author also wishes to express his thanks to the Foundation for a Summer Fellowship. We also wish to acknowledge gratefully the kindness of the staff of the Sterling-Winthrop Research Institute for the analytical determinations and the use of library facilities.

The Acid-catalyzed Thermal Decomposition of Some N,N'-Diaryl-α,ω-diaminoalkanes

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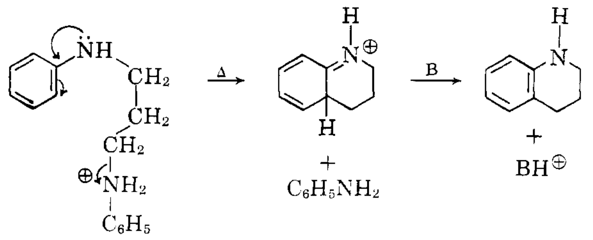
The acid-catalyzed cyclization reported[1] for diphenyltrimethylenediamine (I) has been examined further. When positions *ortho* to the amino nitrogen are vacant, julolidines are formed. Diphenyl- and dinaphthylethylenediamines give piperazine derivatives and the tetramethylene analog of (I) gives N-phenylpyrrolidine.

It has been reported[1] that N,N'-diphenyltrimethylenediamine (I) breaks down smoothly at 230–250°, in the presence of hydrobromic acid, to give anilines and 1,2,3,4-tetrahydroquinoline (II). The following mechanism (Scheme I) was suggested for the formation of these products:

Scheme I



The yield of aniline, based on Scheme I, was almost quantitative, while that of II was *ca.* 50%. An analogous reaction occurred with N,N'-di-*o*-tolyltrimethylenediamine, but here the yield of primary amine was slightly greater than that required by the simple reaction scheme.

We now report further data on the behavior of diamines, of the general formula $ArNH(CH_2)_nNHAr$, when heated in the presence of 0.1 mole of hydrobromic acid.

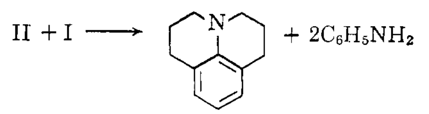
N,N'-Diaryltrimethylenediamines ($n = 3$).—We examined the breakdown of six such diamines, including the diphenyl and di-*o*-tolyl compounds. In all cases the amount of released primary amine was roughly in accord with Scheme I. However, in at least half of these cases, such approximation must be fortuitous because in each of these instances, further treatment of the residue left after distillation of the tetrahydroquinoline resulted in the isolation of significant quantities of a julolidine (III). For each of the trimethylenediamines examined, the average product composition (over two experiments) is listed in Table I.

Table I

Yields from $ArNH(CH_2)_3NHAr$ (+0.1 Mole HBr) at 230–260° (in Moles Product from 1 Mole Diamine)

Ar	Primary amine	(II) derivative	(III) derivative
Phenyl	1.02	0.46	0.17
o-Tolyl	1.05	.57	...
m-Tolyl	1.02	.37	.23
p-Tolyl	1.13	.28	.21
1-Naphthyl	1.04	.69	...
2-Naphthyl	0.85	.62	...

The julolidine may arise from the tetrahydroquinoline:



On this, as on other reasonable schemes, the over-all production of julolidine from diamine requires the release of three moles of primary amine from two moles of diamine.

Of the three diamines failing to yield julolidines, the *o*-tolyl and the 1-naphthyl compounds cannot do so. With the 2-naphthyl compound, neither the formation of 5,6-benzo-1,2,3,4-tetrahydroquinoline (to the exclusion of the 6,7-benzo product) nor the failure to yield a julolidine is surprising. Julolidine formation, or 5,6-benzo-1,2,3,4-tetrahydroquinoline formation, would involve ring closure at the unreactive 3-position of a naphthalene nucleus. On the other hand, the *m*-tolyl compound affords not only 8-methyljulolidine, but the expected pair of tetrahydroquinolines, in the ratio of three parts of 7-methyl isomer to two parts of 5-methyl isomer. This favoring of the 7-derivative by an electron-rich substituent is similar to the known trend in the Skraup closure, although the latter synthesis gives rise to no appreciable proportion of 5-isomer.[2]

N,N'-Diphenyltetramethylenediamine ($n = 4$).—This compound was found to break down smoothly

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[1] A. Fischer, R. D. Topsom, and J. Vaughan, *J. Org. Chem.*, **25**, 463 (1960).

[2] L. Bradford, T. J. Elliott, and F. M. Rowe, *J. Chem. Soc.*, 437 (1947).

above 180°, in the presence of 0.1 mole of hydrobromic acid, to give aniline and N-phenylpyrrolidine. No discernible decomposition occurs below 170°, while in the absence of acid the diamine can be vacuum distilled above 200° without breakdown. Therefore, although tetramethylene dibromide reacts with an excess of aniline to give N-phenylpyrrolidine as the sole product,[3] such reaction does not proceed *via* the diphenyltetramethylenediamine. A possible intermediate is 4-bromo-1-anilinobutane.

N,N′-Diarylethylenediamines ($n = 2$).—N,N′-Diphenylethylenediamine was found to decompose at 250°, in the presence of hydrobromic acid, to give mainly aniline and N,N′-diphenylpiperazine. An examination of reaction products failed to reveal the presence of any indoline which, from analogy with the breakdown of I, was a possible product. However, indoline formation involves substitution at an aromatic carbon, and this presumably implies a lateral attack on the aromatic ring. Models confirm that such attack is much less favored with the ethylenediamine and therefore the preferred reaction in this case is piperazine formation.

N,N′-Di-2-naphthylethylenediamine also fails to give an indoline derivative on breakdown, despite the greater activation to ring closure. It was, however, possible that N,N′-di-1-naphthylethylenediamine might yield some 1-azaperinaphthane on breakdown, provided that the *peri* position were sufficiently active. Such reaction did not occur. Thus from all three ethylenediamines examined, the only isolated products were primary amine and N,N′-diarylpiperazine. The relative amounts are given in Table II. It is seen that in no case are the results in accord with the simple scheme above, but it was noted that much deepseated decomposition occurred at the temperature required for these experiments.

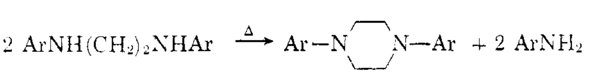

TABLE II

YIELDS FROM $ArNH(CH_2)_2NHAr$ AT 250–280° (0.1 MOLE HBr) (IN MOLES PRODUCT FROM 1 MOLE DIAMINE)

Ar	Primary amine	Diarylpiperazine
Phenyl	1.03	0.38
1-Naphthyl	1.03	.27
2-Naphthyl	0.77	.1[a]

[a] Minimum figure; extraction and purification of this was extremely difficult.

Experimental[4]

N,N′-Diphenyltrimethylenediamine and N,N′-di-*o*-tolyltrimethylenediamine were prepared as previously reported.[1] By the same method were obtained **N,N′-di-*p*-tolyltrimethylenediamine** (52% yield, m.p. 66–67°) and **N,N′-di-*m*-tolyltrimethylenediamine**. The latter compound was obtained in 71% yield as a light yellow oil boiling at 210–220° at 0.5 mm.

Anal. Calcd. for $C_{17}H_{22}N_2$: C, 80.4; H, 8.65; N, 11.0. Found: C, 80.4; H, 8.4; N, 10.9.

The compound gave a dihydrochloride with m.p. 214–216°.

N,N′-Di-1-naphthyltrimethylenediamine.[5]—To a stirred mixture of 190 g. (1.33 moles) of 1-naphthylamine and 45 g. (0.43 mole) of sodium carbonate, at 160°, was added 67 g. (0.33 mole) of trimethylene dibromide at a rate sufficient to keep the temperature at 150–160°. When addition, and the resulting effervescence, was complete the mixture was poured into water and extracted with chloroform. The chloroform layer was dried and was then distilled to remove solvent (at 760 mm.) and excess of 1-naphthylamine (at 0.5 mm.). The diamine was collected at 290–310° at 0.5 mm. Addition of ether gave 32 g. (30%) of white crystals, m.p. 100–102°.

Anal. Calcd. for $C_{23}H_{22}N_2$: C, 84.65; H, 6.75; N, 8.6. Found: C, 84.85; H, 6.65; N, 8.4.

It formed a dihydrochloride, m.p. 227–230°.

N,N′-Di-2-naphthyltrimethylenediamine[5] was obtained in 37% yield as a glassy solid by a procedure similar to that used for the 1-naphthyl isomer. It had b.p. 290–310° at 1 mm.

Anal. Calcd. for $C_{23}H_{22}N_2$: C, 84.65; H, 6.75; N, 8.6. Found: C, 84.3; H, 6.55; N, 8.15.

The dihydrochloride had m.p. 235–237°.

N,N′-Diphenyltetramethylenediamine.—The dihydrochloride, obtained by the method of Caswell and Billman,[6] was neutralized with aqueous alkali. The diamine was extracted into ether, dried, and purified by distillation, b.p. 205° at 0.5 mm.

N,N′-Diphenylethylenediamine.—A mixture of 720 g. of freshly distilled aniline (7.74 moles) and 163 g. of ethylene dibromide (0.87 mole) was heated on a steam bath for 2 hr. The reaction mixture was cooled and dissolved by shaking with 500 ml. of concentrated ammonium hydroxide and 2 l. of ether. The ethereal layer was washed with water, dried over potassium carbonate, and the ether distilled. Distillation under reduced pressure afforded the excess aniline followed by the product. Redistillation at 0.5 mm. gave 149 g. (81%) of material b.p. 158–160° (m.p. 65–66°; diacetyl derivative, m.p. 157–158°).

N,N′-Di-1-naphthylethylenediamine.—While maintaining the temperature at 130° and with constant shaking, 54 g. (0.29 mole) of ethylene dibromide was added in portions to 250 g. (1.75 moles) of redistilled 1-naphthylamine. Reaction was allowed to continue for a further hour at 130°. The product was treated as in the preparation of the previous compound and the excess 1-naphthylamine was removed by distillation at 0.5 mm. The residue was dissolved in 100 ml. of hot benzene, and the cooled solution was poured into 350 ml. of ethanol. The precipitated diamine (45.3 g., 43.5% yield, m.p. 122–124°) was recrystallized from benzene and from benzene–ethanol to give material m.p. 132–133°.

N,N′-Di-2-naphthylethylenediamine.—Ethylene dibromide (54 g., 0.29 mole) was added in one portion, and with vigorous agitation, to 200 g. (1.4 moles) of recrystallized 2-naphthylamine held at 130°. On reheating to 130°, an exothermic reaction commenced and the vigor of this reaction was reduced by cooling the vessel in an ice–salt bath. Reaction was then completed by keeping the mixture at 130° for 2 hr. After cooling, the flask was broken and the pulverized solid product was stirred for 8 hr. as a slurry with 1 l. of concentrated ammonium hydroxide. It was then filtered off, washed with water, dried, and re-

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[3] A. H. Sommers, *J. Am. Chem. Soc.*, **78**, 2439 (1956).

[4] Melting and boiling points are uncorrected. Analyses were by the Microanalytical Laboratory of the University of Otago.

[5] The compounds cannot be prepared by direct interaction in the absence of carbonate owing to the exothermicity of the reaction.

[6] J. H. Billman and L. A. Caswell, *J. Org. Chem.*, **16**, 1041 (1951).

crystallized from ethanol to give 63 g. (83%) of crude product. Recrystallization from acetone and from ethanol gave material m.p. 150–151° (diacetyl derivative m.p. 181–182°).

Breakdown of N,N′-Diaryltrimethylenediamines.—Decomposition of the diamines (0.1–0.2 mole) was carried out in a simple Claisen distillation apparatus at *ca.* 250° and 20 mm. The catalyst was added as 48% hydrobromic acid. Heating was continued until little further material distilled. The distillate (86–90% of original weight except for the *o*-tolyl- and 2-naphthyldiamines for which it was *ca.* 80%) was fractionated and the final separation of intermediate fractions was achieved by chemical methods. With these mixtures, Hickinbottom's method[7] of separating primary amines as their zinc chloride complexes proved far less satisfactory than the Hinsberg method.

The tetrahydroquinolines obtained from the phenyl-, *o*-tolyl-, *p*-tolyl-, and naphthyldiamines were fully characterized by physical constants, infrared spectra, preparation of derivatives, and dehydrogenation to the corresponding quinolines. The tetrahydroquinoline fraction from the breakdown of N,N′-di-*m*-tolyltrimethylenediamine had b.p. 144–150° at 17 mm.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.6; H, 8.85; N, 9.5. Found: C, 81.8; H, 8.45; N, 9.3.

It was separated into components using a Beckman "Megachrom" gas chromatograph, with columns packed with 35% w./w. Apiezon J on C22 firebrick and with a column temperature at 180°. The first fraction (60% of total) was 7-methyltetrahydroquinoline; its benzoyl derivative had m.p. 77–78° and its hydrochloride had m.p. 205–206° (literature values are 70–72° and 175°, respectively). The second fraction (40% of total) was 5-methyltetrahydroquinoline; benzoyl derivative m.p. 125–126°, hydrochloride m.p. 239–240° (literature values are 121° and 238–240°, respectively).

The julolidines obtained in the decomposition were:

Julolidine, b.p. 130–140° at 7 mm., m.p. 37° (from acetone). Analytical figures were good and the compound gave a picrate of m.p. 173°, a methiodide of m.p. 218° and a hydrochloride of m.p. 211° (literature figures are 171, 186, and 218°, respectively).

9-Methyljulolidine[8] (from N,N′-di-*p*-tolyltrimethylenediamine), b.p. 158–160° at 10 mm.

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.4; H, 9.1; N, 7.5. Found: C, 83.15; H, 9.05; N, 7.95.

This compound gave a picrate of m.p. 167°, a methiodide of m.p. 230° and a hydrochloride of m.p. 230°.

8-Methyljulolidine[9] (from N,N′-di-*m*-tolyltrimethylenediamine), b.p. 172–180° at 17 mm.

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.4; H, 9.1; N, 7.5. Found: C, 83.3; H, 9.3; N, 7.6.

This compound gave a picrate of m. p. 158° and a methiodide of m.p. 209–210°.

Breakdown of N,N′-diphenyltetramethylenediamine was carried out in a similar manner. The diamine (15.1 g.) gave 14.1 g. of distillate which on fractionation gave 4.6 g. of aniline and 8.0 g. of N-phenylpyrrolidine, b.p. 142–145° at 27 mm. (picrate m.p. 115.5°, not depressed by addition of an authentic sample).

Breakdown of N,N′-diarylethylenediamines was carried out as above except that the residue in the decomposition flask was examined for involatile products. Thus in the breakdown of 61 g. of N,N′-diphenylethylenediamine, with 2.25 ml. of hydrobromic acid (s.g. 1.46), at 250° and 100 mm., the distillate (28.7 g.) was shown to consist mainly of aniline with lesser amounts of N,N′-diphenylpiperazine and unchanged diamine. Using the gas chromatograph, no evidence was obtained for the presence of indoline in the intermediate fractions. The residue (34.7 g.) was neutralized and distilled to give a fraction b.p. 195 to 200° at 1 mm. which was fractionally recrystallized to give mainly N,N′-diphenylpiperazine and some unchanged diamine. No further compounds could be isolated from the residue (*ca.* 7 g.).

The two N,N′-dinaphthylethylenediamines were decomposed at 280–290° and 18 mm. The distillate in each case consisted of the almost pure naphthylamine; a trace of impurity in the 2-naphthylamine proved to be N-(2-naphthyl)piperazine when isolated as its benzenesulphonyl derivative, m.p. 193.5–194.5°.

Anal. Calcd. for $C_{20}H_{20}N_3O_2S$: C, 68.2; H, 5.7; N, 8.0; mol. wt., 352. Found: C, 67.8; H, 5.6; N, 8.2; mol. wt. (Signer's method), 349.

The distillation residues were neutralized and fractionally recrystallized from chloroform to give the N,N′-dinaphthylpiperazines. Evaporation of the mother liquors deposited intractable tars, of b.p. greater than 300° at 1 mm., and these defied further separation.

Acknowledgment.—The authors are indebted to the New Zealand Universities Research Committee for financial assistance.

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[7] W. J. Hickinbottom, *J. Chem. Soc.*, 992 (1930).

[8] Only literature reference, Pinkus, *Ber.*, **25**, 2804 (1892), gives no analysis or constants.

[9] Only literature reference, *Chem. Abstr.*, **50**, 717 (1956), lists only b.p. 179–180° at 19 mm.

Photosensitive Quinoxaline Pseudo Bases[1a]

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Two photosensitive quinoxaline pseudo bases, similar to one described previously, were prepared and their photoreactions studied. The previously reported pseudo base was found to give a photosensitive intermediate in its photoreaction. No analogous intermediates were observed in the case of the two new pseudo bases. Base-catalyzed dark reactions of the pseudo bases gave the same products, except one, as the photoreactions. A mechanism for the photoreactions is suggested.

The photoreaction of the pseudo base, I, to give the quinoxalone, IV, has been reported.[1b] It has been found that II and III undergo analogous photoreactions when irradiated within their long wave length absorption bands. The pseudo base, II, gives IV, identical with the photoproduct from I, while III gives V and VI.

The structure assigned to V is supported by its formation from VI in a base-catalyzed, ring-closing reaction of known type,[2] by its slow, acid hydroly-

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[1] (a) Contribution No. 2283 from the Kodak Research Laboratories; (b) P. M. Mader, *J. Org. Chem.*, **27**, 2217 (1962).

[2] A. A. Morton, "The Chemistry of Heterocyclic Compounds," McGraw-Hill Book Co., Inc., New York, N.Y., 1946, pp. 267, 270.