

THE PREPARATION OF N,N'-DIMETHYL (DIETHYL)-4,4'-DIAMINO-1,1'-BINAPHTHYL
AND N-METHYL (ETHYL)-1-NAPHTHYLAMINE

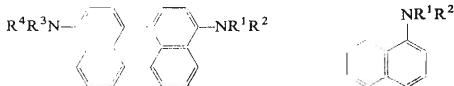
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When studying the mechanism and kinetics of oxidation of N-alkyl derivatives of 1-naphthylamine (VII) and of 4,4'-diamino-1,1'-binaphthyl (naphthidine I), we were faced with the problem of synthesis of the hitherto unreported N,N'-dimethyl-(V) and N,N'-diethyl-4,4'-diamino-1,1'-binaphthyl (VI). We succeeded in preparing these two N,N'-dialkyl derivatives by tosylation of naphthidine (I), alkylation of the tosyl derivative and of its hydrolysis. This method has already been used by Arient and Dvořák¹ for the preparation of N-methyl-o-cumidine. Tosylation of naphthidine was carried out in pyridine at 100°C; the formed tosyl derivative was alkylated by dimethyl (diethyl) sulphate in an aqueous alkaline medium. Of the known methods¹⁻⁵ of the splitting-off of tosyl group, the hydrolysis by concentrated hydrochloric acid at 140–150°C in sealed ampoules proved to be the best one in our case. Compounds V and VI were isolated in the form of their bases.

We used the above method with success also in the preparation of N-methyl-1-naphthylamine and N-ethyl-1-naphthylamine. When compared to other known methods of synthesis of these substances⁶⁻¹⁰, the advantage of the method employed by us lies in that it unambiguously leads to the formation of monoalkyl derivatives. These were isolated, after hydrolysis of the corresponding alkyl tosyl derivatives, as hydrochlorides.



- I, $R^1 = R^2 = R^3 = R^4 = H$
 II, $R^1 = R^3 = H$; $R^2 = R^4 = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$
 III, $R^1 = R^3 = \text{CH}_3$; $R^2 = R^4 = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$
 IV, $R^1 = R^3 = \text{C}_2\text{H}_5$; $R^2 = R^4 = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$
 V, $R^1 = R^3 = \text{CH}_3$; $R^2 = R^4 = H$
 VI, $R^1 = R^3 = \text{C}_2\text{H}_5$; $R^2 = R^4 = H$
 VII, $R^1 = R^2 = H$
 VIII, $R^1 = H$; $R^2 = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$
 IX, $R^1 = \text{CH}_3$; $R^2 = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$
 X, $R^1 = \text{C}_2\text{H}_5$; $R^2 = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$
 XI, $R^1 = \text{CH}_3$; $R^2 = \text{H.HCl}$
 XII, $R^1 = \text{C}_2\text{H}_5$; $R^2 = \text{H.HCl}$

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EXPERIMENTAL

The melting points were measured on a Kofler block. Unless stated otherwise, analytical samples were obtained by crystallization of the substances from ethanol. 4,4'-Diamino-1,1'-binaphthyl (*I*) was prepared according to literature¹¹. 1-Naphthylamine (*VI*) was a commercial product of Východočeské chemické závody, Pardubice-Rybitví.

N,N'-Di-*p*-toluenesulphonyl-4,4'-diamino-1,1'-binaphthyl (*II*)

To a solution of 13 g of dihydrochloride of the base *I* in 40 ml of pyridine was added 20 g of *p*-toluenesulphochloride (m.p. 65–66°C, cyclohexane) over the period of 20 min. The temperature of the reaction mixture raised to 95°C, this temperature being maintained for another 15 min. The reaction mixture was then poured into 300 ml of water warmed up to 60°C. The precipitate was filtered with suction, washed by 250 ml of water and dissolved in 120 ml of 5% aqueous sodium hydroxide solution. The solution was shaken with activated charcoal and then filtered. The filtrate, while stirring, was made slightly acidic with hydrochloric acid (1 : 3) on a Congo-red test paper. The gel-like precipitate was allowed to stand at room temperature for 12 hours, then was decanted by two 150 ml portions of water, filtered and dried at 100°C, affording 8 g of the pink product. The analytical product, m.p. 236–237°C. For $C_{34}H_{28}N_2O_4S_2$ (592.7) calculated: 68.89% C, 4.76% H, 4.73% N, 10.82% S; found: 68.52% C, 4.75% H, 4.49% N, 10.41% S.

N,N'-Dimethyl-*N,N'*-di-*p*-toluenesulphonyl-4,4'-diamino-1,1'-binaphthyl (*III*)

To a solution of 9 g of compound *II* in 60 ml of 5% aqueous sodium hydroxide, 10.3 ml of dimethyl sulphate were added in portions. After standing for 2–4 minutes, a portion of the product precipitated from the emulsion formed. The suspension was shaken for 4 hours, then it was allowed to stand for 1 hour. The precipitate was collected by filtration, washed by water until neutral, and then dried at 110°C, affording 7.5 g of product. The analytical product, m.p. 221–222°C. For $C_{36}H_{32}N_2O_4S_2$ (620.8) calculated: 69.65% C, 5.19% H, 4.51% N, 10.33% S; found: 69.62% C, 5.13% H, 4.81% N, 10.54% S.

N,N'-Diethyl-*N,N'*-di-*p*-toluenesulphonyl-4,4'-diamino-1,1'-binaphthyl (*IV*)

This compound (3.9 g) was prepared from 3.7 g of compound *II*, 25 ml of 5% aqueous sodium hydroxide and 6 ml of diethyl sulphate, using the same procedure as in the preparation of compound *III*. The analytical product, m.p. 261–262°C. $C_{38}H_{34}N_2O_4S_2$ (648.8) calculated: 70.34% C, 5.59% H, 4.32% N, 9.88% S; found: 69.96% C, 5.65% H, 4.29% N, 9.76% S.

N,N'-Dimethyl-4,4'-diamino-1,1'-binaphthyl (*V*)

A mixture of 4 g of compound *III* and 30–40 ml of concentrated hydrochloric acid was heated in a sealed ampoule to 140°C for 4–5 hours. After unsealing, the content of the ampoule was warmed up nearly to its boiling point and the undissolved residue was separated by filtration. The filtrate was diluted by water and then made neutral by addition of 20% aqueous sodium hydroxide, while stirring. It was then allowed to stand for 1 hour. The precipitate was filtered, washed by water until neutral and dried at 100°C, affording 2 g of the product. The crude product (c. 0.5 g) was then added to 60 ml of hot methanol with stirring; the undissolved portion was filtered. The filtrate was warmed up nearly to its boiling point and then gradually diluted by water until the solution turned cloudy. Then, the methanol was partially distilled off from the solution under vacuum. The product, which precipitated after cooling the solution to room temperature, was then filtered and dried at 110°C. The purification was twice repeated, affording the product of chromatographic purity, m.p. 235–236°C. For $C_{22}H_{20}N_2$ (312.4) calculated: 84.58% C, 6.45% H, 8.96% N; found: 84.11% C, 6.32% H, 8.87% N.

N,N'-Diethyl-4,4'-diamino-1,1'-binaphthyl (VI)

The same procedure as in the preparation of compound V afforded 5.6 g of compound VI from 10 g of compound IV. The product of chromatographic purity was obtained after twofold purification of the crude product; m.p. 195–196°C. For $C_{24}H_{24}N_2$ (340.45) calculated: 84.66% C, 7.11% H; 8.22% N; found: 84.16% C, 6.98% H, 8.21% N.

N-*p*-Toluenesulphonyl-1-naphthylamine (VIII)

Treatment of 28.8 g of 1-naphthylamine (VII) with 39.8 g of *p*-toluenesulpho chloride in 20 g of pyridine, described in detail in the preparation of compound II, afforded 48.5 g of the tosyl derivative VIII, m.p. 153–157°C. The analytical product, m.p. 156–157°C. For $C_{17}H_{15}NO_2S$ (297.4) calculated: 68.66% C, 5.89% H, 4.71% N, 10.78% S; found: 68.48% C, 5.16% H, 4.89% N, 10.96% S.

N-Methyl-N-*p*-toluenesulphonyl-1-naphthylamine (IX)

The alkylation of 10 g of compound VIII in 60 ml of 5% aqueous sodium hydroxide solution by 15 ml of dimethyl sulphate furnished 7 g of compound IX, m.p. 124–127°C. The analytical product, m.p. 127–128°C. For $C_{18}H_{17}NO_2S$ (311.4) calculated: 69.42% C, 5.50% H, 4.49% N, 10.29% S; found: 69.02% C, 5.74% H, 4.59% N, 10.20% S.

N-Ethyl-N-*p*-toluenesulphonyl-1-naphthylamine (X)

The alkylation of 10 g of substance VIII, dissolved in 60 ml of 5% aqueous sodium hydroxide, with 12.5 ml of diethyl sulphate yielded 8 g of the compound having m.p. 145–153°C. The analytical product, m.p. 154–155°C. For $C_{19}H_{19}NO_2S$ (325.4) calculated: 70.12% C, 5.89% H, 4.31% N, 9.85% S; found: 69.64% C, 6.14% H, 4.48% N, 9.53% S.

TABLE I
 R_f -Values

Compound	S_1^b	S_2^b	Spray ^c
XI ^a	0.55 bv	0.79 b	violet
N,N-Dimethyl-1-naphthylamine	0.90 v	0.50 b	red-violet
XII ^a	0.73 b	0.69 b	violet
N,N-Diethyl-1-naphthylamine	0.94 bv	0.28 bv	red-violet
V	0.13 bg	0.78 b	violet
N,N,N',N'-Tetramethyl-4,4'-diamino-1,1'-binaphthyl	0.96 gb	0.17 v	pink
VI	0.54 bg	0.54 b	violet
N,N,N',N'-Tetraethyl-4,4'-diamino-1,1'-binaphthyl	0.93 gb	0.18 b	pink

^a The hydrochlorides of the bases XI and XII were deposited and the bases were released by contacting the spots at the start with ammonia vapours; ^b fluorescence, b blue, v violet, g green; ^c the colour after spraying by diazotated *p*-nitroaniline.

N-Methyl-1-naphthylamine hydrochloride (XI)

A mixture of 7 g of compound IX and 30 ml of concentrated hydrochloric acid was heated in a sealed ampoule to 150°C for 4 hours. Then the ampoule was discharged, its content was warmed up and the insoluble residue was filtered. The filtrate was diluted with water and, while stirring, made neutral with 20% aqueous sodium hydroxide. After shaking with ethyl acetate, saturated with argon, the layer was separated, filtered with activated charcoal, and dried by standing over anhydrous sodium sulphate. After addition of ethyl acetate saturated by dry hydrogen chloride, in the ratio 1 : 1, the solution was allowed to stand for 15 min. Then, about the half volume of the solvent was distilled off under reduced pressure at 40°C. After the period of 2 hours, the precipitated hydrochloride of the base XI was filtered with suction. A total of 3.1 g of the compound melting 154–156°C was obtained. The crude product was purified by decomposition of an aqueous solution of the hydrochloride by 20% aqueous sodium hydroxide and by repeating the procedure described above, which afforded the product of chromatographic purity, m.p. 156–157°C. For $C_{11}H_{12}ClN$ (193.7) calculated: 68.21% C, 6.25% H, 18.31% Cl, 7.23% N; found: 68.45% C, 6.30% H, 18.40% Cl, 7.28% N.

N-Ethyl-1-naphthylamine hydrochloride (XII)

Treatment of 10 g of compound X with 45 ml of concentrated hydrochloric acid, after hydrolysis carried out in the same way as in the case of compound XI, yielded a solution which was filtered, diluted by water 1 : 1 and cooled. The crystalline hydrochloride was then filtered, dissolved in the appropriate amount of boiling 2M-HCl and shaken with activated charcoal. The solution was then filtered and cooled to room temperature. The obtained hydrochloride of the base XII was of chromatographic purity, m.p. 183–184°C. For $C_{12}H_{14}ClN$ (207.7) calculated: 69.39% C, 6.79% H, 17.07% Cl, 6.74% N; found: 69.50% C, 6.85% H, 16.98% Cl, 6.72% N.

Paper Chromatography

The R_F values obtained by descending paper chromatography of compounds V, VI, XI, and XII carried out on a Whatman No 3 paper using the systems 30% dimethylformamide in methanol/n-hexane (S_1) and 5% paraffin oil in n-hexane/80% methanol (S_2), are listed in Table I.

The elemental analyses were carried out in the Center of Organic Elemental Analyses of this Institute under the direction of Mr J. Bulušek.

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