Russian Journal of Organic Chemistry, Vol. 38, No. 5, 2002, pp. 699–708. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 5, 2002, pp. 737–746.

peri-Naphthalenediamines: XXXIV. 1,4,5,8-Tetrakis(dimethylamino)naphthalene: Alternative Approaches to Synthesis*

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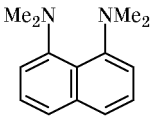
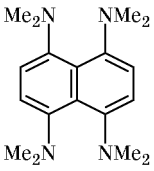
Abstract—New methods were proposed for synthesizing 1,4,5,8-tetrakis(dimethylamino)naphthalene with an overall yield of 4 to 12% to replace the known procedure ensuring an overall yield of 2%. Catalytic hydrogenation was shown to be inapplicable for preparation of polyaminonaphthalenes from nitro compounds having 3 or 4 nitro gruops in the α-positions. Nucleophilic amination of 1,5-dinitronaphthalene in the system NH_2OH/NaOH/MeOH yields 1-amino-4-nitronaphthalene. The nitration of 1,5-bis(*p*-tolylsulfonylamino)-naphthalene leads to formation of 2,6-dinitro rather than 4,8-dinitro derivative, as it was believed formerly. This was confirmed by transformation of the latter into 1,2,5,6-tetrakis(dimethylamino)naphthalene. 3-Nitro, 2,6-dinitro, 2,6-diamino, and 2,4,6,8-tetranitro derivatives of 1,5-bis(dimethylamino)naphthalene, nitro and amino derivatives of 1,4,5-tris(dimethylamino)naphthalene, and 4,5-diamino-1,8-bis(methylamino)naphthalene were synthesized. By treatment with perchloric acid 1,4,5,8-tetrakis(dimethylamino)naphthalene was oxidized to 2,3-dihydroperimidinium salt.

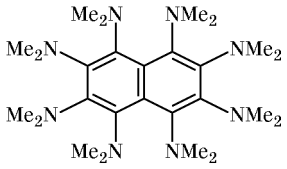
Physical and chemical properties of 1,8-bis(dimethylamino)naphthalene (**I**, "proton sponge") have been extensively studied [1]. However, analogous properties of 1,4,5,8-tetrakis(dimethylamino)naphthalene (**II**, "double proton sponge"), which was synthesized in 1991, remain almost unknown: only its protonation [2] and oxidation [3] have been reported. Nevertheless, functional derivatives of tetraamine **II** could form the basis for synthesizing multidentate organic bases, e.g., compound **III**.



I



II



III

The main reason which restricts the use of compound **II** in chemical transformations is that it is difficult to obtain. Staab *et al.* [2] proposed a multistep scheme for preparation of compound **II** in an overall yield of ~2% (Scheme 1). Taking into account that perimidinone **IV** is obtained from 1,8-diaminonaphthalene in two steps, the overall number of steps connecting the initial compound (1,8-diaminonaphthalene) with target product **II** amounts to seven.

The goal of the present study was to develop alternative routes to tetraaminonaphthalene **II**. First of all, we have found that the transformations shown in Scheme 1 [2] are not always optimal. For example, the synthesis of **V** from **IV** is more efficient when the reaction is carried out in two steps through mononitro derivative **IX**. In such a way, the yield of **V** is raised to 44% against 33% in [2] (cf. [4]). Furthermore, the number of steps in Scheme 1 can be reduced via direct transformation of **VI** into **II** through amine **X** without loss in efficiency (see Experimental). Thus, modification of the procedure given in [2] allowed us to increase the overall yield of "double proton sponge" **II** up to 3%.

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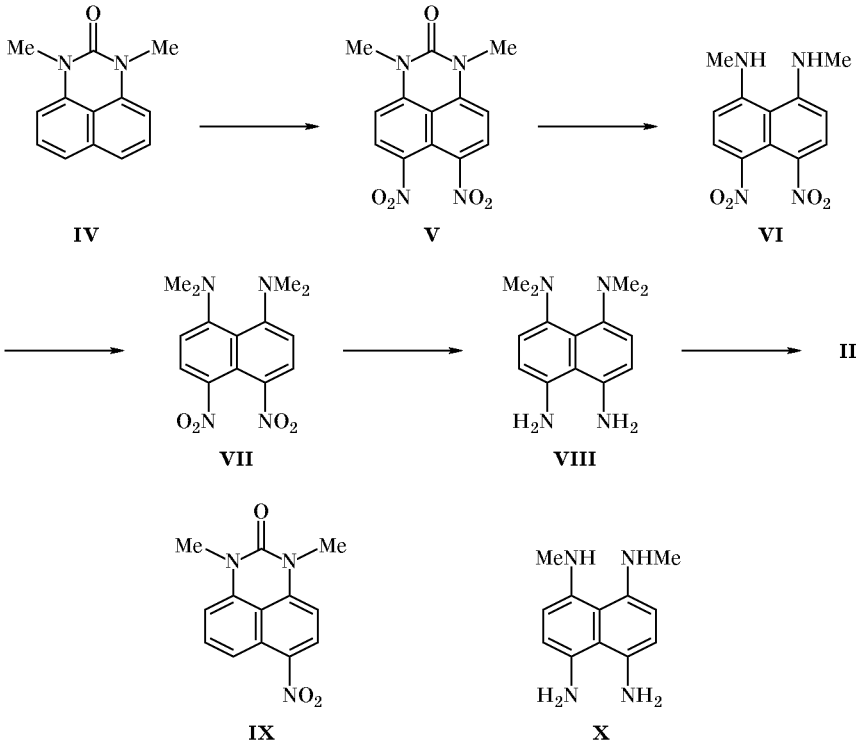
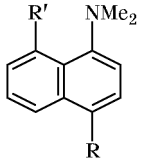
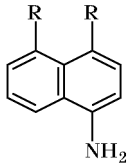
Scheme 1.



An alternative route to proton sponge **II** involves its most obvious precursor, 1,4,5,8-tetranitronaphthalene (**XI**), as starting compound. However, we have encountered with a number of difficulties while developing this approach. First, the yield of **XI** from 1,5-dinitronaphthalene does not exceed 25% [5], which makes the procedure insufficiently effective at the startup. Second, our attempt to synthesize 1,4,5,8-tetraaminonaphthalene (**XII**) by catalytic hydrogenation with hydrogen over Pd/C, N_2H_4 over $FeCl_3$/C, and N_2H_4 over Raney nickel rather than by reduction of nitronaphthalene **XI** with tin(II) chloride [6] resulted in formation of 1,5-diaminonaphthalene in high yield instead of the expected tetraamino derivative; i.e., the hydrogenation was accompanied by elimination of two nitrogen-containing groups. We have found that an analogous transformation (to give 1,5-diaminonaphthalene) also occurs in the catalytic hydrogenation of 1,4,5-trinitronaphthalene (**XIII**) in which the nitro groups are arranged similarly. These results suggest that the number of nitro groups and their positions are the key factors responsible for the observed elimination process: 1,5- and 1,8-dinitronaphthalenes are smoothly hydrogenated to the corresponding diamines [7] (see Experimental). We have found no published data on analogous transformations. Some similarity may be drawn with the formation of compound **XIV** by hydrogenation of 1,8-bis(dimethylamino)-4-nitronaphthalene (**XV**) over Pd/C [8]. However, in the latter case the group being lost is dimethylamino and its elimination occurs on prolonged reduction from amine **XVI** rather than from compound **XV**. We failed to detect formation of tetra- (**XII**) or triamino derivative (**XVII**) in the hydrogenation of the corresponding nitro compounds. This means that elimination of nitrogen-containing groups occurs from some intermediate product. In fact, 1-amino-4,5-dinitronaphthalene (**XVIII**) can be obtained by reduction of **XIII** in the system H_2/Pd/C. Therefore, the first stage of the process is reduction of the least sterically hindered nitro group.



XIV–XVI



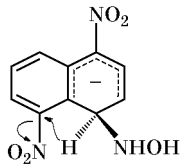
XVII, XVIII

XIV, R = NH_2, R′ = H; **XV**, R = NO_2, R′ = NMe_2; **XVI**, R = NH_2, R′ = NMe_2; **XVII**, R = NH_2; **XVIII**, R = NO_2.

Compound **XVIII** was also obtained in a small yield by independent synthesis, via nucleophilic

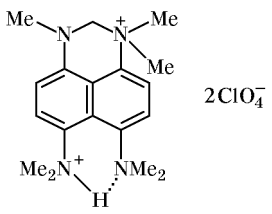
amination of 1,8-dinitronaphthalene in the system $NH_2OH/NaOH/MeOH$ [9]. It should be noted that monoamine **XVIII** is formed even in the presence of a 10-fold amount of the aminating agent. We failed to detect in the reaction mixture 1,8-diamino-4,5-dinitronaphthalene which we planned to use as precursor of compound **II**.

One more example of elimination of nitrogen-containing group was observed in the amination of 1,5-dinitronaphthalene performed under analogous conditions ($NH_2OH/NaOH/MeOH$). Contrary to the expectations, we obtained 1-amino-4-nitronaphthalene (**XIX**), i.e., nucleophilic replacement was accompanied by elimination of the nitro group. Presumably, the replacement occurred in intermediate σ-adduct **XX** as a result of hydride ion migration (cf. [10, 11]).



XX

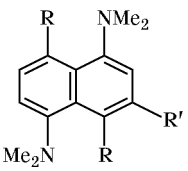
Insofar as we failed to obtain tetraamine **XII** by catalytic hydrogenation, we synthesized it in more than 80% yield from nitro compound **XI** by modified procedure [6]. We were the first to characterize compound **XII** in the pure state rather than its derivatives. Unfortunately, our attempts to effect the transformation **XII** → **II** with the aid of various alkylating agents [MeI/KOH//DMSO (DMF), $MeI/K_2CO_3/MeOH$, and $Me_2SO_4/Na_2CO_3/H_2O$] were unsuccessful. The only procedure which gave a positive result was the so-called Quast method [12] utilizing the system $Me_2SO_4/NaH/THF$. In this case the yield of **II** was 14%. We tried to isolate compound **II** as a salt with perchloric acid but obtained dihydroperimidinium salt **XXI** instead of the expected diperchlorate $\mathbf{II} \cdot 2HClO_4$. However, there was no problem, for salt **XXI**, like other dihydroperimidinium salts [13], can readily be converted into tetraamine **II** with a high yield by the action of $NaBH_4$ in acetonitrile.



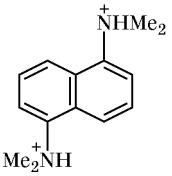
XXI

Barth *et al.* [3] previously synthesized an analogous salt containing I_3^- as counterion by oxidation of proton sponge **II** with iodine. The ^1H NMR spectra of this salt and salt **XXI** are almost similar. Up to now, no formation of oxidation products was observed in the synthesis of salts of diamine **I** derivatives, which indicates strong donor properties of molecule **II** [2]. For instance, compound **II** smoothly gives the corresponding salt with HBF_4 which has no oxidizing properties.

It seemed very promising to make use of previously unknown 1,5-bis(dimethylamino)-4,8-dinitronaphthalene (**XXII**) as precursor of **II**. For this purpose, it was necessary to develop a convenient procedure for synthesizing dinitrodiamine **XXII**. As a possible way we examined nitration of 1,5-bis(dimethylamino)-naphthalene (**XXIII**).



XXII–**XXIV**



XXIII·$2H^+$

XXII, R = NO_2, R′ = H; **XXIII**, R = R′ = H; **XXIV**, R = H, R′ = NO_2.

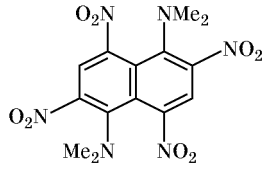
Compound **XXIII** was synthesized by (1) alkylation of 1,5-diaminonaphthalene with methyl iodide in the system KOH/DMF (yield 84%) and (2) reductive methylation of 1,5-diaminonaphthalene in the system $CH_2O/NaBH_4/H_3O^+$ following the procedure reported in [14] (yield 62%). Both these methods turned out to be more efficient than that described in [15].

Treatment of diamine **XXIII** with 2 equiv of concentrated nitric acid in sulfuric acid at 0°C led to formation of previously unknown nitronaphthalene **XXIV** as the major product (yield 40%). Its structure was unambiguously confirmed by the ^1H NMR spectrum which displayed spin–spin couplings between 2-H and 4-H (^4J = 2.3 Hz) and between 4-H and 8-H (^5J = 0.8 Hz).

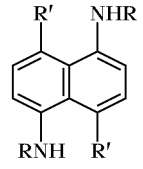
meta-Substitution by the action of nitrating mixture is typical for most tertiary arylamines, e.g., for *N*,*N*-dimethylaniline [16]. Under these conditions, the nitration occurs with dication **XXIII**·$2H^+$. In acetic acid or acetonitrile, the major product was tetranitro derivative **XXV** (30–32%) even when the nitration was carried out using 2 equiv of HNO_3. Thus, we cannot accomplish selective nitration of neutral base **XXIII** because of strong activation of the naphthalene

ring by the dimethylamino groups. The same factor was responsible for our failure to effect selective transformation **I → VII** [17].

According to Nielsen *et al.* [18], amides **XXVI** and **XXVII** which are less reactive 1,5-diaminonaphthalene derivatives are selectively nitrated to the corresponding dinitro compounds **XXVIII** and **XXIX** in ~70% yield. However, as well as the authors of [18], we failed to remove the *N*-acetyl groups from compound **XXVIII** by acid or alkaline hydrolysis.



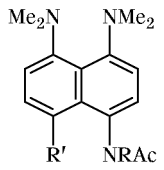
XXV



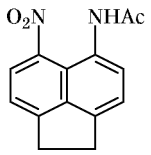
XXVI–XXIX

XXVI, R = Ac, R′ = H; **XXVII**, R = Ts, R′ = H; **XXVIII**, R = Ac, R′ = NO_2; **XXIX**, R = Ts, R′ = NO_2.

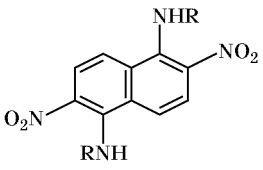
A similar problem arose with nitro derivative **XXX** which is obtained in 86% yield by nitration of acetamide **XXXI**. Compound **XXX** was readily alkylated to give amide **XXXII**, but the *N*-acetyl group therein remained unchanged under hydrolysis conditions (10% or concentrated hydrochloric acid, 25% H_2SO_4, 10% KOH, K_2CO_3, NaOAc, piperidine in water or ethanol). The observed behavior of nitroamides **XXVIII**, **XXX**, and **XXXII** may be interpreted in terms of steric shielding of the acetyl carbonyl group by the bulky nitro group in the neighboring *peri* position. Indeed, acenaphthene derivative **XXXIII** in which the nitro and acetylamino groups are more distant from each other (presumably, due to shrinking effect of the ethylene bridge [19]) is readily hydrolyzed to the corresponding amine in 10% hydrochloric acid [20].



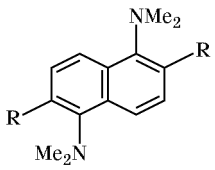
XXX–XXXII



XXXIII



XXXIV, XXXV

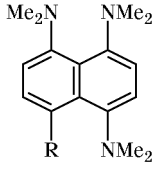


XXXVI–XXXVIII

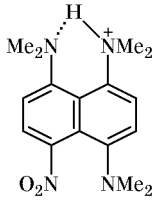
XXX, R = H, R′ = NO_2; **XXXI**, R = R′ = H; **XXXII**, R = Me, R′ = NO_2; **XXXIV**, R = Ts; **XXXV**, R = H; **XXXVI**, R = NO_2; **XXXVII**, R = NH_2; **XXXVIII**, R = NMe_2.

While attempting to reproduce the synthesis of 1,5-diamino-4,8-dinitronaphthalene from bis(*p*-tolylsulfonyl) derivative **XXIX**, reported in [18], we have found that the product obtained by nitration of **XXVII** was assigned invalid structure. In the system HNO_3–AcOH nitro groups enter positions *2* and *6* (to give dinitro compound **XXXIV**) rather than *4* and *8* (as was assumed in [18]). The nitration direction is confirmed by a series of consecutive transformations including hydrolysis of **XXXIV** to diamine **XXXV**, alkylation to **XXXVI** (the best results were obtained in the system MeI/KOH/acetone or acetonitrile, yield 50%), reduction with $SnCl_2$ in hydrochloric acid to diamine **XXXVII**, and methylation of the latter with dimethyl sulfate in H_2O/Na_2CO_3. As a result, we obtained 1,2,5,6-tetrakis(dimethylamino)naphthalene (**XXXVIII**) which was described in [21]. It should be noted that the above sequence leading to proton sponge **XXXVIII** is much more efficient than the procedure proposed in [21].

The best procedure for preparation of double proton sponge **II** is now that developed by us starting from 1,4,5-tris(dimethylamino)naphthalene (**XXXIX**) [8]. In the present communication we describe an alternative route to compound **XXXIX** which is available directly from triamine **XVII**. The latter is prepared by reduction of 1,4,5-trinitronaphthalene. The proposed procedure is characterized by the same efficiency as that described in [8], but it includes two steps less. Here, one of the ways of effecting the transformation **XVII → XXXIX**, namely exhaustive methylation in the system $Me_2SO_4/Na_2CO_3/H_2O$ according to the modified procedure [22], is very simple. It was also applied to a series of naphthylamines (see Experimental). It should be noted that triamine **XXXIX** is not oxidized with perchloric acid, and stable perchlorate **XXXIX** · $HClO_4$ is obtained [8].



XXXIX–XLI



XL · H^+

XXXIX, R = H; **XL**, R = NO_2; **XLI**, R = NH_2.

We expected that in acid medium compound **XXXIX** will give rise to a cation stabilized by intra-

Synthetic routes to 1,4,5,8-tetrakis(dimethylamino)naphthalene (**II**)

Method no.	Starting compound	Reaction sequence	Number of steps *N*	Overall yield of **II**, Σ%	Efficiency, Σ%/*N*
1 (original)	1,8-Diamino-naphthalene	→ → **IV** → **V** → **VI** → **VII** → **VIII** → **II**	7	~2	0.3
1 (modified)	1,8-Diamino-naphthalene	→ → **IV** → **IX** → **V** → **VI** → **X** → **II**	7	~3	0.4
2	1,5-Dinitro-naphthalene	→ **XI** → **XII** → **II**	3	4	1.3
3	1,8-Diamino-naphthalene	→ **I** → **XV** → **XVI** → **XXXIX** → **XL** → **XLI** → **II**	7	12	1.7
4	1,5-Dinitro-naphthalene	→ **XIII** → **XVII** → **XXXIX** → **XL** → **XLI** → **II**	6	10	1.6

molecular hydrogen bond, so that the nitration will occur at the only vacant *peri* position. In fact, by treatment of **XXXIX** with 1 equiv of nitric acid in concentrated sulfuric acid at –30°C (4 min) we succeeded in isolating for the first time 1,4,5-tris-(dimethylamino)-8-nitronaphthalene (**XL**) in 40% yield. Also, some tarry products were formed. The best results were obtained when the nitration was performed with the salt of **XXXIX** with HBF_4. In this case the yield of nitro derivative **XL** attained 50%. The use of milder nitrating systems, e.g., HNO_3/Ac_2O or NO_2BF_4/MeCN, resulted in strong tarring, and no target product **XL** was isolated.

Compound **XL** is the first proton sponge having both donor and acceptor groups in differents rings of the naphthalene system. Analysis of the ^{1}H NMR spectrum of perchlorate **XL** · $HClO_4$ in CD_3CN showed that the NH proton in **XL** · H^+, which is involved in intramolecular hydrogen bond, is displaced toward the 4-NMe_2 group by 63% (calculated from the corresponding coupling constants); however, this displacement is not so strong as expected. A possible reason is that the 8-NO_2 and 1-NMe_2 groups are not coplanar because of *peri* interaction. Compound **XL** is a much weaker base than proton sponge **I**; its pK_a^1 value in DMSO is 5.0 (estimated by the trans-protonation technique [8]) against to 7.5 for diamine **I** [23]. These data suggest that the 1-dimethylamino group which does not participate in intramolecular H-bonding deviates from the naphthalene ring plane more strongly than the nitro group. Hence the latter determines the reduced basicity of **XL**. The pK_a value of nitroamide **XXX** is even smaller: it is equal to 3.8.

Compound **XL** is smoothly reduced to amine **XLI** with $SnCl_2$ in hydrochloric acid (yield ~80%), and methylation of **XLI** with the system MeI/KOH/DMF or Me_2SO_4/NaH/THF gives up to 30% of proton sponge **II**. The best results were obtained by alkylation of **XLI** according to the modified procedure [22] ($Me_2SO_4/Na_2CO_3/H_2O$). In such a way, the yield of **II** was raised to 40%. This procedure allowed us to convert 1,8-diaminonaphthalene into compound **I** in more than 90% yield without resorting to inert atmosphere. Thus, it is the simplest and cheapest among all known methods for synthesis of compound **I** (cf. [1]). The principal results of the present study, as well as comparative analysis of the proposed and previously known approaches to tetraamine **II**, are given in table.

It is seen that, despite a number of steps, method no. 3 turns out to be the most efficient. It combines proton sponges **I**, **XXXIX**, and **II** into a single synthetic sequence. On the other hand, method no. 2 may be regarded as one of the most convenient, for it includes the least number of steps.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker DPX-250 instrument at 250 MHz using tetramethylsilane as internal reference. The IR spectra were obtained on a Specord 75IR spectrometer. The UV spectra were measured on a Specord M-40 spectrophotometer. Column chromatography was performed using Al_2O_3 or silica gel L 40/100 μm (Chemapol). The progress of reactions and the purity of products were monitored by TLC on Al_2O_3 and Silufol plates; development with iodine vapor. The melting points were determined in a sealed capillary using a PTP device and were not corrected. Sodium hydride was used as a 50% dispersion in mineral oil (Aldrich).

1,3-Dimethyl-6-nitroperimidin-2(1*H*)-one (IX). The reaction was carried out following the procedure

described in [4]. A solution of 0.35 g (5.1 mmol) of $NaNO_2$ in 2 ml of water was added to a solution of 1.06 g (5 mmol) of dimethylperimidinone **IV** [24] in 50 ml of glacial acetic acid. The mixture was stirred for 1 h at 20°C, and the resulting orange suspension was poured into 200 ml of water. The product was filtered off, washed with water, dried at 100°C, and recrystallized from toluene. Yield 1.08 g (84%). Orange needles, mp 261–262°C (published data [4]: mp 262°C). IR spectrum (mineral oil), ν, cm^{-1}: 1680 (C=O); 1628, 1583 ($C-C_{arom}$); 1519, 1325 (NO_2). UV spectrum (MeOH), λ_{max}, nm ($\log\varepsilon$): 255 (4.09), 276 (4.05), 345 (3.09).

1,3-Dimethyl-6,7-dinitroperimidin-2(1*H*)-one (V). Concentrated nitric acid (d = 1.41), 0.14 ml (2.2 mmol), was added in one portion to a solution of 0.5 g (1.9 mmol) of compound **IX** in 90 ml of AcOH, stirred at 100°C. The bright orange mixture was stirred for 1.5 h at 100°C and cooled to 20°C. The product was filtered off and washed with acetic acid and water on a filter. Yield 0.32 g (54%). Yellow–orange powder which did not melt below 340°C (published data [2]: decomposes at 310°C). IR spectrum (mineral oil), ν, cm^{-1}: 1691 (C=O); 1625, 1580 ($C-C_{arom}$); 1519, 1321 (NO_2).

General procedure for the reduction of compounds with tin(II) chloride. Nitro compound, 0.05 g, was thoroughly mixed with 2 ml of EtOH, and a solution of 2 equiv of $SnCl_2\cdot 2H_2O$ in 3 ml of concentrated hydrochloric acid was added to the resulting solution or suspension. The mixture was stirred for a definite time at a required temperature (indicated below for each compound). The mixture was then poured in portions into a large excess of a concentrated solution of sodium hydroxide (on cooling with ice), each time with stirring until tin compounds dissolved completely. The product was extracted into diethyl ether (peroxide-free), the extract was evaporated, and the resulting amine was brought into further transformations.

1,8-Bis(methylamino)-4,5-dinitronaphthalene (VI) was synthesized from nitro derivative **V** by the procedure described in [2]. mp 263–264°C (from DMF) (published data [2]: decomposes at 235°C). IR spectrum (mineral oil), ν, cm^{-1}: 3340 (NH); 1600, 1500 ($C-C_{arom}$).

4,5-Diamino-1,8-bis(methylamino)naphthalene (X) and its transformation into 1,4,5,8-tetrakis(dimethylamino)naphthalene (II). Following the above general procedure, nitronaphthylamine **VI**, 0.1 g (0.36 mmol), was reduced with 1.2 g (4.6 mmol) of $SnCl_2\cdot 2H_2O$ (2.5 h, 25°C) to obtain tetraamine **X**. The yield of **X** was not determined, for the amine undergoes very fast oxidation on exposure to air. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.74 s (6H, NMe), 4.8 br.s (6H, NH), 6.60 d (2H, 3-H, 6-H, $J_{2,3}$ = 7.9 Hz), 6.66 d (2H, 2-H, 7-H).

Amine **X** was alkylated according to Quast [12]. It was dissolved in 40 ml of anhydrous THF, and 0.036 g (0.76 mmol) of NaH and 0.07 ml (0.74 mmol) of dimethyl sulfate were added to the solution under stirring in an inert atmosphere. The mixture was stirred for 10 min at 25°C and for 6 h at 60°C, carefully diluted (while stirring) with 60 ml of 20% aqueous KOH, and extracted with hexane (4 × 10 ml). The extract was evaporated, and the residue was subjected to column chromatography on Al_2O_3 (Brockman activity grade II; eluent ethyl acetate). From the yellow fraction with R_f 0.50 we isolated 0.01 g (9%) of 1,4,5,8-tetrakis(dimethylamino)naphthalene (**II**). Yellow needles, mp 193–194°C (from pentane) (published data [2]: mp 193.5°C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.76 s (24H, NMe_2), 6.79 s (4H, H_{arom}). UV spectrum (EtOH), λ_{max}, nm ($\log\varepsilon$): 245 (4.42), 361 (4.11), tail absorption up to 450 nm.

Catalytic hydrogenation of 1,4,5,8-tetranitronaphthalene (XI). Compound **XI** was synthesized by the procedure reported in [5]. Decomposition point 343°C (from acetone–EtOH, 1:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.82 s (4H, H_{arom}). The hydrogenation was performed at 25°C using 0.05 g (0.16 mmol) of nitronaphthalene **XI**, 30 ml of MeOH, and 0.05 g of the catalyst (2% Pd/C). After 15 h, the mixture was filtered, and the solvent was removed to obtain 0.023 g (90%) of 1,5-diaminonaphthalene. The product was identical to a sample prepared by hydrogenation of 1,5-dinitronaphthalene under analogous conditions. Following the same procedure, from 1,8-dinitronaphthalene we obtained in 5 h 95% of 1,8-diaminonaphthalene.

Catalytic hydrogenation of 1,4,5-trinitronaphtalene (XIII). Compound **XIII** was synthesized by the procedure reported in [5]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.10 t (1H, 7-H, $J_{6,7}$ = 7.9, $J_{7,8}$ = 8.6 Hz), 8.56 d (1H, 8-H, $J_{6,8}$ = 1.0 Hz), 8.62 m (3H, 2-H, 3-H, 6-H, $J_{2,3}$ = 8.2 Hz). By hydrogenation of **XIII** for 10 h at 20°C we obtained almost 100% of 1,5-diaminonaphthalene.

When the hydrogenation was terminated after 3 h, the solvent was removed, and the residue was subjected to column chromatography on silica gel with ethyl acetate as eluent, a bright yellow fraction was collected (R_f 0.87) from which we isolated 10% of 1-amino-4,5-dinitronaphthalene (**XVIII**). Red crystals,

mp 245–246°C (from butanol) (cf. [25]). IR spectrum (mineral oil), ν, cm^{-1}: 3485, 3370, 1640 (NH_2); 1525, 1340 (NO_2). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.79 d (1H, 3-H, $J_{2,3}$ = 9.0 Hz), 7.71 t (1H, 7-H, $J_{6,7}$ = 8.4 Hz), 7.78 br.s (2H, NH_2), 8.30 m (2H, 2-H, 8-H), 8.65 d (1H, 6-H).

Amination of 1,8-dinitronaphthalene. The reaction was carried out by the modified procedure [9]. To a solution of 0.05 g (0.23 mmol) of 1,8-dinitronaphthalene in 5 ml of MeOH we added 0.1 g (1.4 mmol, 6 equiv) of $NH_2OH \cdot HCl$ and then 0.16 g (2.9 mmol) of powdered KOH. The mixture was heated to the boiling point and was refluxed for 1 h. The yellow–orange solution was poured into 20 ml of water, and the bright yellow precipitate was filtered off and subjected to column chromatography on Al_2O_3 of Brockman activity grade III (eluent benzene–ethyl acetate, 2 : 1). An orange fraction, R_f 0.60, was collected. We isolated 0.01 g (19%) of compound **XVIII** which was identical to a sample obtained by incomplete hydrogenation of trinitronaphthalene **XIII**.

Amination of 1,5-dinitronaphthalene. A solution of 0.16 g (2.9 mmol) of powdered KOH in 5 ml of MeOH was added in one portion to a suspension of 0.05 g (0.23 mmol) of 1,5-dinitronaphthalene and 0.1 g (1.4 mmol) of $NH_2OH \cdot HCl$ in 8 ml of MeOH. The mixture was stirred for 2 h at 50°C and poured into 30 ml of water, and the yellow precipitate was filtered off and subjected to column chromatography on Al_2O_3 of Brockman activity grade III (eluent chloroform). A yellow fraction, R_f 0.30 was collected. Yield of 1-amino-4-nitronaphthalene (**XIX**) 0.02 g (46%), mp 190–191°C (published data [11]: 191°C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.68 d (1H, 2-H, $J_{2,3}$ = 8.9 Hz), 7.54 d.d.d (1H, 6-H, $J_{6,8}$ = 0.7 Hz), 7.58 br.s (2H, NH_2), 7.75 d.d.d (1H, 7-H, $J_{6,7}$ = 7.4, $J_{5,7}$ = 1.4 Hz), 8.30 d.d (1H, 5-H, $J_{5,6}$ = 8.5 Hz), 8.39 d (1H, 3-H), 8.91 d.d (1H, 8-H).

1,4,5,8-Tetraaminonaphthalene (XII) and its transformation into 1,4,5,8-tetrakis(dimethylamino) naphthalene (II). Following the general procedure (see above), nitronaphthalene **XI** was reduced with tin(II) chloride (2.5 h, 40°C). Yield of **XII** 82%, bluish powder which rapidly turns dark on exposure to air and undergoes very ready oxidation in solution, mp 160–162°C. The product is well soluble in dilute mineral acids. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.1 br.s (8H, NH_2), 6.57 s (4H, H_{arom}).

The alkylation of **XII** was carried out by a procedure similar to the alkylation of amine **X**. Amine **XII** prepared from 0.1 g (0.32 mmol) of nitro derivative **XI** was treated with 0.48 ml (5 mmol) of Me_2SO_4 in the presence of 0.24 g (5 mmol) of NaH. The yield of **II** was 0.014 g (14%). It was identical in physical properties to a sample obtained by alkylation of compound **X**. Treatment of the hexane extract with 0.055 ml (0.64 mmol) of 70% perchloric acid gave 0.028 g of a solid which was recrystallized from methanol to obtain 6,7-bis(dimethylamino)-1,1,3-trimethyl-2,3-dihydro-1*H*-perimidinium diperchlorate (**XXI**) as a grayish powder decomposing at 280–282°C. ^1H NMR spectrum (CD_3CN), δ, ppm: 3.04 d (6H, 7-NMe_2, $J_{NH,NMe}$ = 1.1 Hz), 3.19 d (6H, 6-NMe_2, $J_{NH,NMe}$ = 3.5 Hz), 3.36 s (3H, 3-NMe), 3.53 br.s (6H, 1-NMe_2), 4.85 s (2H, 2-H), 7.24 d (1H, 4-H, $J_{4,5}$ = 8.7 Hz), 7.99 d (1H, 9-H, $J_{8,9}$ = 8.8 Hz), 8.04 m (2H, 5-H, 8-H), 18.27 br.s (1H, NH).

Addition of a small excess of $NaBH_4$ to a solution of salt **XXI** in acetonitrile at 25°C almost instantaneously gave 1,4,5,8-tetrakis(dimethylamino)naphthalene (**II**) in nearly quantitative yield [13].

1,4,5,8-Tetrakis(dimethylamino)naphthalene bis(tetrafluoroborate) (II · 2HBF$_4$). Compound **II**, 0.02 g (0.067 mmol), was dissolved in 2 ml of ether, 0.016 ml (0.13 mmol) of 60% HBF_4 was added, the mixture was vigorously shaken for 2 min, and the precipitate was separated by decanting and washed with ether. Yield quantitative. Grayish powder, mp 341–343°C (from methanol); published data [2]: decomposition point 280°C. ^1H NMR spectrum (CD_3CN), δ, ppm: 3.12 s (24H, NMe_2), 8.12 s (4H, H_{arom}), 19.03 br.s (2H, NH).

1,5-Bis(dimethylamino)naphthalene (XXIII). A solution of 1.58 g (0.01 mol) of 1,5-diaminonaphthalene in 20 ml of DMF was stirred for 3 min in an inert atmosphere, 4.48 g (0.08 mol) of powdered KOH was added, the mixture was stirred for 5 min, and 5 ml (0.08 mol) of methyl iodide was added. The mixture was stirred for 1 h at 20°C and for 1 h at 100°C, diluted with 100 ml of water, made alkaline by adding ammonia until persistent odor, and extracted with benzene (5 × 20 ml). The solvent was removed from the extract to obtain 1.8 g (84%) of compound **XXIII** as grayish crystals with mp 87–88°C (from EtOH); published data [15]: mp 87–88°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.87 s (12H, NMe_2), 7.05 d.d (2H, 2-H, 6-H, $J_{2,3}$ = 7.4, $J_{2,4}$ = 1.0 Hz), 7.38 d.d (2H, 3-H, 7-H, $J_{3,4}$ = 8.4 Hz), 7.92 d.d (2H, 4-H, 8-H).

Nitration of 1,5-bis(dimethylamino)naphthalene (XXIII). *a.* Compound **XXIII**, 0.05 g (0.23 mmol), was dissolved in 2 ml of H_2SO_4 (d = 1.84) at 0°C, 0.03 ml (0.047 mmol) of concentrated nitric acid

(d = 1.41) was added, and the mixture was vigorously stirred for 30 min at 0°C. It was then diluted with 15 ml of cold water, neutralized with concentrated aqueous ammonia until persistent odor, and extracted with chloroform (4 × 10 ml). The extract was evaporated to a minimal volume and was applied to a column charged with silica gel. The column was eluted with chloroform, and an orange–red fraction with R_f 0.60 was collected, from which we isolated 0.024 g (40%) of 1,5-bis(dimethylamino)-3-nitronaphthalene (**XXIV**) as an oily substance which crystallized on cooling to 0°C. Orange needles, mp 75–76°C (from MeOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.91 s and 2.92 s (6H each, 5-NMe_2 and 1-NMe_2), 7.11 d.d (1H, 6-H, $J_{6,7}$ = 7.6, $J_{6,8}$ = 0.9 Hz), 7.52 d.d (1H, 7-H, $J_{7,8}$ = 8.6 Hz), 7.71 d (1H, 2-H, $J_{2,4}$ = 2.3 Hz), 7.86 d.t (1H, 8-H), 8.85 d.d (1H, 4-H, $J_{4,8}$ = 0.8 Hz). UV spectrum (EtOH), λ_{max}, nm (log ε): 282 (4.10), 334 sh (3.57), 419 (3.55). Found, %: C 64.80; H 6.58. $C_{14}H_{17}N_3O_2$. Calculated, %: C 64.85; H 6.61.

b. Compound **XXIII**, 0.05 g (0.23 mmol), was dissolved in 2 ml of glacial acetic acid, 0.03 ml (0.47 mmol) of concentrated nitric acid (d = 1.41) was added at 20°C, and the mixture was stirred for 30 min at 20°C. The dark red solution was diluted with 50 ml of water, and the precipitate was filtered off, dried in air, and recrystallized from chloroform. Yield of 1,5-bis(dimethylamino)-2,4,6,8-tetranitronaphthalene (**XXV**) 0.028 g (30%). Dark red crystals with a yellow luster, decomposition point 218–219°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.75 s (12H, NMe_2), 8.06 s (2H, H_{arom}). UV spectrum (acetone), λ_{max}, nm (log ε): 355 sh (3.77), 449 (3.55), 530 sh (3.29). Found, %: C 42.62; H 3.55. $C_{14}H_{14}N_6O_8$. Calculated, %: C 42.65; H 3.58. The nitration in the system HNO_3/MeCN gave 32% of compound **XXV**.

Nitration of 4-acetamido-4,5-bis(dimethylamino)naphthalene (XXXI). A mixture of 0.085 ml (1.3 mmol) of HNO_3 (d = 1.41) and 3 ml of concentrated sulfuric acid was added dropwise with vigorous stirring to a solution of 0.36 g (1.3 mmol) of amide **XXXI** [8] in 6 ml of concentrated sulfuric acid (d = 1.84), cooled to –20°C. The red–orange mixture was stirred for 3 min at –20°C, poured onto 100 g of crushed ice, neutralized with 55 ml of concentrated aqueous ammonia, and extracted with chloroform. By column chromatography on Al_2O_3 of Brockman activity grade V (eluent chloroform) we isolated a red fraction with R_f 0.43. Yield of 1-acetamido-4,5-bis-(dimethylamino)-8-nitronaphthalene (**XXX**) 0.36 g (86%). Dark red crystals with mp 161–163°C (from octane). IR spectrum (mineral oil), ν, cm^{-1}: 3240 (NH); 1665 (C=O); 1580, 1495 (C–C_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.12 s (3H, COMe); 2.79 s and 2.97 s (6H each, 4-NMe_2 and 5-NMe_2); 6.64 d, 6.99 d, 7.53 d, and 7.91 d (1H each, 6-H, 3-H, 2-H, 7-H, $J_{2,3}$ = 8.3, $J_{6,7}$ = 8.8 Hz); 7.54 s (1H, NH). Found, %: C 61.02; H 6.43; N 17.51. $C_{16}N_{20}N_4O_3$. Calculated, %: C 60.75; H 6.37; N 17.71.

1-(*N*-Acetylmethylamino)-4,5-bis(dimethylamino)-5-nitronaphthalene (XXXII). Powdered KOH, 0.019 g (0.33 mmol), and methyl iodide, 0.076 ml (1.2 mmol), were added to a solution of 0.095 g (0.3 mmol) of nitroamide **XXX** in 5 ml of acetone. The mixture was stirred for 7 days at room temperature, the solvent was removed, the residue was dissolved in a small amount of chloroform, and the solution was applied to a column charged with Al_2O_3 of Brockman activity grade V. The column was eluted with chloroform, and the first red fraction, R_f 0.90, was collected, from which 0.094 g (95%) of amide **XXXII** was isolated. Red–orange leaflets, mp 154–155°C (from octane). IR spectrum (mineral oil), ν, cm^{-1}: 1670 (C=O); 1580, 1510 (C–C_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.80 s (3H, COMe); 2.83 s and 2.88 s (6H each, 1-NMe_2 and 8-NMe_2); 3.07 s (3H, CONMe); 6.72 d, 6.87 d, 7.13 d, and 7.52 d (1H each, 6-H, 3-H, 2-H, 7-H, $J_{2,3}$ = 8.2, $J_{6,7}$ = 8.4 Hz). Found, %: C 61.52; H 6.44; N 16.90. $C_{17}H_{22}N_4O_3$. Calculated, %: C 61.80; H 6.71; N 16.96.

2,6-Dinitro-1,5-bis(*p*-tolylsulfonylamino)naphthalene (XXXIV), which was assigned in [18] the structure of 4,8-dinitro derivative **XXIX**, was synthesized by the procedure reported in [18] with the difference that the product was filtered off after 2 days rather than immediately after nitration. Yield 72%. Lemon-yellow crystals with mp 262–263°C (from aqueous pyridine) (cf. [18]). IR spectrum (mineral oil), ν, cm^{-1}: 3280 (NH); 1600, 1540 (C–C_{arom}); 1170, 1080 (SO_2).

1,5-Diamino-2,6-dinitronaphthalene (XXXV). The hydrolysis of compound **XXXIV** was carried out as described in [18]. However, we failed to attain the yield given in [18] (97%) by repeated experiments. The yield of **XXXV** was 80%. In order to obtain product **XXXV** as a readily filterable precipitate it is advisable to pour the mixture into hot water with special precautions.

1,5-Bis(dimethylamino)-2,6-dinitronaphthalene (XXXVI). Diamine **XXXV**, 0.05 g (0.2 mmol), was dissolved in 20 ml of acetone or acetonitrile, 0.09 g (1.6 mmol) of powdered KOH was added, the dark violet solution was stirred for 1 min, and 0.1 ml

(1.6 mmol) of methyl iodide was added. The reaction flask was tightly capped and was left to stand for 4 days with intermittent shaking. Additional amounts of KOH and MeI (the same as above) were added, and the mixture was kept for 4 days. The solvent was evaporated, and the residue was washed with chloroform. The extract was subjected to a column charged with silica gel, and the column was eluted with chloroform to collect a bright orange fraction with R_f 0.90. Yield of **XXXVI** 0.031 g (50%). Bright orange leaflets with mp 170–171°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$–CCl_4, 1 : 1), δ, ppm: 2.89 s (12H, NMe_2), 7.62 d and 7.98 d (2H each, 4-H, 8-H, 3-H, 7-H, $J_{3,4}$ = 9.2 Hz). UV spectrum (MeOH), λ_{max}, nm (log ε): 255 s (4.15), 282 (4.05), 328 (3.94), 433 (3.47). Found, %: C 54.86; H 4.92. $C_{14}H_{16}N_4O_4$. Calculated, %: C 55.26; H 5.30.

2,6-Diamino-1,5-bis(dimethylamino)naphthalene (XXXVII) was synthesized from dinitro derivative **XXXVI**, following the general procedure for reduction with tin(II) chloride (2 h, 25°C). Yield 85%. Gray powder (relatively stable to oxidation with atmospheric oxygen), mp 157–159°C. IR spectrum (mineral oil), ν, cm^{-1}: 3380, 3300 (NH_2); 1630; 1600, 1500 (C–C_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.96 s (12H, NMe_2), 3.9 br.s (4H, NH_2), 6.96 d and 7.55 d (2H each, 3-H, 7-H, 4-H, 8-H, $J_{3,4}$ = 8.8 Hz).

General procedure for exhaustive alkylation of naphthylamines with the system Me_2SO_4–Na_2CO_3–H_2O. The alkylation was carried out by the modified procedure [22]. To 1 mmol of naphthylamine we added in succession dimethyl sulfate (4 mmol per amino group), 5 ml of water, and $Na_2CO_3 \cdot 10H_2O$ in an amount equimolar to the dimethyl sulfate taken. The mixture was vigorously stirred for 1–2 h at room temperature until the initial compound disappeared (TLC). The resulting suspension was neutralized with concentrated aqueous ammonia until persistent odor and was extracted with benzene. If necessary, the product was purified by chromatography on Al_2O_3. In such a way, the following compounds were synthesized: **I** (yield 93%, from 1,8-diaminonaphthalene); **XXIII** (65%, from 1,5-diaminonaphthalene), and **XXXIX** (52%, from 1,4,5-triaminonaphthalene).

1,2,5,6-Tetrakis(dimethylamino)naphthalene (XXXVIII). Amine **XXXVII** was alkylated with the system $Me_2SO_4/Na_2CO_3/H_2O$, following the above general procedure. Yield of **XXXVIII** 60%. The product was identical in physical and spectral parameters to that described in [21]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.72 s and 2.98 s (12H each, 2-NMe_2, 6-NMe_2, 1-NMe_2, 5-NMe_2), 7.27 d and 7.91 d (2H each, 3-H, 7-H, 4-H, 5-H, $J_{3,4}$ = 9.1 Hz).

1,4,5-Tris(dimethylamino)naphthalene (XXXIX) was synthesized both as described in [8] and by the following procedure. 1,4,5-Triaminonaphthalene (**XVII**) [13], 0.5 g (2.9 mmol), was dissolved in 200 ml of anhydrous THF. The solution was stirred for 5 min in an inert atmosphere, 2.2 g (46 mmol) of powdered NaH was added, the mixture was heated to the boiling point, and 4.4 ml (46 mmol) of Me_2SO_4 in 20 ml of THF was added dropwise with stirring to the boiling mixture. The mixture was then refluxed for 3 h, cooled to 20°C, diluted with 200 ml of concentrated aqueous sodium hydroxide, and vigorously shaken. The organic phase was separated, and the aqueous phase was extracted with hexane (2 × 50 ml). The extracts were combined with the organic phase, and the solvent was removed to obtain 0.3 g (60%) of compound **XXXIX** as a reddish oily substance which was identical to a sample prepared by the procedure described in [8].

1,4,5-Tris(dimethylamino)naphthalene hydrotetrafluoroborate (XXXIX · HBF_4) was synthesized as described above for bis(hydrotetrafluoroborate) **II** · 2HBF_4. Yield quantitative. Colorless powder, mp 204–205°C (from MeOH).

1,4,5-Tris(dimethylamino)-8-nitronaphthalene (XL). Salt **XXXIX** · HBF_4, 0.2 g (0.6 mmol), was dissolved at –20°C in 12 ml of concentrated sulfuric acid (d = 1.84), and 0.04 ml (0.64 mmol) of concentrated nitric acid (d = 1.41) was added with stirring at –20°C. The mixture was kept for 5 min with occasional stirring, poured onto 80 g of ice, neutralized with concentrated aqueous ammonia until persistent odor, and extracted with chloroform (5 × 20 ml). The solvent was removed from the extract, and the residue was subjected to column chromatography on silica gel using chloroform as eluent. A yellow–brown fraction, R_f 0.30, was collected. We isolated 0.088 g (50%) of nitronaphthalene **XL** as an orange oily substance which crystallized on cooling to 0°C, mp 86–87°C (from MeOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.55 s (6H, 1-NMe_2), 2.74 br.s and 2.84 br.s (6H each, 4-NMe_2, 5-NMe_2), 6.70 br.d and 6.93 br.d (1H each, 3-H, 6-H, $J_{2,3}$ = 8.2, $J_{6,7}$ = 8.1 Hz), 7.21 d and 7.34 d (1H each, 2-H, 7-H). UV spectrum (EtOH), λ_{max}, nm (log ε): 355 (4.02), 420 sh (3.46). Found, %: C 63.43; H 6.90. $C_{16}H_{22}N_4O_2$. Calculated, %: C 63.56; H 7.33.

Perchlorate **XL** · $HClO_4$. Yellowish needles. Decomposition point 222–223°C (from water). ^{1}H NMR spectrum (CD_3CN), δ, ppm: 2.62 s (6H, 1-NMe_2); 3.07 d (6H, 5-NMe_2, $J_{NH,NMe}$ = 1.9 Hz); 3.17 d (6H, 4-NMe_2, $J_{NH,NMe}$ = 3.3 Hz); 7.69 d, 7.81 d, 7.95 d,

and 8.02 d (1H each, 2-H, 6-H, 7-H, 3-H, $J_{2,3}$ = 8.2, $J_{6,7}$ = 8.4 Hz); 18.66 br.s (1H, NH). Found, %: C 47.50; H 5.43; Cl 8.89. $C_{16}H_{23}ClN_4O_6$. Calculated, %: C 47.70; H 5.76; Cl 8.80.

1-Amino-4,5,8-tris(dimethylamino)naphthalene (XLI) was synthesized by reduction of nitro derivative **XL** according to the general procedure (1 h, 25°C). Yield 80%. Yellow oily substance which rapidly turns green on exposure to air. IR spectrum (film), ν, cm^{-1}: 3420, 3273 (NH_2); 2913, 2847, 2806, 2760 (CH_3); 1580, 1487 ($C-C_{arom}$). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.68 s, 2.70 s, and 2.73 s (6H each, 4-NMe_2, 8-NMe_2, 5-NMe_2); 6.52 d, 6.80 d, 6.82 d, and 7.04 d (1H each, 2-H, 3-H, 7-H, 6-H, $J_{2,3}$ = 8.1, $J_{6,7}$ = 8.2 Hz).

Transformation of 1-amino-4,5,8-tris(dimethylamino)naphthalene (XLI) into 1,4,5,8-tetrakis(dimethylamino)naphthalene (II). Compound **XLI** was alkylated following the general procedure with the system $Me_2SO_4/Na_2CO_3/H_2O$. Yield of **II** 40%. The product was identical to samples of **II** prepared by the other methods.

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