1(2H)-3,4-Dihydro-6-methoxy-7-hydroxynaphthalenone (VII).—A 20-g. sample of X dissolved in aqueous alkali was acetylated with acetic anhydride, giving 19 g. of the acetyl derivative (XI) which, after crystallization from water, melted at 65.5–66.5°.

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.72; H, 6.30.

To a cooled stirred solution of 20 g. of XI in 130 ml. of dry benzene at 0°, was added 20 g. of phosphorus pentachloride in portions. The mixture was warmed to room temperature to complete the reaction and then cooled until benzene began to solidify. At this point, a solution of 20 g. of anhydrous stannic chloride in 20 ml. of dry benzene was added with stirring. After standing for 3 hr. at 0°, the mixture was hydrolyzed by the addition of ice followed by 60 ml. of concentrated hydrochloric acid. A 120-ml. portion of ether was added and the mixture was shaken until complete solution occurred. The organic layer was then washed with 5% hydrochloric acid, 5% sodium hydroxide, and water. After evaporation of the ether, 11 g. of residue, melting at 118–120°, was obtained. This residue was saponified with 10% potassium hydroxide, whereupon 8 g. of VII, melting at 150.2–150.9° after crystallization from water, was obtained.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29; OCH_3, 16.14. Found: C, 68.46; H, 6.16; OCH_3, 16.0.

By methylation with dimethyl sulfate, 1(2H)-3,4-dihydro-6,7-dimethoxynaphthalenone was obtained, m.p. 98–98.5° (from *n*-heptane), lit.[11] m.p. 99°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; OCH_3, 30.06. Found: C, 69.61; H, 6.54; OCH_3, 30.01.

The semicarbazone had m.p. 226.5–227° (from ethanol).

Anal. Calcd. for $C_{13}H_{17}N_3O_3$: N, 15.96. Found: N, 15.81.

(11) K. N. Campbell, A. Scharge, and B. K. Campbell, *J. Org. Chem.*, **15**, 1135 (1950).

The Synthesis of 7-Alkylamino-1-naphthols

DANIEL L. ROSS AND JULIA J. CHANG

Research Laboratories, Polaroid Corporation, Cambridge 39, Massachusetts

Received April 10, 1963

1,7-Dihydroxynaphthalene, when heated with aqueous solutions of methylamine, ethylamine, isopropylamine, and dimethylamine, gave good yields of the corresponding 7-alkylamino-1-naphthols uncontaminated with the other position isomer. The selectivity of the reaction is explained in terms of steric effects.

In the course of searching for new couplers for the preparation of azo dyes, it became desirable to develop a synthesis of 7-alkylamino-1-naphthols. The method described for the primary amine, alkali fusion of 7-aminonaphthalene-1-sulfonic acid,[1a,b] was not suitable for the substituted derivatives. Although the precursors, the 7-alkylaminonaphthalene-1-sulfonic acids, were easily prepared by the Bucherer reaction with 2-naphthol-8-sulfonic acid, alkali fusion of the N-methyl compound was accompanied by at least 50% demethylation and gave a mixture of 7-methylamino-1-naphthol (**8a**) and 7-amino-1-naphthol, while fusion of the N-isopropyl compound resulted in extensive degradation of the molecule. The Bucherer reaction using various primary aliphatic amines with 1,7-dihydroxynaphthalene, under a wide variety of conditions, gave only mixtures of both possible monosubstitution products, 1,7-diamine, and recovered starting material.

An early report[2] that 1,7-dihydroxy-2-naphthoic acid gave 7-amino-1-naphthol when heated at 180° with concentrated ammonia solution led us to investigate the reaction of aliphatic amines with 1,7-dihydroxynaphthalene in the absence of the bisulfite usually used in the Bucherer reaction.

Uncatalyzed reactions of amines with naphthols have been previously reported.[3] For example, N-methyl-β-naphthylamine was obtained in 80% yield on heating β-naphthol with aqueous methylamine at 200–220° for 7 hr.[4] Depending on the reaction temperature, either 3-amino-2-naphthol or 2,3-naphthalenediamine could be obtained from 2,3-dihydroxynaphthalene,[5] while the corresponding diamines were formed when 1,5-,[6] 1,8-,[6] and 2,7-dihydroxynaphthalenes[7] were heated to 250–300° with aqueous ammonia. Similar conditions were used to prepare α- and β-naphthylamine from the corresponding naphthols.[8] However, there is but a single example reported in which a simple dihydroxynaphthalene, containing both an α- and a β-hydroxy group, has been treated under these conditions. When 1,3-dihydroxynaphthalene was heated with ammonia at 130–140°, 3-amino-1-naphthol (preferential replacement of the β-hydroxy group) and some diamine were obtained.[9] Treatment with aniline gave 3-anilino-1-naphthol.

In the present work, when aqueous methylamine was heated with 1,7-dihydroxynaphthalene, a single aminonaphthol was produced. Reasonable yields of 7-methylamino-1-napthol (**8a**) were obtained over a considerable range of temperature (130–180°) and molar ratios of amine to dihydroxynaphthalene. In addition, it was only when forcing conditions were used (180°, four equivalents of methylamine) that any significant amount of 1,7-diamine was formed. There was no detectable amount of the other isomer, 8-methylamino-2-naphthol, present. Ethylamine, isopropylamine, and dimethylamine also reacted, at increasingly higher temperatures, to give the corresponding 7-amino-1-naphthols uncontaminated by the other possible position isomers and with no significant formation of diamines. In a single experiment, using aqueous ammonia at 130°, only starting material was recovered. Similarly, none of the desired product was obtained when *t*-butylamine was used.

(1) (a) A. C. Mueller and C. S. Hamilton, *J. Am. Chem. Soc.*, **66**, 860 (1944); (b) V. V. Perekalin and N. M. Slabachevskaya, *J. Gen. Chem. USSR*, **21**, 985 (1951).

(2) P. Friedländer and S. Zinberg, *Ber.*, **29**, 37 (1896).

(3) For a comprehensive discussion of the preparation of amines by substitution of the hydroxy group, see H. Glaser, "Methoden der Organischen Chemie," Vol. XI/1, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1957, p. 160.

(4) G. T. Morgan and F. P. Evans, *J. Chem. Soc.*, 1140 (1919).

(5) P. Friedlander and S. Zakrzewski, *Ber.*, **27**, 761 (1894).

(6) H. Erdmann, *Ann.*, **247**, 306 (1888).

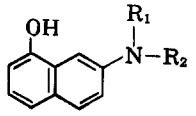
(7) F. Kaufler and V. Karrer, *Ber.*, **40**, 3262 (1907).

(8) V. V. Kozlov and I. K. Veselovskaya, *Zh. Obshch. Khim.*, **31**, 2662 (1961); *Chem. Abstr.*, **56**, 11508 (1962).

(9) P. Friedlander and H. Rudt, *Ber.*, **29**, 1609 (1896).

TABLE I

PROPERTIES OF AMINONAPHTHOLS



8

Compound	R_1	R_2	M.p., °C., dec.	λ_{max}, mμ (EtOH)	$\epsilon_{max} \times 10^{-3}$	Analyses, % Calcd. C	H	N	Found C	H	N
8a	H	CH_3	132–133[a]	250, 291, 301, 350	37.0, 9.0, 8.0, 2.04	76.27	6.40	8.09	76.37	6.30	7.79
8b	H	CH_2CH_3	89–90[b]	251, 292, 303, 347	33.2, 7.8, 6.9, 1.8	76.97	7.00	7.48	77.06	7.14	7.72
8c	H	$CH(CH_3)_2$	88–89[b]	253, 293, 304, 349	46.0, 11.6, 10.6, 2.68	77.58	7.51	6.96	77.61	7.48	7.22
8d	CH_3	CH_3	106.5–108.0[c]	256, 296, 306, 350	32.4, 9.4, 8.6, 1.92	76.97	7.00	7.48	76.89	6.86	7.39

Recrystallization solvents: [a] Carbon tetrachloride. [b] Hexane. [c] Cyclohexane.

TABLE II

DERIVATIVES OF N-SUBSTITUTED 7-AMINO-1-NAPHTHOLS

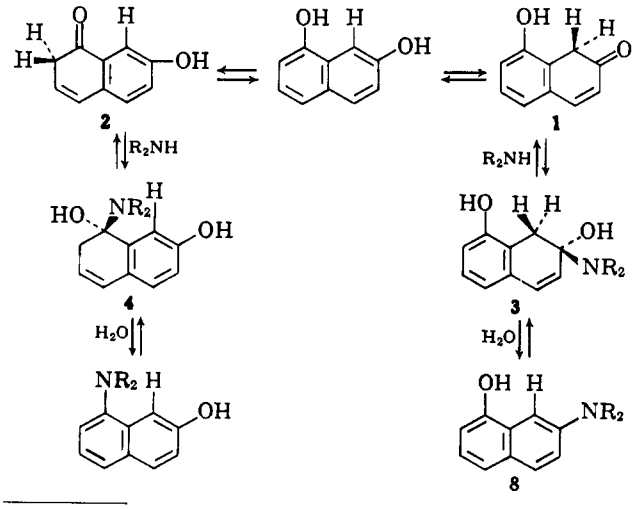
	Derivative	M.p., °C.	Analyses, % Calcd. C	H	N	Found C	H	N
8a	O,N-Bis(3,5-dinitrobenzoyl)	214–215[a]	53.48	2.69	12.48	53.52	2.91	12.69
8b	Picrate	170–171 dec.[b]	51.92	3.87	13.46	52.39	4.12	13.21
8c	Picrate	147–148 dec.[c]	53.02	4.22	13.02	53.36	4.26	12.91
8d	Picrate	178.5–179.5 dec.[d]	51.92	3.87	13.46	51.87	3.96	13.16

Recrystallization solvents: [a] Acetonitrile. [b] Toluene. [c] Chloroform. [d] Ethanol.

To confirm the structures assigned to these products, an authentic sample of 7-ethylamino-1-naphthol (**8b**) was prepared by the lithium aluminum hydride reduction of 7-acetamido-1-naphthol[1a] and proved to be identical with the product of the reaction of ethylamine with 1,7-dihydroxynaphthalene. The properties of the aminonaphthols and their derivatives are listed in Tables I and II.

It seems reasonable to assume that this reaction proceeds by addition of the amine to the carbonyl group of the keto form of the naphthol[3,10] as shown in Scheme I. What appears remarkable about the present reaction is the high degree of preference for replacement of the β-hydroxy group. The differences in reactivities of α- and β-naphthol would be expected to be small. Wheland[11] calculated that there is no difference in ΔE (−10 kcal. per mole) between α- and β-naphthol upon conversion to their keto forms.

SCHEME I



(10) A. Rieche and H. Seeboth, *Ann.*, **638**, 43, 52, 66, 78 (1960).

(11) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 405.

Quantitative kinetic and thermodynamic data which permit direct comparison between α- and β-naphthol are largely lacking in the literature. A few scattered observations have been reported, however. The heat of formation[12] of β-naphthol (34.2 kcal./mole) exceeds that of α-naphthol (31.3 kcal./mole) by 2.9 kcal./mole, while the difference for the corresponding acetates is 3.5 kcal./mole. The rate of esterification with acetic anhydride in acetic acid is slower for α-naphthol.[13] When α- and β-naphthol were treated with aqueous ammonia[8] for 3 hr. at 250°, β-naphthylamine was obtained in 58% yield, while the α isomer gave only 23.2%. In the Bucherer reaction, β-naphthols react more readily than α-naphthols with arylamines,[14] even if, as in 1,6-dihydroxynaphthalene-4-sulfonic acid where both α- and β-positions are available, the α-position is activated by a 4-sulfo group, a situation which normally leads to preferential replacement by ammonia of the activated group.

Although the above information is hardly adequate enough to allow any definitive conclusions to be drawn, we believe that the selectivity of the reaction reported here can be best interpreted in terms of the effects that steric interactions with the *peri*-position of the naphthalene ring have on three aspects of the proposed reaction sequence: namely, the positions of the keto–enol equilibria of the α- and β-hydroxyl groups; the ease of addition of amine to the two ketonic forms, **1** and **2** (or the relative positions in the equilibria between **1** and **3** *vs.* **2** and **4**); and the relative ease of the loss of water from intermediates **3** and **4**. Such effects would be expected to be small but significant, especially when bulkier groups are involved. In general, a reaction leading to an increase in spatial requirements at an α-position should be less favorable energetically than the same reaction at a β-position. Similarly, a reaction which re-

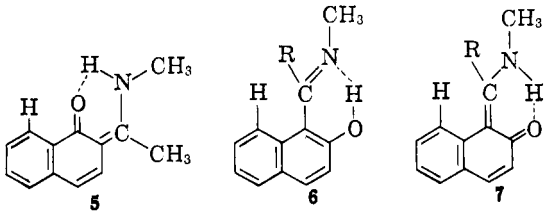
(12) A. Leman and G. Lepoutre, *Compt. rend.*, **226**, 1978 (1948).

(13) A. Leman, *Ann. chim.*, **9**, 357 (1938).

(14) N. L. Drake, "Organic Reactions," Vol. 1, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 105; see also ref. 3, p. 148.

sults in a decrease in *peri*-interactions should be correspondingly more favorable. Thus, a greater relief of *peri*-interactions should result on going from the dihydroxynaphthalene (OH· · · ·H interaction) to the β-keto form (**1**, Scheme I, no interaction) than on going to the α-form, **2** (=O· · · ·H interaction), and, consequently, at equilibrium, there should be a higher concentration of **1** than **2**. Addition of a primary or secondary amine might be expected to proceed more readily with the β-keto form than the α-form, because in the latter there is the possibility of steric repulsion by interaction of the incoming (solvated) amine with the *peri*-hydrogen atom. Finally, rearomatization of the addition products **3** and **4** should be less favorable for **4**, in that a bulky amino group would be brought into a position coplanar with the *peri*-hydrogen atom.

Recent work by Dudek[15] has shown that *peri*-effects can influence the direction and ease of the ketonization of substituted α- and β-naphthols. Thus, N-methyl-1-hydroxy-2-acetonaphthoneimine exists in the ketoamine form **5**, while N-methyl-2-hydroxy-1-acetonaphthoneimine (**6**, R = CH_3) is more stable in the hydroxyimine form because interactions between the C-methyl group and the *peri*-hydrogen atom can be relieved by rotation about the single bond to the α-substituent, a condition not possible in the ketoamine form (**7**, R = CH_3). In N-methyl-2-hydroxy-1-naphthaldehydeimine (**6**, R = H), where the methyl group has been replaced by a less bulky hydrogen atom, the ketoamine form is again more stable (**7**, R = H).



5 **6** **7**

With a large excess of ammonia at 250°, 1,7-dihydroxynaphthalene was reported to give 79.5% of "aminonaphthol" and 21.5% of diamine.[16] Addition of 1 equiv. of sodium hydroxide increased the yield of "aminonaphthol" to 90%. Although the authors describe their product as 7-amino-1-naphthol, the combination of the more vigorous conditions and the smaller size of the amine has resulted in the loss of selectivity, for the melting point given (130°) is considerably less than that reported for this compound (156–158°,[1a] 155–156°[1b]), and suggests that the product was a mixture of both isomers.

Experimental[17]

1,7-Dihydroxynaphthalene.—The melting point of a commercial grade, from Aldrich Chemical Co., Inc., was raised from 175–176° to 179–181° (lit.[18] m.p. 181°) by recrystallization from 1% aqueous hydrochloric acid containing a trace of stannous chloride.

7-Methylamino-1-naphthol (**8a**).—In a 250-ml. steel bomb were placed 40 g. (0.25 mole) of 1,7-dihydroxynaphthalene, 43.5 ml. (0.5 mole) of 40% aqueous methylamine, and 55 ml. of water. The bomb was sealed and heated while rocking at 140° for 8 hr. After cooling and opening the bomb, the contents were dissolved in 100 ml. of 50% sodium hydroxide solution and 300 ml. of water. The solution was filtered from a little crude 1,7-di(methylamino)naphthalene (4.21 g., m.p. 74–75°). The filtrate was acidified with 300 ml. of concentrated hydrochloric acid and chilled in an ice bath. The precipitated solid was collected by suction filtration and dissolved in 300 ml. of water. In other preparations (using different ratios of reactants and temperatures) from which 1,7-dihydroxynaphthalene was recovered, it was separated from the product at this point by filtration. The acidic solution of the product was neutralized with aqueous ammonium carbonate (prepared by saturating concentrated ammonium hydroxide solution with carbon dioxide), and the precipitated product was collected, washed with a little cold water, and dried to give 27.7 g. of crude product, m.p. 124–127° dec. Neutralization of the strongly acidic filtrate from above gave an additional 3.1 g. of product, total yield 71%. An analytical sample was prepared by crystallization to constant melting point from carbon tetrachloride. The properties of the aminonaphthols are reported in Table I.

7-Ethylamino-1-naphthol (**8b**). **A.**—In a 250-ml. steel bomb were placed 40 g. (0.25 mole) of 1,7-dihydroxynaphthalene, 41.2 ml. (0.5 mole) of 70% aqueous ethylamine, and 60 ml. of water. The bomb was sealed and heated while rocking at 155° for 8 hr. The contents of the bomb were dissolved in 100 ml. of 50% aqueous sodium hydroxide solution and 300 ml. of water and were filtered from a trace of solid. The filtrate was acidified with 300 ml. of concentrated hydrochloric acid and chilled in an ice bath. The aqueous phase was decanted from the heavy oil which separated, the oil was mixed with 300 ml. of water, and the mixture was filtered from 8.6 g. of recovered starting material. The filtrate was neutralized with ammonium carbonate solution and the precipitated product was collected, washed with water, and dried to give 22.4 g. of crude product, m.p. 68–70° dec. An additional 2.1 g. of product was obtained by neutralization of the above decanted hydrochloric acid solution to give a total yield of 52% (66% corrected for recovered starting material). An analytical sample was prepared by crystallization to constant melting point from hexane.

B.—By Lithium Aluminum Hydride Reduction.—To a suspension of 2 g. of lithium aluminum hydride in 50 ml. of dry tetrahydrofuran was added, over 20 min., a solution of 5.03 g. (0.025 mole) of 7-acetamido-1-naphthol[1a] in 75 ml. of tetrahydrofuran. The mixture was stirred under reflux for 15 hr. A solution of 2 ml. of water in 20 ml. of tetrahydrofuran was then added slowly to the mixture with cooling, and the entire reaction mixture was evaporated to dryness under reduced pressure. The residue was heated with two 100-ml. portions of acetic acid and filtered. The combined acetic acid extracts were evaporated to dryness, and the residue was stirred with 200 ml. of 6 *N* hydrochloric acid. The solution was filtered through a pad of Celite and neutralized with ammonium carbonate solution to give, after washing with water and drying, 3.04 g. (65%) of 7-ethylamino-1-naphthol which, after recrystallization from hexane, proved to be identical in all respects (melting point, mixture melting point, infrared and ultraviolet spectra) with the product obtained from 1,7-dihydroxynaphthalene and ethylamine.

Hydrochloride of 7-Isopropylamino-1-naphthol (**8c**).—In a 250-ml. steel bomb were placed 40 g. (0.25 mole) of 1,7-dihydroxynaphthalene, 42.5 ml. (29.5 g., 0.5 mole) of isopropylamine, and 55 ml. of water. The bomb was sealed and heated while rocking at 170° for 16 hr. The contents of the bomb were dissolved in 100 ml. of 50% sodium hydroxide solution and 300 ml. of water, the solution was filtered through a Celite pad, and the filtrate was acidified with 300 ml. of concentrated hydrochloric acid. The resulting heavy oil was separated by decanting the aqueous layer and mixed with 200 ml. of ethyl acetate. The solid which separated was collected, washed with a second 200-ml. portion of ethyl acetate, and dried to give 33.0 g. (56%) of the hydrochloride, m.p. 198–202° dec.

An analytical sample of the hydrochloride, obtained by two recrystallizations from 5% hydrochloric acid, melts at 117–118°, resolidifies, and decomposes at 222–224°. This compound was hygroscopic.

(15) G. O. Dudek, *J. Am. Chem. Soc.*, **85**, 694 (1963); *Spectrochim. Acta*, **19**, 691 (1963).

(16) V. V. Kozlov and I. K. Veselovskaya, *Zh. Obshch. Khim.*, **31**, 3030 (1961); *Chem. Abstr.*, **57**, 739 (1962).

(17) Melting points are uncorrected and were obtained on a Mel-Temp capillary melting point apparatus. Elemental analyses were by Dr. S. M. Nagy of the Microchemical Laboratory, Massachusetts Institute of Technology, and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Ultraviolet spectra were determined on a Cary Model 11 spectrophotometer.

(18) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds," Edward Arnold Ltd., London, 1958, p. 286.

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.

(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

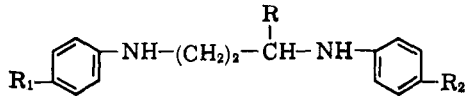
I. K. LEWIS, G. B. RUSSELL, R. D. TOPSOM, AND J. VAUGHAN

The Department of Chemistry, University of Canterbury, Christchurch, New Zealand

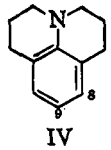
Received September 25, 1963

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

(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).