peri-Naphthylenediamines
35.* Unusual behavior of "proton sponge"-derived Mannich bases

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Aminomethylation of 1,8-bis(dimethylamino)naphthalene ("proton sponge") afforded a series of its 4-dialkylaminomethyl-substituted derivatives. An attempt to introduce the second *peri*-dialkylaminomethyl group unexpectedly led to the formation of salts with the 2,2-dialkyl-6,7-bis(dimethylamino)-2-azonia-2,3-dihydrophenalene cation. The structure of one of these salts was established by X-ray diffraction analysis. Treatment of 1,8-bis(dimethylamino)-4-piperidinomethylnaphthalene with iodomethane gave a spiro compound rather than the expected *N*-[4,5-bis(dimethylamino)-1-naphthylmethyl]-*N*-methylpiperidinium iodide. This spiro compound was generated through cyclodimerization of the 1-naphthylmethyl carbocations. These transformations provide evidence that "proton sponge"-derived Mannich bases quaternized at the dialkylaminomethyl group are unstable and undergo the spontaneous transformation into the resonance-stabilized 4,5-bis(dimethylamino)-1-naphthylmethyl carbocation. By contrast, 4-dialkylamino-1-dimethylaminomethylnaphthalenes gave methoiodides, which are stable under standard conditions. The latter compounds undergo the nucleophilic substitution of the NR_3 group typical of such salts.

Key words: 1,8-bis(dimethylamino)naphthalene, 1-dimethylaminonaphthalene, "proton sponge", Mannich bases, aminomethylation, naphthylmethyl carbocations, 2-azonia-2,3-dihydrophenalene, spiro compounds, X-ray diffraction analysis.

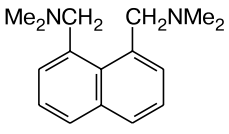
The previous studies of 1,8-bis(dialkylamino)naphthalenes ("proton sponges") have demonstrated that these compounds are of interest not only (and even not primarily) because of their high basicity but also because of their reactivity, which is untypical of most of usual naphthalene derivatives (see the review[3]). Cyclodimerization of 4,5-bis(dimethylamino)-1-naphthylmethyl carbocation **2** is perhaps the most prominent example (Scheme 1). Depending on the mode of generation of this carbocation from alcohol **1**, this reaction afforded spiro compounds **3** or **4**,[4—7] which are structurally similar to the known cyclohexadienone alkaloids.[8]

In continuation of these investigations, we found that the tendency to produce carbocations of type **2** in the series of "proton sponges" is so high that it has a strong effect on the reactivities of many other derivatives of "proton sponges." In particular, in the present study we report on the unusual behavior of 1,8-bis(dimethylamino)naphthalene-derived Mannich bases.

The reactions of 1,8-bis(dimethylamino)naphthalene (**5**) with equimolar amounts of formaldehyde and piperidine, morpholine, or diethylamine in an AcOH medium afforded previously unknown Mannich bases **6a—c** in good yields (Scheme 2).

Mannich base **6d** was prepared by treating compound **5** with an equimolar amount of bis(dimethylamino)methane in an AcOH medium[9] or with *N,N*-dimethylmethyleneammonium chloride in anhydrous MeCN [10] in 79 and 47% yields, respectively (Scheme 3).

Taking into account considerable interest in 1,8-bis(dimethylaminomethyl)naphthalene (**7**),[11] it seemed attractive to us to introduce the second dialkylaminomethyl group at the free *peri* position of Mannich bases **6**. Treatment of compound **5** with two equivalents of bis(dimethylamino)methane or a piperidine—formaldehyde mixture in acidic conditions did not lead to bis-aminomethylation. At room temperature, the reaction stopped at the step of formation of monosubstitution products **6a** or **6d**. At 55—60 °C, the reaction gave rise to a complex



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* For Part 34, see Ref. 1. This paper simultaneously presents Part 6 of the series "Resonance-stabilized α-naphthylmethyl carbocations and derived spiro compounds;" for Part 5, see Ref. 2.

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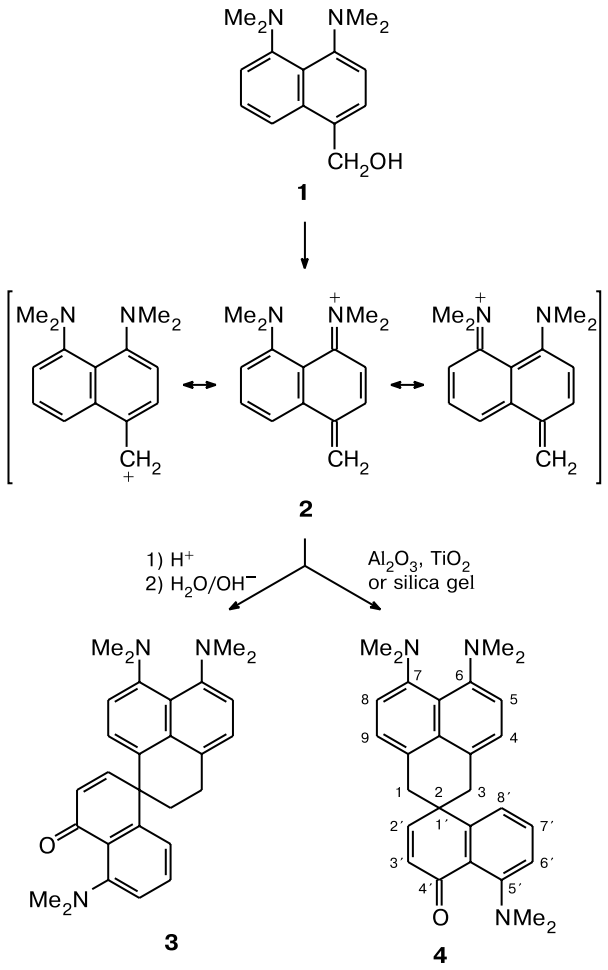
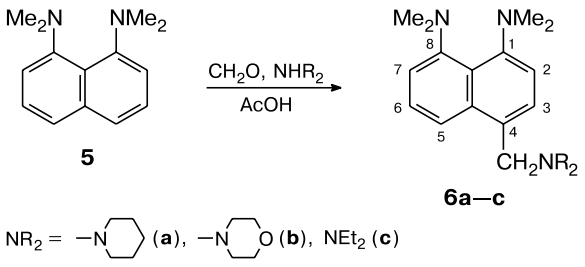
Scheme 1

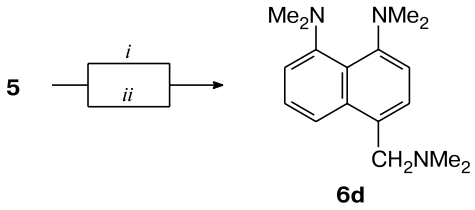


Scheme 2



mixture of compounds, which were difficult to separate. Compound **6a** also did not undergo further aminomethylation under the action of a piperidine—formaldehyde mixture. Thus, the reaction mixture underwent only resinification upon its storage at 55—60 °C until the starting compound disappeared. At lower temperatures, the reaction did not proceed at all. In a neutral medium, the reaction of 1,8-bis(dimethylamino)naphthalene (**5**) with two equivalents of *N,N*-dimethylmethyleneammonium

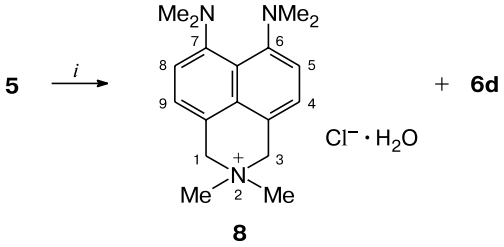
Scheme 3



i. $Me_2NCH_2NMe_2$ (1 equiv.), AcOH;
ii. $CH_2{=}N^+Me_2Cl^-$ (1 equiv.), MeCN.

chloride unexpectedly afforded 6,7-bis(dimethylamino)-2,2-dimethyl-2-azonia-2,3-dihydrophenalene chloride monohydrate (**8**) (in 47% yield) along with 4-dimethylaminomethyl derivative **6d** (27%) (Scheme 4). The structure of compound **8** was confirmed by the ^{1}H NMR and IR spectroscopic data and results of elemental analysis.

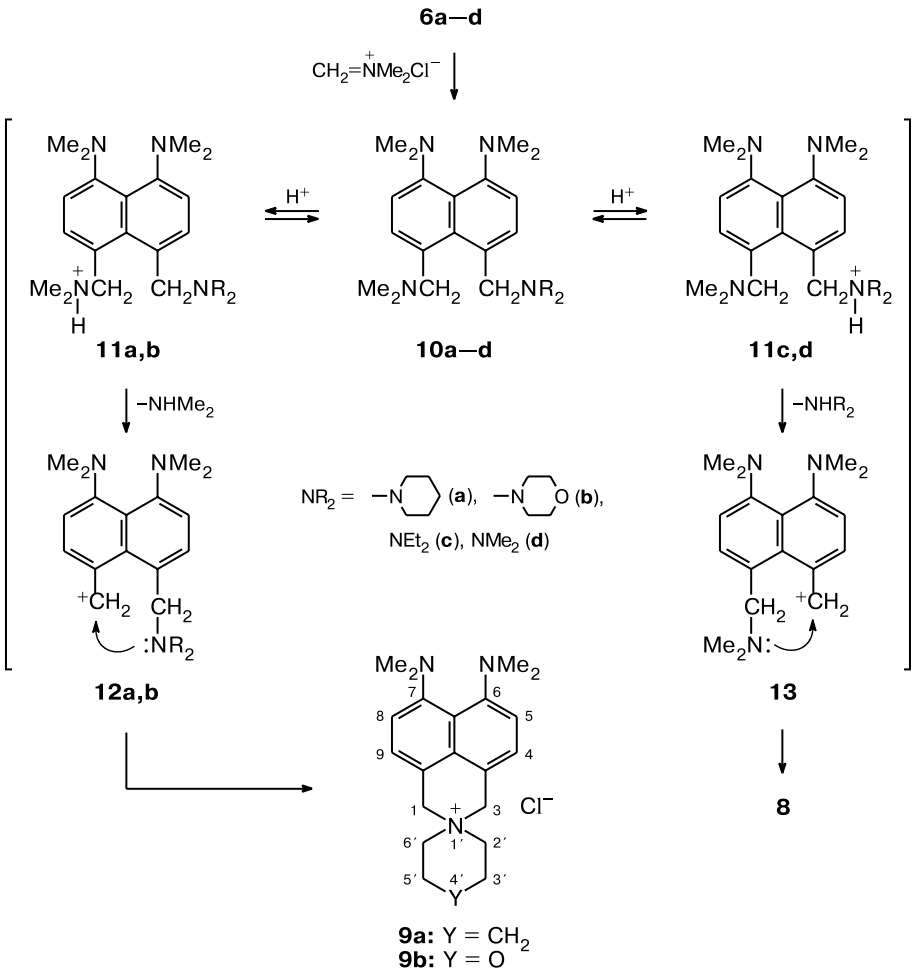
Scheme 4



i. $CH_2{=}N^+Me_2Cl^-$ (2 equiv.), MeCN.

Under similar conditions, aminomethylation of 4-dimethylaminomethyl-1,8-bis(dimethylamino)naphthalene (**6d**) and, which is particularly interesting, of 4-diethylaminomethyl derivative **6c** also produced salt **8** in 20 and 29% yields, respectively. However, the aminomethylation products derived from Mannich bases **6a,b** have structures **9a,b**, which differ in that the onium center is involved in the piperidine or morpholine rings (37—38% yields). The probable mechanism of the formation of compounds **8** and **9a,b** is shown in Scheme 5. Undoubtedly, the first step of this reaction gives Mannich bis-base **10**, which is in equilibrium with protonated forms **11a,b** or **11c,d** (protonation can proceed through the proton eliminated upon aminomethylation). Cations **11a,d** undergo further rapid intramolecular substitution of the Me_2NH or R_2NH group. Most likely, the direction of cyclization is controlled by the accessibility of the lone electron pairs of the NR_2 groups. Taking into account that Mannich bis-base **7** is stable in an acidic medium,[11] it is evident that the driving force for the observed cyclization is the strong electron-donating effect of the *peri*-dimethylamino groups, which ensure constant stability of carbocations **12a,b** and **13** and, hence, facilitate the S_N1 mechanism.

Scheme 5



The ^{1}H NMR spectra of salts **8** and **9a,b** are characterized by simplicity typical of symmetrical 4,5-disubstituted "proton sponge" derivatives. In particular, these spectra have doublets for two pairs of the equivalent *ortho*- and *meta*-protons of the naphthalene ring, *viz.*, H(5) and H(8), H(4) and H(9), and singlets for the protons of two methylene groups of the dihydroazaphenalene fragment. The equivalence of the geminal protons of the latter groups indicates that the piperidinium ring in cation **8** undergoes rapid inversion under standard conditions by analogy with the inversion of the CH_2—X—CH_2 bridge (X = CH_2, O, S, Se, or Te) in the corresponding *peri*-disubstituted naphthalenes.[12]

We succeeded in growing crystals of diperchlorate **14** suitable for X-ray diffraction analysis. The crystals contain two independent and virtually identical dications (Fig. 1) and four independent anions two of which are disordered. The piperidinium ring in the dications adopts a half-chair conformation. The back of the half-chair forms dihedral angles of 51.9(2) and 50.1(3)° with the remaining plane of the piperidine fragment. The fragment of protonated 1,8-bis(dimethylamino)naphthalene, like that in other analogous compounds,[3,13] is virtually planar although the N(1) and N(2) atoms deviate from the plane of the naphthalene ring by −0.075(5) and 0.064(5) Å, respectively, in one dication and by −0.020(5) and 0.190(5) Å in another dication. The parameters of the hydrogen bridge (see Table 1) are indicative of its noticeable asymmetry and are, on the whole, very

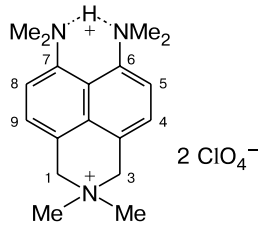


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Table 1. Geometric parameters of the N—H...N hydrogen bonds for two independent cations **14** (distances (d/Å) and angles (ω/deg)) according to the results of X-ray diffraction analysis

Distance	d(N—H)	d(H...N)	d(N...N)	ω(NH...N)
N(2)H...N(1)	1.08	1.48	2.55	172
N(5)H...N(4)	1.19	1.44	2.57	157

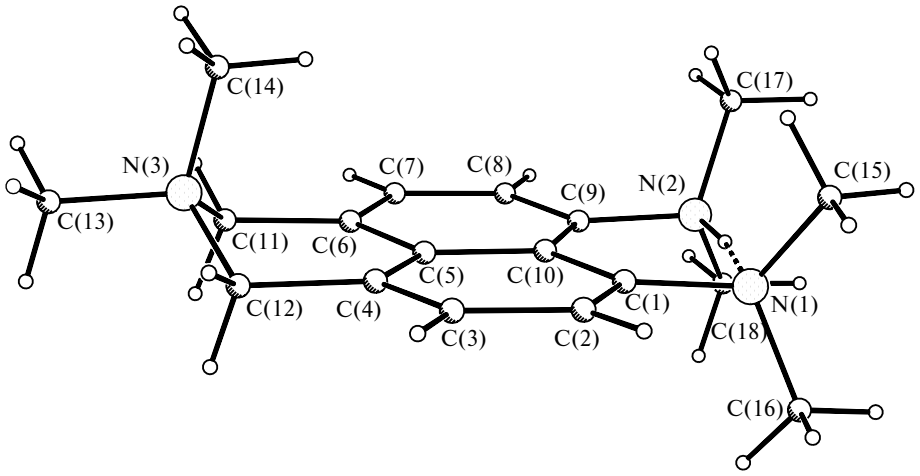


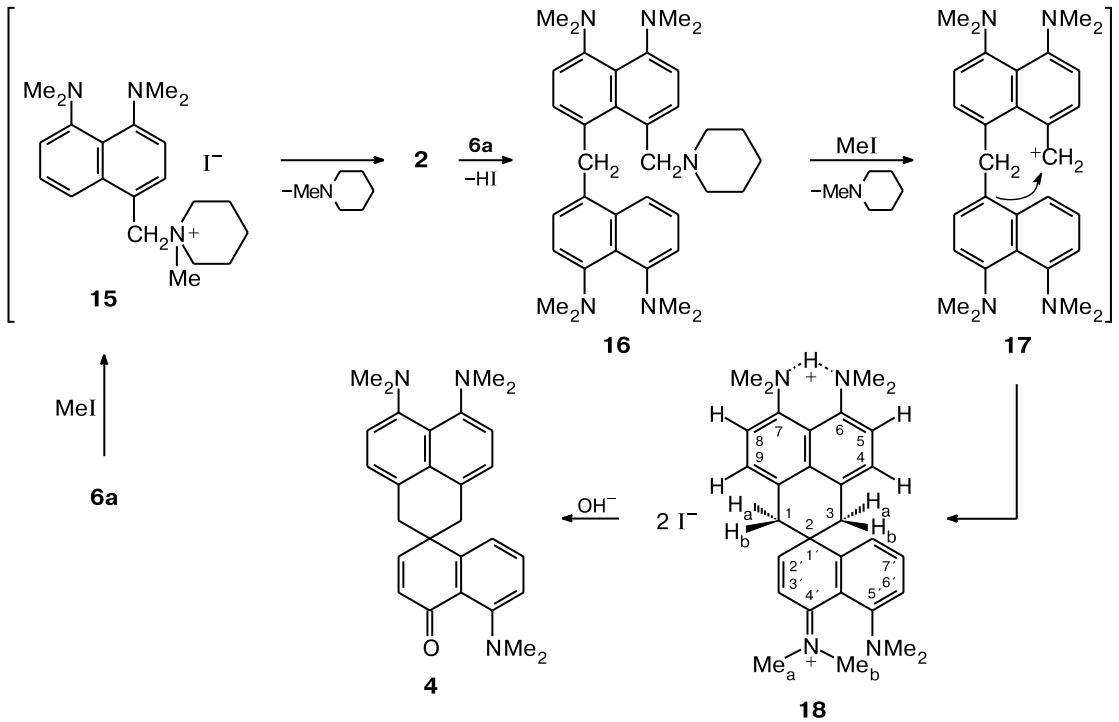
Fig. 1. Overall view of one of the independent cations in the crystal structure of **14**.

similar to the characteristics of the hydrogen bonds in other unsymmetrical salts of "proton sponges."[3]

The fact that the naphthylmethyl carbocations can be readily generated from "proton sponge"-derived Mannich bases is also confirmed by another our observation. Methylation of Mannich base **6a** with a small excess of MeI in acetone afforded immonium salt **18**. Refluxing of the latter salt in aqueous alkali over a short period of time gave rise to spiro compound **4** (in ~40% yield, see Scheme 6), which has been prepared earlier according to another procedure.[6,7]

The ^{1}H NMR spectrum of compound **18** has two three-proton singlets at δ_H 3.29 and 3.77 belonging, apparently, to the nonequivalent methyl groups of the $=N^+Me_2$ fragment. In addition, the spectrum shows doublets for the quinoid protons at δ_H 6.57 and 7.20 with the characteristic spin-spin coupling constant J_o = 10.8 Hz. The presence of a singlet at δ_H 18.52 signifies that the 1,8-bis(dimethylamino)naphthalene fragment in salt **18** is protonated, *i.e.*, this salt occurs as the dication. Apparently, the intramolecular hydrogen bond in this fragment is asymmetrical as evidenced by

Scheme 6

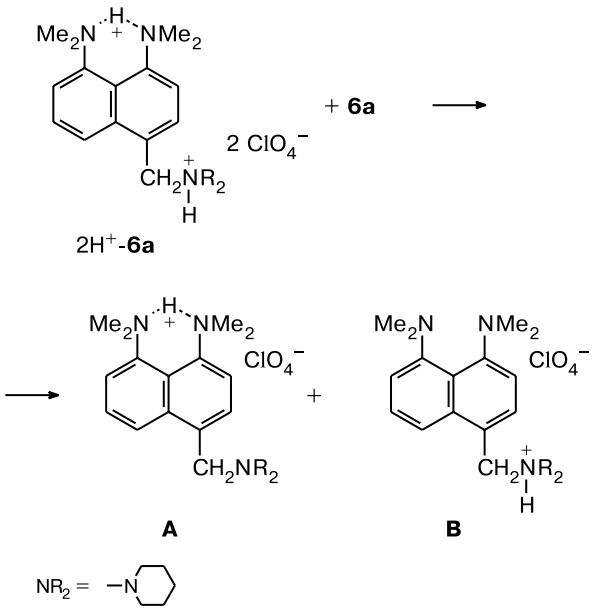


the nonequivalence of the H(5), H(8) and H(4), H(9) protons.

Evidently, the transformation **6a** → **4** started with the formation of quaternary salt **15**, which dissociated to produce resonance-stabilized carbocation **2**. The attack of the latter on position 5 of molecule **6a** afforded intermediate **16** from which carbocation **17** was generated in an analogous way. The subsequent intramolecular *ipso*-attack of the carbenium center on position 4 of another residue of "proton sponge" of carbocation **17** gave immonium salt **18**, which was hydrolyzed to form spiro product **4** (see Scheme 6).

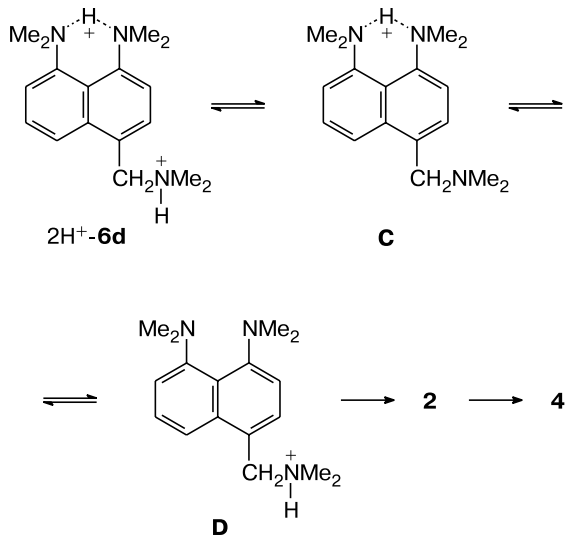
One would expect that carbocation **2** and then spiro compound **4** will be generated from an analog of quaternary salt **15**, which is a monoprotonated form of Mannich base. However, this situation is in actuality realized only partially because pK_a of the dialkylaminomethyl group is close to that of the fragment including the *peri*-dimethylamino groups. Thus, in attempting to prepare monocations of Mannich bases by treating them with one equivalent of $HClO_4$, we invariably isolated the corresponding diperchlorate. In the ^1H NMR spectrum of the latter compound, the proton chelated by the NMe_2 groups and the proton bound to the CH_2NR_2 group are manifested as slightly broadened peaks at δ_H 18.7 and 9.2, respectively. The addition of one equivalent of Mannich base **6a** to a solution of diperchlorate **6a** · $2HClO_4$ afforded an equilibrium mixture of monocations consisting of the form **A** (62%) and the form **B** of the cation H^+-**6a** (38%) (Scheme 7).

Scheme 7



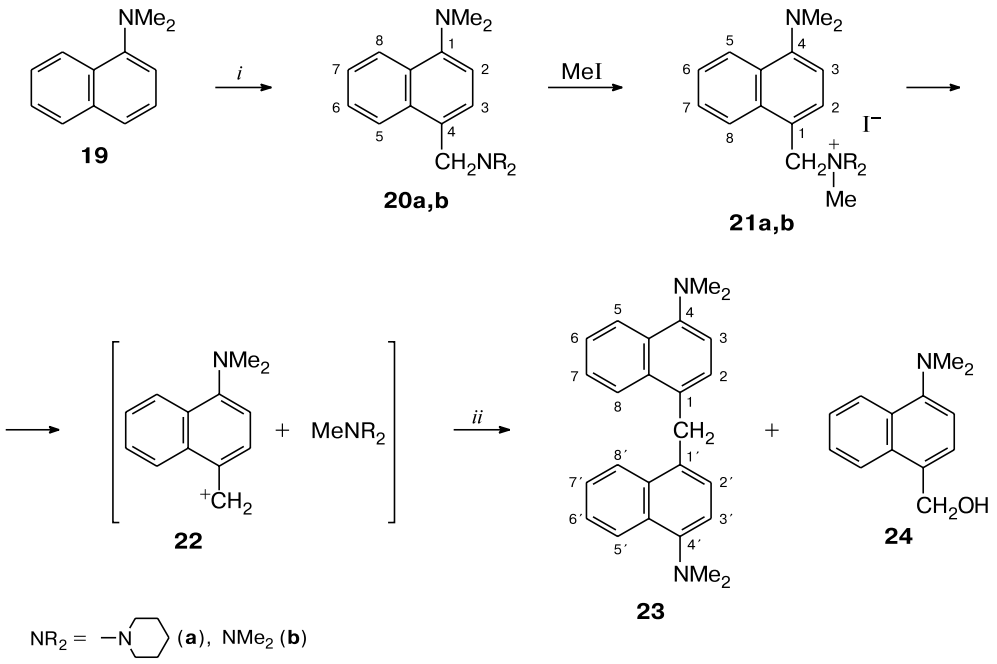
Further experiments on protonation were carried out predominantly with the use of base **6d** (Scheme 8). Evidently, carbocation **2** must be generated primarily from the form **D** of the monocation H^+-**6d** through elimination of dimethylamine. However, the equilibrium in a strongly acidic medium is virtually completely shifted to the dication $2H^+$-**6d**. Because of this, the Mannich base remained virtually intact even upon prolonged refluxing of **6d** in HCl or HBr. However, heating of diperchlorate in water (85 °C, 120 h) did afford spiro compound **4** in 44% yield. Apparently, this yield reflects the fact that equilibrium amounts of the form **D** of the monocation H^+-**6d** are involved in the process (see Scheme 8).

Scheme 8



Unlike the "proton sponge," 1-dimethylaminonaphthalene-derived Mannich bases produce carbocations not so readily and, consequently, behave traditionally.[14,15] Aminomethylation of 1-dimethylaminonaphthalene (**19**) with an equimolar amount of a piperidine—formaldehyde mixture or bis(dimethylamino)methane in an AcOH medium gave Mannich bases **20a,b** in 77 and 53% yields, respectively. Upon treatment with iodomethane, the latter compounds readily underwent quaternization at the dialkylamino group to form stable salts **21a,b**. Further refluxing of these salts in water or a 10% KOH solution gave rise to binaphthylmethane **23** [16] and 4-hydroxymethyl-1-dimethylaminonaphthalene **24** (Scheme 9). It should be noted that the reaction in water afforded binaphthylmethane **23** as the major product (~70%), whereas the yield of the alcohol varied from trace amounts (for salt **21a**) to 9% (for **21b**). By contrast, the reaction in an alkaline medium gave alcohol **24** as the predominant product (~60%), whereas compound **23** was isolated in low yield (6—8%). The reason for this difference is quite evident. In water, alcohol **24** coexists, apparently, with equilibrium amounts of carbocation **22**, and the *ipso*-replacement of the CH_2OH group with carbocation **22** (by

Scheme 9



i. CH_2O, HN⟨⟩, AcOH or $Me_2NCH_2NMe_2$, AcOH; *ii*. H_2O or aqueous KOH.

analogy with other similar reactions[3,7]) gives rise to binaphthylmethane **23**. Being a very weak nucleophile, water competes with this process to only a small extent. By contrast, the nucleophilic substitution with the use of a much stronger nucleophile, such as alkali, gives predominantly alcohol **24**.

Therefore, the presence of the second *peri*-dimethylamino group in compounds **6a—d** leads to a qualitative change in the reactivity of Mannich bases of the naphthalene series. Under appropriate conditions, these compounds can readily generate the resonance-stabilized 4,5-bis(dimethylamino)-1-naphthylmethyl carbocations, which undergo various, including synthetically valuable, transformations.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker DPX-250 spectrometer (250 MHz), and the ^{1}H NMR spectra of compounds **6a,b** were measured on a Unity-300 instrument (300 MHz) with $SiMe_4$ as the internal standard. The IR spectra were recorded on a UR-20 spectrometer in Nujol mulls. Chromatography was carried out on columns with Al_2O_3 (for activity grade according to Brockmann, see below). The course of the reactions and purities of the resulting compounds were monitored by TLC on glass plates with a nonfixed Al_2O_3 layer (the eluents are indicated in each experiment); visualization was carried out with iodine vapor (unless otherwise specified). The melting points were measured in sealed glass tubes and were not corrected. Commercially available 1,8-bis(dimethylamino)naphthalene (Merck) and *N,N*-dimethylmethyleneammonium chloride (Fluka) were used. Acetone was dried over $CaCl_2$.

Colorless crystals of diperchlorate **14** suitable for X-ray diffraction analysis were prepared by isothermal evaporation of its aqueous solution at 50 °C. The crystallographic characteristics and principal details of X-ray diffraction study are given in Table 2. The structure was solved by direct methods and refined by the least-squares method based on F^2_{hkl}. The oxygen atoms of two disordered anions were refined with occupancies of 0.58/0.42 and 0.63/0.37. The coordinates and thermal parameters of the nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference electron density maps and refined isotropically. All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[17] The atomic coordinates and complete crystallographic data for the structure of **14** were deposited with the Cambridge Structural Database (refcode CCDC 176387).

4-Dialkylaminomethyl-1,8-bis(dimethylamino)naphthalenes (6a—c) (general procedure). An ice-cooled mixture of secondary amine (1 mmol) and 40% formalin (0.07 mL, 1 mmol) was added to a solution of 1,8-bis(dimethylamino)naphthalene (**5**) (214 mg, 1 mmol) in glacial AcOH (0.15 mL). The resulting transparent solution was kept for several days (see below) at 25 °C, after which the reaction mixture was diluted with water and slowly made alkaline with a 20% aqueous solution of KOH to pH 12. The reaction products were extracted with AcOEt (3×5 mL). The solution was concentrated to dryness *in vacuo*. The residue was chomatographed on Al_2O_3 (IV) (d = 2 cm, l = 5.5 cm, hexane as the eluent), and the main colorless fraction was collected (R_f in the TLC conditions are reported below). The ^{1}H NMR spectroscopic data for compounds **6a—c** are given in Table 3.

Table 2. Crystallographic characteristics and details of X-ray diffraction study for compound **14**

Parameter	Characteristic
Molecular formula	$C_{18}H_{27}Cl_2N_3O_8$
Molecular weight	484.33
Space group	$P\bar{1}$
a/Å	9.4663(12)
b/Å	12.0213(14)
c/Å	20.547(2)
α/deg	81.564(3)
β/deg	81.812(3)
γ/deg	73.198(3)
V/Å^3	2201.7(5)
Z	4
d_{calc}/g cm^{-3}	1.461
F(000)	1016
μ/cm^{-1}	3.45
Diffractometer	«Bruker SMART 1000 CCD»
T/K	140(2)
Scan mode	ω
θ_{max}/deg	1.78—28.04
Number of measured reflection	22826
Number of independent reflections (R_{int})	10472 (0.0829)
Number of independent reflection with $I \geq 2\sigma(I)$	4589
R_1 (based on F for reflections with $I \geq 2\sigma(I)$)	0.0870
wR_2 (based on F^2 for all reflections)	0.1427
Number of refinable parameters	633
GOOF	0.883

Colorless crystals of diperchlorate were obtained (quantitative yield) by treatment of compounds **6a,c,d** with two equivalents of 70% $HClO_4$ in AcOEt followed by the addition of ether. The ^{1}H NMR spectroscopic data for salts **6a,c,d**·2$HClO_4$ are given in Table 4.

1,8-Bis(dimethylamino)-4-piperidinomethylnaphthalene (6a). The reaction time was 36 h. The yield was 86%. Colorless viscous oil, R_f 0.07. Found (%): C, 76.98; H, 9.37. $C_{20}H_{29}N_3$. Calculated (%): C, 77.12; H, 9.38.

Diperchlorate 6a·2$HClO_4$, colorless crystals, m.p. 236—237 °C (with decomp., from MeCN). Found (%): C, 46.68; H, 6.05; Cl, 13.45. $C_{20}H_{31}Cl_2N_3O_8$. Calculated (%): C, 46.88; H, 6.09; Cl, 13.84.

1,8-Bis(dimethylamino)-4-morpholinomethylnaphthalene (6b). The reaction time was 3 days. The yield was 85%. Colorless viscous oil, R_f 0.03. Found (%): C, 72.51; H, 8.67. $C_{19}H_{27}N_3O$. Calculated (%): C, 72.81; H, 8.68.

4-Diethylaminomethyl-1,8-bis(dimethylamino)naphthalene (6c). The reaction time was 2 days. The yield was 45% (when the reaction was carried out at 5 °C, the yield was 67%). Pale-straw-colored viscous oil, R_f 0.04. Found (%): C, 75.93; H, 9.74. $C_{19}H_{29}N_3$. Calculated (%): C, 76.20; H, 9.76.

Diperchlorate 6c·2$HClO_4$, colorless crystals, m.p. 193—194 °C (with decomp., from EtOH). Found (%): C, 45.46; H, 6.23; Cl, 13.92. $C_{19}H_{31}Cl_2N_3O_8$. Calculated (%): C, 45.61; H, 6.24; Cl, 14.17.

4-Dimethylaminomethyl-1,8-bis(dimethylamino)naphthalene (6d). ***A.*** Bis(dimethylamino)methane (0.33 mL, 2.55 mmol)[18] was added to a solution of 1,8-bis(dimethylamino)naphthalene (**5**) (0.5 g, 2.33 mmol) in glacial AcOH (0.34 mL) on cooling with ice. The resulting colorless solution was vigorously shaken for 5 min and then kept at 25 °C for 24 h. The reaction mixture was diluted twice with water and slowly made alkaline with a 20% aqueous solution of KOH to pH 12. The reaction products were extracted with AcOEt (3×5 mL). The solvent was evaporated *in vacuo*. The residue was chromatographed on Al_2O_3 (IV) (d = 3 cm, l = 5.5 cm, hexane as the eluent), and the main colorless fraction was collected (R_f 0.06). The yield was 0.5 g (79%). Compound **6d** was obtained as a colorless viscous oil whose ^{1}H NMR spectrum corresponds to the data published earlier.[6]

Diperchlorate 6d·2$HClO_4$, colorless crystals, m.p. 227—228 °C (with decomp., from MeCN). Found (%): C, 43.00; H, 5.76; Cl, 14.79. $C_{17}H_{27}Cl_2N_3O_8$. Calculated (%): C, 43.23; H, 5.76; Cl, 15.01.

B. A solution of 1,8-bis(dimethylamino)naphthalene (**5**) (300 mg, 1.4 mmol) in anhydrous MeCN (3 mL) was added to a suspension of *N,N*-dimethylmethyleneammonium chloride

Table 3. Parameters of the ^{1}H NMR spectra ($CDCl_3$, δ, J/Hz) of compounds **6a—c**

Compound	NMe_2 (both s, 6 H each, 1-, 8-NMe_2)	H(2)	H(3)	H(5)	H(6), t	H(7)	$ArCH_2N$, s	R
6a	2.79 and 2.80	6.85 (d, $J_{2,3}$ = 7.7)	7.26 (d, $J_{3,2}$ = 7.7)	7.84 (dd, $J_{5,6}$ = 8.4, $J_{5,7}$ = 0.95)	7.35 ($J_{6,7}$ = 7.7, $J_{6,5}$ = 8.2)	6.95 (dd, $J_{7,6}$ = 7.5, $J_{7,5}$ = 0.84)	3.73	1.45 (m, 2 H, C(4′)H_2); 1.57, 2.46 (both m, 4 H each, C(3′)H_2, C(5′)H_2; C(2′)H_2, C(6′)H_2)
6b	2.771 and 2.776	6.80 (br.d, $J_{2,3}$ = 7.6)	7.21 (br.d, $J_{3,2}$ = 7.6)	7.80 (br.d, $J_{5,6}$ = 8.1)	7.33 ($J_{6,7}$ = 7.8, $J_{6,5}$ = 8.0)	6.93 (br.d, $J_{7,6}$ = 7.5)	3.74	2.47, 3.67 (both m, 4 H each, C(3′)H_2, C(5′)H_2; C(2′)H_2, C(6′)H_2)
6c	2.772 and 2.783	6.83 (d, $J_{2,3}$ = 7.7)	7.29 (br.d, $J_{3,2}$ = 7.7)	7.81 (dd, $J_{5,6}$ = 8.4, $J_{5,7}$ = 0.94)	7.32 ($J_{6,7}$ = 7.6, $J_{6,5}$ = 8.3)	6.92 (dd, $J_{7,6}$ = 7.6, $J_{7,5}$ = 0.94)	3.84	1.06 (t, 6 H, $N(CH_2C\underline{H}_3)_2$; 2.58 (q, 4 H, $N(C\underline{H}_2CH_3)_2$

Table 4. Parameters of the ^{1}H NMR spectra (DMSO-d_6, δ, *J*/Hz) of diperchlorates of compounds **6a,c,d**

Compound	NMe_2 (d, 12 H, 1-, 8-NMe_2)	H(2), d	H(3), d	H(5), dd	H(6), t	H(7), dd	$C\underline{H}_2N^+H$, s	H_{chel}, br.s	$CH_2N^+\underline{H}$, s	R
6a · $2HClO_4$	3.14	8.21, $J_{2,3}$ = 7.7	7.98, $J_{3,2}$ = 7.9	8.49, $J_{5,6}$ = 8.6	7.90, $J_{6,7}$ = 8.0, $J_{6,5}$ = 8.2	8.21, $J_{7,6}$ = 7.7	4.84	18.69	9.22	1.60 (m, 6 H, C(3′)H_2, C(4′)H_2, C(5′)H_2); 3.16 (m, 4 H, C(2′)H_2, C(6′)H_2)
6c · $2HClO_4$	3.15	8.23, $J_{2,3}$ = 7.6	7.99, $J_{3,2}$ = 7.9	8.39, $J_{5,6}$ = 8.6	7.92, $J_{6,7}$ = 8.0, $J_{6,5}$ = 8.2	8.21, $J_{7,6}$ = 7.9	4.86	18.72	9.29	1.26 (t, 6 H, $N(CH_2C\underline{H}_3)_2$); 3.15 (q, 4 H, $N(C\underline{H}_2CH_3)_2$)
6d · $2HClO_4$	3.16	8.22, $J_{2,3}$ = 7.7	7.97, $J_{3,2}$ = 7.9	8.48, $J_{5,6}$ = 8.6	7.91, $J_{6,7}$ = 8.0, $J_{6,5}$ = 8.2	8.22, $J_{7,6}$ = 7.7	4.86	18.70	9.64	2.83 (s, 6 H, NMe_2)

(145 mg, 1.55 mmol) in anhydrous MeCN (5 mL) under argon. The reaction mixture was stirred at 20 °C for 2.5 h. The acetonitrile was evaporated *in vacuo*. The residue was diluted with water (2 mL) and made alkaline with a 20% aqueous solution of KOH to pH 12. The reaction products were extracted with AcOEt (3×5 mL). The solvent was removed *in vacuo*. The residue was chomatographed on Al_2O_3 (IV) (*d* = 2 cm, *l* = 5.5 cm) and compound **6d** was eluted with hexane in a yield of 178 mg (47%).

C. A solution of 1,8-bis(dimethylamino)naphthalene (**5**) (170 mg, 0.79 mmol) in anhydrous MeCN (2 mL) was added to a suspension of *N,N*-dimethylmethyleneammonium chloride (160 mg, 1.71 mmol) in anhydrous MeCN (5 mL) under argon. The reaction mixture was stirred at 20 °C for 2.5 h. The acetonitrile was evaporated *in vacuo*. The residue was diluted with water (2 mL), made alkaline with a 20% aqueous solution of KOH to pH 12, and extracted with AcOEt (3×3 mL). The solvent was evaporated. The residue was chromatographed on Al_2O_3 (IV) (*d* = 1 cm, *l* = 3 cm, hexane as the eluent), and a colorless fraction of compound **6d** was collected in a yield of 59 mg (27%).

The aqueous phase was concentrated to dryness *in vacuo*. The residue was treated with hot MeCN (2 mL) and the undissolved precipitate was filtered off. After evaporation of the solvent, a pale-beige powder of compound **8** was obtained in a yield of 127 mg (47%). **6,7-Bis(dimethylamino)-2,2-dimethyl-2-azonia-2,3-dihydrophenalene chloride monohydrate (8)** was obtained as small pale-beige crystals, which darkened upon heating above 235 °C, m.p. 253—254 °C (with decomp., from a MeCN—C_6H_6 mixture, 1 : 1). Found (%): C, 63.53; H, 8.35; Cl, 9.93; N, 12.20. $C_{18}H_{26}ClN_3 \cdot H_2O$. Calculated (%): C, 63.98; H, 8.35; Cl, 10.49; N, 12.44. IR, ν/cm^{-1}: 3480, 3400 (H_2O), 1589 (C—C_{ar}). ^{1}H NMR ($CDCl_3$), δ: 2.77 (s, 12 H, 6-, 7-NMe_2); 3.55 (s, 6 H, C(2)N^+Me_2); 5.02 (s, 4 H, C(1)H_2, C(3)H_2); 6.85 and 7.22 (both d, 2 H each, H(5), H(8) and H(4), H(9), $J_{4,5}$ = $J_{8,9}$ = 7.8 Hz).

A 70% $HClO_4$ solution (0.01 mL, 0.118 mmol) was added to a solution of salt **8** (20 mg, 0.059 mmol) in anhydrous EtOH (2 mL). The colorless precipitate of **6,7-bis(dimethylamino)-2,2-dimethyl-2-azonia-2,3-dihydrophenalene diperchlorate (14)** that formed was filtered off, washed with ether, and dried in air. The yield was quantitative. Colorless crystals (darkened upon heating above 210 °C), m.p. 278—279 °C (with decomp., from H_2O). Found (%): C, 44.39; H, 5.61; Cl, 14.19; N, 8.35. $C_{18}H_{27}Cl_2N_3O_8$. Calculated (%): C, 44.64; H, 5.62; Cl, 14.64; N, 8.68. ^{1}H NMR (DMSO-d_6), δ: 3.16 (s, 12 H, 6-, 7-NMe_2); 3.28 (s, 6 H, C(2)N^+Me_2); 5.25 (s, 4 H, C(1)H_2, C(3)H_2); 7.76 and 8.26 (both d, 2 H each, H(4), H(9) and H(5), H(8), $J_{4,5}$ = $J_{8,9}$ = 7.8 Hz); 18.22 (br.s, 1 H, NH).

Reaction of 4-dialkylaminomethyl-1,8-bis(dimethylamino)naphthalenes 6a—d with *N,N*-dimethylmethyleneammonium chloride (general procedure). A solution of the corresponding Mannich base **6a—d** (2 mL) in anhydrous MeCN (0.40 mmol) was added to a suspension of *N,N*-dimethylmethyleneammonium chloride (40 mg, 0.43 mmol) in anhydrous MeCN (2 mL) under argon. The reaction mixture was stirred at 20 °C for 2.5 h after which the solvent was concentrated to dryness. Water (2 mL) was added to the residue and the mixture was made alkaline with a 20% aqueous solution of KOH to pH 12. The aqueous phase was concentrated *in vacuo*. The residue was triturated with hexane and decanted. The precipitate was treated with hot MeCN (2 mL, for **8**) or hot $CHCl_3$ (5 mL, for **9a,b**). The undissolved residue was filtered off. After evaporation of the solvent, compounds **8** and **9a,b** were obtained as colorless or pale-cream powders. The yields of salts **8** from the starting compounds **6d** and **6c** were 20% and 29%, respectively. The yields of **9a** and **9b** were 37% and 37%, respectively.

6,7-Bis(dimethylamino)-spiro[2,3-dihydro-2-azoniaphenalene-2,1′-piperidinium] chloride (9a) was obtained as small pale-cream crystals, which darkened upon heating above 290 °C, m.p. 315—316 °C (with decomp., from MeCN). Found (%): C, 69.82; H, 8.39; Cl, 9.76; N, 11.24. $C_{21}H_{30}ClN_3$. Calculated (%): C, 70.08; H, 8.40; Cl, 9.85; N, 11.67. IR, ν/cm^{-1}: 1590 (C—C_{ar}). ^{1}H NMR ($CDCl_3$), δ: 1.84 (m, 6 H, C(3′)H_2, C(4′)H_2, C(5′)H_2); 2.77 (s, 12 H, 6-, 7-NMe_2); 3.80 (m, 4 H, C(2′)H_2, C(6′)H_2); 5.13 (s, 4 H, C(1)H_2, C(3)H_2); 6.85 and 7.23 (both d, 2 H each, H(5), H(8) and H(4), H(9), $J_{4,5}$ = $J_{8,9}$ = 7.9 Hz).

6,7-Bis(dimethylamino)-spiro[2,3-dihydro-2-azoniaphenalene-2,1′-morpholinium] chloride (9b) was obtained as small pale-yellow crystals, which darkened at a temperature higher than 270 °C, m.p. 309—310 °C (with decomp., from MeCN). Found (%): C, 66.05; H, 7.80; Cl, 9.49; N, 11.54. $C_{20}H_{28}ClN_3O$. Calculated (%): C, 66.38; H, 7.80; Cl, 9.79; N, 11.61. IR, ν/cm^{-1}: 1590 (C—C_{ar}). ^{1}H NMR (DMSO-d_6), δ: 2.76 (s, 12 H, 6-, 7-NMe_2); 3.44 and 3.99 (both br.s, 4 H each, C(2′)H_2, C(6′)H_2 and C(3′)H_2, C(5′)H_2); 5.08 (s, 4 H, C(1)H_2, C(3)H_2); 7.01 and 7.34 (both d, 2 H each, H(5), H(8) and H(4), H(9), $J_{4,5}$ = $J_{8,9}$ = 7.8 Hz).

6,7,5′-Tris(dimethylamino)-spiro[1,3-dihydrophenalene-2,1′-1′,4′-dihydronaphthalene]-4′-one (4). ***A.*** A mixture of compound **6a** (200 mg, 0.642 mmol), freshly distilled MeI (0.05 mL, 0.803 mmol), and anhydrous acetone (3 mL) was stirred at 20 °C for 2 h. The orange precipitate of immonium salt **18** that formed was filtered off and washed with benzene and ether. The yield was 93 mg, m.p. 205—206 °C (with decomp., from MeOH). ^{1}H NMR (DMSO-d_6), δ: 3.18 (br.m, 18 H, 5′,6,7-NMe_2); 3.29 and 3.77 (both s, 3 H each, $=N^+Me_2$); 3.60 and 4.04 (both d, 2 H* each, C(1)H_a, C(3)H_a, C(1)H_b, C(3)H_b, ^2J = −15.8 Hz); 6.57 (d, 1 H, H(3′), $J_{3',2'}$ = 10.8 Hz); 7.20 (d, 1 H, H(6′), $J_{6',7'}$ = 8.5 Hz); 7.34 (m, 2 H, H(2′), H(8′)); 7.48 (d, 1 H, H(4 or 9), ^3J = 7.7 Hz); 7.65 (m, 2 H, H(7′), H(9 or 4)); 8.07 (d, 1 H, H(5 or 8), ^3J = 7.8 Hz); 8.13 (d, 1 H, H(8 or 5), ^3J = 7.8 Hz); 18.58 (br.s, 1 H, NH).

Salt **18** (93 mg) was refluxed with a 20% aqueous solution of KOH (5 mL) for 20 min. Then yellow crystals of spiro compound **4** were filtered off. The product was chromatographed on Al_2O_3 (II) (d = 2 cm, l = 7 cm, $CHCl_3$ as the eluent), and the first yellow fraction was collected. The yield was 65 mg (40%), m.p. 158—159 °C (with decomp., from a EtOH—H_2O mixture, 5 : 1), which agrees with the published data.[6,7] The spectroscopic characteristics (^{1}H NMR and IR spectra) of the reaction product were identical with those of the authentic sample.

B. A solution of diperchlorate **6d**·$2HClO_4$ (200 mg, 0.42 mmol) in H_2O (5 mL) was kept at 85 °C for 120 h. Then the reaction mixture was cooled. The aqueous phase was decanted and concentrated (fraction 1). The resinous residue was treated with $CHCl_3$ (4×10 mL) and the solvent was distilled off (fraction 2). Each fraction was treated with a 20% aqueous solution of KOH (3 mL) (was brought to boiling). Then the solutions were cooled and the reaction products were extracted with $CHCl_3$ (3×2 mL). After evaporation of the chloroform from fraction 1, 4-dimethylaminomethyl-1,8-bis(dimethylamino)naphthalene (**6d**) was obtained in a yield of 17 mg (15%). Fraction 2 was chromatographed on Al_2O_3 (II) (d = 1.5 cm, l = 7 cm, $CHCl_3$ as the eluent), and the first yellow fraction was collected (R_f 0.14). The yield of compound **4** was 40 mg (44%). The ^{1}H NMR spectrum and m.p. of the product were identical with those of the authentic sample.

Transformation of 4-dimethylaminomethyl-1,8-bis(dimethylamino)naphthalene (6d) in hydrochloric acid. A solution of 4-dimethylaminomethyl-1,8-bis(dimethylamino)naphthalene (**6d**) (150 mg, 0.55 mmol) in 35% HCl (5 mL) was kept at 40 °C for 3 h. Then the reaction mixture was diluted twice with water and added to a 20% aqueous solution of KOH (10 mL). The product was extracted with $CHCl_3$ (3×5 mL) and the chloroform was distilled off. The starting base **6d** was obtained in a yield of 128 mg (85%); its physicochemical properties were identical with those of the authentic sample.

The use of concentrated HBr (5 mL) instead of hydrochloric acid (refluxing for 10 h) led only to more substantial resinification.

1-Dimethylamino-4-piperidinomethylnaphthalene (20a). An ice-cooled mixture of piperidine (0.37 mL, 3.74 mmol) and 40% formalin (0.25 mL, 3.74 mmol) was added to an emulsion of 1-dimethylaminonaphthalene (**19**) (0.63 g, 3.66 mmol) in glacial AcOH (0.21 mL); 95% EtOH (1 mL) was added for homogenization of the mixture. Then the reaction mixture was kept at 70—80 °C for 12 h, diluted with water (2 mL), and made alkaline with a 20% aqueous solution of KOH to pH 12. The reaction products were extracted with $CHCl_3$ (3×5 mL). The solution was concentrated to dryness *in vacuo*. The red-brown mixture was chromatographed on Al_2O_3 (II) (d = 2.5 cm, l = 6 cm, hexane as the eluent), and the main colorless fraction was collected (R_f 0.05; visualization of TLC with Br_2 vapor). The yield was 0.48 g (77%). Compound **20a** was obtained as a colorless viscous oil. Found (%): C, 80.03; H, 9.00. $C_{18}H_{24}N_2$. Calculated (%): C, 80.55; H, 9.01. ^{1}H NMR ($CDCl_3$), δ: 1.47 (m, 2 H, C(4′)H_2); 1.59 (m, 4 H, C(3′)H_2, C(5′)H_2); 2.48 (br.s, 4 H, C(2′)H_2, C(6′)H_2); 2.91 (s, 6 H, 1-NMe_2); 3.83 (s, 2 H, ArC$\underline{H}_2$N); 7.03 and 7.36 (both d, 1 H each, H(2) and H(3), $J_{2,3}$ = $J_{3,2}$ = 7.6 Hz); 7.53 and 8.33 (both m, 2 H each, H(6), H(7) and H(5), H(8)).

4-Dimethylaminomethyl-1-dimethylaminonaphthalene (20b). Bis(dimethylamino)methane (0.9 mL, 6.57 mmol) was added to a solution of 1-dimethylaminonaphthalene (**19**) (1 g, 5.83 mmol) in glacial AcOH (0.9 mL) on cooling with ice. The resulting transparent solution was vigorously shaken for 5 min and then kept at 50—52 °C for 12 h. Then the reaction mixture was diluted twice with water and made alkaline with a 20% aqueous solution of KOH to pH 12. The reaction products were extracted with $CHCl_3$ (3×5 mL). The solvent was distilled off *in vacuo*. The residue was chromatographed on Al_2O_3 (IV) (d = 2.5 cm, l = 9 cm, hexane as the eluent), and the main colorless fraction was collected (R_f 0.07; visualization of TLC with Br_2 vapor). The yield was 0.71 g (53%). Compound **20b** was obtained as a colorless viscous oil. Found (%): C, 78.36; H, 8.82. $C_{15}H_{20}N_2$. Calculated (%): C, 78.90; H, 8.83. ^{1}H NMR ($CDCl_3$), δ: 2.30 (s, 6 H, $CH_2N\underline{Me}_2$); 2.89 (s, 6 H, 1-NMe_2); 3.76 (s, 2 H, ArC$\underline{H}_2$N); 7.00 and 7.30 (both d, 1 H each, H(2) and H(3), $J_{2,3}$ = 7.6 Hz); 7.51 and 8.27 (both m, 2 H each, H(6), H(7) and H(5), H(8)).

Methylation of 4-dialkylaminomethyl-1-dimethylaminonaphthalenes (20a,b) (general procedure). A mixture of 4-dialkylaminomethyl-1-dimethylaminonaphthalene **20a,b** (0.745 mmol) and freshly distilled MeI (0.05 mL, 0.803 mmol) in anhydrous acetone (3 mL) was stirred at 20 °C for 1 h. The colorless precipitate that formed was filtered off, washed with benzene and ether, and dried in air. The yields of salts **21a** and **21b** were 82% and 86%, respectively.

***N*-Methyl-*N*-(4-dimethylamino-1-naphthylmethyl)piperidinium iodide (21a)** was obtained as colorless crystals, m.p. 134—135 °C (with decomp.), the compound decomposed upon recrystallization. Found (%): C, 55.48; H, 6.61; I, 30.22. $C_{19}H_{27}IN_2$. Calculated (%): C, 55.61; H, 6.63; I, 30.93. ^{1}H NMR (DMSO-d_6), δ: 1.41 and 1.63 (both br.s, 1 H each, C(4′)H_a and C(4′)H_e); 1.84 (br.s, 4 H, C(3′)H_2, C(5′)H_2); 2.89 (s, 6 H, 4-NMe_2); 2.93 (s, 3 H, $CH_2N^+(C\underline{H}_3)$); 3.36 (m, 4 H, C(2′)$H_2$, C(6′)$H_2$); 4.99 (s, 2 H, $ArCH_2N$); 7.18 (d, 1 H, H(3), $J_{3,2}$ = 7.9 Hz); 7.63 (m, 3 H, H(2), H(6), H(7)); 8.25 (m, 1 H, H(5)); 8.45 (d, 1 H, H(8), $J_{8,7}$ = 7.6 Hz).

***N,N,N*-Trimethyl-*N*-(4-dimethylamino-1-naphthylmethyl)ammonium iodide (21b)** was obtained as colorless crystals, which darkened at a temperature higher than 250 °C, m.p. 294—295 °C (with decomp.), the compound decomposed upon recrystallization. Found (%): C, 51.15; H, 6.26; I, 33.91.

* The intensities of these signals are rather low due, apparently, to the partial H/D exchange in the deuterated solvent used. Presumably, the fact that this exchange proceeds readily is associated with the electron-withdrawing effect of the $=N^+Me_2$ group.

$C_{16}H_{23}IN_2$. Calculated (%): C, 51.90; H, 6.26; I, 34.27. ^{1}H NMR (DMSO-d_6), δ: 2.88 (s, 6 H, 4-NMe_2); 3.08 (s, 9 H, $CH_2N^+(C\underline{H}_3)_3$); 4.99 (s, 2 H, $ArC\underline{H}_2N$); 7.19 (d, 1 H, H(3), $J_{3,2}$ = 7.9 Hz); 7.62 (m, 2 H, H(6), H(7)); 7.70 (d, 1 H, H(2), $J_{2,3}$ = 7.9 Hz); 8.24 (m, 1 H, H(5); 8.44 (d, 1 H, H(8), $J_{8,7}$ = 7.8 Hz).

Hydrolysis of *N*-methyl-*N*-(4-dimethylamino-1-naphthylmethyl)piperidinium iodide (21a). ***A.*** A suspension of iodide **21a** (178 mg, 0.434 mmol) in H_2O (5 mL) was refluxed for 5 h. The reaction products were extracted with $CHCl_3$ (3×3 mL). The solvent was distilled off to 1/3 of the initial volume of the reaction mixture. The residue was chromatographed on Al_2O_3 (II) (d = 1.5 cm, l = 8 cm, $CHCl_3$ as the eluent), and the colorless fraction that moved with the solvent front was collected. After evaporation of the solvent, **4,4´-dimethylamino-1,1´-bis(dinaphthyl)methane (23)** was obtained in a yield of 53 mg (69%) as colorless crystals, m.p. 180—181 °C (from heptane) (*cf.* lit. data[16]: m.p. 181—182.5 °C). Found (%): C, 84.39; H, 7.40; N, 7.86. $C_{25}H_{26}N_2$. Calculated (%): C, 84.70; H, 7.40; N, 7.91. ^{1}H NMR ($CDCl_3$), δ: 2.87 (s, 12 H, 4-NMe_2, 4´-NMe_2); 4.74 (s, 2 H, CH_2); 6.93 and 6.98 (both d, 2 H each, H(3), H(3´) and H(2), H(2´), $J_{2,3}$ = 7.7 Hz); 7.48 (m, 4 H, H(6), H(6´), H(7), H(7´)); 8.02 and 8.32 (both m, 2 H each, H(8), H(8´) and H(5), H(5´)).

B. A suspension of iodide **21a** (240 mg, 0.585 mmol) in a 10% aqueous KOH solution (20 mL) was refluxed for 15 min. The reaction products were extracted with $CHCl_3$ (3×5 mL). The solvent was distilled off to 1/3 of the initial volume of the reaction mixture. The residue was chromatographed on Al_2O_3 (II) (d = 1.5 cm, l = 8 cm, $CHCl_3$ as the eluent), and the colorless fraction that moved with the solvent front was collected. The solvent was distilled off and compound **23** was obtained in a yield of 8 mg (8%). A mixture with the sample prepared according to the method *A* did not give a melting point depression.

Then the next colorless fraction containing **4-hydroxymethyl-1-dimethylaminonaphthalene (24)** was collected (R_f 0.35; visualization of TLC with Br_2 vapor). The yield was 67 mg, (57%). Compound **24** was obtained as colorless viscous oil. Found (%): C, 77.44; H, 7.52; N, 6.88. $C_{13}H_{15}NO$. Calculated (%): C, 77.57; H, 7.52; N, 6.96. ^{1}H NMR ($CDCl_3$), δ: 1.95 (br.s, disappeared upon deuteration, 1 H, OH); 2.87 (s, 6 H, 1-NMe_2); 5.04 (s, 2 H, $ArCH_2N$); 6.99 and 7.38 (both d, 1 H each, H(2), H(3), $J_{2,3}$ = 7.6 Hz); 7.52 (m, 2 H, H(6), H(7)); 8.12 and 8.27 (both m, 1 H each, H(5), H(8)).

Hydrolysis of *N,N,N*-trimethyl-*N*-(4-dimethylamino-1-naphthylmethyl)ammonium iodide (21b). ***A.*** A suspension of iodide **21b** (100 mg, 0.27 mmol) in H_2O (3 mL) was refluxed for 1 h. The reaction products were extracted with $CHCl_3$ (3×3 mL). The solvent was distilled off to 1/3 of the initial volume of the reaction mixture. The residue was chromatographed on Al_2O_3 (II) (d = 1.5 cm, l = 8 cm, chloroform as the eluent), and the colorless fraction that moved with the solvent front was collected. Then the solvent was distilled off and compound **23** was obtained in a yield of 35 mg (73%). A mixture with the authentic sample did not give a melting point depression.

Then the colorless fraction containing alcohol **24** was collected. The yield of the compound whose ^{1}H NMR spectrum was identical with that of the authentic sample was 5 mg (9%).

B. A suspension of iodide **21b** (200 mg, 0.54 mmol) in a 10% aqueous solution of KOH (17 mL) was refluxed for 5 min. The reaction products were extracted with $CHCl_3$ (3×5 mL). The solvent was distilled off to 1/3 of the initial volume of the reaction mixture. The residue was chromatographed on Al_2O_3 (II) (d = 1.5 cm, l = 8 cm, $CHCl_3$ as the eluent), and the fractions containing dinaphthylmethane **23** and alcohol **24** were collected. The yields of compounds **23** and **24** were 6 mg (6%) and 65 mg (60%), respectively. The physicochemical characteristics (m.p. and ^{1}H NMR spectra) of both compounds are identical with those of the samples prepared as described above.

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