

XCII.—*Studies in the Tetrahydronaphthalene Series.**I. The Diazoamino-compounds of ar-Tetrahydro- β -naphthalene.*

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ar-TETRAHYDRO- β -NAPHTHYLAMINE, according to Bamberger, is a base having the properties of a benzenoid amine, and in this respect differs from its alicyclic isomeride and also from β -naphthylamine (Bamberger, *Ber.*, 1887, **20**, 2915; Bamberger and Müller, 1888, **21**, 847, 1112; Bamberger and Bordt, 1889, **22**, 625; Bamberger and Kitchelt, 1890, **23**, 876).

The reactions of the aromatic base have not been exhaustively studied owing to the fact that it is the bye-product of the hydrogenation of β -naphthylamine, the main reaction resulting in the formation of its isomeride. *ar*-Tetrahydro- β -naphthylamine can be diazotised, and is stated to yield *azo*-colouring matters with diazonium salts (*Ber.*, 1890, 23, 883), but no experimental evidence has been published in support of the latter assertion.

The production of *azo*-compounds without the intermediate formation of diazoamines, if it could be substantiated, would tend to show that the aromatic base still retains its naphthalenoid character, but the results established in the present paper show that this is not the case, and that *ar*-tetrahydro- β -naphthylamine behaves towards diazonium salts as would be expected from its formula, yielding diazoamines and not aminoazo-compounds, thus confirming Bamberger's view that it resembles the monoamines of the benzene series.

This result is of much interest, because Bamberger and Bordt (*Ber.*, 1889, 22, 625) have shown that *ar*-tetrahydro- α -naphthylamine, which, from its formula, might be expected to behave like 2:3-xylylidine and produce diazoamino-compounds, does not react in this way, but, contrary to expectation, forms aminoazo-compounds, in this respect resembling the parent substance, α -naphthylamine.

The diazoamines of *ar*-tetrahydro- β -naphthalene have the general colour and appearance of the benzenoid diazoamines, are decomposed by cold concentrated hydrochloric acid, and can be obtained in accordance with Griess's observation, either by the action of a benzenediazonium salt on the tetrahydro-base, or by condensing the benzenoid amine with *ar*-tetrahydro- β -naphthalenediazonium chloride. For example, the compound produced by the interaction of diazotised *p*-toluidine and *ar*-tetrahydro- β -naphthylamine is identical with that obtained by condensing *p*-toluidine with the diazotised aromatic base. The same holds true in the case of *p*-bromoaniline and the hydrogenised base.

The results recorded in this paper may be summed up as follows :

Diazoamines of *ar*-tetrahydro- β -naphthalene have been prepared from the diazonium salts of *ar*-tetrahydro- β -naphthylamine; β -naphthylamine; *p*-toluidine; *o*-toluidine; *p*-nitroaniline; *o*-nitroaniline; and *p*-bromoaniline.

Azo-compounds have been obtained from the diazotised aromatic base with β -naphthylamine and with β -naphthol.

The behaviour of the diazonium salts of *m*-nitroaniline and of *m*-chloroaniline towards *ar*-tetrahydro- β -naphthylamine is peculiar. Undoubtedly, diazoamines are produced in each case. They cannot be isolated, however, for they change, slowly at 0° and instantly at the ordinary temperature, into exceedingly viscid, dark red substances.

That this transformation is not due to the subsequent formation of aminoazo-compounds, brought about by the presence of an open para-position in the benzene nucleus, is proved by the fact that *o*-nitro-aniline gives a stable diazoamino-compound.

A satisfactory explanation of the change has not yet been obtained, and the point will receive further attention.

If *ar*-tetrahydro- β -naphthylamine retains in any degree the characteristics of β -naphthylamine, it ought to be an easy matter to transform diazoaminotetrahydro- β -naphthalene in such a manner that the diazo-group enters the α -position contiguous to the aminic nitrogen, thus giving rise to an azo-compound. Since such a transformation has not been effected, the conclusion may be drawn that in the diazoamines of tetrahydro- β -naphthalene the tendency of the diazo-group to migrate into the contiguous α -position is not, at the most, greater than its tendency to enter the ortho-position in the amines of the benzene series.

EXPERIMENTAL.

p-Toluenediazoaminotetrahydro- β -naphthalene, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_3\text{H} \cdot \text{C}_{10}\text{H}_{11}$.

This compound is slowly precipitated as a light yellow, ochreous solid on adding excess of sodium acetate solution to a hydrochloric acid solution containing equivalent quantities either of *p*-toluenediazonium chloride and *ar*-tetrahydro- β -naphthylamine, or of *ar*-tetrahydro- β -naphthalenediazonium chloride and *p*-toluidine.

After 15 hours, the product is collected, washed, dried, and crystallised from a hot mixture of alcohol and toluene in equal volumes; it separates from this solvent in straw-coloured flakes which melt at 107° . The substance is readily soluble in alcohol, benzene, or chloroform, but only sparingly so in light petroleum. The product obtained by each of the methods of preparation was analysed:

1st Preparation:

0.1439 gave 19.1 c.c. moist nitrogen at 15° and 758 mm. $\text{N} = 15.50$.

2nd Preparation:

0.0870 gave 11.7 c.c. moist nitrogen at 15° and 758 mm. $\text{N} = 15.75$.

$\text{C}_{17}\text{H}_{19}\text{N}_3$ requires $\text{N} = 15.85$ per cent.

A mixture of the two preparations has a melting point identical with that of either product taken separately.

Decomposition of p-Toluenediazoaminotetrahydro- β -naphthalene by Cold Hydrochloric Acid.—The method employed was that devised by Meldola and Streatfeild (Trans., 1887, 51, 438). Three grams of the diazoamine were treated for 3 hours with 15 c.c. of concentrated hydrochloric acid at 0° . The contents of the beaker, slightly diluted

with water, were slowly filtered into a cooled alkaline solution of β -naphthol containing a small quantity of ammonium hydroxide, the odour of which served to indicate the alkalinity of the mixture. The residue on the filter was again digested with hydrochloric acid and filtered into the β -naphthol solution. The bright red precipitate thus obtained was collected, washed once with water, extracted three times with hot dilute hydrochloric acid, and finally washed with hot water and dried.

The dried substance was separated by fractional crystallisation from hot alcohol into two portions, the one consisting of vermilion-red crystals with a green reflex, very sparingly soluble in hot alcohol and melting at 153° , the other of bright red crystals melting at 109° .

The former substance was identified as *ar-tetrahydronaphthaleneazo- β -naphthol*, $C_{10}H_{11} \cdot N_2 \cdot C_{10}H_6 \cdot OH$, a compound prepared by adding a solution of *ar*-tetrahydro- β -naphthalenediazonium chloride to an alkaline solution of β -naphthol. This substance separates from hot alcohol in vermilion-red crystals having a green reflex and melting at 153° . It is insoluble in caustic soda, sparingly soluble in alcohol, and gives a crimson colour with concentrated sulphuric acid :

0.1048 gave 8.7 c.c. moist nitrogen at 20° and 766 mm. $N = 9.57$.

$C_{20}H_{18}ON_2$ requires $N = 9.27$ per cent.

The bright red crystals melting at 109° consist probably of a mixture of *ar*-tetrahydronaphthaleneazo- β -naphthol and *p*-tolueneazo- β -naphthol (m. p. 134°).

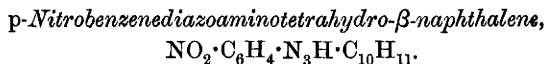
The basic products of the decomposition remaining in the acid filtrates from the azo-compounds were set free and acetylated by boiling for 3 hours with glacial acetic acid and acetic anhydride. The mixed acetyl derivatives, obtained by adding water to the glacial acetic acid solution, were extracted with hot water. The greater part dissolved, leaving an oily residue, and the solution, on cooling, yielded a crop of white crystals which, after recrystallisation, melted at 146° and proved to be identical with aceto-*p*-toluidide (m. p. 147°), a mixture of the two substances having the same melting point.

The insoluble oily residue from the aqueous extract crystallised from hot dilute acetic acid in needles melting at 101° . The quantity obtained was too small for further purification, but it did not depress the melting point of aceto-*ar*-tetrahydro- β -naphthalide (m. p. 106°) by more than 1° .

These results show that the decomposition of this mixed diazoamine of the tetrahydro- β -naphthalene series by cold hydrochloric acid follows the usual mode of fission already noticed in the case of its benzene analogues, the compound yielding two primary amines, *p*-toluidine and

ar-tetrahydro- β -naphthylamine and two diazonium salts, *p*-toluenediazonium chloride and *ar*-tetrahydro- β -naphthalenediazonium chloride.

The brown, oily product obtained when *o*-toluidine is employed instead of *p*-toluidine appears to be a diazoamine, since it is decomposed by cold hydrochloric acid, the products of fission yielding azo-compounds with β -naphthol.

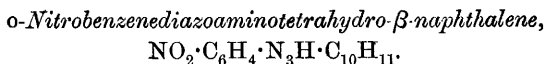


This was prepared by adding sodium acetate to a solution of *p*-nitrobenzenediazonium chloride and *ar*-tetrahydro- β -naphthylamine hydrochloride; it separated as a bulky, reddish-brown precipitate, which after repeated crystallisation from alcohol and toluene was obtained in well-defined, chocolate-brown prisms melting at 179° with violent decomposition:

0.1051 gave 16.9 c.c. moist nitrogen at 15.5° and 770 mm. $N = 19.05$.
 $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_4$ requires $N = 18.92$ per cent.

The diazoamine is readily soluble in alcohol, benzene, or chloroform, but dissolves only sparingly in light petroleum. When mixed with alcoholic sodium hydroxide, it yields a deep purple solution of its sodium derivative.

In this instance, it is not possible to prepare the diazoamine by the interaction of *ar*-tetrahydro- β -naphthalenediazonium chloride and *p*-nitroaniline; the condensation does not occur in aqueous, alcoholic, or glacial acetic acid solutions.



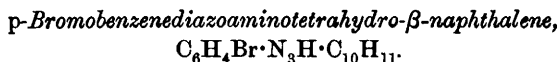
This substance is readily obtained by coupling *o*-nitrobenzenediazonium chloride with tetrahydro- β -naphthylamine in dilute acetic acid, although the latter base, when diazotised, does not, under these conditions, condense with *o*-nitroaniline. The product, a reddish-brown, ochreous precipitate, is easily soluble in alcohol or benzene, but dissolves only sparingly in light petroleum. After three crystallisations from alcohol and toluene, it separates in yellow plates which melt at 134°:

0.0631 gave 10 c.c. nitrogen at 15.5° and 770 mm. $N = 18.78$.
 $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_4$ requires $N = 18.92$.

Although the diazonium salts derived from the *o*- and *p*-nitroanilines combined with tetrahydro- β -naphthylamine, yielding well-defined diazo-

amines, it was not possible to isolate the isomeride from *m*-nitroaniline.

A solution of diazotised *m*-nitroaniline and tetrahydro- β -naphthylamine, when treated with excess of sodium acetate, gave rise to a salmon-pink precipitate which slowly changed at 0° into a viscid, dark-red liquid, the same transformation occurring rapidly at the ordinary temperature. All attempts at crystallisation have failed, the substance separating in the viscid form and gradually acquiring the consistence of sealing wax. A diazoamine is probably present, since the products of decomposition with hydrochloric acid yield red azonaphthols.



This compound can be prepared in two ways, either by condensing *p*-bromobenzenediazonium chloride with *ar*-tetrahydro- β -naphthylamine, or by treating the diazotised tetrahydro-base with *p*-bromoaniline. The former method is preferable. The diazoamine, when thrice crystallised from alcohol and toluene, separates in primrose-yellow, silky needles which melt at 134°. The identity of the products obtained by the two methods of condensation is proved by comparing the melting point of each with that of a mixture of the two, and also by analysis :

1st Preparation :

0.1684 gave 0.0961 AgBr. Br = 24.28.

0.1029 ,, 11.4 c.c. moist nitrogen at 18.5° and 756 mm. N = 12.69.

2nd Preparation :

0.0676 gave 0.0384 AgBr. Br = 24.17.

$C_{16}H_{16}N_3Br$ requires Br = 24.24 ; N = 12.72 per cent.

An attempt to condense diazotised *m*-chloroaniline with tetrahydro- β -naphthylamine gave a result comparable with that obtained in the case of *m*-nitroaniline ; the yellowish-brown solid precipitated on the addition of sodium acetate rapidly changed to a viscid, red, oily product from which nothing crystalline could be extracted.

The peculiar behaviour of meta-substituted amines is still under investigation, and it is worthy of note that the effect just described only occurs with *m*-amines and with β -naphthylamine.



This is obtained by adding sodium acetate to a hydrochloric acid solution of tetrahydro- β -naphthalenediazonium chloride, and tetrahydro- β -naphthylamine ; when crystallised from light petroleum it separates in well-defined, amber-coloured prisms melting at 104° ; it is readily soluble in the ordinary organic solvents :

0.1374 gave 15.8 c.c. nitrogen at 14° and 756 mm. $N = 13.46$.

$C_{20}H_{23}N_3$ requires $N = 13.77$ per cent.

The following experiment was performed with the view of transforming diazoaminotetrahydro- β -naphthalene into the aminoazo-compound.

Four grams of the substance, 0.5 gram of *ar*-tetrahydro- β -naphthylamine, and 0.5 gram of the chloride dissolved in alcohol were allowed to stand for four days. Evaporation of the solvent yielded a tarry residue, from which neither alcohol nor dilute acid extracted any azo-compound. The tar was then shaken with sodium hydroxide and benzoyl chloride, but a solid product could not be isolated.

The fact that transformation does not occur in this case indicates that the hydrogen in the α -position contiguous to the aminic nitrogen in tetrahydro- β -naphthylamine is not more reactive than that in the ortho-position in an amine of the benzene series.

β -Naphthalenediazoaminotetrahydro- β -naphthalene, $C_{10}H_7 \cdot N_3H \cdot C_{10}H_{11}$.

This compound is produced by filtering a diazotised solution of β -naphthylamine into one containing tetrahydro- β -naphthylamine dissolved in dilute hydrochloric acid, and treating the mixture with sodium acetate. The precipitated diazoamine, which at first is yellow, slowly assumes a red colour. It crystallises from light petroleum in lustrous yellow plates which melt at 137.5°:

0.1202 gave 14.6 c.c. moist nitrogen at 21.5° and 764 mm. $N = 13.87$.

$C_{20}H_{19}N_3$ requires $N = 13.95$ per cent.

Tetrahydro- β -naphthaleneazo- β -naphthylamine, $C_{10}H_{11} \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$.

This substance is produced in the calculated quantity when sodium acetate is added to a hydrochloric acid solution of tetrahydro- β -naphthalenediazonium chloride and β -naphthylamine. The yellow solid at first precipitated changes into a dark red substance which crystallises from alcohol in dark red tablets melting at 130°. It is much less soluble in the ordinary solvents than the isomeric diazoamine:

0.0771 gave 9.2 c.c. nitrogen at 18° and 764 mm. $N = 13.86$.

$C_{20}H_{19}N_3$ requires $N = 13.95$ per cent.

It might be mentioned that tetrahydro- β -naphthylamine is much more easily diazotised than β -naphthylamine itself, the solution not being rendered turbid by the formation of bye-products.

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