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THE THERMAL DECOMPOSITION
OF SOME
N,N'-DIARYLETHYLENEDIAMINE
HYDROBROMIDES.
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A few N,N'-diarylethylenediamines have been prepared, and decomposed with hydrogen bromide at elevated temperatures. An examination of the products has shown that the expected fused-ring heterocyclic compounds, e.g. indoline, are not formed; instead the main products are the corresponding 1,4-diphenylpiperazines and primary arylamines. Small quantities of other compounds have also been found. The significance of the various products has been discussed, and the total relevant evidence used in proposing a reaction scheme. The absence of fused-ring heterocyclics has been explained on steric and electronic grounds, and a comparison with syntheses of five-membered fused-ring compounds made.
The Hofmann-Martius reaction involves the thermal decomposition of the hydrochlorides and hydrobromides of N-alkylanilines and N,N'-dialkylanilines to give the salts of ring-alkylated primary or secondary anilines. Typical reactions are shown diagrammatically below:

In both cases some polyalkylation occurs. Our knowledge of the scope and mechanism of this reaction is due mainly to the extensive investigations of Hickinbottom which have been reviewed in recent years.\(^1,2\) The following facts concerning the reaction have been found.

(1) The temperatures required are high, usually 250\(^\circ\)-300\(^\circ\), although 200\(^\circ\) and less have been found sufficient where the alkyl groups are secondary or tertiary.

(2) Polyalkylation may occur, even in the rearrangement of
secondary anilines.

(3) Olefins and alkyl halides are by-products, and their production is accompanied by reduced yields of ring-alkylated anilines.

(4) Where suitable alkyl groups are used, the alkyl substituted aniline and the olefin formed contain rearranged alkyl groups, but the alkyl halide does not. For example, N-isoamylaniline yields isoamyl bromide, trimethylethylene, and p-tert-amylaniline.3,4

(5) Olefins or easily ionized alkyl halides can be used to introduce alkyl groups into the aromatic nucleus of an aniline in the presence of its hydrohalide under the conditions of the reaction.

Both intramolecular and intermolecular mechanisms were suggested by early work on this reaction, and both have found supporters in recent times. Thus Dewar,5 in supporting an intramolecular mechanism, assumes a π-complex intermediate. The difficulty with this suggestion is revealed by an examination of reaction products (see (3) and (4) above). These results are not readily explained on Dewar’s theory.

The generally accepted mechanism at present is that of Hughes,1,2 who has developed the earlier ideas of Hickinbottom and Michael. His suggested mechanism is as follows:

\[
\begin{align*}
C_6H_5\cdotNH_2^+\cdot R + X^- & \longrightarrow C_6H_5\cdot NH_2 + R\cdot X^- \\
R\cdot X & \rightleftharpoons R^+ + X^- \\
R^+ + C_6H_5\cdot NH_2 & \rightleftharpoons \text{Olefin} + C_6H_5\cdot NH_3^+ \\
R^+ + C_6H_5\cdot NH_2 & \longrightarrow R\cdot C_6H_4\cdot NH_2 + H^+ 
\end{align*}
\] (1) (ii) (iii) (iv)
This mechanism appears to contain an anomaly in that step (i) is shown as irreversible. It might be anticipated, by analogy with the well known reaction of alkyl halides and anilines to give N-alkylated anilines, that this would be reversible even under the conditions of the rearrangement, viz., high temperatures and high halide ion concentration.

It was decided in this department to attempt to carry out such a rearrangement with N-phenylazetidine (I) to establish whether or not 1, 2, 3, 4-tetrahydroquinoline (II) is produced according to the scheme:

\[ \text{H}^+ + \text{C}_6\text{H}_5\cdot\text{NH}_2 \rightleftharpoons \text{C}_6\text{H}_5\cdot\text{NH}_3^+ \] (v)

Such a rearrangement would be a case of the Hofmann-Martius reaction, unusual in that it would be an ortho-rearrangement and intramolecular.

To this end, attempts were made to prepare N-phenylazetidine. The only recorded preparation was that of Scholtz who claimed to prepare it from the interaction of 1,3-dibromopropane and aniline. Not only was this the sole recorded preparation of an azetidine from a dihalide and an amine, but also the only claim to have prepared an
N-arylazetidine. Scholtz obtained the compound as a low-boiling fraction when distilling his main product N,N'-diphenyltrimethylenediamine (III). Hanssen previously prepared the diamine by this method, but failed to distil it owing to extensive decomposition. Veer later carried out the same preparation. He differed from Hanssen in being able to distil his product, and from Scholtz in that the fraction distilling before the diamine contained only aniline. Sommers also prepared the diamine without signs of decomposition.

Fischer, Topsom and Vaughan found, in repeating Scholtz's preparation, that the low-boiling fraction could be separated into aniline and a compound answering to Scholtz's description of N-phenylazetidine. This description also fitted 1, 2, 3, 4-tetrahydroquinoline (II) with which the compound was readily identified.

When the reaction mixture from the preparation was carefully freed from acid, N,N'-diphenyltrimethylenediamine (III) could in fact be distilled. However, the monohydrobromide of III was found to break down smoothly at 230° - 250° to give II and aniline. With smaller amounts of acid present, the decomposition was less rapid, but the products remained unchanged. The yield of the reduced quinoline was about 50%, and of aniline slightly greater than quantitative on the reaction scheme below.

It seems that II is formed as the result of an interesting Hofmann-Martius reaction, the mechanism of which may be formulated in various ways. Firstly it may be
represented as mechanistically the same as the normal Hofmann-Martius reaction:

\[
\begin{align*}
\text{III} & \xrightarrow{HBr} \text{IV} & \xrightarrow{\Delta} \text{V} \\
\text{V} & \rightarrow \text{VI} & + \text{H}^+ \\
\end{align*}
\]

However it is possible that at the low acid, and therefore halide ion, concentrations used (usually a 10:1 molar ratio of III to HBr) the carbonium ion (a) might be produced by a direct unimolecular decomposition of (a) rather than via an alkyl halide intermediate. As a further extension, the mechanism could involve a synchronous ring closure and aniline elimination process as shown below:

\[
\begin{align*}
\text{VII} & \xrightarrow{\Delta} \text{VIII} & + \text{C}_6\text{H}_5\cdot\text{NH}_2 \\
& & + \text{H}^+ \\
\end{align*}
\]

An analogous mechanism does not occur in the normal Hofmann-
Martius reaction, but it must be remembered that in that case a 1:1 molar ratio of acid to amine is used.

At present in this department investigations are being carried out into the scope, mechanism and synthetic value of this reaction. A variety of \( N,N' \)-diaryltrimethylenediamines are therefore being prepared and decomposed. It has been found that not only are reduced quinolines formed, but julolidines are also found where the aryl group of the diamine does not carry an ortho substituent.

![Julolidine IV](image)

In the cases where the aryl group is ortho substituted, thus excluding julolidine formation, unidentified dark-coloured high molecular-weight materials are produced in addition to the reduced quinolines.

The present work is the result of a concurrent investigation into the rearrangements of \( N,N' \)-diarylethylene-diamines under similar conditions. It was decided firstly to investigate the breakdown of \( N,N' \)-diphenylethlenediamine (V). Irrespective of other products, this could conceivably rearrange to yield indoline (VI) and aniline as shown on the reaction scheme below:
No analogues of julolidine containing two five-membered rings are expected since such ring systems would be highly strained, and have not in fact been reported in the literature.

In order to introduce the further work undertaken, it is necessary to anticipate the results obtained to the extent of pointing out that the main product of the breakdown of V was found to be 1,4-diphenylpiperazine (VII), and no indoline could be separated from the reaction products. The investigation was therefore extended to \( N,N' \)-di-2-naphthylethlenediamine (VIII) and \( N,N' \)-di-1-naphthylethlenediamine (IX). In the former case ring closure to the unknown 4,5-benzoindoline (X) might possibly be easier than that to indoline because of the greater activation to electrophilic attack of the 1-position of a 2-naphthylamine than of the ortho position of an aniline.
With the 1-naphthyl analogue of VII the steric conditions for ring closure to the unknown 1-azaperinaphthane (XI) are almost as good as for the formation of tetrahydroquinoline from III. In spite of the "meta-like" nature of the "peri" position of the naphthylamine, XI may indeed be regarded as a likely product.
II

PREPARATION OF N,N'-DIARYLETHYLENEDIAMINES

General

(1) Melting points are uncorrected.

(2) Reference melting points are given in brackets after the measured figures. Unless otherwise stated they are the highest given in "Beilstein's Handbuch der Organischen Chemie."

(3) All microanalyses were carried out at Otago University.

DISCUSSION

The N,N'-diarylethlenediamines were prepared by the interaction of ethylene dibromide with an arylamine at elevated temperatures. This method, which was first described by Morley 11, is the only practical one found in the literature. The alternative procedure of reacting the sodio-derivatives of acetylated amines with dibromoalkanes fails to give practical yields with ethylene dibromide 14.

The direct interaction may be formulated as follows:

$$2Ar\cdot NH_2 + Br\cdot CH_2\cdot CH_2\cdot Br \longrightarrow Ar\cdot NH\cdot CH_2\cdot CH_2\cdot NH\cdot Ar + 2HBr$$

Earlier workers 11,12,13 used a 4:1 molar ratio of arylamine to ethylene dibromide so that the hydrogen bromide liberated in the reaction could combine to give arylamine hydrobromide. The salt was then dissolved out of the reaction mixture with water. This procedure would be inefficient because some of the product may be present as its salt and
therefore lost. It thus seemed preferable to neutralize the reaction mixture and then remove the primary amine by taking advantage either of its greater solubility in common organic solvents, or of its lower boiling point.

The earlier workers mentioned above found appreciable amounts of 1,4-diarylpiperazines in their reaction products.

\[ 2\text{ArNH}_2 + 2\text{BrCH}_2\text{CH}_2\text{Br} \rightarrow \text{ArNCH}_2\text{CH}_2 \cdot \text{NAr} + 2\text{HBr} \]

The extent of this side reaction depends on the relative proportions of arylamine to dibromide, and is reduced by using excess arylamine (see, for example, Garzino 15). This procedure was followed in the present work, the actual excess depending on the ease of purification of the particular arylamine used.

The three diamine forming reactions were found to be exothermic. While this caused no embarrassment in the formation of the phenyl diamine, cooling was certainly necessary during the preparation of \( N,N'-\text{di-2-naphthylethylene-diamine} \) where it proved advisable to add all the reactant ethylene dibromide at once, otherwise it could not be stirred into the rapidly solidifying mass. During the first attempt with the 1-naphthylamine reaction, the mixture did not solidify at 130°, (the temperature of the reaction) and the ethylene dibromide was added slowly with stirring during the second and third preparations. Cooling was then unnecessary.

In each preparation, the amines were liberated from their salts with concentrated ammonia before any separation
was attempted. In the preparations of \( \text{N,\text{N}'-diphenylethylene-diamine} \) and of \( \text{N,\text{N}'-di-1-naphthylethylene-diamine} \), the free amines could be dissolved in diethyl ether, and their extraction could be accomplished through simultaneous addition of ether and neutralizing ammonia. However, with the ether-insoluble \( \text{N,\text{N}'-di-2-naphthylethylene-diamine} \), the rock-hard reaction mixture was pulverized and stirred as a slurry with concentrated ammonia before the acid-free amines were filtered off.

Where the reaction products are ether-soluble, the ether could be distilled off at normal pressures followed by the primary arylamine under reduced pressure. However, in the preparation of \( \text{N,\text{N}'-di-2-naphthylethylene-diamine} \), the 2-naphthylamine was not distilled off as its melting - and boiling - points are high and it was present in large quantity. It was therefore a simpler procedure to separate it from the diamine by extracting it with ethanol, in which it is very soluble.

Morley 11 repeatedly recrystallized crude \( \text{N,\text{N}'-diphenylethylene-diamine} \) from aqueous ethanol to yield glossy plates, m.p.63°, but in the present work the melting-point could not be raised above 59° by this procedure. However a good yield of pure product, m.p. 65° - 66° (66°), was obtained by distilling twice under reduced pressure.

Purification of \( \text{N,\text{N}'-di-1-naphthylethylene-diamine} \) was effected by dissolving the crude material in hot benzene, and the solution cooled and poured into ethanol. This yielded a crystalline solid which was purified to constant melting point by recrystallizing repeatedly from benzene and
from benzene-alcohol. This proved more efficient than simple recrystallization from benzene.\textsuperscript{12}

Bischoff\textsuperscript{13} purified N,N\textsuperscript{-}di-2-naphthylethylenediamine by recrystallizing it from ethanol, but this was found to be inadequate and also cumbersome owing to the low solubility of the diamine in hot ethanol. Purification via the amine sulphate (successful with N,N\textsuperscript{-}diphenylethylenediamine\textsuperscript{14}) was also unsatisfactory, as was attempted purification through the hydrochloride. In addition, chromatography, using an alumina column, was unsuccessful.

An attempt to distill some of the material under reduced pressure at 170\degree\textsuperscript{1}-180\degree\textsuperscript{1} yielded mostly di-2-naphthylamine. The identity of this compound was confirmed by the formation of suitable derivatives and by a satisfactory analysis. Although on the surface, it may seem surprising to meet this compound as a major product of the distillation, it has often been produced in reactions involving 2-naphthylamines at high temperatures.\textsuperscript{16,17,18,19,20} 1-Naphthylamines do not, as a rule, give di-1-naphthylamines under the same conditions.

Recrystallization of the crude diamine from acetone gave a fairly pure material. Losses were incurred by this procedure, but it was the most satisfactory method attempted.

\textit{Experimental}

\textbf{Ethylene dibromide Purification}. Reagent grade ethylene dibromide was dried over calcium chloride and distilled, the fraction boiling at 130\degree\textsuperscript{1}-132\degree\textsuperscript{1} (131.7\degree\textsuperscript{1}) being collected and used in the following preparations.
**N,N'-diphenylethlenediamine.** Reagent grade aniline was purified by distilling twice off zinc dust under reduced pressure, the fraction boiling at 76° - 78°/15 mm being collected each time.

A solution of aniline (720g) and ethylenedibromide (163g, 75ml.) was heated on a water bath for two hours in a 1-litre flask fitted with a reflux condenser. Crystals of aniline hydrobromide began to appear after half an hour. After cooling, the reaction mixture was dissolved in concentrated ammonia solution (500ml., S.G. 0.880) and diethyl ether (2 litres). The aqueous layer was separated and the ethereal solution washed with distilled water (4 x 500 ml.), dried over potassium carbonate, and the ether distilled off. The aniline was then removed by distillation under reduced pressure, and the residue distilled twice. The product, b.p. 158° - 160°/ca. 0.5 mm. weighed 149g (81%) m.p. 65° - 66° (66°). The diacetyl derivative, made by boiling with acetic anhydride, melted at 157° - 158° (158°).

**N,N'-di-2-naphthylethlenediamine.** Reagent grade 2-naphthylamine was recrystallized twice from ethanol-water, m.p. 110°-111° (112°-113°). The naphthylamine (200g) was heated to 130° in a 500ml. flask fitted with a thermometer and a reflux condenser. Ethylene dibromide (54g, 25ml.) was added with vigorous agitation, and the contents of the flask brought to 130° again, at which temperature the reaction began. In spite of cooling in an ice-salt bath, the reaction mixture reached 170°, but soon cooled down. Finally it was
heated for two hours at 130° on the oil bath. After cooling, the flask was broken, the hard yellow product being then pulverized and stirred for eight hours as a slurry with concentrated ammonia (1 litre, S.G. 0.880). The solid was filtered off, washed with water, dried, and recrystallized from ethanol to give 63g (83%) of crude material, m.p. 124°-145°. Four recrystallizations from acetone followed by one from dried distilled ethanol yielded 25g of product, m.p. 150°-151° (149°-150°), diacetyl derivative, m.p. 181°-182° (175°-176°). A second preparation gave similar results.

**N,N'-di-1-naphthylethylenediamine.** Commercial grade 1-naphthylamine was purified by distilling once under reduced pressure, the fraction boiling at 120°-130°/ca.0.5mm. being collected and recrystallized once from diethyl ether. m.p. 49°-50° (49°-50°). 1-Naphthylamine (250g) was heated to 130° in a flask fitted with a thermometer and a reflux condenser. Ethylene dibromide (54g, 25ml.) was carefully added in 5ml. amounts, the temperature being maintained at 130° and the mixture being constantly shaken. Finally the purple glutinous mass was heated on an oil bath at 130° for an hour.

After cooling, the contents of the flask were dissolved in ether (1litre) and ammonia (700ml., S.G. 0.880) before the aqueous layer was removed and the ether solution washed with water (4x500 ml.). A small amount of solid (probably 1,4-di-1-naphthylpiperazine, see p. 11) was filtered off, the solution dried over calcium carbonate, and the ether distilled off. Vacuum distillation allowed recovery of the 1-naphthylamine (b.p. 100°-140°/ca. 0.5mm), and left a
brown glassy residue. This was dissolved in hot benzene (100 ml), the solution cooled and poured into absolute alcohol (350 ml.), and the solid filtered off to yield 45.3 g. (43.6%) of crude product, m.p. 122°-124°. Three recrystallizations from benzene followed by two from benzene-ethanol yielded 21.2 g of pale yellow N,N'-di-1-naphthylethylenediamine, m.p. 132°-133° (133°-134°).
III
DECOMPOSITIONS OF \( N,N' \)-DIARYLETHYLENEDIAMINES

Discussion

The normal Hofmann-Martius reaction is carried out under conditions of reflux or in sealed tubes, and the products thus remain with the reactants. This is necessary since the products have boiling-points similar to those of the reactants, and therefore cannot be separated by distillation during the reaction. The procedure does, however, lead to polyalkylation, that is, alkylation of already rearranged products.

However, in the decomposition of \( N,N' \)-diaryltrimethylene-diamines already mentioned (p. 6), the products are of lower molecular weight and boiling-point than the reactants. Thus the conditions were chosen so that the products were distilled off the reaction mixture as they were formed. Provided that the reaction temperature is above that necessary for the decomposition, the pressure can be adjusted till the reactant diamine does not quite boil. This, in the case of the trimethylene-diamines, resulted in the immediate distillation of the aniline and the tetrahydroquinoline and prevented their participation in any subsequent reactions. This procedure resulted in a distillate accounting for about 90% of the reactant by weight. A similar situation was expected with the ethylene-diamine reactions, most of the reactant being converted to low-boiling indolines and anilines.

It was found that for the phenyl-diamine, the
FIG. I. Boiling Points.

- \( \text{NH}_2 \) group: 184°
- \( \text{NHCH}_3 \) group: 196°
- \( \text{NHET} \) group: 205°
- 177° +
- 228° - 230°
- 100° - 101°/12 mm.

- \( \text{NH}_2 \) group: 306°
- \( \text{NHCH}_3 \) group: 308° +
- \( \text{NHET} \) group: 315° - 316° +
- 295° +
- 70°/0.01 mm.

† From "Elsevier's Encyclopaedia of Organic Chemistry." Publisher, ref. 27.

* From G. Lock and G. Gergely, Ber., 77, 465 (1944-45)

decomposition temperature (230°) was above the boiling points of aniline (184°) and indoline (228°-230°), and by reducing the pressure it was anticipated that these products would be readily distilled off the reaction mixture. For the decomposition of the dinaphthylethylenediamines, pressure reduction was necessary to ensure distillation of the naphthylamines, whose boiling points are shown on Fig. 1. The other likely products, i.e. 4,5-benzoindoline and 1-azaperinaphthane, are not recorded in the literature, but it can be predicted, by a comparison with known related compounds, that their boiling points will be about 330°-350°. (See Fig. 1).

In carrying out the decompositions, the Claisen flask containing the reactants was heated slowly on an oil bath, and the temperature was taken when the first volatile products appeared above the level of the oil bath. Subsequently the oil bath was kept 20°-30° above this critical temperature. Temperature variation within a 50° range above the critical temperature had no apparent effect on the rate of distillation of product. Reactions were in all cases continued until the rate of distillation became negligible, although consistency in this was difficult to achieve.

Although Fischer, Topsom and Vaughan 6 found it convenient in their work to use a 10:1 molar ratio of diamine to hydrogen bromide, a 30:1 molar ratio is used here. The amount of acid used had no obvious effect on the rate of decomposition for the decompositions attempted.
A. Decomposition of N,N'-diphenylethylenediamine

The breakdown of this compound in the presence of hydrogen bromide was conveniently conducted at 250° and 110-120 mm. pressure, when the bulk of the reaction was completed in three hours. At this stage only about half the reaction mixture had distilled over. Further heating of the residue resulted in the extremely slow distillation of some liquid products, and a little volatile matter which was lost down the vacuum line. This later reaction would seem to represent some secondary breakdown as it does not occur initially, and thus the majority of the decompositions were continued for only 3-4 hours. These decompositions gave fairly consistent percentages of distillate and residue as summarized below.

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Distillate (1)</th>
<th>Residue (2)</th>
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<tr>
<td></td>
<td>43.2-45.8%</td>
<td>53.2-55.3%</td>
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This makes it obvious that the N,N'-diphenylethylenediamine is not simply decomposing to aniline and indoline. The distillate and the residue were thus examined to establish their constituents.

Examination of "Reaction Distillate" (1).

An attempt was first made to separate any constituents from (1) by fractional distillation under reduced pressure. The first product to pass over was aniline, (b.p. 74-76/12 mm.) which was found to make up at least 93% of the sample. A
small amount of higher boiling material (b.p 76°-140°/12 mm.)
then passed over without any obvious fraction appearing.
(Indoline boils at 100°-101°/12 mm.)

To investigate the higher boiling fraction more
thoroughly, a second method of separation was sought. Aniline
should be the only primary amine present, and a chemical
method was thus attempted. Primary aromatic amines form
complexes with zinc chloride which are insoluble in organic
solvents, and this is the basis of Hickinbottom's 21 method
for the quantitative separation of primary and secondary
amines. This appeared better than the Hinsberg method
because the primary amine is removed more quickly, and
because the secondary amine is recovered as such, not as its
benzene-sulphonamide.

The distillate from a decomposition was first
fractionated in a short column containing glass helices, this
removing much of the aniline. The column was then washed
down with ether and the primary amines precipitated with
zinc chloride. The amines remaining in the ether solution
were then converted to their hydrobromides to facilitate
separation. Recrystallization yielded only N,N'-diphenylethy-
lenediamine dihydrobromide and aniline hydrobromide. The
latter compound was not expected in view of the previous
treatment with zinc chloride, and its presence suggests that
Hickinbottom's method does not give a clean separation. This
has since been confirmed by Russell. 22 The method is thus
inefficient as far as estimation of the amount of aniline is
concerned.
The investigation of the reaction distillate thus shows it to contain at least 92% aniline and at least 1.8% of \(N,N'\)-diphenylethylenediamine, with no evidence for the presence of other products.

**Examination of "Reaction Residue" (2)**

A consideration of the volatile reaction products obtained, combined with the fact that the reaction appeared to have finished when about half the original volume had distilled, gave added interest to the residue. The average reaction gave 44% distillate (mostly aniline) and 53.3% residue, and this corresponds well with the partial reaction.

\[
\begin{align*}
\text{100\%} & \\
\text{56.2\%} & \\
\text{43.8\%} & 
\end{align*}
\]

The residue therefore seemed likely to consist of residues in a fairly high molecular weight compound. On this basis the most likely compound was 1,4-diphenylpiperazine (VII), and this was accordingly sought.

Since, 1,4-diphenylpiperazine was known to be soluble in chloroform but in no other common organic solvents, the residue was dissolved in chloroform, neutralized with ammonia, washed, dried, and recrystallized from ethanol-chloroform.
This gave a poor yield of the impure piperazine which could not be purified by repeated or fractional recrystallizations from ethanol-chloroform. However it was noted that the least soluble fraction melted far above the melting-point of 1,4-diphenylpiperazine.

Separation by a vacuum distillation method was then attempted, the residue being first neutralized to avoid decomposition during distillation. The distillation temperature of the piperazine was found to be only slightly above its melting point, and it was convenient to distil it directly into a wide air condenser where it solidified on the walls. This was entirely satisfactory. It gave good yields of fairly pure product, the purification of which could be completed by one recrystallization from ethanol-chloroform. A small amount of N,N'-diphenylethylenediamine, which distilled with the piperazine, was isolated during the recrystallization, but no evidence for any other products was obtained.

The examination of the residue (2) can now be summarized thus:

Residue (2)
Distillation

Distillate ca. 80%
Recrystallization
1,4-diphenylpiperazine ca. 72.4%

Residue (3). ca. 18%

N,N'-diphenylethylenediamine ca. 3.5%
All percentages are calculated from weights of substances referred to residue (2) as 100%.

The residue (3) was now examined. Treatment always began with fractional recrystallization from ethanol-chloroform. The first crop (5-10% of the original residue (2)) was a high-melting amorphous or microcrystalline solid. Subsequent fractions proved to be impure 1,4-diphenylpiperazine, N,N'-diphenylethlenediamine, and a sticky black material in that order.

Many attempts were made to purify the high melting solid (4) (m.p. 213°-219°). Repeated recrystallization from chloroform-ethanol accomplished nothing, and no separation could be achieved by column chromatography using activated alumina. Similarly, the melting point could not be appreciably raised by recrystallization from carbon tetrachloride, di-n-butyl ether, benzene, chlorobenzene and mixtures of these solvents. Extraction of a chloroform solution of the material with dilute hydrochloric acid, followed by neutralization of the acid extract, gave back the amorphous solid with little increase in purity. An attempt was also made to purify this substance via its presumed hydrochloride (decomposes 250°) which was precipitated when a chloroform solution was treated with hydrogen chloride. However, no solvent could be found to allow successful recrystallization of this substance, the best purification being partial precipitation of it from an ethanol solution by ether addition. By adding sodium hydroxide to a hydrochloric acid solution of the material and subsequently recrystallizing from ethanol-chloroform, a poor yield of
amorphous solid, m.p. 227°-229°, was obtained.

The molecular weight of a sample (m.p. 224°-228°) was determined by Signer's method using methylene dichloride as the solvent. Two determinations gave values of 398 and 390. Analysis gave C, 80.9; H, 7.4; N, 11.4%. The empirical formula is therefore close to C₈H₉N, but could also be C₈H₁₀N which allows the possibility of the compound being composed of \( \text{C}_8\text{H}_9\text{N} \) units. If this were so, the molecular weight suggests about 69% trimer and 31% tetramer; the material has no sharp melting point and could well be a mixture.

An infra-red spectrum of the material is shown opposite together with one of 1,4-diphenylpiperazine. The differences in the region 1360-1280 cm\(^{-1}\) probably indicate differences in the C-N bonds of the two compounds, while the peak at 830 cm\(^{-1}\) indicates that the unknown contains a para-substituted aromatic ring. Other peaks at 1515 cm\(^{-1}\) and 1180 cm\(^{-1}\) can be related to 1,4-substitution, but there is no certainty in this interpretation. A reduction in the intensity of the "monosubstituted aromatic" peaks at 760 cm\(^{-1}\) and 690 cm\(^{-1}\) possibly indicates a reduction in the number of monosubstituted aromatic rings. The peak at 990 cm\(^{-1}\), given by both the unknown and the diphenylpiperazine, occurs at a frequency known to be characteristic of the cyclohexane ring, and is probably due to the piperazine ring. Overall, the spectra are very similar, and the two compounds are probably closely related.

The above evidence indicates that the solid may contain:
Both require C, 80.6; H, 7.6; N, 11.8%. The spectrum does not show a peak in the region 3500 cm$^{-1}$ to 3300 cm$^{-1}$ as expected for a secondary amine. (a) and (b) contain secondary nitrogen atoms.

**Summary**

The compounds definitely found in the products of decomposition of N,N'-diphenylethylenediamine are given below together with their minimum amounts expressed as percentages by weight of the original diamine:

- (i) Aniline, 39%
- (ii) N,N'-Diphenylethylenediamine, 4.5%
- (iii) 1,4-Diphenylpiperazine, 39.2%
- (iv) Probable mixture of (a) and (b) 3.1%

**B. Decomposition of N,N'-Di-2-naphthylethylenediamine**

The pure diamine was found to distil at 284°-288°/ca 0.5mm. In this case therefore, the pressure was kept at ca. 4.0mm., which should allow reaction temperatures of about 300° without loss of reactant by distillation.
In a preliminary experiment the decomposition
temperature was found to be 275°, and the temperature was kept at 
280°-290° for seven hours, most of the product distilling
during the first five hours. This yielded 39% of the original
weight as distillate and 46% as residue, (some of the fine
flaky solid having been lost on initial evacuation).
Resolution of the residue was difficult, and it was thought that
unreacted diamine may have been a contributing factor. The
second decomposition was therefore carried out under a pressure
of 1mm. After seven hours, 41.7% of the reaction mixture had
distilled off leaving 51.7% residue. Further material was
found as a low-boiling evil-smelling liquid in the liquid air
trap of the vacuum line.

Examination of Reaction Distillate

It was found that while the distillate was mainly
2-naphthylamine, a small quantity of other material was
present which caused a melting point depression of 6° to 20°,
depending on the sample tested. Little separation could be
achieved by recrystallization, but redistillation gave a good
yield of better quality 2-naphthylamine which could be purified
by one recrystallization.

The redistillation also yielded a small quantity of
higher-boiling product which probably contained some
naphthylamine. To separate this into primary and secondary
amines the Hinsberg method was used, since the zinc chloride
method previously used was not satisfactory. It yielded a
small amount of the sulphonamide of a secondary amine which
was purified by recrystallization. A molecular weight
determination and elemental analysis suggested that this was the benzene sulphonamide of 1-(2-naphthyl) piperazine. Although such a compound was unexpected, it was isolated only in very small quantities. Examination of comparable reactions (see p. 13 and references 16, 17, 18, 19, 20) indicate that such a product is not unreasonable if di-2-naphthylamine formation occurred at the same time. The latter compound was not detected in the reaction residue, perhaps because of the small quantities involved.

Thus there is no sign of any 4,5-benzoindoline which, if formed, would be expected in the distillate under the reaction conditions used.

**Examination of Reaction Residue**

In the preliminary decomposition, the residue was dissolved in chloroform, and dried and neutralized over anhydrous potassium carbonate. Evaporation and cooling precipitated a poor yield of impure 1,4-di-2-naphthylpiperazine. Purification was effected by boiling with glacial acetic acid, in which the piperazine is insoluble, and recrystallization from chloroform.

Further boiling down of the mother liquor from above with addition of ethanol yielded a dark intractable syrup. (The original solution was slightly yellow, but it soon darkened.) In an attempt to separate more 1,4-di-2-naphthylpiperazine and to prepare a crystalline derivative of the syrup, this was boiled with the glacial acetic acid used in the purification of the piperazine. A small amount of the piperazine separated, but the other object of the process was
not achieved. The remainder of the material could be separated from the acetic acid as a black unanalysable gum.

It was thought that the rapid coloration of the chloroform solution in the above separation was caused by incomplete removal of acid with potassium carbonate. Hence in the major decomposition, the chloroform solution of the residue was washed with sodium hydroxide solution. The solution still darkened rapidly and the separation was carried out as quickly as possible. Boiling down of the chloroform solution yielded only 21.3% of the residue as impure 1,4-di-2-naphthylpiperazine which could this time be satisfactorily purified by recrystallization from chloroform. From a knowledge of the solubility of this compound in chloroform at the temperature of filtration, it was calculated that 1,4-di-2-naphthylpiperazine could not comprise more than 31% of the original residue.

The material recovered from the remaining solvent was a dark resinous solid. This was distilled under reduced pressure to give a yellow oil which hardened on cooling but did not crystallize, and could not be recrystallized from any of the variety of solvents tried. It could not be steam-distilled, and could not be further separated or identified. This was disappointing because it is in this fraction that any di-2-naphthylamine produced could be expected.

The decomposition also produced a low boiling liquid which was collected in the liquid air trap of the vacuum line. Its smell was not recognized as that of an alkene or simple amine, but it may have been vinylamine or ethyleneimine.
A similar compound (seemingly identical in odour) is produced by the decomposition of \(N,N'\)-di-1-naphthylethylene-diamine, and is investigated later.

**Summary**

The minimum amounts of products separated are shown below as weight percentages of the original reactant:

1. 2-Naphthylamine, 36.0%
2. 1-(2-Naphthyl)piperazine, a trace
3. 1,4-Di-2-naphthylpiperazine, 10.9%

There was no evidence for any 4,5-benzoindoline, and the rest of the decomposition material not accounted for was mostly a high boiling intractable mixture.

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**C. Decomposition of \(N,N'\)-di-1-naphthylethylene diamine**

\(N,N'\)-di-1-naphthylethylene diamine was found to distil at 260°/ca.0.5mm.

In the initial reaction the temperature of decomposition appeared to be a function of pressure, suggesting that the reaction occurred in the gas phase. This was probably caused by inefficient mixing of the small quantity of hydrogen bromide used.

For the major decomposition the pressure was 18mm. The first signs of decomposition occurred about 250°±5° at this pressure, and for the next 2½ hours the temperature was kept at 280°. A liquid product then distilled at 180°-200°. The residue was now very dark in colour, and it was decided to distil it off the reaction mixture at low pressures. A total of 82.7% of the reactant weight was finally distilled; the
residue (11%) was a black intractable solid which was not further investigated. A loss of 6.3% occurred, the material being lost either down the vacuum line or in the condenser.

The liquid air trap of the system was found to contain a small amount of the same evil-smelling liquid that occurred in the breakdown of \(N,N'\)-di-2-naphthylethylenediamine. An attempt was made to identify this by making its benzene sulphonamide, but the melting point of the resulting crystals corresponded to none found in literature for likely compounds. There was insufficient material for analysis.

**Examination of Reaction Distillate**

Careful fractionation of the distillate from the preliminary decomposition through a Vigreux column did not separate it into distinct fractions. The main fraction melted at 35°-45° which suggests that it is mostly 1-naphthylamine. Application of the Hinsberg method of separation of primary and secondary amines yielded only the benzene sulphonamide of 1-naphthylamine, so this method was not used in the major breakdown.

From the second decomposition, in which 82.7% of the reactants were distilled off, the distillate was redistilled to yield 59.2% by weight (referred to the original reactant as 100%) as a low-melting yellowish solid, mostly 1-naphthylamine as shown by mixed melting point. (The theoretical yield of 1-naphthylamine on the basis of 1,4-di-1-naphthylpiperazine formation is 45.8%).

Since neither fractionation nor the Hinsberg method gave satisfactory separation, the distilled material was
acetylated under stringent conditions to ensure complete acetylation of any secondary amines present. The 1-naphthylamine was then removed as its monoacetyl and diacetyl derivatives by fractional recrystallization. The impurity, which has a peculiar odour and still contains some monoacetyl-1-naphthylamine, was concentrated in a small quantity of dark oil. The amount of this impurity was estimated as less than 3% of the original reactants.

**Examination of Distillation Residue**

Separation of the residue by solvent methods resulted in only 35% of it being obtained as impure 1,4-di-1-naphthylpiperazine. The remainder consisted of a small amount of needle-like crystals mixed with plate-like crystals (probably of the piperazine) and a black oil. This could not be further separated by recrystallization from a variety of solvents including ethanol, chloroform, petroleum ether, and benzene. Column chromatography in ether removed little of the colour, and afforded no separation.

**Summary**

The products of the decomposition of \( \text{N,N'}-\text{di-1-naphthylethylenediamine} \) which were separated are expressed below as weight percentages of the original reactant.

(i) 1,4-di-1-naphthylpiperazine, ca. 8.0%
(ii) 1-naphthylamine, ca. 47.0%

Any 1-azaperinaphthane formed could be expected in the distillate, and since most of the latter has been identified, this compound must be present in very small quantity, if at all.
<table>
<thead>
<tr>
<th>Diamine Weight</th>
<th>HBr* Weight</th>
<th>Decomp. Time</th>
<th>Pressure</th>
<th>Temp.</th>
<th>Residue Weight</th>
<th>Residue %</th>
<th>Distillate Weight</th>
<th>Distillate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.5g</td>
<td>1.04g</td>
<td>7 hours</td>
<td>30mm.</td>
<td>250°</td>
<td>16.11g</td>
<td>42.9</td>
<td>16.92g</td>
<td>50.4</td>
</tr>
<tr>
<td>36.5g</td>
<td>1.42g</td>
<td>4 hours</td>
<td>80mm.</td>
<td>250°</td>
<td>20.80g</td>
<td>55.3</td>
<td>16.30g</td>
<td>44.2</td>
</tr>
<tr>
<td>25.2g</td>
<td>0.75g</td>
<td>3 hours</td>
<td>25mm.</td>
<td>260°</td>
<td>13.82g</td>
<td>53.2</td>
<td>11.21g</td>
<td>43.2</td>
</tr>
<tr>
<td>58.0g</td>
<td>1.49g</td>
<td>3 hours</td>
<td>120mm.</td>
<td>250°</td>
<td>31.70g</td>
<td>53.2</td>
<td>27.32g</td>
<td>45.6</td>
</tr>
<tr>
<td>37.1g</td>
<td>0.37g</td>
<td>2.5 hrs</td>
<td>25mm.</td>
<td>250°</td>
<td>20.20g</td>
<td>53.8</td>
<td>16.30g</td>
<td>43.4</td>
</tr>
</tbody>
</table>

* These weights are of 48% solution of hydrobromic acid.
Experimental

A. N,N'-Diphenylethylenediamine

(i) Decomposition

In a typical decomposition, N,N'-diphenylethylenediamine (36.5g) and hydrobromic acid (1.50g, 48%) were placed in a simple Claisen distillation apparatus, and heated, on an oil bath, under a pressure of 100mm. Product began to distil when the oil bath reached 230°, and the temperature was maintained at 250° for four hours. (Most distillation occurred during the first two hours). Total distillate 16.3g, residue 20.8g.

The results of the five decompositions performed are shown on Fig. II opposite. Samples used in the investigation of the residue and the distillate were from the last four decompositions.

(ii) Examination of Distillate

(a) Fractional Distillation. A sample of the distillate (14.5g) was distilled under reduced pressure (12 mm.) to yield the following fractions:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Weight</th>
<th>nD</th>
</tr>
</thead>
<tbody>
<tr>
<td>74° - 76°</td>
<td>13.9g</td>
<td>1.5874</td>
</tr>
<tr>
<td>76° - 110°</td>
<td>ca. 0.1g</td>
<td></td>
</tr>
<tr>
<td>110° - 140°</td>
<td>ca. 0.1g</td>
<td></td>
</tr>
</tbody>
</table>

(b) Chemical Separation. A sample of the distillate (38.8g) was fractionated through a short column of helices to give aniline, (25.8g) b.p. 69°-72°/12 mm., acetyl derivative
m.p. 113°-114° (114°). The column was washed down into the distilling flask with diethyl ether (100 ml.) and the solution treated with zinc chloride solution (50 ml. of 50%) and filtered. The precipitate was washed with ether and dried. The weight, 4.1g, corresponds to 2.4g. of aniline, and the total aniline recovered is thus 74% of the distillate weight (compare 87% which was separated in one attempt). The aqueous layer was separated and the ether solution washed with water (4 x 50 ml) and dried over potassium carbonate. Treatment with hydrogen bromide, from a bromine-tetralin generator, gave 2.8g of highly coloured precipitate. Recrystallization of this from ethanol yielded 1.2g of impure N,N'-diphenylethylenediamine dihydrobromide, m.p. 245°-250° (248°-250°), not depressed by addition of an authentic sample. Further boiling down yielded a brown solid which sublimed to give aniline hydrobromide (0.4g), m.p. 290° (286°), not depressed by addition of an authentic sample.

(iii) Examination of Residue

The residue (20.8g) was dissolved in chloroform (500 ml.) and dried and neutralized over anhydrous potassium carbonate. After filtration, the solution was boiled down to 150 ml. and ethanol (350 ml.) added before it was further reduced to 200 ml. and cooled to -10° C. This yielded 16.4 g of solid. Further boiling down to 100 ml. and addition of water (300 ml.) brought the total recovered material up to 19.9 g. This was distilled at 194.5° - 195.5°/ca 0.5 mm. yielding 14.5 g. of distillate (A), m.p. 160°-162°, and 4.7 g of residue (B).
Recrystallization of A from chloroform-ethanol yielded 1,4-diphenylpiperazine (11.2g) m.p. 165°-166° (165°), trinitrobenzene derivative, m.p. 172°-173° (171°). The mother liquor, on boiling down to 100 ml., yielded impure 1,4-diphenylpiperazine (0.7g) m.p. 155°-160°, not depressed by addition of an authentic sample. Addition of water (500 ml.) gave N,N'-diphenylethylenediamine (2.1g), m.p. 45°-55° (65°) not depressed by addition of an authentic sample.

B, on recrystallization from ethanol-chloroform, yielded 1.2g of solid, m.p. 215°-220°, raised to 220°-224° by five recrystallizations from ethanol-chloroform. The hydrochloride was precipitated from a chloroform solution of the amine with hydrogen chloride. It was dissolved in ethanol, precipitated with ether, filtered, and the solid obtained dissolved in dilute hydrochloric acid. The amine was regenerated with sodium hydroxide, and recrystallized from ethanol-chloroform to give a poor yield of the substance, m.p. 227°-229°. The remainder of B was recovered by boiling off more solvent with addition of ethanol to yield N,N'-diphenylethylenediamine (1.8g), m.p. 50°-55° (65°) after two recrystallizations from ethanol-water, not depressed by addition of an authentic sample. In some cases a small amount of 1,4-diphenyl-piperazine was also separated.

B. N,N'-di-2-naphthylethylenediamine

(1) Decomposition

A mixture of N,N'-di-2-naphthylethylenediamine (23.3g) and hydrobromic acid (0.45g, 48%) in a Claisen distillation flask was carefully heated on an oil bath. Material began to
distil when the oil bath reached 275°, and the temperature was maintained at 280°-290° for seven hours. Most of the volatile product distilled at 140°-150° during the first five hours, while during the last hour a slight rise in temperature was accompanied by distillation of a small amount of yellow oil. The total yield was 9.7g of distillate, 12.0g of residue, and a small amount of evil-smelling liquid in the liquid air trap.

(ii) Examination of Distillate

The distillate (9.69g, m.p. 86°-90° and 104°-106° depending on the sample taken) was redistilled to give the following fractions:

<table>
<thead>
<tr>
<th>Pressure (approx)</th>
<th>Temperature</th>
<th>Weight</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1mm. 90°-132°</td>
<td>0.62g</td>
<td>98°-104°</td>
</tr>
<tr>
<td>B</td>
<td>1mm. 132°-142°</td>
<td>7.54g</td>
<td>100-104°</td>
</tr>
<tr>
<td>C</td>
<td>1mm. 142°-160°</td>
<td>0.75g</td>
<td>60°-84°</td>
</tr>
<tr>
<td>D</td>
<td>0.5mm. 146°-160°</td>
<td>0.10g</td>
<td>Liquid.</td>
</tr>
</tbody>
</table>

A and B, mixed and recrystallized from ethanol water, gave 2-naphthylamine (6.5g) m.p. 109°-110° (112°-113°) not depressed by addition of an authentic sample. Acetyl derivative, m.p. 132°-133° (132°).

C and D were dissolved in acetone (10 ml.), added to dilute sodium hydroxide solution (50 ml., 10%), and the acetone boiled off. Application of the Hinsberg method 25 for removal of primary amines yielded, after recrystallization from absolute ethanol, flaky green crystals of the sulphonamide of a secondary
amine, (0.10g), m.p. 191°-193°, raised to 193.5°-194.5° by a further recrystallization. The molecular weight, determined by Signer's method 24 using methylene dichloride, was 349.

(Found C, 67.8; H, 5.6; N, 8.2%; 1-(2-naphthyl)piperazine benzene sulphonamide, \( \text{C}_{20}\text{H}_{20}\text{N}_{2}\text{O}_{2} \) requires C, 68.2; H, 5.7; N, 8.0%; molecular weight 352.)

(iii) Examination of Residue

The yellow residue (12.0g) was dissolved in chloroform (1 litre), washed thoroughly with dilute sodium hydroxide (250 ml.), and with distilled water (5x200 ml.). The chloroform solution was dried over anhydrous magnesium sulphate, filtered, boiled down to 80 ml., cooled to \(-10^\circ\), and filtered to yield impure 1,4-di-2-naphthylpiperazine (2.5g), m.p. 170°-200°, not depressed by addition of an authentic sample. Two recrystallizations from chloroform brought the melting point to 237°-238° (227°-228°). (Found C, 85.2; H, 5.9; N, 8.1%; \( \text{C}_{24}\text{H}_{22}\text{N}_{2} \) requires C, 85.2; H, 6.6; N, 8.3%.)

Further boiling down of the filtrate with addition of ethanol yielded a black intractable gum. This was distilled under reduced pressure (200°-260°/ca. 0.5 mm), to give a yellow oil which hardened on cooling, but did not crystallize. It could not be recrystallized from ethanol, acetone, benzene or chloroform, or steam distilled. Attempts to further purify it were unsuccessful.

\[ \text{C, } \text{N,N'-Di-1-naphthylethylenediamine} \]

(i) Decomposition

A mixture of N,N'-di-1-naphthylethylenediamine (43.8g) and hydrobromic acid (0.75g, 48%) in a Claisen flask was
carefully heated on an oil bath at a pressure of 18 mm. The first product began to distil when the oil bath reached 250°± 5°, and heating was continued at 280° for 2½ hours, by which time 25 ml. of liquid had distilled at 180°-200°. Finally the flask was heated to 360° under a pressure of ca. 0.5 mm., this causing distillation of a solid (b.p. 200°-300°). The total distillate was 36.28 g. while 4.82 g was left as a black intractable residue which was not further investigated. The distillate was redistilled to yield another distillate (25.88 g) b.p. 80-120°/ca 0.5 mm., and a solid residue (10.39 g).

(i) Examination of Distillate

The distillate (25.88 g) was acetylated by boiling for half an hour with acetic anhydride (200 ml., 216 g), and the resulting solution poured into boiling water (4 litres). The solid precipitated was filtered off and fractionally recrystallized from ethanol-water. The first fraction was N,N'-diacetyl-1-naphthylamine (25.51 g, m.p. 123°-126°, raised to 131°-132° (130°) by two recrystallizations from aqueous ethanol). This was followed by a brown tar (1.4 g), and some N-acetyl-1-naphthylamine (3.02 g, m.p. 116°-142°, not depressed by addition of an authentic sample) which was purified by recrystallization from aqueous ethanol.

The total residues from the acetyl derivatives (including the brown tar) were taken into ether and dried over anhydrous magnesium sulphate. Evaporation and chilling in dry ice yielded further monoacetyl derivative (2.7 g, m.p. 150°-155°, undepressed by addition of an authentic sample). The residue on evaporation of the ether was a dark viscous oil (1.37 g) of
peculiar odour.

The total material recovered was therefore \( \text{N,}\text{N-diacetyl-1-naphthylamine (25.5g)} \) and \( \text{N-acetyl-1-naphthylamine (5.7g)} \), this corresponding to 20.72g of 1-naphthylamine.

(iii) Examination of Residue

The residue after distillation (10.39g) was extracted with acetone (150 ml.) and an insoluble material (A) filtered off (3.26g, m.p. 271°-273°). Evaporation of the filtrate to ca. 70 ml. and cooling yielded a further solid (B) (0.36g, m.p. 265°-273°) and a filtrate (C).

A and B were mixed and recrystallized twice from chloroform to yield 1,4-di-1-naphthylpiperazine (2.3g, m.p. 272°-273°, (265°)) (Found: C, 84.4; H, 6.3; N, 8.1%; \( \text{C}_{24}\text{H}_{22}\text{N}_{2} \) requires C, 85.2; H, 6.6; N, 8.3%)

The acetone solution C was allowed to stand for four hours, when 0.50 g of grey solid (D) precipitated, leaving a filtrate (E). D was recrystallized from chloroform to give a mixture of plates and needles, m.p. 208°-211°, raised by addition of 1,4-di-1-naphthylpiperazine. This mixture could not be further separated by recrystallizations from alcohol, benzene, and chloroform-ethanol, or by extracting a chloroform solution with dilute hydrochloric acid.

E was boiled down with addition of ethanol till 80 ml. of ethanol remained. From this black crystals (F) (0.18g) were separated, and after recrystallization from ethanol gave the same mixture as D.

The ethanol solution was boiled down to 20 ml., ligroin (200 ml.) added, and the solution boiled down to 50 ml.
and cooled. A black gum slowly precipitated, but this was not separated by recrystallization from benzene, ligroin or ethanol, or chromatography using activated alumina and diethyl ether solvent.
IV
DISCUSSION OF RESULTS

(1) Summarized Results

It has been indicated in the introduction that it was expected that \( N,N' \)-diarylethlenediamines in the presence of hydrogen bromide at high temperatures might break down to yield cyclized products of the indoline series, and primary arylamines. Investigation of these reactions has shown that such cyclization occurs to a negligible extent if at all, and the distillate, in which such compounds would occur, was composed almost entirely of primary arylamines. Only distillate from the breakdown of \( N,N' \)-di-1-naphthylethlenediamine contained a little unidentified material.

The products of the decomposition of the ethlenediamines also differ from those of the trimethylenediamines in that considerable amounts of high-boiling residue occurred. The residue from the decomposition of \( N,N' \)-diphenylethlenediamine was found to be mostly 1,4-diphenylpiperazine with a small amount of higher boiling material, probably para substituted, and di-para substituted, 1,4-diphenylpiperazines. The residues from the decomposition of the naphthylamines also contained the corresponding diarylpiperazines, but, in addition, considerable resinous material was found.

(ii) Possible Reaction Schemes

For the usual Hofmann-Martius reaction a carbonium ion has been proved, \( ^1,28,29 \) and it seems likely that at least in the decomposition of trimethylenediamines to tetrahydroquinolines,
FIG. III

\[ \text{Ar.NH.CH}_2\text{CH}_2\text{NH.Ar} \xrightarrow{(1)} \text{Ar.NH.CH}_2\text{CH}_2\text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(4)} \text{Ar.NH.CH}_2\text{CH}^+ + \text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(ii)} \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(iii)} \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(v)} \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(vi)} \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(vii)} \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(viii)} \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(ix)} \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(x)} \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \]

\[ \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \xrightarrow{(xi)} \text{Ar.NH.CH}_2\text{CH}_2.\text{NH}_2\text{Ar} \]
a carbonium ion is also formed. By analogy, it is possible that a carbonium ion participates in piperazine formation.

By consideration of the compounds formed and by analogy with the Hofmann-Martius reaction, it is possible to formulate the reaction scheme shown in Fig. III.

Apart from the assumption of a carbonium ion, a further simplification is to be noted. It is possible that the decomposition may involve the equivalent of the alkyl bromide intermediate shown to occur in the normal Hofmann-Martius reaction and which, in the latter reaction, yields a carbonium ion. This is not shown, partly in the interests of simplification, partly because no evidence for its occurrence is at present available. However, direct evidence for it would not be expected in view of its probable instability under the reaction conditions. (Compare the instability of N-(3-bromopropy1) aniline on attempted distillation 30).

The reaction scheme proposed involves, at two stages, fission of a protonated amine to yield a primary arylamine and a carbonium ion intermediate (steps (2) and (6)). Both are formally reversible, but under the reaction conditions used the primary arylamine is distilled off, this preventing the reverse reaction.

The carbonium ion (iii) may react in one of several ways. It may attack an amine nitrogen atom as shown in reaction (4). Reaction (3), cyclization by attacking the ortho position of its own aromatic ring, is also a possibility, but no products are found to support this. A third possibility is attack on another aromatic ring of the system, and evidence
for this is found in the para-substituted diphenylpiperazines produced from the decompositions of $N,N'$-diphenylethylenediamine.

The reaction paths (3) and (4) are in fact truly competitive despite the reversibility of step (4). This results from the irreversibility of the later step (6) by distillation of the primary arylamine. Apparently some factor (to be discussed later) makes the reactions (4), (5) and (6) preferable to (3). This is possibly contrary to the situation for the equivalent carbonium ion derived from a trimethylenediamine, but not necessarily so.

The carbonium ion (vi) may also react in one of the three ways mentioned for (iii), but para attack on another aromatic ring will not be considered. In this case (7) is truly reversible and (9) is not. The latter reaction would be expected to give a fused ring product, but since this is not formed it must be concluded that (9) is not a possible reaction.

It should be noted that the reaction scheme proposed also fits well the reaction of trimethylenediamines to tetrahydroquinolines and julolidines. Julolidines may be formed from the trimethylene equivalent of (vi), tetrahydroquinolines from (iii) or (vi).

A mechanism of synchronous ring closure and aniline formation was mentioned in the introduction (p. 6) for formation of the reduced quinoline. This would allow the following scheme:
This scheme is attractive mainly because it does not involve high energy carbonium ion intermediate. The apparent isolation of para-substituted diphenylpiperazines would favour the choice of the carbonium ion mechanism, but little evidence is really available to allow distinction, and similar deductions may be made from both schemes.

(iii) Conditions for Fused Ring formation

The non-formation of "fused-ring" compounds may be readily explained if it is assumed that the reactive entity, whether it be carbonium ion or alkyl bromide, must attack the aromatic nucleus at right angles to the plane of the ring. Such an assumption is clearly reasonable, and it is generally accepted that such a lateral approach involves the lowest energy
barrier to reaction.

The ease of lateral approach during fused ring formation is obviously influenced by the length of the closing chain. Models of the appropriate carbonium ion intermediates (a), (b) and (c) show that such an approach is possible when the product will be a reduced quinoline (a), but is not possible for similar five-membered ring formation (b). The steric conditions for ring closure on to the "peri" position of a 1-naphthylamine (c), while better than for the formation of a five-membered ring, are not as favourable as those occurring in the formation of a reduced quinoline.

Furthermore, the improved distribution of bonds in the 1-azaperinaphthane case (c), as compared with the indoline case (a), is to a large extent offset by the fact that the peri position is far less activated for carbonium ion attack, because the peri carbon atom is analogous to a meta carbon with respect to the amino substituent. Thus tetrahydroquinoline formation is favoured over indoline formation by more suitable steric conditions, and is favoured by comparison with 1-azaperinaphthane formation by more suitable steric and electronic conditions.

A further argument against the formation of "fused-ring"
products in these reactions may be the availability of an alternative reaction, namely substituted piperazine formation. However, this is unlikely since, in the reaction scheme proposed, piperazine formation from (vi) (Fig. III) is a reversible reaction whereas cyclization to "fused-ring" compounds is not.

(iv) Methods of Formation of Fused Five-membered Rings.

A survey of the main methods of fusing a five-membered ring to an aromatic ring reveals that the most popular methods do not involve a ring closure at the bridging carbon atom. From the above discussion, the reason possibly lies in the terminal carbon atom of a three-membered side-chain not having available any low-energy approach to the ortho carbon of the benzene ring. In other syntheses where such ring closure occurs, a Lewis acid is used as a catalyst and the nitrogen is usually alkylated, i.e., it is a tertiary nitrogen atom. This is difficult to understand on the above assumption, but mechanisms of such reactions are not fully established.

Typical ring closures in the syntheses of indolines are shown below, and none necessarily involves closure at the bridging carbon atom.

\[
\text{NH}_2 + \text{CH}_2 - \text{CH}_2 \text{OH} \xrightarrow{\text{HCl, 5hrs}} 130^\circ - 140^\circ \rightarrow \text{NH}
\]
Other common syntheses involve the reduction of indoles, hydroxyindoles, and isatins. A reaction of particular interest is the synthesis of 1-methylindoline by von Braun, Heider and Müller who condensed N-(2-bromoethyl)-N-methylindaniline in the presence of aluminium chloride.

Presumably the aluminium chloride is present as a Lewis acid, but it may have some further effect in aiding ring closure. Thus Julian et al. observe that N-methylated indoles are much easier to form by ring closure with aluminium chloride than are non-alkylated indoles. The reason for this is not known.

On this basis, it would be interesting to decompose \( N,N'- \text{dimethyl}-N,N'- \text{diphenylethylene diamine} \) in the presence of hydrogen bromide and possibly aluminium chloride to see if it would form 1-methylindoline according to the scheme:
By starting with this compound, reaction steps of the type (4) (Fig. III) would be prevented, and a reaction such as (3) (Fig. III) might occur. However, the methyl group might also be transferred to an aromatic ring by a normal Hofmann-Martius reaction, and the reaction could continue along path (4) (Fig. III).

It will be noted that the above discussion is concerned with syntheses in which the reduced five-membered ring is formed. However it appears that direct indole syntheses, in which the spatial disposition of bonds is somewhat different from the above examples (because of the double bond) may also be covered by the above argument. Again the cyclization step does not appear, in general, to involve the ortho carbon of the aromatic ring.

Thus indoles are most commonly made by the Fischer synthesis starting from an arylhydrazone, and treating it with a Lewis acid.

This is thought to proceed via a six-membered ring with
later elimination of ammonia. Several modifications of the synthesis are known.

Of the other main indole syntheses, only one apparently involves closure on the aromatic nucleus, and that is the Bischler synthesis, which is represented by

\[
\begin{align*}
R_1-C=O & \xrightarrow{C_6H_5NH_3X} R_2-CH-NH-C_6H_5 \\
\end{align*}
\]

The mechanism for this reaction has not yet been established, but of the reaction schemes which have been proposed, the two possibilities finding most support at present both involve some sort of direct closure on the ortho carbon atom of the aromatic ring. However, the mechanistic problem is far from solved, and it has been asserted that the reaction scheme follows the steps set out below.

\[
\begin{align*}
\text{Ph}^+ + H_2O & \rightarrow \text{Ph}NH_2 + \text{CH}_2\text{CO-Ph} + Br^- \\
\rightarrow \text{CH}_2\text{CO-Ph} & \rightarrow \text{PhNH}_2 + H_2O
\end{align*}
\]

(v) Naphthylamines and the Hofmann-Martius Reaction

In closing, it may be pointed out that in the thermal breakdowns involving naphthalene nuclei investigated in the
present project, it has been assumed that a Hofmann-Martius type of rearrangement is quite feasible under these conditions. Current work in the department indicates that the assumption is valid with dinaphthyltrimethylenediamines. However, a literature survey revealed that only one attempt has in fact been made to rearrange a simple N-alkylnaphthylamine hydrochloride. Heap \(^{36}\) heated 2-naphthylisopropylamine hydrochloride at 300\(^\circ\)-320\(^\circ\) for six hours, but found mostly propylene and 2-naphthylamine in his products with no evidence for ring alkylated naphthylamines. 

Hey \(^{37}\) has found that anilines may also be ring-methylated by heating their hydrochlorides with methanol, and it is thought that the reaction involves rearrangement of the N-methylated aniline hydrochloride first formed. Attempts at similar reactions with naphthylamine hydrochlorides were not successful, the only ring-alkylated products found being methylated naphthols\(^{18}\). The applicability of the Hofmann-Martius reaction to the simple N-alkyl naphthylamines might therefore prove worthy of investigation.
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