Anal. Calcd. for $C_{13}H_{16}ClNO$: C, 65.68; H, 6.78; Cl, 14.91; N, 5.89. Found: C, 65.35; H, 7.05; Cl, 14.60; N, 5.97.

Evaporation of the ethyl acetate extracts gave 16 g. of recovered starting material. The yield of hydrochloride, corrected for recovered starting material, is 92%.

7-Isopropylamino-1-naphthol (8c).—The free amine was obtained by neutralization of an aqueous solution of its hydrochloride with sodium acetate. An analytical sample was obtained by two recrystallizations from hexane.

7-Dimethylamino-1-naphthol (8d).—In a 250-ml. steel bomb were placed 40 g. (0.25 mole) of 1,7-dihydroxynaphthalene and 96 ml. (90 g., 0.5 mole) of 25% aqueous dimethylamine. The bomb was sealed and heated while rocking at 180° for 8 hr. The reaction mixture was worked up as described for **8b**. No starting material was recovered, and there was obtained 27 g. of crude product (m.p. 101–104° dec.) from the oily precipitated hydrochloride and 4 g. of additional product by neutralization of the hydrochloric acid solution; the yield was 66%. An analytical sample was obtained by crystallization from cyclohexane.

Derivatives.—The derivatives were prepared by conventional means[19] and crystallized to constant melting point. Their properties are reported in Table II.

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(19) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956.

The Acid-Catalyzed Decomposition of N,N'-Diaryl-1,3-diaminopropanes

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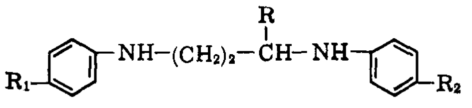
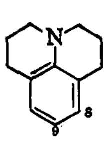
The scope of the previously reported acid-catalyzed thermal decomposition of N,N'-diaryl-1,3-diaminopropanes to give arylamines, tetrahydroquinolines, and julolidines has now been investigated. The aryl groups that can be employed are probably limited to alkyl-, aryl-, alkoxy-, and halophenyl. Further, decomposition of *ortho*- and *para*-substituted diaryldiamines gives considerable quantities of N-alkylanilines, making purification of the tetrahydroquinolines difficult. Nevertheless, the method offers useful syntheses for 5- and 7-substituted tetrahydroquinolines and for alkyl- and halojulolidines. The results presented support the previously suggested mechanism. The investigation has been extended to the breakdown of the trimethylenediamines formed from indoline, tetrahydroquinoline, and carbazole. The first two diamines gave indoline and lilolidine, and tetrahydroquinoline and julolidine, respectively; the third is remarkably stable and a reason is suggested for this. The breakdown of N'-benzyl-N'-phenyl-1,2-diaminoethane gives toluene, aniline, benzylamine, and N-phenyl-1,2-diaminoethane, but tetrahydroisoquinoline was not detected.

We have recently reported[1,2] that N,N'-diphenyl-1,3-diaminopropane (I) decomposes smoothly at about 230° in the presence of hydrogen bromide to give aniline, tetrahydroquinoline (XI), and julolidine[3] (IV). It was also shown that the corresponding tolyl- and naphthyldiamines decomposed in a similar manner, although no julolidines were obtained from N,N'-*o*-tolyl-1,3-diaminopropane or from the two naphthyldiamines.



I, $R = R_1 = R_2 = H$
II, $R = CH_3$, $R_1 = R_2 = H$
III, $R = H$, $R_1 = CH_3$, $R_2 = Cl$



IV

This reaction offered the possibility of synthesizing both tetrahydroquinolines and julolidines in a simple manner from the corresponding arylamines, the diaryldiamines being readily prepared by heating the arylamines with 1,3-dibromopropane. Substituted tetrahydroquinolines are usually prepared by the reduction of the respective quinolines, but this does not always lead to readily purified products and may also remove halogen atoms.[4] Thus, only one of the four possible chlorotetrahydroquinolines substituted in the aromatic ring has been reported. Julolidines are less well-known. Heating the respective tetrahydroquinolines with 1,3-chlorobromopropane or 1,3-dibromopropane yields julolidine (IV),[5–7] 8-methyl-,[8] 9-methyl-,[6] or 9-methoxyjulolidine.[6] This method is probably of limited further application,[9] and the tetrahydroquinoline must first be obtained. A number of 9-substituted julolidines have also been prepared[9] by electrophilic substitution in the parent compound, but oxidizing conditions must be avoided.

Results and Discussion

Decompositions were carried out in a simple Claisen apparatus under a pressure suitably reduced to ensure that any products significantly more volatile than the diamine would be distilled. Decompositions in sealed tubes were found to give much larger quantities of inseparable residues.

The effect of various amounts of hydrogen bromide on the decomposition of N,N'-diphenyl-1,3-diaminopropane was studied. The relative amounts of the volatile products were little affected, but, while the rate of decomposition increased with larger amounts of the acid, so also did the amount of intractable residue; 0.1 mole of acid was judged to be the best compromise, giving about 90% of the diamine as volatile material in a reasonable time. Other catalysts such as sulfuric acid

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

(2) G. B. Russell, G. J. Sutherland, R. D. Topsom, and J. Vaughan, *ibid.*, **27**, 4375 (1962).

(3) 2,3,6,7-Tetrahydro-1H,5H-benzo[*ij*]quinolizine.

(4) "Heterocyclic Compounds," Vol. 4, R. C. Elderfield, Ed., John Wiley and Son, Inc., New York, N. Y., 1952, p. 286.

(5) Z. J. Vejdelek, B. Kakac, and M. Protiva, *Chem. Listy*, **47**, 1676 (1953); *Chem. Abstr.*, **49**, 1046 (1955).

(6) G. Pinkus, *Ber.*, **25**, 2798 (1892).

(7) D. Glass and A. Weissberger, *Org. Syn.*, **26**, 40 (1946).

(8) M. S. Raasch, U. S. Patent 2,707,681 (May 3, 1955); *Chem. Abstr.*, **50**, 717 (1956).

(9) P. A. S. Smith and T. Y. Yu, *J. Org. Chem.*, **17**, 1281 (1952).

TABLE I

DECOMPOSITIONS OF N,N′-DIARYL-1,3-DIAMINOPROPANES[a]

Compound	Phenyl- (230)	*o*-Tolyl- (235)	*m*-Tolyl- (200)	*p*-Tolyl- (240)	*o*-Methoxyphenyl- (270)	*m*-Methoxyphenyl- (200)	*p*-Methoxyphenyl- (250)	*o*-Chlorophenyl- (300)	*m*-Chlorophenyl- (235)	*p*-Chlorophenyl- (280)
Arylamine	1.09	0.76	1.00	1.04	0.36	0.84	0.70	0.81	1.08	0.35
N-Methylarylamine		0.09		0.08	0.29	0.14	0.20[b]			0.10
N-Ethylarylamine		0.11		0.11	0.13[b]		0.37[b]			0.19
N,N-Dimethylarylamine							0.19[b]			
N-Allylarylamine								0.37		
Aminophenol					0.20	0.03				
Tetrahydroquinoline	0.33	0.82	0.59[c]	0.26	0.15	0.53[c]	0.06	0.35	0.56[c]	0.19
Alkyl tetrahydroquinoline				0.06[b]			0.05	0.08[b]		0.05[b]
Quinoline				0.04[b]			0.05			0.05
Julolidine	0.22		0.19	0.23		0.03[d]	0.05[e]		0.23	0.20

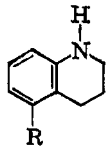
[a] The amount of each component, determined by gas chromatography, is expressed in moles per mole of diamine decomposed. The temperature (°C.) at which decomposition first occurs is shown in parentheses below each diamine. [b] Not isolated; identified by comparison of gas chromatograph retention times, on two columns, with authentic samples. [c] Mixture of 5- and 7-substituted tetrahydroquinolines. [d] Quantity isolated. [e] Provisional identification.

and cobaltous chloride also caused decomposition, but only the aniline could be isolated in significant yield.

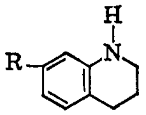
It was found that the ease of reaction depended quite markedly on both the nature and the position of an introduced substituent. Thus Table I shows that for *meta*-substituted diaryldiamines, the ease of breakdown is MeO ~ Me > H ~ Cl, while for *ortho* and *para* substituents it is Me ~ H > MeO > Cl. Each of the chosen substituents allowed the most ready decomposition when in the *meta* position. It has previously been suggested[2] that the reaction involves ring closure synchronous with the splitting off of the arylamine molecule. The above results are consistent with this. It was also found that with *ortho*- and *para*-substituted diaryldiamines, significant cleavage of the trimethylene chain occurred, leading to N-alkylarylamines and similar products. Gas chromatograms showed that such products were not present as impurities in the original diamines. Such cleavage represents reduction, and the corresponding oxidation appears to be the conversion of tetrahydroquinolines into quinolines, some of which were isolated from the reaction products. These additional products made separation and purification of the tetrahydroquinolines difficult. With the *meta* compounds, such fission appears to be absent[10]; the tetrahydroquinolines were formed in satisfactory yield and were easily isolated.

With the chloro-substituted diamines, higher temperatures were required for decomposition and an increased number of products was formed. These features, together with the greater difficulty experienced in isolating products of low volatility indicated that breakdown of diaryldiamines containing more deactivating substituents, such as nitro and carboxyl groups, would be unprofitable. However, N,N′-bis(*o*-biphenylyl)-1,3-diaminopropane decomposed to give the expected *o*-aminobiphenyl and 8-phenyltetrahydroquinoline. It is thus likely that the useful decompositions of simple N,N′-diaryldiamines are limited to alkoxy, alkyl, aryl, and halo substituents.

No julolidine can be formed from *ortho*-substituted diaryldiamines, but these did not in general give increased amounts of the tetrahydroquinolines. In fact, the best yield of tetrahydroquinoline usually resulted from the *meta* isomers. These gave mixtures of the 5- (V) and 7-substituted (VI) tetrahydroquinolines.



V



VI

The separation of these tetrahydroquinolines required a preparative gas chromatograph, but the derived 8-substituted julolidine was readily isolated in each case. The relative amounts of the two isomers obtained with each substituent are shown in Table II, together with the proportions of 5- and 7-substituted quinoline reported[11] for the Skraup reaction with *m*-arylamines. There is a striking similarity between the product ratios obtained in the two reactions, and this may be linked with closely similar cyclizing entities (see ref. 11).

TABLE II

RELATIVE AMOUNTS OF TETRAHYDROQUINOLINES PRODUCED FROM BIS(*m*-SUBSTITUTED PHENYL)-1,3-DIAMINOPROPANES[a]

m-Substituent	Diamine decomposition, % tetrahydroquinoline		Skraup reaction, % quinoline	
	5-	7-	5-	7-
Methyl-	40	60	41	59
Methoxy-	22	78	21	79
Chloro-	47	53	49	51

[a] The relative amounts of the corresponding quinolines produced in the Skraup reaction are also given.

Three other related diaryldiamines were also decomposed. N,N′-Diphenyl-1,3-diaminobutane (II) decomposed to give aniline and both the 2- and 4-methyltetrahydroquinolines as expected. Chain cleavage, particularly to give N-ethylaniline, was extensive and 2-methylquinoline was produced. No julolidines were isolated. The decomposition of N-*p*-chlorophenyl N′-*p*-tolyl-1,3-diaminopropane (III) gave both *p*-chloroaniline and *p*-toluidine. That the former was in considerable excess is consistent with the suggested mechanism. An attempt also was made to obtain

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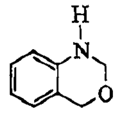
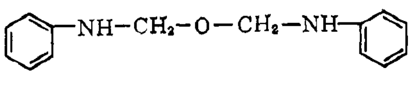
(10) The N-methyl-*m*-anisidine formed probably results from the methylation of initially formed *m*-anisidine. Thus, no N-ethyl-*m*-anisidine was detected.

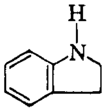
(11) M. H. Palmer, *J. Chem. Soc.*, 3645 (1962).

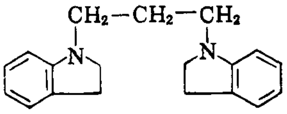
1,2-dihydro-4H-3,1-benzoxazine (VII) by the decomposition of N,N'-diphenylbis(aminomethyl) ether (VIII), but the only volatile product obtained was aniline.

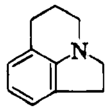

VII


VIII

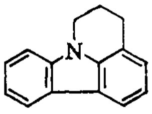
Decomposition of Some Related Diamines.—The diamines discussed above contain only secondary amine groups. Some tertiary diamines were also examined. 1,3-Bis(N-indolinyl)propane (IX) gave, on decomposition, a mixture of indoline (X) and lilolidine[12] (XI).

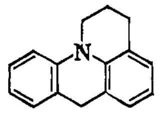

X


IX


XI

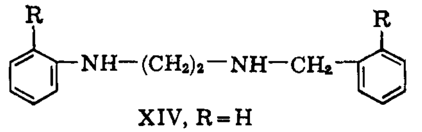
Similarly, 1,3-bis(N-tetrahydroquinolinyl)propane gave tetrahydroquinoline and julolidine. By analogy, the trimethylenediamines derived from carbazole and acridan should yield the previously unreported trimethylenecarbazole[13] (XII) and trimethyleneacridan[14] (XIII).


XII


XIII

Attempts to prepare the bis(acridanyl)propane were unsuccessful and, while the corresponding carbazolyl compound could be made, it proved to be remarkably stable, being recovered unchanged after heating for several hours at 300–350° in the presence of hydrogen bromide. This stability is explicable in terms of a rate-determining cyclization since the 1-position in carbazole is known[15] to be very much less nucleophilic than the corresponding *ortho* carbon of an alkylaniline.[16] This factor probably accounts also for the failure of an attempt to prepare the trimethylenecarbazole by refluxing carbazole with 1,3-bromochloropropane.[17]

N-Benzyl-N'-phenyl-1,2-diaminoethane (XIV) and N-*o*-xylyl-N'-*o*-tolyl-1,2-diaminoethane (XV) were decomposed also. No evidence could be found for the presence of tetrahydroisoquinolines in the reaction products. The compounds detected were the respective aromatic hydrocarbons, benzene and toluene, the arylamines and benzylamines, and the N-aryl-1,2-diaminoethanes.


XIV, R = H
XV, R = CH_3

Experimental

Melting and boiling points are uncorrected. Analyses were by the Microanalytical Laboratory of the University of Otago. The analytical gas chromatograph used was fitted with an integrating amplifier. The column used for analyses was packed with 10% w./w. Apiezon L on Celite 545; the column temperature was 150–200°. The instrument was calibrated for linearity of response and for response to different components. The samples used for these purposes were generally those isolated from the decomposition mixtures, and only with the chloro substituent was the uncorrected peak area estimation significantly in error. A Beckman Megachrom preparative gas chromatograph was used to separate components of similar boiling points. The columns were packed with 35% w./w. Apiezon J on C22 firebrick and were used at a temperature of 180°. Infrared spectra were determined on a Perkin-Elmer Model 221 spectrograph using sodium chloride optics. All starting materials were redistilled or recrystallized before being used.

N,N'-Diaryl-1,3-Diaminopropanes.—N,N'-Diphenyl- and the three N,N'-ditolyl-1,3-diaminopropanes were prepared as already reported.[1,2] The following diamines were similarly obtained, in the yields given, by the interaction at elevated temperatures of 1,3-dibromopropane with a 10 *M* amount of the corresponding arylamine:[18] N,N'-bis(*o*-methoxyphenyl)-1,3-diaminopropane[19] [72%, b.p. 230–240° (1 mm.). *Anal.* Calcd. for $C_{17}H_{22}N_2O_2$: C, 71.32; H, 7.69; N, 9.78. Found: C 71.00; H, 7.81; N, 9.37.], N,N'-bis(*m*-methoxyphenyl)-1,3-diaminopropane [72%, b.p. 220–230° (1 mm.), $n^{20}D$ 1.6415. *Anal.* Calcd. for $C_{17}H_{22}N_2O_2$: C, 71.32; H, 7.69; N, 9.78. Found: C, 71.40; H, 7.42; N, 9.21.], N,N'-bis(*p*-methoxyphenyl)-1,3-diaminopropane [44%, m.p. 99°, lit.[19] m.p. 96.5°. *Anal.* Calcd. for $C_{17}H_{22}N_2O_2$: C, 71.32; H, 7.69; N, 9.78. Found: C, 71.00; H, 8.00; N, 9.52. Dihydrochloride, m.p. 208–209°.], N,N'-bis(*o*-chlorophenyl)-1,3-diaminopropane [86%, b.p. 220–225° (1 mm.), m.p. 77–78°. *Anal.* Calcd. for $C_{15}H_{16}Cl_2N_2$: C, 61.10; H, 5.43; N, 9.49. Found: C, 60.98; H, 5.64; N, 9.47.], N,N'-bis(*m*-chlorophenyl)-1,3-diaminopropane [60%, b.p. 260–270° (1 mm.), $n^{20}D$ 1.6415. *Anal.* Calcd. for $C_{15}H_{16}Cl_2N_2$: C, 61.10; H, 5.43; N, 9.49. Found: C, 60.91; H, 5.55; N, 9.28.], N,N'-bis(*p*-chlorophenyl)-1,3-diaminopropane [58%, b.p. 280–290° (1 mm.), m.p. 77°, lit.[20] m.p. 75°. *Anal.* Calcd. for $C_{15}H_{16}Cl_2N_2$: C, 61.10; H, 5.43; N, 9.49. Found: C, 61.21; H, 5.67; N, 9.80.], and N,N'-bis-(*o*-biphenyl)-1,3-diaminopropane [53%, b.p. 273–274° (0.5 mm.), m.p. 77°. *Anal.* Calcd. for $C_{27}H_{26}N_2$: C, 85.70; H, 6.89; N, 7.40. Found: C, 85.89; H, 7.01; N, 7.14. Dihydrochloride, m.p. 172° (from ethanol).].

Prepared in an analogous manner were N,N'-diphenyl-1,3-diaminobutane [89%, b.p. 210–200° (1 mm.), $n^{20}D$ 1.6060. *Anal.* Calcd. for $C_{16}H_{19}N_2$: C, 80.00; H, 8.33; N, 11.67. Found: C, 80.28; H, 8.61; N, 11.62.], and N,N'-diphenylbis(aminomethyl) ether [36%, b.p. 214–220° (1 mm.), $n^{20}D$ 1.6399. *Anal.* Calcd. for $C_{14}H_{16}N_2O$: C, 73.68; H, 7.02; N, 12.28. Found: C, 73.53; H, 7.63; N, 12.08.].

N-*p*-chlorophenyl-N'-*p*-tolyl-1,3-diaminopropane.—N-(3-Bromopropyl)*p*-toluidine hydrobromide (18 g., m.p. 152–153°, lit.[21] m.p. 151°) was neutralized with 10% sodium hydroxide solution and the free base was extracted with ether. The ether solution was dried over magnesium sulfate and was then added dropwise, over 1.5 hr., to 100 g. of stirred, molten *p*-chloroaniline on a water bath. The ether was distilled as the addition proceeded. The mixture was heated for an additional hour; it then was neutralized and the bases were extracted with ether. The extract was washed with water and dried over magnesium sulfate. Distillation gave 15 g. (91%) of the required compound, b.p. 245–250° (1 mm.).

Anal. Calcd. for $C_{16}H_{19}ClN_2$: C, 69.95; H, 6.92; N, 10.20. Found: C, 70.37; H, 7.23; N, 10.06.

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[12] 1,2,5,6-Tetrahydro-4H-pyrrolo[3,2,1-*ij*]quinoline.

[13] 2,3-Dihydro-1H-pyrido[3,2,1-*jk*]carbazole.

[14] 2,3-Dihydro-1H,7H-pyrido[3,2,1-*de*]acridine.

[15] M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 3079 (1958).

[16] P. B. D. De la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Butterworth and Co., Ltd., London, 1959, p. 139.

[17] T. Y. Yu, *Dissertation Abstr.*, **12**, 254 (1952).

[18] The reactions are exothermic and with *p*-anisidine it is necessary to add the dibromopropane dropwise with stirring.

[19] R. Daniels and B. D. Martin, *J. Org. Chem.*, **27**, 178 (1962).

[20] W. L. C. Veer, *Rec. trav. chim.*, **57**, 589 (1938).

[21] L. W. Deady, G. J. Leary, R. D. Topsom, and J. Vaughan, *J. Org. Chem.*, **28**, 511 (1963).

1,3-Bis(N-indolinyl)propane was available as a by-product of an attempt to prepare lilolidine by refluxing indoline with 1,3-dibromopropane.[22] It had b.p. 220–223° (0.5 mm.).

Anal. Calcd. for $C_{19}H_{22}N_2$: C, 81.98; H, 7.98; N, 10.05. Found: C, 82.34; H, 8.20; N, 9.40.

1,3-Bis(N-tetrahydroquinolinyl)propane was prepared by heating 93 g. of tetrahydroquinoline with 31 g. of 1,3-dibromopropane at 55° for 2.5 hr. The deep red reaction mixture was dissolved by shaking with a mixture of dichloromethane and aqueous sodium hydroxide. The organic layer was washed with aqueous sodium hydroxide and with water and was dried over magnesium sulfate. After evaporation of the solvent, distillation under reduced pressure gave 62 g. of tetrahydroquinoline, 9.0 g. of julolidine, and 9.0 g. of the required diamine.[23] The diamine had b.p. 208–212° (0.5 mm.) and gave a dipicrate, m.p. 162° (from benzene).

Anal. Calcd. for $C_{33}H_{32}N_8O_{14}$: C, 51.83; H, 4.19. Found: C, 51.75; H, 4.30.

1,3-Bis(N-carbazolyl)propane.[24]—Carbazole (16.7 g., 0.1 mole) was fused for 45 min. at 260° with 6 g. (0.107 mole) of potassium hydroxide. The material obtained was pulverized and refluxed for 15 min. in 100 ml. of sodium-dried toluene.

The potassium salt was filtered from the hot toluene and cooled in a vacuum desiccator. The salt (17.6 g., 0.086 mole) was refluxed for 5 hr. with 8.75 g. (0.043 mole) of 1,3-dibromopropane in 50 ml. of sodium-dried toluene. The solvent was removed by steam distillation, and the residue was heated under reduced pressure to sublime carbazole (3 g.). The residue was recrystallized twice from toluene to give 8.7 g. (54%) of the required compound, m.p. 183°.

Anal. Calcd. for $C_{20}H_{24}N_2$: C, 86.58; H, 5.93; N, 7.48. Found: C, 86.45; H, 6.07; N, 7.14.

The picrate had m.p. 152° from benzene.

Attempted Preparation of 1,3-Bis(N-acridanyl)propane.—Refluxing acridan with dibromopropane gave only acridine and an intractible black tar. A preparation analogous to that used to make the carbazole analog could not be attempted because sodio or potassio derivatives of acridan could not be formed under mild conditions with sodium, potassium, or sodium hydride; more stringent conditions gave acridine.[25] Acridanylmagnesium iodide[26] was prepared and refluxed with dibromopropane but only acridan and a black tar were formed.

N-Benzyl-N′-phenyl-1,2-diaminoethane.[27]—N-(2-Bromoethyl)-aniline hydrobromide[28] (74 g., m.p. 138°) was neutralized with 10% sodium hydroxide solution and extracted with 600 ml. of ether. The extract was washed with water and dried over potassium carbonate. Benzylamine (100 g.) was added, and the ether was distilled. The mixture was refluxed for 5 hr. and then shaken with 200 ml. of 10% sodium hydroxide solution and 1 l. of ether. The organic layer was washed with water and dried over potassium carbonate. Distillation gave 42 g. (66.5%) of the product, b.p. 220–223° (20 mm.). The dipicrate had m.p. 161°, lit.[27] m.p. 158–160°.

Anal. Calcd. for $C_{27}H_{24}N_8O_{14}$: C, 47.38; H, 3.51; N, 16.37. Found: C, 47.35; H, 3.72; N, 16.57.

N-*o*-Xylyl-N′-*o*-tolyl-1,2-diaminoethane (36.6 g., 37%) was prepared[29] from 125 g. of *o*-xylamine hydrochloride[30] and 117 g. of N-(2-bromoethyl)-*o*-toluidine hydrobromide[31,32] in a manner similar to the previous preparation. It had b.p. 206–213° (0.5 mm.) and gave a picrate, m.p. 177°.

Anal. Calcd. for $C_{23}H_{25}N_5O_7$: C, 57.14; H, 5.18; N, 14.49. Found: C, 57.18; H, 5.50; N, 14.29.

Breakdown of N,N′-Diaryl-1,3-Diaminopropanes.—Decomposition of the diamines was carried out in a Claisen distillation apparatus at temperatures from 200–300° as necessary and under reduced pressures (20 mm. unless otherwise stated). The catalyst was added as 48% hydrobromic acid. Decomposition always commenced quite suddenly as the temperature was raised, and the temperature at which this first occurred was reproducible to within 5°. Heating was continued until little further material distilled.

The distillate (86–94%, except for the methoxyphenyldiamines where it was 79–86%) was, in general, first analyzed on the gas chromatograph and then separated into components which, after identification, could be used to assign and calibrate the peaks in the original chromatogram. Compounds present in small amounts (<5%) could not always be separated from the decomposition mixture and the corresponding peaks were identified by retention time comparisons, on two columns,[33] with synthetic samples prepared for this purpose by literature methods. Semiquantitative chemical separations, made for the distillates obtained from the breakdown of the diphenyl- and ditolyldiamines,[12] confirmed the v.p.c. analyses.

The separation of pure compounds from the decomposition mixtures obtained from *ortho-* and *para*-substituted diamines was more difficult than with the *meta* isomers. It was usual first to fractionate the distillate. When the v.p.c. indicated the presence of more than one component in a fraction, the compounds were isolated either with the preparative gas chromatograph or by chemical means (particularly by fractional re-recrystallization of picrates), by the Hickinbottom method[34,35] of separating primary amines, and by the Hinsberg method. The latter process, involving treatment of mixtures with benzenesulfonyl chloride, allowed easy recovery of the unaffected julolidines.

The small amounts of tarry residues obtained were, in general, too complex to allow further separation. Significant quantities of the aminophenols were, however, isolated by alkali extraction of the corresponding decomposition residues from the methoxyphenyldiamines.

Compounds isolated were fully characterized by a combination of physical measurements, infrared spectra, preparation of derivatives, and elemental analysis. In cases of ambiguity, authentic samples were synthesized for comparison. Tetrahydroquinolines were also dehydrogenated to the corresponding quinolines by heating with sulfur.

Previously unreported tetrahydroquinolines and julolidines isolated from diamine decompositions are listed below. Infrared spectra, where not specifically mentioned, confirmed the structure.

5-Chlorotetrahydroquinoline, a pale green oil, $n^{20}D$ 1.6137, was obtained *via* the preparative gas chromatograph from the fraction, b.p. 110–120° (1 mm.), resulting from the breakdown of N,N′-bis(*m*-chlorophenyl)-1,3-diaminopropane. The infrared

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[22] Following the method described by J. von Braun [*Ber.*, **51**, 1215 (1918)], except that 1,3-dibromopropane was substituted for 1,3-chlorobromopropane.

[23] The amount of tetrahydroquinoline recovered is greater than the excess originally added and this, with the corresponding presence of julolidine, indicates that some breakdown of the diamine has occurred under the reaction conditions. Indeed, it is hard to purify as distillation leads to some concurrent decomposition.

[24] Refluxing carbazole with dibromopropane for several days gives only a low yield of the diamine, and the product is hard to purify.

[25] Although it has been claimed (A. Albert in "Heterocyclic Compounds," Vol. 4, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1952, p. 537) that acridan forms a sodio derivative with sodium, we could find no reference to this in the literature. It was also stated that acridans substituted on the nitrogen atom may be obtained by reacting N-sodioacridan with an alkyl iodide, but the reference quoted describes only the reaction with the sodio derivative of 5,5-dimethylacridan which is stabilized as it cannot form an acridine.

[26] V. V. Chelintzev and B. V. Tronov, *J. Russ. Phys. Chem. Soc.*, **46**, 1886 (1914); *Chem. Abstr.*, **9**, 2072 (1915).

[27] Only literature references [P. Karrer and C. Gränacher, *Helv. Chim. Acta*, **7**, 763 (1924) and C. Gränacher, V. Schilling, and E. Schlatter, *ibid.*, **8**, 873 (1925)] describe its preparation by a three-stage process from hippuric acid.

[28] W. M. Pearlman, *J. Am. Chem. Soc.*, **70**, 871 (1948).

[29] Preparation by R. G. Mathews of this department.

[30] Prepared in 71% yield from *o*-xylyl bromide *via* the hexamine complex following the procedure described for similar conversions by J. Graymore [*J. Chem. Soc.*, 1116 (1947)].

[31] Prepared by the action of PBr_3, followed by HBr, on N-(3-hydroxypropyl)-*o*-toluidine. This was found preferable to the method described in ref. 32 which, in our hands, led to incomplete reaction.

[32] H. W. Heine, B. L. Kapur, J. L. Bove, R. W. Griener, K. H. Klinger, and C. Mitch, *J. Am. Chem. Soc.*, **76**, 2503 (1954).

[33] The two columns were the Apiezon L on Celite 545 column and one consisting of polyethyleneglycol 4000 also on Celite 545.

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

[35] The method involves the precipitation of the zinc chloride complexes of any primary amine present by treating a mixture with concentrated zinc chloride solution. The complexes, of form $[ArNH_2]_2 \cdot ZnCl_2$, are then washed with water, dried, and weighed. In a previous publication (ref. 2), we suggested that this method of separation was far less satisfactory than the Hinsberg method. We have since found that the difficulty arises from the partial hydrolysis of the arylamine complex on washing with water. Thus, it is preferable to wash the complexes free of other amines with concentrated zinc chloride and with ether and then to deliberately hydrolyze them; the liberated primary amine can be isolated and weighed.

spectrum (pure liquid) showed a medium peak at 14.20 μ and a strong peak at 13.10 μ corresponding to the out-of-plane vibrations of three adjacent aromatic C-H bonds.[36]

Anal. Calcd. for $C_9H_{10}ClN$: C, 64.48; H, 5.97; N, 8.36. Found: C, 64.53; H, 6.21; N, 8.00.

The hydrochloride had m.p. 120–122°.

7-Chlorotetrahydroquinoline was a white solid, m.p. 63–63.5° after recrystallization from petroleum ether (b.p. 30–40°). It was obtained as the 5-chloro isomer above. The infrared spectrum (melt) showed a strong peak at 12.80 μ (2 adjacent aromatic C-H bonds) and a medium peak at 11.95 μ (isolated aromatic C-H bond).[36]

Anal. Calcd. for $C_9H_{10}ClN$: C, 64.48; H, 5.97; N, 8.36. Found: C, 64.31; H, 6.13; N, 8.51.

The hydrochloride had m.p. 206–208°.

8-Chlorotetrahydroquinoline, a light green oil, was obtained by recrystallization of the picrates from the fraction, b.p. 95–110° (1 mm.), obtained in the decomposition of N,N′-bis(*o*-chlorophenyl)-1,3-diaminopropane.

Anal. Calcd. for $C_9H_{10}ClN$: C, 64.48; H, 5.97; N, 8.36. Found: C, 64.71; H, 5.82; N, 8.01.

It gave a benzoyl derivative, m.p. 134°, and a picrate, m.p. 130–131°.

Anal. Calcd. for $C_{15}H_{13}ClN_4O_7$: C, 45.54; H, 3.28; N, 14.14. Found: C, 45.58; H, 3.40; N, 14.07.

It gave 8-chloroquinoline on dehydrogenation (standard procedure using sulfur), b.p. 110° (1 mm.), methiodide m.p. 165° (lit.[37] m.p. 165°).

8-Chlorojulolidine, an oil, was readily obtained as the fraction, b.p. 135–140° (1 mm.), from the decomposition of the N,N′-bis(*m*-chlorophenyl)-1,3-diaminopropane.

Anal. Calcd. for $C_{12}H_{14}ClN$: C, 69.39; H, 6.75; N, 6.75. Found: C, 69.39; H, 6.77; N, 7.12.

It gave a hydrochloride, m.p. 162–163° after recrystallization from ethanol–ether, and a picrate, m.p. 161–162° after recrystallization from ethanol.

Anal. Calcd. for $C_{18}H_{17}ClN_4O_7$: N, 12.83. Found: N, 12.75.

9-Chlorojulolidine was a white solid, m.p. 46° after recrystallization from petroleum ether (b.p. 40–50°). It was easily obtained as the nonvolatile (steam) component of the fraction left after removal of the primary amine from the breakdown of N,N′-bis(*p*-chlorophenyl)-1,3-diaminopropane.

Anal. Calcd. for $C_{12}H_{14}ClN$: C, 69.39; H, 6.75; N, 6.75. Found: C, 69.49; H, 7.01; N, 6.42.

It gave a hydrochloride, m.p. 240–241°, and a picrate, m.p. 152–153°.

Anal. Calcd. for $C_{18}H_{17}ClN_4O_7$: N, 12.83. Found: 12.43.

8-Methoxyjulolidine, an oil, was easily isolated as the fraction, b.p. 140–160° (3 mm.), from the breakdown of the *m*-anisyldiamine after washing with alkali.

Anal. Calcd. for $C_{13}H_{17}NO$: C, 52.78; H, 4.63; N, 12.96. Found: C, 52.50; H, 4.91; N, 12.96.

It gave a picrate, m.p. 147–148° after recrystallization from ethanol.

Anal. Calcd. for $C_{16}H_{16}N_4O_8$: N, 6.90. Found: N, 6.73.

N-Allyl-*o*-chloroaniline, a previously unreported oil, was obtained after fractional recrystallization and decomposition of the picrates from the fraction, b.p. 80–90° (1 mm.), arising from the decomposition of the di-*o*-chlorophenyldiamine.

Anal. Calcd. for $C_9H_{10}ClN$: C, 64.48; H, 5.97; N, 8.36. Found: C, 64.03; H, 5.96; N, 7.82.

It gave a picrate, m.p. 167–168°.

Anal. Calcd. for $C_{13}H_{13}ClN_4O_7$: N, 14.12. Found: N, 14.07.

Breakdown of N,N′-Bis(*o*-biphenyl)-1,3-diaminopropane (32.5 g.) at 245–255° (45 mm.) gave 29.9 g. of distillate. From this was obtained 14.7 g. of *o*-aminobiphenyl and 9.8 g. of 8-phenyltetrahydroquinoline, b.p. 186–202° (15 mm.). The latter gave a picrate, m.p. 160°.[38]

Anal. Calcd. for $C_{21}H_{18}N_4O_7$: C, 57.51; H, 4.11; N, 12.78. Found: C, 57.70; H, 4.41; N, 12.36.

Breakdown of N,N′-diphenylbis(aminomethyl) ether (26.7 g.) at 260–270° gave 9.0 g. of aniline and 16.5 g. of an intractible residue.

Breakdown of N,N′-diphenyl-1,3-diaminobutane (19 g.) at 250–260° gave 16.5 g. of distillate. Gas chromatography showed that the distillate consisted essentially of six components: aniline, 4.8 g.; N-methylaniline, 0.4 g.; N-ethylaniline, 3.7 g.; 2-methylquinoline, 1.3 g.; 2-methyltetrahydroquinoline, 1.9 g.; and 4-methyltetrahydroquinoline, 2.9 g. The aniline was isolated *via* its zinc chloride complex, and the other three major components were obtained using the preparative gas chromatograph.

Breakdown of N-*p*-chlorophenyl-N′-*p*-tolyl-1,3-diaminopropane (9.8 g.) at 260–270° gave 8.8 g. of distillate. The twelve major components in the distillate were identified (retention times on two columns) and estimated by v.p.c. as *p*-chloroaniline, 3 g.; *p*-toluidine, 1.9 g.; N-methyl-*p*-toluidine, 0.1 g.; N-ethyl-*p*-toluidine, 0.4 g.; N-methyl-*p*-chloroaniline, 0.3 g.; N-ethyl-*p*-chloroaniline, 0.3 g.; 6-methylquinoline, 0.1 g.; 6-methyltetrahydroquinoline, 0.65 g.; N-ethyl-6-methyltetrahydroquinoline, 0.3 g.; 6-chlorotetrahydroquinoline, 0.3 g.; 9-methyljulolidine, 1.0 g.; and 9-chlorojulolidine, 0.3 g.

Breakdown of 1,3-bis(N-indolinyl)propane at 270° (45 mm.) gave a distillate consisting almost entirely of indoline and lilolidine (b.p. 150–160° at 20 mm.) in the molar ratio 1:0.7. Lilolidine gave a picrate, m.p. 170° (lit.[39] m.p. 170°).

Anal. Calcd. for $C_{17}H_{16}N_4O_7$: C, 52.59; H, 4.15; N, 14.43. Found: C, 52.65; H, 4.32; N, 14.39.

Breakdown of 1,3-bis(tetrahydroquinolinyl)propane (7.6 g.) at 205° gave a distillate (6.8 g.) which was shown by v.p.c. to consist only of tetrahydroquinoline and julolidine (molar ratio 1:0.82).

Breakdown of N-benzyl-N′-phenyl-1,2-diaminopropane (107 g.) at 255–260° (70 mm.) gave 78.6 g. of distillate and 35.3 g. of an intractible residue. The distillate was shown by fractionation, v.p.c., and infrared spectra to contain 6% toluene, 38% aniline, 8% benzylamine, 21% N-phenyl-1,2-diaminoethane (b.p. 115–116° at 0.5 mm., dibenzoyl derivative m.p. 149°, lit.[40] m.p. 150°, unchanged by addition of an authentic sample[41] of m.p. 150°), and 10% of unchanged diamine.

Breakdown of N-*o*-xylyl-N′-*o*-tolyl-1,2-diaminoethane gave the methyl analogs of the compounds above. The N-*o*-tolyl-1,2-diaminoethane, b.p. 155–160° (18 mm.), gave a picrate, m.p. 148–149° (lit.[42] m.p. 148°), and a bisphenylisothiocyanate derivative, m.p. 128°, unchanged when mixed with an authentic sample.

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[36] The spectral identification of the two isomers was confirmed by the similarity of the spectra of 5-chloro- and 8-chlorotetrahydroquinolines and of 6-chloro- and 7-chlorotetrahydroquinolines in the 11–15-μ region.

[37] A. Claus and M. Scholler, *J. prakt. Chem.*, [2]**48**, 140 (1893).

[38] M. Arramoff and Y. Sprinzak [*J. Org. Chem.*, **22**, 571 (1957)] prepared 8-phenyltetrahydroquinoline, b.p. 160° (3 mm.), and list a picrate, m.p. 164–166°, of the unusual formula $2C_{15}H_{15}N \cdot 3C_6H_3N_3O_7$.

[39] G. Barger and E. Dyer, *J. Am. Chem. Soc.*, **60**, 2414 (1938).

[40] S. C. Dickermann and A. J. Besozzi, *J. Org. Chem.*, **19**, 1855 (1954).

[41] C. Benko and M. Tisle, *Croat. Chem. Acta*, **30**, 243 (1958); *Chem. Abstr.*, **54**, 2221 (1960).

[42] H. E. Newman, *Ber.*, **24**, 2191 (1891).