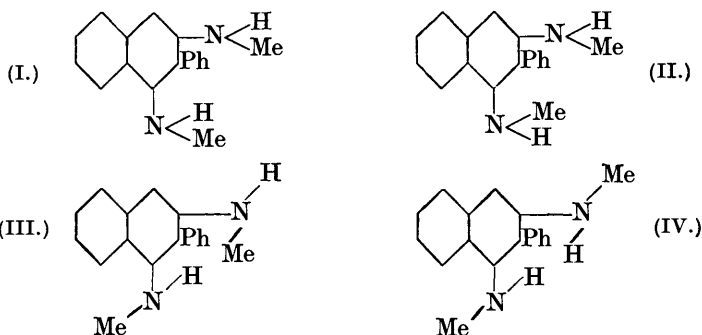


CLV.—N-Methyl Derivatives of 2-Phenylnaphthylene-1:3-diamine.

By WILLIAM SIMPSON KENTISH.

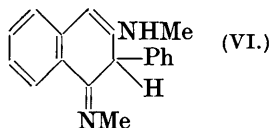
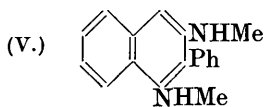
THE isomerism of the α - and β -*NN'*-dimethyl-2-phenylnaphthylene-1:3-diamines, examined by Lees and Thorpe (J., 1907, **91**, 1282) and by Gibson, Kentish, and Simonsen (J., 1928, 2131), can be explained by assuming either definite structural differences between the two isomerides or an interlocking of the phenyl and methyl groups producing *cis-trans* isomerism. On the latter assumption, the molecules of the isomeric dimethyl compounds may be either planar (I and II) or non-planar (III and IV).



The planar model was suggested by Gibson, Kentish, and Simonsen (*loc. cit.*, p. 2133), but there is much evidence against it. In the first place, there is no reason why the methylamino- and phenyl groups should remain in the plane of the ring, since they are rotating continuously and are not fixed as the assumption demands. Moreover, molecular models show that there is not sufficient space for the methyl groups to exist between the nitrogen atoms and the benzene

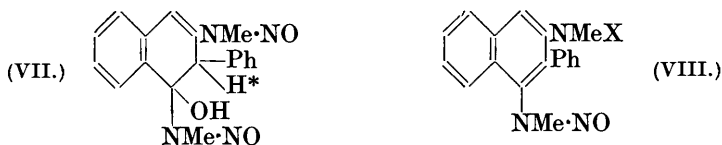
ring. In addition, only two of the four possible isomerides are known. The non-planar model assumes that the phenyl and methylamino-groups interlock and that the former vibrates slightly about the plane of the naphthalene ring, the latter oscillating in planes perpendicular to that of the naphthalene ring. The formation of mono-derivatives of the *cis*- or α -dimethyldiamine (III) is explained if it is assumed that steric hindrance prevents two large substituents from entering the naphthalene ring on the same side. The failure to resolve either of the isomerides cannot be explained by assuming racemisation, because, in that event, the two isomerides themselves should be similarly interconvertible. Both models fail to explain adequately why the α -dimethyldiamine forms only mono-derivatives, since the trimethyldiamine can be readily acetylated and the dimethyldiamines pass very quickly into the tetramethyl compound when heated with methyl sulphate. Also, there is no explanation of the transformation in the presence of nitrous acid (see p. 1171), and why two nitroso-groups can be introduced into the α -dimethyldiamine even though the nitroso- and the methyl group have comparable molecular volumes. There is no reason why the isomerides should not be interconvertible in the presence of strong reagents, as the molecular model shows that the overlapping of groups is not so great as that observed in the case of the enantiomorphic forms of 2:6:2'-trisubstituted diphenyl compounds (Kenner and others, *J.*, 1922, **121**, 614, etc.; Mills, *Chem. and Ind.*, 1926, **45**, 883) and the disubstituted 1:8-nitronaphthylamines (Mills and Elliott, *J.*, 1928, 1291) and also of the exactly comparable isomerides of 5'-chloro-2'-hydroxy-2-benzoyl-*m*-toluic acid (Hayashi, *J.*, 1927, 2516; compare Kentish, *Chem. and Ind.*, 1928, **47**, 952), and yet these are readily interconvertible.

In the light of this evidence, more attention may be given to the structural explanation of the isomerism. Of the many possibilities, the most probable represents the β -form as the simple dimethylnaphthylenediamine (V) and the α -form as a methylimino-compound with a reduced naphthalene ring (VI).



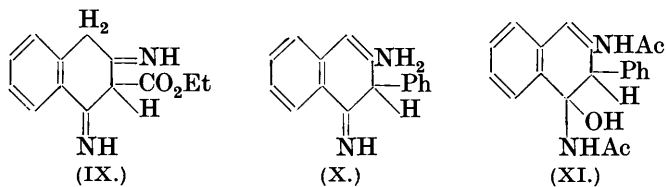
The formulæ explain the formation of mono-derivatives of the α -dimethyldiamine and also the stability of the isomerides in the presence of strong reagents. The anomalous behaviour of nitrous acid, which rapidly transforms the α -dimethyldiamine into the β -dinitrosoamine (very slow transformation in the case of acetic

anhydride and other reagents is not, however, excluded), is probably due to the addition of the reagent at the methylimino double bond giving the compound (VII) and the elimination of the hydroxyl group and the hydrogen atom (marked *) as water, giving the β -dinitrosoamine (VIII; X = NO).



Owing to the intractability of the salts of the dimethyldiamines and optically active acids, the evidence for non-resolvability lies largely in the homogeneity of the methylenecamphor derivatives. Since, however, several cases have already been found where this reagent has not effected resolution, the evidence for non-resolvability cannot be accepted as definitely established. In the case of the β -dimethyldiamine, rapid racemisation would indeed be expected.

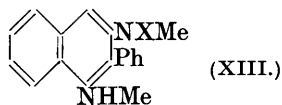
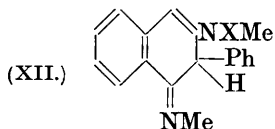
Atkinson and Thorpe (J., 1906, **89**, 1906) considered that ethyl 1 : 3-diaminonaphthalene-2-carboxylate had the di-imino structure (IX), as it had a yellow colour, and that the corresponding carboxylic acid together with 2-phenylnaphthylene-1 : 3-diamine and naphthylene-1 : 3-diamine, being colourless, had the diamino structure. It is, however, very probable that 2-phenylnaphthylene-1 : 3-diamine has the mono-imino structure (X), because the 1-amino-group cannot be diazotised unless there is an acetyl group in the 3-position. Finally, on acetylation of the diamine with acetic anhydride, an "acetyl acetate" is obtained (Atkinson and Thorpe, *loc. cit.*). This is not a true salt, as, on treatment with caustic soda, it passes immediately into the diacetyl compound. It is evident that, during acetylation, acetic acid adds on at the imino double bond, giving the compound (XI) analogous to that obtained with nitrous acid. Loss of water occurs in this case only in the presence of alkalis. The isolation of the intermediate compound undoubtedly strongly supports the imino structure of 2-phenylnaphthylene-1 : 3-diamine.



When 2-phenylnaphthylene-1 : 3-diamine is methylated with methyl sulphate and alkali in the cold, the imino structure is retained in the

case of the α -dimethyldiamine; transformation, however, takes place on further methylation, since the tetramethyldiamine is also obtained (compare the amino structure of 3-acetyl-2-phenylnaphthylene-1:3-diamine). When the diamine is heated with methyl sulphate, transformation occurs and the β -dimethyldiamine is obtained. The transformation is probably due to the addition of methyl sulphate (Me and MeSO₄ being the two addenda) at the imino double bond and the subsequent splitting off of the MeSO₄ and H groups. This addition may only occur under the conditions of the second method of methylation, as alkalis would tend to retain the MeSO₄ addendum.

It seemed to be of considerable interest to examine the mechanism of the action of nitrous acid in converting the α - into the β -dimethyldiamine. The only method of effecting an interchange was described by Gibson, Kentish, and Simonsen (*loc. cit.*) and involved the action of nitrous acid on the α -dimethyldiamine, giving the β -dinitrosoamine, and the subsequent reduction of this to the β -dimethyldiamine. The slowness of the action of nitrous acid on the α -dimethyldiamine in comparison with the normal rate of acetylation, etc., of this base suggests that the acid-soluble α -mononitrosoamine is produced immediately and is slowly transformed into the β -dinitrosoamine. When the α -dimethyldiamine is treated with one molecule of nitrous acid, a good yield of α -3-nitrosomethylamino-1-methylimino-2-phenyl-1:2-dihydronaphthalene (XII; X = NO) is obtained. This is dimorphic like many other compounds of this series. Evidently some peculiarity in the structure presents an alternative method of packing the molecules in the crystals.



As this mononitrosoamine can be reduced to the α -dimethyldiamine, and also slowly converted into the β -dinitrosoamine when treated with nitrous acid, it is evident that the transformation occurs when the second nitroso-group is introduced. The α -mononitrosoamine can be neither methylated nor condensed with *p*-toluenesulphonyl chloride. In order to discover whether the transformation was in any way specifically associated with the first nitroso-group, the action of nitrous acid on the monoacetyl and mono-*p*-toluenesulphonyl derivatives of the α -dimethyldiamine was investigated. The α -monoacetyl compound (XII; X = CO·CH₃) gave a *nitrosoamine* (VIII; X = CO·CH₃) fairly quickly, and this was reduced to a new acetyl compound which could be hydrolysed to the β -dimethyl-

diamine and was therefore β -3-acetylmethylamino-1-methylamino-2-phenylnaphthalene (XIII; $X = \text{CO}\cdot\text{CH}_3$).

The α -mono-*p*-toluenesulphonyl compound (XII; $X = \text{SO}_2\cdot\text{C}_7\text{H}_7$) similarly gave a mononitrosoamine (VIII; $X = \text{SO}_2\cdot\text{C}_7\text{H}_7$) which gave the β -dimethyldiamine after removal of the nitroso- and *p*-toluenesulphonyl groups.

The transformation is thus seen to be unassociated with the nature of the first substituent in the α -dimethyldiamine, and evidence seems now to have accumulated to show that nitrous acid effects a definite structural transformation.

Further support for the structural explanation of the isomerism of the dimethyldiamines was obtained by the preparation of the mononitrosoamine of the β -dimethyldiamine. When the latter was treated with one molecule of nitrous acid, the greater part of the product obtained consisted of the dinitrosoamine and unchanged base, but a small quantity of the β -mononitrosoamine (XIII; $X = \text{NO}$) was also isolated with some difficulty.

The β -mononitrosoamine had a deep red colour and gave intensely coloured solutions, whereas solutions of the α -mononitrosoamine were only slightly coloured. The intensity of colour in the former compound would be expected, as there is a chromophore ($\text{N}\cdot\text{NO}$) and an auxochrome (NHMe) present as substituents in a phenylnaphthalene ring. In the α -mononitrosoamine, the naphthalene ring is absent.

It is proposed to see whether absorption spectra will furnish proof of the structure of the derivatives of 2-phenylnaphthylene-1 : 3-diamine.

EXPERIMENTAL.

α -3-Nitrosomethylamino-1-methylimino-2-phenyl-1 : 2-dihydro-naphthalene (XII; $X = \text{NO}$).— α -*NN'*-Dimethyl-2-phenylnaphthylene-1 : 3-diamine (VI) (7 g.) was dissolved in 15% hydrochloric acid (70 c.c.), and sodium nitrite (1.95 g.) in aqueous solution (10 c.c.) added slowly with mechanical stirring at the ordinary temperature. After a few minutes, a slight precipitate of dinitrosoamine was filtered off and the filtrate was basified with ammonia. The red oil obtained quickly solidified (7.3 g.), and on crystallising from alcohol the α -mononitrosoamine was isolated in 70% yield (Found : N, 14.5. $\text{C}_{18}\text{H}_{17}\text{ON}_3$ requires N, 14.4%). It had m. p. 154° and was dimorphic; the unstable α_1 -form separated first from solutions as a mass of fine yellow glistening needles and quickly passed into the glistening orange-red prisms of the stable α -form. Both had the same melting point. The mononitrosoamine gave the Liebermann reaction and was soluble only in fairly concentrated hydrochloric acid.

A solution of the mononitrosoamine (4 g.) in glacial acetic acid (60 c.c.) was heated with excess of tin and concentrated hydrochloric

acid (30 c.c.) on the water-bath for 20 minutes. Excess of solid caustic soda was added to the decanted liquid, and the solution boiled for a few minutes to decompose double salts of tin. The product was extracted with hot benzene and was worked up in the usual way. A nearly theoretical yield of the α -dimethyl base (VI) was obtained (m. p. 169° after crystallising from light petroleum, b. p. $60\text{--}80^\circ$).

The α -mononitrosoamine (1 g.) was dissolved in 20% hydrochloric acid (40 c.c.), and excess of sodium nitrite solution added. The β -dinitrosoamine (VIII; X = NO) separated slowly and had m. p. 179° after crystallising from alcohol.

When the α -mononitrosoamine was heated with *p*-toluenesulphonyl chloride in pyridine solution for 4 hours at 100° , and methylated with methyl sulphate and caustic soda in methylalcoholic solution in the usual way, it was recovered unchanged.

Action of Nitrous Acid on α -3-Acetylmethylamino-1-methylimino-2-phenyl-1:2-dihydronaphthalene.—The α -monoacetyl compound (XII; X = CO \cdot CH₃) (8 g.), dissolved in 10% hydrochloric acid (150 c.c.), was treated with a slight excess of sodium nitrite solution. After $\frac{1}{2}$ hour, the precipitate was collected, washed with water, and crystallised from alcohol, in which it was readily soluble; β -3-acetylmethylamino-1-nitrosomethylamino-2-phenylnaphthalene (VIII; X = CO \cdot CH₃) separated in pale yellow lustrous plates, m. p. 198° (Found: N, 12.8. C₂₀H₁₉O₂N₃ requires N, 12.6%). It gave the Liebermann reaction.

The acetylnitrosoamine (4 g.) was dissolved in acetic acid (40 c.c.) and reduced with tin and hydrochloric acid, giving β -3-acetylmethylamino-1-methylamino-2-phenylnaphthalene (XIII; X = CO \cdot CH₃) (3 g.). This was very soluble in the ordinary solvents and crystallised from dilute alcohol in prisms, m. p. 147° (Found: N, 9.2. C₂₀H₂₀ON₂ requires N, 9.2%).

The β -monoacetyl compound was not appreciably hydrolysed by boiling with 40% caustic soda solution or alcoholic sulphuric acid. When it was refluxed for 4 hours with concentrated hydrochloric acid, and the product crystallised from alcohol, a good yield of the β -dimethyldiamine (V) (m. p. 158°) was obtained.

*Action of Nitrous Acid on *p*-Toluenesulphonyl- α -NN'-dimethyl-2-phenylnaphthylene-1:3-diamine.*—The α -mono-*p*-toluenesulphonyl compound (XII; X = SO₂ \cdot C₇H₇) (5 g.) was dissolved in concentrated hydrochloric acid (80 c.c.) and an equal volume of water was added, followed by a slight excess of sodium nitrite solution. A pale yellow precipitate formed fairly quickly, and after 30 minutes this was collected, washed with water, and crystallised from alcohol, in which it was fairly soluble; nitroso-*p*-toluenesulphonyl- β -NN'-

dimethyl-2-phenylnaphthylene-1 : 3-diamine (VIII; $X = SO_2 \cdot C_7H_7$) separated in pale yellow plates, m. p. 183° , which gave the Liebermann reaction (Found : N, 9.5. $C_{25}H_{23}O_3N_3S$ requires N, 9.4%).

The β -nitroso-*p*-toluenesulphonyl compound (3 g.) was reduced with tin and hydrochloric acid in acetic acid solution. The solid resin obtained was at once hydrolysed by heating at 120° with 20 c.c. of a mixture of glacial acetic acid (30 parts) and concentrated sulphuric acid (70 parts) until the whole had dissolved. On pouring the mixture into water and basifying it with ammonia, 1 g. of the β -dimethyldiamine (m. p. 159° after crystallising from alcohol) was obtained.

β -3-Nitrosomethylamino-1-methylamino-2-phenylnaphthalene.—The β -dimethyl base (7 g.), dissolved in 20% hydrochloric acid (100 c.c.), was treated with sodium nitrite (2.02 g.) in aqueous solution (10 c.c.) at 0° . After 15 minutes, the dinitrosoamine was filtered off; the filtrate, basified with ammonia, gave a deep red solid. This consisted mainly of the β -dimethyl base, which was removed by digesting the solid several times with 10% hydrochloric acid. The residue was basified with ammonia and crystallised from a mixture of 3 parts of alcohol and 1 part of benzene, the β -*mononitrosoamine* (XIII; $X = NO$) separating in minute, deep red needles with a violet fluorescence, m. p. 248° (Found : N, 14.6. $C_{18}H_{17}ON_3$ requires N, 14.4%). It was fairly readily soluble in alcohol and readily soluble in benzene, giving intensely coloured crimson solutions. The hydrochloride was yellow and rather sparingly soluble in water. Owing to the small amount of β -mononitrosoamine obtained in this reaction, it was not possible to prove the constitution by conversion either into the dinitrosoamine or into the β -dimethyldiamine; but it was not considered likely that the nitroso-group had entered the naphthalene ring, as no similar compound was obtained when excess of nitrous acid was used or when the α -dimethyldiamine was treated with nitrous acid.

Acetyl Acetate Derivative of 2-Phenylnaphthylene-1 : 3-diamine.—The acetyl acetate compound (XI) was dissolved in alcohol and treated in the cold with excess of 5% aqueous caustic soda, and the solution poured into water after a few minutes. The precipitate, m. p. 272° , was the pure diacetyl-2-phenylnaphthylene-1 : 3-diamine (Atkinson and Thorpe, J., 1906, **89**, 1935, give m. p. 267°).

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