CCXXXII.—*Studies in the Dihydronaphthalene Series.*
Part II. The ar-Dihydro- α -naphthols and their
Derivatives.

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OUR investigations of the hydrogenation of α -naphthylamine (T., 1918, **113**, 955; *J. Soc. Dyers and Col.*, 1919, **35**, 128; *J. Soc. Chem. Ind.*, 1920, **39**, 241T; T., 1920, **117**, 1574) have shown that the base is converted into *ar*-tetrahydro- α -naphthylamine by the action of sodium and amyl alcohol, but that when the reduction is effected under suitable conditions with sodium and ethyl alcohol in the presence of an inert solvent of high boiling point, such as solvent naphtha or toluene, the intermediate 5 : 8-dihydro- α -naphthylamine only is obtained. The latter is isomerised by the action of sodium ethoxide at a suitable temperature and concentration to 5 : 6(or 7 : 8)-dihydro- α -naphthylamine, a compound which differs from its isomeride in that it may be converted into the tetrahydro-derivative by the action of sodium and ethyl alcohol.

In the case of α -naphthol also the action of sodium and amyl alcohol leads to the formation of the *ar*-tetrahydro-derivative (Bamberger and Bordt, *Ber.*, 1890, **23**, 215; Jacobson and Turnbull, *ibid.*, 1898, **31**, 897). The *ar*-dihydro- α -naphthols corresponding with the two *ar*-dihydro- α -naphthylamines have not been described hitherto, and it appeared of interest, therefore, to prepare and examine these compounds.

In the first place, attempts were made to prepare these compounds by the direct hydrogenation of α -naphthol in a similar manner to that used for the preparation of the dihydro- α -naphthylamines (*loc. cit.*), with the exception that an increased quantity of sodium

was employed on account of the acidic nature of the product. The reduction mixture was diluted and distilled in a current of steam to remove the volatile solvent. The residue was then acidified, distilled in a current of steam, and the distillate examined.

(a) When α -naphthol, ethyl alcohol, toluene or solvent naphtha, and sodium were employed, the distillate contained a product, melting at 56° , which proved to be a mixture of 5 : 8-dihydro- α -naphthol and 5 : 6(or 7 : 8)-dihydro- α -naphthol, together with a small quantity of unreduced α -naphthol.

(b) When α -naphthol, ethyl alcohol, solvent naphtha or toluene, and sodium were employed, and the mixture, after all the sodium had disappeared, was distilled slowly to remove the volatile solvent, and then heated for one hour at 125° , the product proved to be a mixture of 5 : 6(or 7 : 8)-dihydro- α -naphthol with some unreduced α -naphthol. Separation of this mixture was at first effected by means of fractional distillation in a current of steam, as the hydrogenated naphthol is more volatile than α -naphthol, but later, when it was found that the hydrogenated naphthol did not form a picrate, it proved more satisfactory to remove the α -naphthol from the mixture by conversion into the picrate. 5 : 6(or 7 : 8)-Dihydro- α -naphthol forms colourless plates or needles, melting at 71° .

As a result of these experiments it appears that, in the case of α -naphthol, it is more difficult to determine conditions suitable for the preparation of the 5 : 8-dihydro-derivative than is the case with α -naphthylamine, for, although the conditions were varied, in all cases where hydrogenation occurred, the product was a mixture of the two dihydro- α -naphthols, owing to the fact that some of the 5 : 8-dihydro-derivative was isomerised during the reaction. This is, however, not surprising, for in view of the increased concentration of alkali used in these experiments, it is probable that conditions which are favourable for the hydrogenation of α -naphthol to its 5 : 8-dihydro-derivative are equally favourable for the isomerisation of this compound to the 5 : 6(or 7 : 8)-dihydro- α -naphthol.

Therefore, whilst the method (b) outlined above was suitable for the preparation of 5 : 6(or 7 : 8)-dihydro- α -naphthol, the method (a) was unsuitable for the preparation of the 5 : 8-derivative, as we were unable to separate the mixture of the two dihydro-compounds formed.

Attention was next directed to the preparation of the dihydro- α -naphthols from the corresponding amines by diazotisation and boiling the diazonium compound.

It is noteworthy that whilst this method gives good results in the case of the preparation of *ar*-tetrahydro- α -naphthol from *ar*-tetrahydro- α -naphthylamine (Bamberger and Althausse, *Ber.*, 1888,

21, 1892), the yields of the dihydro- α -naphthols from the corresponding dihydro-amines are low, and these compounds are always formed together with a considerable proportion of naphthalene.

5 : 8-Dihydro- α -naphthol forms colourless plates or needles, melting at 75°, with a pronounced phenolic odour, whilst 5 : 6- (or 7 : 8)-dihydro- α -naphthol also forms colourless plates or needles, melting at 71°, identical with the product previously described and obtained by the direct hydrogenation of α -naphthol and isomerisation of the intermediate 5 : 8-dihydro- α -naphthol.

The following table indicates the behaviour of aqueous solutions of α -naphthol, 5 : 8-dihydro- α -naphthol, 5 : 6(or 7 : 8)-dihydro- α -naphthol, and *ar*-tetrahydro- α -naphthol on the addition of ferric chloride and calcium hypochlorite respectively :

	α -Naphthol.	5 : 8-Dihydro- α -naphthol.	5 : 6(or 7 : 8)-Dihydro- α -naphthol.	<i>ar</i> -Tetrahydro- α -naphthol.
Ferric chloride.	Violet colour and precipitate.	A more reddish-violet colour and precipitate which develops more slowly than is the case with α -naphthol.	Brown colour and precipitate.	Yellow colour and precipitate.
Calcium hypochlorite.	„ „	A much redder colour and precipitate than with α -naphthol.	„ „	Faint white precipitate.

An important difference in the properties of 5 : 8-dihydro- α -naphthol and 5 : 6(or 7 : 8)-dihydro- α -naphthol is shown by their behaviour on treatment with sodium and ethyl alcohol, for the 5 : 8-isomeride remains unchanged, whilst the 5 : 6(or 7 : 8)-isomeride is converted into *ar*-tetrahydro- α -naphthol.

It is clear, therefore, that the course of the reaction in the conversion of α -naphthol into *ar*-tetrahydro- α -naphthol by means of sodium and an alcohol is completely analogous to the course of the reactions in the hydrogenation of naphthalene and α -naphthylamine under similar conditions, and the intermediate dihydro-derivatives in each case exhibit a similar behaviour when treated with sodium and ethyl alcohol.

The behaviour of the two dihydro- α -naphthols when sulphonated and nitrated under conditions similar to those employed for *ar*-tetrahydro- α -naphthol (*loc. cit.*) was next examined. When the dihydro- α -naphthols are treated with twice their weight of concentrated sulphuric acid for two days at the ordinary temperature,

they are converted, for the greater part, into water-soluble products, although sulphonation is accompanied to a certain extent by resinification. The crude sodium salts of the sulphonic acids could be isolated from the sulphonation mixtures in the usual manner. The sulphonic acids are readily hydrolysed by dilute acids with regeneration of the dihydro- α -naphthols. From analogy to the monosulphonic acid of *ar*-tetrahydro- α -naphthol it was to be expected that the sulphonic group would enter the *para*-position with respect to the hydroxyl group in the dihydro- α -naphthols, and that this was the case is obvious from the behaviour of the sulphonic acids on nitration.

5 : 8-Dihydro- α -naphthol-4-sulphonic acid and 5 : 6(or 7 : 8)-dihydro- α -naphthol-4-sulphonic acid possess similar properties to *ar*-tetrahydro- α -naphthol-4-sulphonic acid, and, for example, in alkaline solution do not combine with diazonium compounds to form azo-dyes.

For the nitration experiments it is unnecessary to isolate the sulphonic acids, but the diluted sulphonation mixtures were nitrated directly, and 2-nitro-5 : 8-dihydro- α -naphthol, yellow needles, melting at 98°, volatile with steam, 2-nitro-5 : 6(or 7 : 8)-dihydro- α -naphthol, yellow needles, melting at 55°, volatile with steam, and 2 : 4-dinitro-5 : 8-dihydro- α -naphthol, yellow, prismatic needles, melting at 127°, were obtained.

Both dihydro- α -naphthols exhibited behaviour similar to that of *ar*-tetrahydro- α -naphthol when treated with nitrous acid, and yielded 4-nitro-5 : 8-dihydro- α -naphthol, brown needles, melting at 161°, and 4-nitro-5 : 6(or 7 : 8)-dihydro- α -naphthol, yellow needles, melting at 162°, respectively.

All attempts to obtain 2 : 4-dinitro-5 : 6(or 7 : 8)-dihydro- α -naphthol either by nitration of the dihydronaphtholsulphonic acid with two molecules of nitric acid or by the further nitration of 4-nitro-5 : 6(or 7 : 8)-dihydro- α -naphthol with nitric acid resulted in complete resinification of the compound.

It should be noted that whereas the nitration of *ar*-tetrahydro- α -naphthol under the conditions described results in almost theoretical yields of the nitro-derivatives in all cases, the dihydro- α -naphthols are, on nitration, more readily oxidised under the existing conditions, and give extremely low yields of the nitro-derivatives. This behaviour is not surprising, however, in view of the unsaturated character of the hydrogenated ring in the dihydro- α -naphthols.

E X P E R I M E N T A L .

(1) A mixture of 400 c.c. of dry toluene or solvent naphtha (b. p. 139°) and 70 grams of sodium was boiled in a flask fitted with a reflux condenser, and a solution of 30 grams of α -naphthol in rather more ethyl alcohol than is necessary to dissolve the sodium was added drop by drop through the condenser. Boiling was continued until all the sodium had disappeared, and the mixture was then distilled until the internal temperature rose to 125° , at which temperature heating was continued for one hour. The mixture was poured into water and distilled in a current of steam to remove the remainder of the toluene. The residue was acidified with hydrochloric acid and distilled in a current of steam. The distillate was saturated with sodium chloride, as the dihydronaphthol is appreciably soluble in water, and the crystalline product separated. Any unaltered α -naphthol was removed by conversion into its picrate.

5 : 6(or 7 : 8)-*Dihydro- α -naphthol* forms colourless, silky needles or plates, melting at 71° (corr.) (Found : C = 82.19; H = 6.79. $C_{10}H_{10}O$ requires C = 82.19; H = 6.85 per cent.).

(2) Fifteen grams of 5 : 6(or 7 : 8)-dihydro- α -naphthylamine were stirred into 25 grams of sulphuric acid diluted with 100 c.c. of water, and the crystalline paste, cooled to 2° , was diazotised with a solution of 7.2 grams of sodium nitrite in 100 c.c. of water. The yellowish-red solution was kept for half an hour, warmed gently until the evolution of nitrogen ceased, distilled in a current of steam, and the distillate saturated with sodium chloride. The product, a mixture of 5 : 6(or 7 : 8)-dihydro- α -naphthol and naphthalene, was extracted with sodium hydroxide, the extract was acidified, and the regenerated dihydronaphthol purified by distillation in a current of steam. The product was identical with that obtained by the direct hydrogenation of α -naphthol (Found : C = 81.99; H = 6.66 per cent.).

ar-Tetrahydro- α -naphthol is readily obtained from 5 : 6 (or 7 : 8)-dihydro- α -naphthol by the gradual addition of 30 grams of sodium to a boiling solution of 10 grams of this dihydro- α -naphthol in 400 c.c. of dry ethyl alcohol. The *ar*-tetrahydro- α -naphthol was isolated in the usual manner,

This compound was prepared from 5 : 8-dihydro- α -naphthylamine in a similar manner to that described for the preceding compound. 5 : 8-Dihydro- α -naphthol forms colourless plates or needles, melting at 75° (Found : C = 81.99; H = 6.92. $C_{10}H_{10}O$ requires C = 82.19; H = 6.85 per cent.). When heated with a solution of sodium ethoxide, it is converted into 5 : 6 (or 7 : 8)-dihydro- α -naphthol.

Sulphonation of 5 : 8-Dihydro- α -naphthol.

Ten grams of finely powdered 5 : 8-dihydro- α -naphthol having been completely dissolved in 20 grams of cold concentrated sulphuric acid, the solution was kept for two days at the ordinary temperature, and the mixture was then diluted with water and filtered from a trace of unsulphonated 5 : 8-dihydro- α -naphthol. The filtrate was neutralised with milk of lime, and the calcium salt, after removal of calcium sulphate, was converted into the sodium salt and evaporated to dryness. The sodium salt could not be obtained in a pure condition for analysis owing to the presence of resinous matter. It is very readily soluble in water, and the sulphonic group is readily hydrolysed by boiling with dilute acids, 5 : 8-dihydro- α -naphthol being regenerated. 5 : 8-Dihydro- α -naphthol-4-sulphonic acid, in neutral or alkaline solution, does not couple with diazonium salts to form azo-compounds.

Sulphonation of 5 : 6(or 7 : 8)-Dihydro- α -naphthol.

This sulphonation was effected in a similar manner to that described for the preceding compound. The product, which could not be obtained in a sufficiently pure condition for analysis, possesses similar properties to those of its isomeride.

Two grams of 5 : 8-dihydro- α -naphthol were dissolved in 4 grams of cold concentrated sulphuric acid. The solution was allowed to

remain for two days, diluted with 6.5 c.c. of water, cooled in ice and nitrated with 0.9 c.c. of nitric acid (d 1.4; 1 mol.) diluted with 2 c.c. of water. The nitrosulphonic acid did not separate from the mixture as did the corresponding compound during the nitration of *ar*-tetrahydro- α -naphthol-4-sulphonic acid under the same conditions. The nitrosulphonic acid, therefore, was not isolated in this case, but the nitration mixture was boiled with dilute sulphuric acid (1 : 1) in order to hydrolyse the sulphonic group, and then distilled in a current of steam. 2-Nitro-5 : 8-dihydro- α -naphthol forms yellow needles, melting at 98°. It is readily volatile with steam and possesses a sweet, pleasant odour. It dissolves in sodium hydroxide solution with an orange coloration, forms an orange-red sodium salt, and couples with diazonium compounds forming azo-dyes (Found : C = 62.71; H = 4.80; N = 7.13. $C_{10}H_9O_3N$ requires C = 62.82; H = 4.71; N = 7.33 per cent.).

This compound was prepared in the same manner as that described for the preceding compound. It forms yellow needles, melting at 55°, and possesses similar properties to those of 2-nitro-5 : 8-dihydro- α -naphthol (Found : C = 62.71; H = 4.84; N = 7.50. $C_{10}H_9O_3N$ requires C = 62.82; H = 4.71; N = 7.33 per cent.).

Five grams of 5 : 8-dihydro- α -naphthol were dissolved in sodium hydroxide, the solution being diluted with water to 150 c.c. To this, an aqueous solution of 3.6 grams of sodium nitrite (2 mols.) was added together with 100 grams of ice. Fifty c.c. of 10 per cent. sulphuric acid contained in a dropping funnel, the end of which dipped below the surface of the liquid, were then slowly run into the mixture with constant agitation. The sticky, yellowish-white precipitate was collected and washed with cold water. The major portion dissolved in sodium carbonate solution, and was filtered from a quantity of a tarry residue. From the filtrate, the

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product was precipitated by dilute acetic acid. 4-Nitro-5:8-dihydro- α -naphthol crystallises from dilute alcohol in brown needles, melting at 161° (with decomp.). It is not volatile with steam. It dissolves in sodium hydroxide solution with a yellowish-brown coloration, and on addition of excess of alkali, the sodium salt crystallises in brown needles. 4-Nitro-5:8-dihydro- α -naphthol does not couple with diazonium compounds (Found: C = 62.79; H = 4.78; N = 7.15. $C_{10}H_9O_3N$ requires C = 62.82; H = 4.71; N = 7.33 per cent.).

4-Nitro-5:6(or 7:8)-dihydro- α -naphthol,

This compound was prepared in the same manner as that described for the preceding compound. It crystallises from dilute alcohol in yellow needles, melting at 162° (with decomp.). Its properties are similar to those of 4-nitro-5:8-dihydro- α -naphthol (Found: C = 62.99; H = 4.75; N = 7.15. $C_{10}H_9O_3N$ requires C = 62.82; H = 4.71; N = 7.33 per cent.).

Four grams of 5:8-dihydro- α -naphthol were dissolved in 8 grams of cold concentrated sulphuric acid, the solution was allowed to remain for two days, and diluted with 10 c.c. of water. The clear liquid was cooled in ice, and nitrated with 4.7 c.c. of nitric acid (d 1.4; 2.5 mols.) diluted with 5.5 c.c. of water. After all the nitric acid had been added, the mixture was allowed to remain at the ordinary temperature for some time. It was then warmed on the water-bath at 50° until a semi-crystalline product, insoluble in water, had separated. A quantity of resinous impurity was removed from the product by careful washing with cold toluene.

2:4-Dinitro-5:8-dihydro- α -naphthol crystallises from ether in long, yellow, prismatic needles, melting at 127° . It dissolves in sodium hydroxide solution with an orange-brown coloration, and the sodium salt crystallises from the solution in orange needles

SILBERRAD : RESEARCHES ON SULPHURYL CHLORIDE. PART I. 2029

(Found : C = 50·75; H = 3·36; N = 11·99. $C_{10}H_8O_5N_2$ requires C = 50·85; H = 3·39; N = 11·87 per cent.).

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