydrogen sulphide passed to saturation. At first, the barium compound assumed a more intense green colour, which, however, rapidly disappeared as the solution became saturated with hydrogen sulphide, the green precipitate being replaced by almost colourless scales of the amido-compound. After passing a gentle current of hydrogen sulphide for about an hour longer, the vessel containing the mixture was tightly corked and allowed to stand several hours, with occasional agitation. The precipitate was then collected, washed with a very dilute solution of hydrogen sulphide, and dissolved by suspending it in 140 parts of water, and adding dilute sulphuric acid in excess. It was also found advisable to add a little sulphurous acid solution, as otherwise the amido compound oxidised rapidly during filtration. The clear filtrate containing the strongly acid solution of amido- $\beta$ -naphthol sulphate was immediately poured into a filtered solution of two parts of potassium dichromate in 20 of water, when the quinone at once separated in slender needles of a bright orange colour. It was collected without delay, thoroughly washed with distilled water, and dried at the ordinary temperature. It was found on

incineration to contain traces of chromium; but as it decomposes very readily, it was not practicable to remove the chromium by crystallisation from any solvent. When the solutions are carefully filtered, and the operations rapidly performed, the quinone is quite pure, with the exception just mentioned. It melts at  $96^{\circ}$ . The substance was dried *in vacuo* and analysed with the following results, in which a correction has been made for the chromium present.

I. .142 gram of substance gave .396 gram of carbonic anhydride and .050 gram of water.

II. .139 gram of substance gave .387 gram of carbonic anhydride and .050 gram water.

		Theory.	I.	II.	Mean.
$C_{10}$	= 120	75.95	76.05	75.93	75.99
$H_6$	= 6	3.80	3.91	4.00	3.95
$O_2$	= 32	20.25	—	—	—
	<hr/>	<hr/>			
	158	100.00			

The analytical results correspond very closely with those required by the formula  $C_{10}H_6O_2$ , showing it to be an isomeride of the naphthoquinone previously discovered by one of us (Groves, this Journal, xxvi, 209). As its general characters and reactions moreover correspond with those of the quinones, we have called it  *$\beta$ -naphthaquinone*, distinguishing the readily volatile quinone formed by the direct oxidation of naphthalene or of amido- $\alpha$ -naphthol as  *$\alpha$ -naphthaquinone*.

Like the ordinary quinones,  *$\beta$ -naphthaquinone*, when treated with hydriodic acid, yields a hydroquinone crystallising in colourless needles, which appeared to be reconverted into the quinone by the action of oxidising agents. The same compound is produced by the action of sulphurous acid; the quinone dissolves readily in aqueous sulphurous acid, forming a colourless solution, which deposits the hydroquinone when concentrated by evaporation at a gentle heat. When alcoholic solutions of the quinone and hydroquinone are mixed, water added, and the solution gently heated, dark-coloured crystals are deposited resembling those obtained from the corresponding  $\alpha$ -compounds under similar circumstances. The  *$\beta$ -naphthaquinone* dissolves, when heated with dilute nitric acid, and the solution, on cooling, deposits a crystalline substance of a magnificent crimson colour. If, however, the quinone be boiled with nitric acid for some time, it is completely oxidised to phthalic acid, which may be obtained by evaporating the solution to dryness and recrystallising the residue from water. The phthalic acid readily yields a sublimate of phthalic anhydride, which, with resorcin, gives the characteristic fluorescein reaction.

Adopting Graebe's symbol for naphthalene, it is evident that both

oxygen atoms in the  $\beta$ -quinone are in the same benzene nucleus, since it yields phthalic acid on oxidation; moreover, one of the oxygen atoms occupies the  $\beta$ -position, since it is a derivative of  $\beta$ -naphthol. The relation of the two oxygen atoms to one another is undetermined, although considering the readiness with which the quinone is attacked and decomposed, and the difficulty with which it is volatilised, it is more probable that the oxygen atoms have a meta-relation than an ortho one.

This substance is of special interest, as being the first instance of an isomeric quinone derived from the same hydrocarbon, although it should not be forgotten that in the benzene series we have a brominated compound  $C_6HBr_3O_2$ , the "tribromoresorquinone" of Liebermann and Dittler, which, unless the formula be doubled, is isomeric with tribromoquinone.

We purpose continuing our investigation of the new substances mentioned in this paper, and also of instituting a careful comparison of the two isomeric naphthaquinones.

---