peri-Naphthylenediamines

32*. Reactions of 4,5-bis(dimethylamino)-1-naphthyllithium and 4,5-bis(dimethylamino)-1-naphthylmagnesium bromide with electrophilic agents. New representatives of double naphthalene "proton sponges" with the structures of 1,1′-binaphthyl ketone and 1,1′-binaphthylmethanol

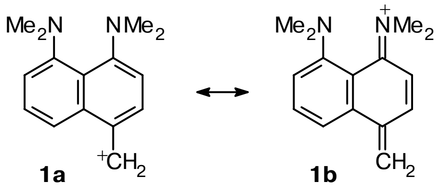
O. V. Ryabtsova, A. F. Pozharskii, V. A. Ozeryanskii, and N. V. Vistorobskii*

Rostov State University,
7 ul. Zorge, 344090 Rostov-on-Don, Russian Federation.
Fax: (8 632) 22 3958. E-mail: pozharsk@pozhar.rnd.runnet.ru

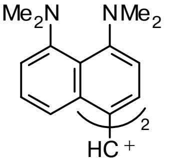
The 4-deuterio, 4-methyl, 4-iodo, 4-methylthio, 4-trimethylsilyl, and 4-ethoxycarbonyl derivatives of 1,8-bis(dimethylamino)naphthalene ("proton sponge") and some related alcohols were prepared by the reactions of 4,5-bis(dimethylamino)-1-naphthyllithium or 4,5-bis(dimethylamino)-1-naphthylmagnesium bromide with the corresponding electrophilic reagents. New representatives of double "proton sponges" with the structures of 1,1′-binaphthyl ketone and 1,1′-binaphthylmethanol were synthesized. The pK_a values of selected compounds in DMSO were measured by competitive protonation.

Key words: 1-bromo-4,5-bis(dimethylamino)naphthalene, organolithium and organomagnesium compounds, addition at the C=O group, acylation, 1,1′-binaphthyl ketone, 1,1′-binaphthylmethanol, "proton sponges".

The strong electron-donating effect of two dimethylamino groups with respect to the naphthalene ring is an important feature of 1,8-bis(dimethylamino)naphthalene ("proton sponge").[2] In addition to the fact that electrophilic substitution proceeds exceptionally readily, this effect is manifested, in particular, in the ability of the NMe_2 groups to efficiently stabilize carbocationic centers. Thus, carbocations of type **1** generated *in situ* readily enter into [4π+2π]-cyclodimerization due to a substantial contribution of resonance structure **1b** containing the *exo-endo*-1,3-diene fragment.[3,4] Taking into account that, on the one hand, naphthylmethyl carbocations have attracted considerable interest[5] and, on the other hand, their reactivities are untypical of the chemistry of naphthalenes, the synthesis of carbocations **2** and **3** containing two or three residues of the "proton sponge" is of importance.



1a **1b**



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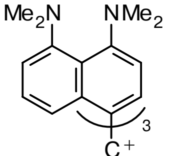

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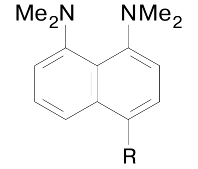
The most evident procedure for the preparation of these carbocations involves the synthesis of the corresponding alcohols with the formation of organometallic derivatives of "proton sponge" **4a** in one of the stages. Until recently, these compounds remained unknown, except for the only example, *viz.*, 4,5-bis(dimethylamino)naphthyllithium[6] (**4b**) and its conversion into the corresponding aldehyde under the action of DMF.

The aim of the present study was to examine the procedures for the preparation of lithium (**4b**) and magnesium (**4c**) derivatives of the "proton sponge" in detail and to study the reactivities of these compounds with respect to typical electrophiles.



4a—c

R = H (**a**), Li (**b**), MgBr (**c**)

Results and Discussion

As in the study performed previously,[6] organometallic compounds **4b,c** were generated using 1-bromo-4,5-bis(dimethylamino)naphthalene (**5a**) as the starting compound. Since **5a** is the key compound in the synthesis of metal derivatives, we simplified the procedure for its preparation. Previously,[6] the procedure, which involved successive treatment of compound **4a** with bromine and concentrated H_2SO_4 at −10 °C, took ~12 h to form the target product **5a** in 73% yield. The reaction of the "proton sponge" with a solution of NBS in THF at

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* For Part 31, see Ref. 1.

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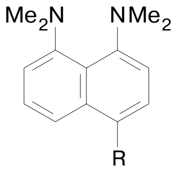
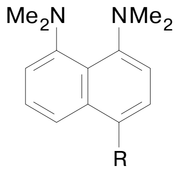

5a,b

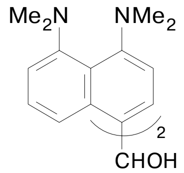
R = Br (**a**), CHO (**b**)

−5 °C [7] proved to be a more convenient procedure. In the latter case, the reaction time was 2 h and the yield of derivative **5a** reached 75%. Magnesium derivative **4c** was then prepared by the reaction of bromide **5a** with magnesium in anhydrous ether or THF at ~20 °C. It should be noted that the "proton sponge," unlike *N*,*N*-dimethylaniline,[8] 1-dimethylaminonaphthalene,[9] and 1,5-bis(dimethylamino)naphthalene,[10] is not metallated with *n*-butyllithium. Its reactions with sodium metal[11] (−20 °C, dimethoxyethane) or lithium metal[12] (−50 °C, THF) afforded a stable radical anion or its conversion products (1-dimethylaminonaphthalene, 1,1′-binaphthyl, naphthalene, *etc.*).

In addition, we found that bromide **5a** did not react with lithium metal in boiling ether; however, lithium derivative **4b** was formed in the presence of an equimolar amount of Bu^{n}Br. This procedure is an alternative to the synthesis involving Bu^{n}Li, which is less convenient to use. The reaction performed at 35 °C was completed in 1.5—2 h. All experiments described below were carried out with compound **4b** generated *in situ* from Bu^{n}Li and bromide **5a**.

The subsequent reactions of organometallic compounds **4b,c** with different electrophiles (D_2O, MeI, Me_2S_2, Me_3SiCl, iodine, benzaldehyde, benzophenone, diethyl carbonate, and aldehyde **5b**) afforded the previously unknown compounds **6a—i** in yields from moderate to high (Table 1).


6a—h


6i

R = D (**a**), Me (**b**), SMe (**c**), $SiMe_3$ (**d**), I (**e**), CH(OH)Ph (**f**), $C(OH)Ph_2$ (**g**), CO_2Et (**h**)

Compounds **4b** and **4c** would be expected to possess high nucleophilicity due to the presence of the electron-donating dimethylamino groups. As can be seen from Table 1, naphthyllithium **4b** is the most efficient reagent in the majority of reactions due, apparently, to the higher ionicity of the C—Li bond.[13] At the same time, the preparation of Grignard reagent **4c** is less laborious and the synthesis involving this reagent does not require an inert atmosphere.

The reactions of organometallic compounds **4b,c** with MeI afforded methylnaphthalene **6b**. This is the second example of the synthesis of C-alkylated "proton sponges." Previously,[14] these compounds have been prepared by alkylation of compound **4a** with alkene complexes of platinum.

Treatment of compounds **4b,c** with carbonyl compounds, including 4,5-bis(dimethylamino)naphthalene-

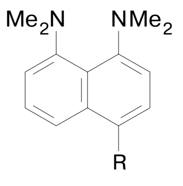
Table 1. Results of the reactions of organometallic compounds **4b** and **4c** with different substrates and the data from elemental analysis for products **6a—i**

Reagent	Reaction product	Yield (%) from		M.p. /°C	Found/Calculated (%)			Molecular formula
		4b	**4c**		C	H	N	
D_2O	**6a**	100	97	271—272[a]	78.02 78.10	8.84[b] 8.89[b]	13.05 13.01	$C_{14}H_{17}DN_2$
MeI	**6b**	57	40	213—214[a]	78.88 78.90	8.80 8.83	12.24 12.27	$C_{15}H_{20}N_2$
Me_2S_2	**6c**	90	30	196—197[a]	69.27 69.19	7.83 7.74	10.82 10.76	$C_{15}H_{20}N_2S$
Me_3SiCl	**6d**	42	31	240—241[a]	71.35 71.28	9.33 9.16	9.75 9.79	$C_{17}H_{26}N_2Si$
I_2	**6e**	87	30	215—216[a]	49.59 49.43	5.11 5.04	8.20 8.23	$C_{14}H_{17}IN_2$
PhCHO	**6f**	88	67	102—104	78.90 78.72	7.63 7.55	8.79 8.74	$C_{21}H_{24}N_2O$
Ph_2CO	**6g**	40	73	141—142[c]	82.00 81.78	7.39 7.12	7.02 7.06	$C_{27}H_{28}N_2O$
$(EtO)_2CO$	**6h**	44	40	223—224[a]	71.46 71.30	7.87 7.74	9.84 9.87	$C_{17}H_{22}N_2O_2$
5b	**6i**	54	22	114—115	76.55 76.28	8.13 7.95	12.23 12.27	$C_{29}H_{36}N_4O$

[a] M.p. of the corresponding perchlorate (with decomp., from water).

[b] H + D.

[c] From 95% EtOH.



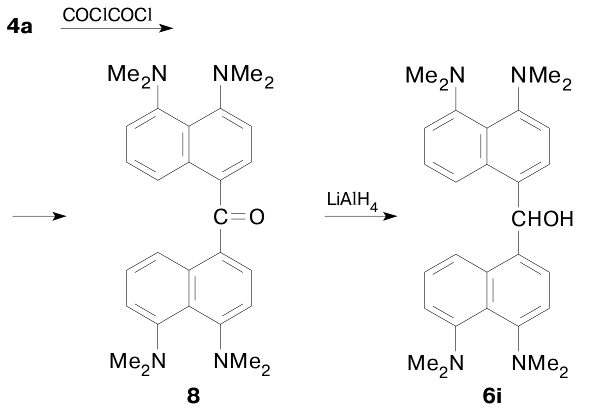
7a,b

R = COPh (**a**), CN (**b**)

1-carbaldehyde (**5b**), gave rise to secondary and tertiary alcohols **6f,g,i**. Interestingly, the preparation of alcohol **6f** in the presence of more than one equivalent of benzaldehyde was accompanied by the formation of ketone **7a**. We established that the latter occurred due to oxidation of intermediate alkoxide by an excess of benzaldehyde (see also Ref. 15). The reactions with the use of an excess (from two- to fivefold) of all other reagents (see Table 1) afforded no by-products. It should be noted that tertiary alcohol **6g** has been synthesized previously[16] in low yield from phenylmagnesium bromide and ketone **7a** (the major product of this reaction was an 1,4-addition product involving the carbonyl group and the naphthalene ring).

The addition—elimination-type reactions of diethyl carbonate with derivatives **4b,c** gave rise to new carbonyl compound **6h**. By analogy with the latter reactions, we attempted to perform the reaction of an organometallic compound with ether **6h** to prepare the previously unknown ketone **8**. However, this attempt failed due, apparently, to an essential decrease in the partial positive charge on the carbon atom of the C=O group.

Presumably, compounds **7a** and **7b** [6] and, in particular, ketone **8** proved to be inert with respect to organometallic compounds for the same reason. We prepared the latter compound independently in 60% yield by acylation of 1,8-bis(dimethylamino)naphthalene hydrochloride with oxalyl chloride in the presence of $AlCl_3$.* The structure of compound **8** was confirmed by spectral data, including mass spectra, and by its reduction to alcohol **6i**.



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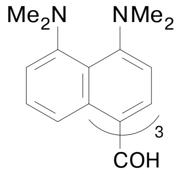
6i

Table 2. Hammett constants (σ_n) of the substituents and the basicity constants pK_a of compounds **4a**, **5a**, and **6b—e,h**

Compound	R	σ_n(H_2O)	pK_a*
4a	H	0	7.5
6b	Me	−0.14	7.7
6d	$SiMe_3$	−0.07	7.2
6c	SMe	0	7.1
6e	I	0.21	6.6
5a	Br	0.23	6.5
6h	CO_2Et	0.45	5.6

* DMSO, 25 °C.

Binaphthyl derivatives **6i** and **8** are new representatives of double naphthalene "proton sponges." At the same time, the reaction of ketone **8** with one more molecule **4b** or **4c** would be expected to produce very interesting alcohol **9** containing three residues of diamine **4a**. Unfortunately, attempts to perform this reaction failed. Apparently, aldehyde **5b** is the "limiting" carbonyl compound capable of reacting with organometallic compounds **4b,c**. The low reactivity of ketone **8** resulting from the +M effect of four NMe$_2$ groups is consistent with the position of the C=O stretching vibration band in its IR spectrum (ν(C=O) is 1633 cm^{-1} compared to 1685 cm^{-1} for aldehyde **5b**).[6]



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We estimated the influence of the substituents on the basic properties of the compounds synthesized by competitive protonation based on the data from ^{1}H NMR spectroscopy.[19] The pK_a values for derivatives **6b—e,h** and bromide **5a** in DMSO* and the Hammett constants (σ_n) of the corresponding substituents[20] are given in Table 2. In addition, the basicity of compound **4a**[21] is given for comparison. As expected, the +*I* effect of the Me group in 4-methyl derivative **6b** leads to an increase in the basicity by 0.2 pK_a units compared to that of compound **4a**.

The presence of other functional groups leads more likely to a decrease in basicity of the resulting "proton sponges" rather than to its increase in spite of the negative (for $SiMe_3$) or zero (for SMe) values of some Hammett constants.

Therefore, although there is no strict quantitative dependence of the pK_a values on the σ_n constants, the qualitative relationship between these parameters in the series of compounds under consideration persists: the higher the basicity, the lower the σ_n constants. In our opinion, a slight quantitative inconsistency between the σ_n and pK_a values may be due both to steric and solvent

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* *N,N*-Dimethylaniline reacted with oxalyl chloride to form the corresponding diketone.[17] Acylation of other substrates under the conditions of the Friedel—Crafts reaction is often accompanied by the cleavage of the C—C bond in oxalyl chloride to form carboxylic acids or their chlorides along with monoketones.[18] Apparently, acylation of compound **4a** with oxalyl chloride also gave rise initially to the 4-chloroformyl derivative, which then acylated one more molecule **4a** to form finally monoketone **8**.

* The basicity constant of deuterated derivative **6a** and the pK_a value of diamine **4a** are equal within the experimental error (±0.03 pK_a units).

effects associated with the use of different solvents (water or DMSO) in the quantitative measurements.

Experimental

The ^1H NMR spectra were recorded on a Bruker DPX-250 instrument (250 MHz) in $CDCl_3$ with $SiMe_4$ as the internal standard. The IR spectra were measured on a Specord IR-71 spectrometer. The mass spectra were obtained on a Finnigan 4021 instrument (EI, 70 eV, direct inlet of the sample). Chromatography was performed and the purities of the compounds were monitored by TLC on Al_2O_3 (Brockmann II) using $CHCl_3$ as the eluent; visualization was carried out with iodine vapor. The melting points were determined in sealed glass tubes on a PTP instrument and were not corrected. Commercial *n*-butyllithium (a 1.6 *M* solution in *n*-hexane, Fluka), 1,8-bis(dimethylamino)naphthalene (Merck), oxalyl chloride (Aldrich), trimethylchlorosilane, and dimethyl disulfide (Fluka) were used. Other reagents and solvents used in the synthesis of organometallic compounds and in their reactions were purified and dried according to standard procedures.[23] The physicochemical and spectral characteristics of the resulting compounds are given in Tables 1 and 3.

1-Bromo-4,5-bis(dimethylamino)naphthalene (5a). A solution of NBS (0.266 g, 1.5 mmol) in THF (20 mL) was added dropwise with vigorous stirring to a solution of compound **4a** (0.32 g, 1.5 mmol) in THF (10 mL) cooled to −5 °C for 30 min. Then the reaction mixture was stirred at ~20 °C for 2 h, concentrated to 2 mL, and chromatographed. The first major fraction of bromo derivative **5a** was collected (0.33 g, 75%) as a pale-yellow oil. The properties of **5a** are analogous to those of the specimen prepared previously.[6]

4,5-Bis(dimethylamino)-1-naphthyllithium (4b). A 1.6 *M* solution of Bu^nLi (1.2 mL) in *n*-hexane (1.9 mmol) was added with stirring to a solution of bromide **5a** (0.3 g, 1 mmol) in Et_2O (2 mL) using a microdispenser (or a syringe) under an atmosphere of Ar at −30 °C. The reaction was accompanied by the immediate appearance of the bright-yellow color. The resulting solution of compound **4b** (1 mmol) was kept at −30 °C in a freezing chamber for 30 min and compound **4b** was used in subsequent conversions without isolation.

4,5-Bis(dimethylamino)-1-naphthylmagnesium bromide (4c). Magnesium chips (0.1 g, 4 mmol; activated with 0.02 mL of dry *n*-butyl bromide) and THF (2 mL) were placed into a flask equipped with a stirrer, a reflux condenser, and a dropping funnel with protection from atmospheric moisture. Then a solution of bromide **5a** (0.3 g, 1 mmol) in THF (1.5 mL) was added with stirring so that the reaction mixture boiled spontaneously. After completion of the addition, the transparent solution was stirred at 50—55 °C for ~1 h until compound **5a** was completely consumed (TLC control). The solution of the resulting Grignard reagent **4c** (1 mmol) was used in subsequent reactions without isolation.

1,8-Bis(dimethylamino)-4-methylnaphthalene (6b). *A.* Iodomethane (1 mL) was added with stirring to a solution of lithium derivative **4b** (1 mmol) prepared as described above at −30 °C. The reaction mixture was kept at −30 °C for 3 h, allowed to warm to ~20 °C, and poured into water. The yellow ethereal layer was separated and the aqueous layer was extracted with $CHCl_3$ (2×2 mL). The solvents were removed. The residue was chromatographed (*n*-hexane as the eluent) and the major colorless fraction was collected (TLC control). Compound **6b** was obtained in a yield of 0.13 g (57%) as a colorless oil readily soluble in dilute mineral acids. Perchlorate **6b • HClO$_4$**. Found (%): C, 54.75; H, 6.40; Cl, 10.67; N, 8.49. $C_{15}H_{21}ClN_2O_4$. Calculated (%): C, 54.80; H, 6.44; Cl, 10.78; N, 8.52. ^1H NMR (DMSO-d_6), δ: 2.70 (br.s, 3 H, Me); 3.11 and 3.13 (both d, 6 H each, C(1)NMe_2 and C(8)NMe_2, $J_{NH,C(1)NMe}$ = 2.7 Hz, $J_{NH,C(8)NMe}$ = 2.4 Hz); 7.61 (dd, 1 H,

Table 3. ^1H NMR spectra of compounds **6a—f**,**h**,**i** and **7a**

Compound	δ (*J*/Hz)						
	NMe_2	H(2), d	H(3), d	H(5), dd	H(6), dd	H(7), dd	R
6a	2.83 (s, 12 H, NMe_2)	6.96 (7.9)	7.33 (7.9)	7.39 (7.9)*	7.33 (7.3, 7.9)	6.96 (7.3)*	—
6b	2.76 (s, 6 H, C(1)NMe_2); 2.80 (s, 6 H, C(8)NMe_2)	6.84 (7.7)	7.16 (7.7)	7.50 (1.1, 8.3)	7.36 (7.5, 8.3)	6.96 (1.1, 7.5)	2.57 (br.s, 3 H, Me)
6c	2.80 (s, 6 H, C(8)NMe_2); 2.81 (s, 6 H, C(1)NMe_2)	6.86 (8.0)	7.40 m	7.98 (1.1, 8.3)	7.40 m	6.97 (1.1, 7.5)	2.47 (s, 3 H, SMe)
6d	2.77 (s, 6 H, C(1)NMe_2); 2.80 (s, 6 H, C(8)NMe_2)	6.86 (7.6)	7.50 (7.6)	7.57 (0.9, 8.3)	7.31 (7.7, 8.3)	6.91 (0.9, 7.7)	0.40 (s, 9 H, $SiMe_3$)
6e	2.76 (s, 6 H, C(8)NMe_2); 2.77 (s, 6 H, C(1)NMe_2)	6.61 (8.1)	7.84 (8.1)	7.59 (1.1, 8.3)	7.35 (7.6, 8.3)	6.95 (1.1, 7.6)	—
6f	2.78 (br.s, 12 H, NMe_2)	6.84 (7.9)	7.32 m	7.63 (8.1)*	7.32 m	6.92 (7.5)*	2.24 (br.d, 1 H, CHO<u>H</u>, *J* = 3.1); 6.42 (d, 1 H, C<u>H</u>OH, *J* = 3.1); 7.32 (m, 5 H, Ph)
6h	2.74 (s, 6 H, C(8)NMe_2); 2.86 (s, 6 H, C(1)NMe_2)	6.78 (8.3)	8.04 (8.3)	8.55 (1.1, 8.5)	7.39 (7.6, 8.5)	6.91 (1.1, 7.6)	1.40 (t, 3 H, CH_2<u>Me</u>); 4.38 (q, 2 H, C<u>H$_2$</u>Me)
6i	2.78 (s, 12 H, C(1,1′)NMe_2); 2.81 (s, 12 H, C(8,8′)NMe_2)	6.83 (8.0) 2H	7.29 m 2H	7.61 (8.5)* 2H	7.29 m 2H	6.92 (7.5)* 2H	2.18 (br.d, 1 H, OH, *J* = 4.1); 7.05 (br.d, 1 H, CH, *J* = 4.1)
7a	2.78 (s, 6 H, C(8)NMe_2); 2.88 (s, 6 H, C(1)NMe_2)	6.74 (8.1)	7.43 m	8.04 (1.1, 8.4)	7.34 (7.6, 8.4)	6.94 (1.1, 7.6)	7.43, 7.53, 7.81 (all m, 2 H, 1 H, 2 H, Ph)

Note. For convenience, the atomic numbering scheme for the naphthalene ring in all compounds under consideration is identical with that used for 1,8-bis(dimethylamino)naphthalene derivatives.

* If the $J_{5,7}$ constant was not observed in the NMR spectrum, only one value is given.

H(3), $J_{H(3),Me}$ = 0.8 Hz, J = 7.8 Hz); 7.78 (dd, 1 H, H(6), J_1 = 7.6 Hz, J_2 = 8.5 Hz); 7.99 (d, 1 H, H(2), J = 7.8 Hz); 8.09 (dd, 1 H, H(5), J_1 = 0.8 Hz, J_2 = 7.6 Hz); 8.17 (dd, 1 H, H(7), J_1 = 0.8 Hz, J_2 = 8.5 Hz); 18.59 (br.s, 1 H, NH).

B. A solution of MeI (0.5 mL, 8 mmol) in THF (1.5 mL) was added to a solution of Grignard reagent **4c** (0.34 mmol) prepared as described above. The reaction mixture was stirred at 50 °C for 2 h, decomposed with a saturated NH_4Cl solution, and extracted with $CHCl_3$ (3×2 mL). The solvent was removed. The residue was chromatographed (*n*-hexane as the eluent) and the major colorless fraction was collected (TLC control). Compound **6b** was isolated in a yield of 0.03 g (40%). It was identical in properties to the specimen synthesized according to procedure ***A***.

The reaction with the use of D_2O instead of MeI afforded **4-deuterio-1,8-bis(dimethylamino)naphthalene (6a)** in virtually quantitative yield as a colorless oil whose physicochemical characteristics are very similar to those of crystalline **1,8-bis(dimethylamino)naphthalene (4a)**. Perchlorate **6a · HClO$_4$**. Found (%): C, 53.14; H+D, 6.40; Cl, 11.47; N, 8.48. $C_{14}H_{18}ClDN_2O_4$. Calculated (%): C, 53.25; H+D, 6.38; Cl, 10.78; N, 8.52. ^{1}H NMR (DMSO-d$_6$), δ: 3.12 (d, 12 H, NMe$_2$, $J_{NH,NMe}$ = 2.5 Hz); 7.73 (m, 2 H, H(3), H(6), J_1 = 7.7 Hz, J_2 = 8.2 Hz); 8.08 (d, 2 H, H(2), H(7), J = 7.7 Hz); 8.09 (d, 1 H, H(5), J = 8.2 Hz); 18.35 (br.s, 1 H, NH).

Next we describe the procedures giving the best results (see Table 1).

[4,5-Bis(dimethylamino)-1-naphthyl]methyl sulfide (6c). A solution of lithium derivative **4b** (5.5 mmol), which was prepared according to the procedure described above, was added with stirring to a solution of dimethyl disulfide (1 mL) in Et_2O (2 mL) at −70 °C. The mixture was kept at −70 °C for 2 h and then at ~20 °C for 3 h and poured into water. The ethereal layer was separated and the aqueous layer was extracted with $CHCl_3$ (3×2 mL). The combined organic extracts were concentrated to the minimum volume and chromatographed (*n*-hexane as the eluent). Compound **6c** was obtained in a yield of 0.13 g (90%) as a dark-yellow oil with weak "sulfide" odor. Perchlorate **6c · HClO$_4$**. Found (%): C, 49.78; H, 5.80; Cl, 9.77; N, 7.71, S, 8.76. $C_{15}H_{21}ClN_2O_4S$. Calculated (%): C, 49.93; H, 5.83; Cl, 9.85; N, 7.77; S, 8.88. ^{1}H NMR (DMSO-d$_6$), δ: 2.65 (s, 3 H, SMe); 3.11 and 3.13 (both d, 6 H each, C(4)NMe$_2$ and C(5)NMe$_2$, $J_{NH,C(4)NMe}$ = 2.3 Hz, $J_{NH,C(5)NMe}$ = 2.7 Hz); 7.60 (d, 1 H, H(2), J = 8.3 Hz); 7.80 (t, 1 H, H(7), J_1 = 7.6 Hz, J_2 = 8.5 Hz); 8.06 (d, 1 H, H(3), J = 8.3 Hz); 8.14 (br.d, 1 H, H(6), J = 7.6 Hz); 8.26 (br.d, 1 H, H(8), J = 8.5 Hz); 18.54 (br.s, 1 H, NH).

4,5-Bis(dimethylamino)-1-napthyltrimethylsilane (6d). A solution of lithium derivative **4b** (5 mmol), which was prepared as described above, was added to a solution of Me_3SiCl (1 mL, 0.8 g, 7 mmol) in Et_2O (2 mL) at −70 °C under Ar. The reaction mixture was kept at −70 °C for 2 h and then at ~20 °C for 3 h, poured into water, and alkalized with ammonia until a persistent odor appeared. The ethereal layer was separated and the aqueous layer was extracted with $CHCl_3$ (4×2 mL). A needle-like colorless precipitate of compound **6d** was obtained in a yield of 0.06 g (42%). Perchlorate **6d · HClO$_4$**. Found (%): C, 52.48; H, 7.27; Cl, 9.10; N, 7.19. $C_{17}H_{27}ClN_2O_4Si$. Calculated (%): C, 52.77; H, 7.03; Cl, 9.16; N, 7.24. ^{1}H NMR (DMSO-d$_6$), δ: 0.46 (s, 9 H, SiMe$_3$); 3.12 and 3.15 (both d, 6 H each, C(5)NMe$_2$ and C(4)NMe$_2$, $J_{NH,C(4)NMe}$ = 2.5 Hz, $J_{NH,C(5)NMe}$ = 2.2 Hz); 7.82 (m, 2 H, H(2), H(7)); 8.04 (d, 1 H, H(3), J = 7.6 Hz); 8.11 (dd, 1 H, H(6), J_1 = 0.8 Hz, J_2 = 7.6 Hz); 8.22 (dd, 1 H, H(8), J_1 = 0.8 Hz, J_2 = 8.3 Hz); 18.69 (br.s, 1 H, NH).

1,8-Bis(dimethylamino)-4-iodonaphthalene (6e). A solution of I_2 (~0.2 g, 0.78 mmol) in Et_2O was added portionwise to a solution of compound **4b** (0.68 mmol) prepared as described above at −30 °C until the brown color of iodine persisted. The reaction mixture was kept at −30 °C for 1 h and decomposed by pouring into water. The ethereal layer was washed successively with a solution of $Na_2S_2O_3$ and water and concentrated to dryness. The residue was chromatographed (*n*-hexane as the eluent) and the first colorless fraction containing iodide **6e** was collected. Compound **6e** was obtained as a pale-yellow oil in a yield of 0.2 g (87%). Perchlorate **6e · HClO$_4$**. Found (%): C, 38.09; H, 4.01; Cl+I, 36.73; N, 6.30. $C_{14}H_{18}ClIN_2O_4$. Calculated (%): C, 38.16; H, 4.12; Cl+I, 36.84; N, 6.36. ^{1}H NMR (DMSO-d$_6$), δ: 3.11 and 3.15 (both d, 6 H each, C(4)NMe$_2$ and C(5)NMe$_2$, $J_{NH,C(4)NMe}$ = 1.9 Hz, $J_{NH,C(5)NMe}$ = 2.2 Hz); 7.89 (m, 2 H, H(2), H(7)); 8.22 (m, 2 H, H(3), H(6)); 8.41 (br.d, 1 H, H(8), J = 8.0 Hz); 18.61 (br.s, 1 H, NH).

[4,5-Bis(dimethylamino)-1-naphthyl]phenylmethanol (6f). Freshly distilled benzaldehyde (0.33 mL, 1 mmol) was slowly added with stirring to a solution of lithium derivative **4b** (1 mmol) at −30 °C. The reaction mixture was kept at −30 °C for 1 h and then at ~20 °C for 4 h and poured into water. The ethereal layer was separated and the aqueous layer was extracted with $CHCl_3$ (4×3 mL). The combined extracts were concentrated. The residue was washed with a 10% solution of NaOH and chromatographed to isolate alcohol **6f** from the colorless zone with R_f 0.34 (0.28 g, 88%). Compound **6f** was obtained as a colorless caramel, which was crystallized upon prolonged evacuation and freezing to −20 °C.

The reaction with the use of an excess of benzaldehyde afforded also **1-benzoyl-4,5-bis(dimethylamino)naphthalene (7a)** as orange crystals in 10—30% yield. Compound **7a** was present in the yellow-orange fraction with R_f 0.55. The properties of the crystals are identical with those reported in the literature.[22]

[4,5-Bis(dimethylamino)-1-naphthyl]diphenylmethanol (6g). A solution of benzophenone (0.74 g, 4 mmol) in THF (2.5 mL) was added dropwise with intense stirring to a solution of Grignard reagent **4c** (2.7 mmol), which was prepared as described above, at ~20 °C. The reaction mixture was stirred at 40 °C for 1.5 h and hydrolyzed with a saturated NH_4Cl solution. The aqueous layer was extracted with $CHCl_3$ (3×3 mL) and the solvents were evaporated. The residue was crystallized from *n*-hexane and crystallized from 95% EtOH. Alcohol **6g** was obtained as colorless crystals in a yield of 0.79 g (73%).[16]

1,8-Bis(dimethylamino)-4-ethoxycarbonylnaphthalene (6h). Diethyl carbonate (2 mL) was added with stirring to a solution of lithium derivative **4b** (1 mmol) cooled to −30 °C. The reaction mixture was kept at −30 °C for 2 h, allowed to warm to ~20 °C, and poured into water. The ethereal layer was separated and the aqueous layer was extracted with $CHCl_3$ (3×2 mL). The solvents were removed. The combined residues were chromatographed and the first bright-yellow fraction was collected. Ester **6h** was obtained as a yellow oil in a yield of 0.12 g (44%). Perchlorate **6h · HClO$_4$**. Found (%): C, 52.71; H, 5.90; Cl, 9.20; N, 7.19. $C_{17}H_{23}ClN_2O_6$. Calculated (%): C, 52.78; H, 5.99; Cl, 9.17; N, 7.24. ^{1}H NMR (DMSO-d$_6$), δ: 1.38 (t, 3 H, CH$_2$Me, J = 7.1 Hz); 3.11 and 3.20 (both s, 6 H each, C(1)NMe$_2$ and C(8)NMe$_2$); 4.45 (q, 2 H, C$\underline{H}_2$Me, J = 7.1 Hz); 7.89 (t, 1 H, H(6), J_1 = 7.8 Hz, J_2 = 8.7 Hz); 8.21 (m, 3 H, H(2), H(3), H(7)); 8.73 (br.d, 1 H, H(5), J = 8.7 Hz); 18.59 (br.s, 1 H, NH).

[4,4′,5,5′-Tetrakis(dimethylamino)-1,1′-dinaphthyl]methanol (6i). A solution of aldehyde **5b** [6] (0.25 g, 1 mmol) in Et_2O (2 mL) was added with stirring to a solution of lithium derivative **4b** (1 mmol) cooled to −30 °C. The reaction mixture was kept at −30 °C for 5 h and then at ~20 °C for 30 min and poured into water. The ethereal layer was separated, the aqueous layer was extracted with $CHCl_3$ (4×2 mL), and the extracts were combined and concentrated. The reaction product was isolated by chromatography by collecting the major colorless fraction (TLC control). After removal of $CHCl_3$, a pale-yellow viscous substance was obtained, which was crystallized from *n*-hexane. Compound **6i** was obtained as transparent rhombic crystals in a yield of 0.21 g (54%). The crystals possess strong refracting properties and melted with decomposition. MS, *m/z* (I_{rel} (%)): 456 $[M]^+$ (77), 441 $[M - Me]^+$ (8), 410 $[M - Me - MeNH_2]^+$ (11), 243 (2). IR (CCl_4), ν/cm^{-1}: 3613, 3406, 3255 (OH); 3066, 3014, 2934, 2830, 2772 (CH).

4,4′,5,5′-Tetrakis(dimethylamino)-1,1′-dinaphthyl ketone (8). Freshly sublimed $AlCl_3$ (1 g, 7.5 mmol) and oxalyl chloride (0.4 mL, 4.7 mmol) in CH_2Cl_2 (15 mL) were placed in a flask equipped with a stirrer, a reflux condenser, and a dropping funnel with protection from atmospheric moisture and refluxed with stirring for 20 min. Then 1,8-bis(dimethylamino)naphthalene hydrochloride (1.45 g, 5.8 mmol) was added with stirring to the resulting transparent solution at ~20 °C and the suspension was refluxed for 1 h after which oxalyl chloride (0.4 g) and $AlCl_3$ (0.5 g) were added. The reaction mixture was heated with stirring for 2 h and then carefully poured onto crushed ice (100 g), alkalized with a 20% NaOH solution to pH ~11, and extracted with $CHCl_3$ (3×50 mL). The solvent was distilled off, the residue was chromatographed, and the first yellow-orange fraction containing ketone **8** was collected. Compound **8** was obtained in a yield of 0.78 g (60%) as yellow crystals, m.p. 170—171 °C (from *n*-octane). Found (%): C, 77.01; H, 7.50; N, 12.30. $C_{29}H_{34}N_4O$. Calculated (%): C, 76.62; H, 7.54; N, 12.32. ^1H NMR, δ: 2.78 and 2.86 (both s, 12 H each, C(5,5′)NMe_2 and C(4,4′)NMe_2); 6.69 (d, 2 H, H(3), H(3′), *J* = 8.2 Hz); 6.94 (dd, 2 H, H(6), H(6′), J_1 = 0.9 Hz, J_2 = 7.6 Hz); 7.35 (dd, 2 H, H(7), H(7′), *J* = 8.5 Hz); 7.42 (dd, 2 H, H(2), H(2′), *J* = 8.2 Hz); 8.25 (dd, 2 H, H(8), H(8′), J_1 = 0.9 Hz, J_2 = 8.5 Hz). MS, *m/z* (I_{rel} (%)): 454 $[M]^+$ (100), 439 $[M - Me]^+$ (7), 426 $[M - CO]^+$ (16), 408 $[M - Me - MeNH_2]^+$ (12), 256 (29). IR (Nujol mulls), ν/cm^{-1}: 1633 (C=O); 1561, 1510 (ring).

Reduction of ketone 8 with $LiAlH_4$. A solution of ketone **8** (0.45 g, 1 mmol) in ether (10 mL) was added portionwise to a suspension of $LiAlH_4$ (0.04 g, 1 mmol) in Et_2O (10 mL). The reaction mixture was heated on a water bath to weak reflux, kept for 20 min, and carefully hydrolyzed with water (10 mL). The organic layer was separated and the aqueous layer was extracted with ether (2×5 mL). The extracts were combined and dried with anhydrous Na_2SO_4. The solvent was removed and alcohol **6i** was obtained in a yield of 0.4 g (89%) as colorless crystals. A mixture with the authentic sample did not give a melting point depression.

Analogously, alcohol **6f** was obtained in quantitative yield by reduction of benzoyl **7a**. The physicochemical properties of the resulting compound are identical with the properties of the specimen prepared as described above.

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