XXXIII.—*On the Action of Benzoic Acid on Naphthaquinone.*

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Preparation of Naphthaquinone.

THE naphthaquinone employed in the following experiments was prepared by the method of Groves (*Chem. Soc. J.*, 1873, 209), by the oxidation of naphthalene with chromic anhydride in acetic acid solution. In order to get rid of unattacked naphthalene, Groves recommends that the mixture of naphthalene and naphthaquinone should be exposed to the air for some days in a warm place. This process is somewhat tedious; so, with a view to finding a shorter method, we made some experiments on the relative solubilities of naphthalene and naphthaquinone. We found that a hot mixture of equal volumes of glacial acetic acid and water dissolves naphthalene readily, but deposits very nearly the whole of the hydrocarbon on cooling to 20°; whereas of the naphthaquinone, which is dissolved under similar conditions, a considerable portion is retained in solution in the cold, and may be precipitated by diluting with an equal volume of water, and still more thoroughly by subsequent partial neutralisation with sodium carbonate. Following up this observation we endeavoured to employ in the separation of the naphthalene and naphthaquinone the acetic acid which serves as a solvent during the oxidation. This we have accomplished in the following process:—

Into each of ten flasks, 10 grams of naphthalene and 60 grams of glacial acetic acid are introduced. After heating to dissolve the naphthalene, a solution of 30 grams of chromic acid in 20 c.c. of water is gradually added to each flask. (A preliminary experiment showed that the presence of this proportion of water did not cause a precipitation of naphthalene from the hot solution.) In practice it is best to prepare this solution of chromic anhydride on a large scale, dividing it afterwards into portions of 50 grams each, by means of a measure constructed for this purpose. The chromic solution must be very gradually, taking the flasks in rotation: by hurrying the action the yield is much diminished. When the whole of the oxidising agent has been introduced, the contents of the flasks are united and heated over a water-bath to complete the reaction, after which 300 c.c. of water are added, a portion of this water being employed to rinse out

the small flasks.* The whole is then heated for a few minutes on the water-bath, agitating thoroughly, and is then allowed to cool. As soon as the temperature has sunk to about 20° , the liquid is filtered rapidly through calico. The filtration must not be postponed too long, as part of the naphthaquinone otherwise separates out. The filtrate is diluted with an equal volume of water, which occasions the separation of a great portion of the naphthaquinone, and is then partially neutralised with crystallised sodium carbonate. The naphthalene on the calico filter is again extracted with about 300 c.c. of a hot mixture of equal volumes of glacial acetic acid and water; the liquid is left to cool, filtered from the naphthalene, and treated as above. This second extraction is generally sufficient to exhaust the naphthalene. The finely-divided naphthaquinone is separated by filtration from the partially neutralised liquids, dried, and purified by crystallisation from light petroleum as recommended by Groves. In this way it is freed from a reddish-brown product, insoluble in petroleum. A petroleum of sp. gr. 0.72 was found very suitable.

The yield of pure naphthaquinone was 20 per cent. of the weight of naphthalene employed.

Action of Benzoic Acid on Naphthaquinone.

When naphthaquinone is heated with three times its weight of benzoic acid in a flask to about 160° , the liquefied mass speedily assumes a darker colour, at the same time almost solidifying from the separation of minute crystalline needles. Water is eliminated during the reaction, escaping in bursts of steam from the semi-solid mass and condensing in drops in the upper part of the flask. As soon as the quantity of crystalline substance no longer visibly increases, the reaction is stopped, and the contents of the flask, after cooling, are boiled with alcohol to dissolve the excess of benzoic acid, filtered, and washed with boiling alcohol on the filter. The crude substance, of which the yield is about equal to the weight of naphthaquinone employed, is thus obtained in small reddish-brown needles. It is insoluble in all the usual solvents, even at their boiling points; but aniline and bisulphide of carbon, when heated with it in sealed tubes to 300° , dissolve small quantities, the substance crystallising out in larger needles on the walls of the tube on cooling. Of course as a mode of purification, this last method is not applicable. We found, however, that the greater part of the colouring matter could be removed by

* 500 c.c. of water have thus been added to 600 grams of acetic acid. These proportions, which were found to work well in practice, were employed instead of equal volumes, in order to allow (roughly) for the formation of water during the oxidation and for the presence of a portion of the acetic acid as chromic acetate.

long-continued boiling with aniline. After treatment with aniline, the substance was again boiled with alcohol, and was thus ultimately obtained of a pale reddish-brown colour. Its weight was reduced by one-half in this process of purification. Under the microscope it now presented a perfectly homogeneous appearance, and consisted of fine ramiform needles. It is highly electric. It fuses above the range of the thermometer. Caustic alkalis do not dissolve it. We satisfied ourselves by means of a qualitative test for nitrogen, which gave a negative result, that the aniline employed in the purification had not combined in any way with the substance.

Analysis yielded the following results : —

	Substance.	CO ₂ .	OH ₂ .
I	0.1580	0.4876	0.0456
II	0.1392	0.4294	0.0386
III	0.1510	0.4666	0.0428

These numbers lead to the formula C₉H₄O—

	Calculated for C ₉ H ₄ O.		Found.			
			I.	II.	III.	Mean.
C ₉ ..	108	84.37	84.16	84.13	84.27	84.18
H ₄ ..	4	3.13	3.20	3.06	3.14	3.13
O ..	16	12.50	—	—	—	(12.69)
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	128	100.00				100.00

Analyses I and II were made with one preparation of substance; in III a second preparation was employed.

By tripling the above empirical formula, so as to give the molecular formula C₂₇H₁₂O₃, the formation of this substance might be accounted for by the following equation :—

To this higher molecular weight the physical properties of the substance also point. In view, however, of the difficulty of dealing with a substance which cannot be purified by recrystallisation, which does not possess a fusing point capable of being appealed to in the comparison of different preparations, and of which the only test of purity is the frequently fallacious one of apparent homogeneity under the microscope, we offer the above formula with all reserve. The study of the reactions of the substance, the details of which are given further on, has thrown but little light on its constitution.

An experiment was made to determine whether the compound could

be prepared by heating together benzoic anhydride and naphthaquinone at 160° ; but, though the operation was continued for a long time, no trace of the compound was formed. The experiment was repeated, employing a higher temperature, but again with negative result. From this it would appear that the presence of the hydroxyl group in benzoic acid is necessary to the formation of the compound.

Oxidation.—In order to ascertain whether benzoic acid could be regenerated from the compound by oxidation, 1 gram was boiled with a mixture of potassic dichromate and dilute sulphuric acid. After boiling for about 18 hours, the substance had almost entirely disappeared. The liquid was then distilled with steam, and the distillate, after rendering alkaline, was evaporated to a small bulk and acidified with hydrochloric acid. No trace of benzoic acid could be detected.

In order to test for other acids, a second oxidation was performed with potassium permanganate in aqueous solution. 10 grams of the substance were treated in this way with 5 grams of permanganate. As soon as the permanganate was reduced, the solution was filtered from the mixture of manganic hydroxide and unattacked substance, the filtrate being preserved, and the precipitate subjected afresh to the oxidising action of 5 grams of permanganate. This was repeated several times, the solution being filtered after each operation, in order that any soluble products of oxidation might be withdrawn as quickly as possible from the further action of the permanganate. As soon as the reduction of the permanganate slackened, the process was finally interrupted, and the united filtrates, after evaporating to a small bulk, were acidified with hydrochloric acid and extracted with ether. About a gram of a solid crystalline acid was thus obtained, but, as it was of a yellowish colour, it was converted into a sodium salt and treated in aqueous solution with a very small quantity of permanganate on the water-bath. The resulting colourless solution yielded a perfectly white acid, readily soluble in hot water, and crystallising on cooling in small plates, fusing at 182° , which is the fusing point of phthalic acid. By sublimation, long characteristic needles of phthalic anhydride were obtained, fusing at 128.5 — 129.5° . We could not detect any other acid in the product of oxidation.

All other experiments yielded either negative results or such small quantities of product that examination was impossible.

Action of Hydriodic Acid and Amorphous Phosphorus.—After heating for four hours to 250° , the substance was recovered unaltered.

Distillation with Zinc-dust.—The substance was distilled from combustion-tubing with ten times its weight of zinc-dust. Two experiments were made, each with a gram of substance. In one the heating was carried backwards from the open towards the closed end of the

tube: in the other, forwards, beginning at the closed end. About one drop of an oily liquid, smelling like a high-boiling coal-tar oil, was obtained in each case.

Fusion with Potash.—No action took place till a temperature was reached at which the substance inflamed, and burnt like tinder on the surface of the potash. Even when previously mixed with potash and water, the substance behaved in exactly the same manner, separating out on the surface as soon as the water was driven off.

Distillation with Soda-lime.—The heating was carried forwards from the closed end of the tube. Nothing was obtained beyond a slight sublimate of unaltered substance.

Action of Zinc-ethyl.—Treated with zinc-ethyl at 100° , the substance does not evolve gas. It therefore contains no hydroxyl-group.*

Beyond showing that the compound contains the group $C_6H_4(C_2)^{VI}$ [1 : 2], and that it contains neither the group $C_6H_5-C\equiv$, nor hydroxyl, the above experiments are inconclusive. The absence of the group $C_6H_5-C\equiv$ shows that, assuming the substance to be formed in the manner expressed by the equation, the nucleus of the benzoic acid undergoes modification during the reaction, probably by the direct attachment of carbon of the naphthaquinone. The $C_6H_4(C_2)^{VI}$ group may belong either to a naphthaquinone residue, or—less probably, however—to a modified benzoic acid residue.

We propose provisionally to name the compound *benzonaphthone*.

The reaction is interesting as showing benzoic acid, a substance usually very inert in its behaviour towards neutral organic bodies, in a somewhat new light.

According to preliminary experiments which we have made, naphthaquinone also reacts with the following acids:—Of the formic series—formic, acetic, propionic, butyric, isobutyric, and stearic acids; of the benzoic series—phenylacetic acid—hydrocinnamic acid being, however, apparently without action; of the oxalic series—oxalic and succinic acids. It does not react with lactic acid. In many of these cases mixtures of compounds appear to be formed. We hope, however, to find among the products of these reactions substances somewhat

* In a paper by Japp and Wilcock, the non-evolution of gas when a substance is treated with cold zinc-ethyl is suggested as a general test for the absence of hydrogen directly attached to oxygen or nitrogen (*Chem. Soc. Trans.*, 1881, 665, foot note). I have since found that the test as thus employed frequently leads to erroneous results, inasmuch as, although substances containing the hydroxyl-group or the amido-group evolve gas under these conditions, those containing the imido-group generally require heating with the zinc-ethyl before any evolution of gas occurs. The substance ought to be added to the zinc-ethyl already heated to 100° . - F.R.J.

more amenable to ordinary chemical treatment than the compound here described.

Other quinones, so far as our observations have as yet extended, do not appear to react with acids.