peri-Naphthylenediamines
27.* Transformations of tertiary carbocations stabilized by the 4,5-bis(dimethylamino)-1-naphthyl group

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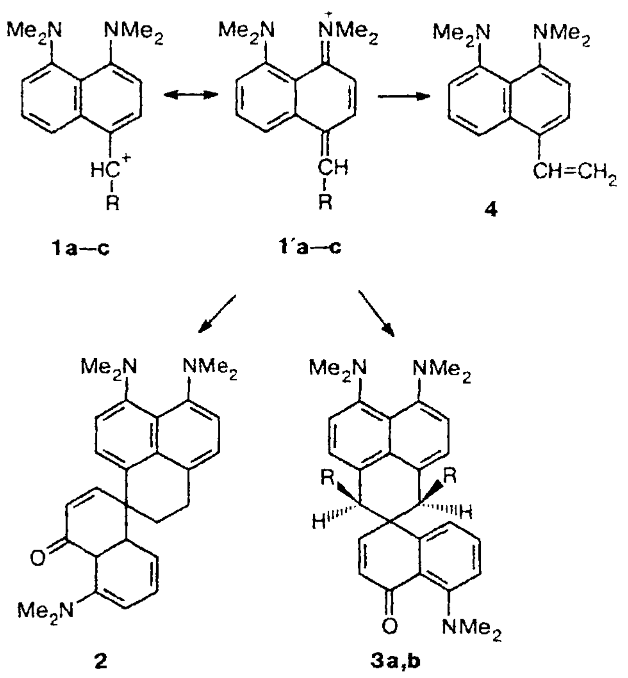
Tertiary alcohols containing the 4,5-bis(dimethylamino)-1-naphthyl group were synthesized. The carbocations that formed from α-methyl-containing alcohols in an acidic medium underwent smooth E1 elimination to give the corresponding unsaturated derivatives of the "proton sponge" in good yields. At the same time, the carbocation generated from 4-(α-hydroxybenzhydryl)-1,8-bis(dimethylamino)naphthalene was converted into a benzo[*a*]fluorene derivative as a result of a complex reaction which has been previously unknown in the chemistry of "proton sponges." The structure of the latter derivative was established by X-ray diffraction analysis.

Key words: 1,8-bis(dimethylamino)naphthalene, "proton sponge," alkenes, tertiary alcohols, carbocations, benzo[*a*]fluorene, dehydration, X-ray diffraction analysis.

Previously, we have reported that 1-naphthylmethyl carbocations containing strong +M substituents, such as NMe_2 or OMe, at positions 4 and 5 exhibit unusual reactivities.[2–7] Thus, the parent cation **1a** based on 1,8-bis(dimethylamino)naphthalene ("proton sponge") formed spiro compounds **2** or **3** (Scheme 1) depending on the procedure for its generation (treatment of the corresponding alcohol with protic[3,4] or Lewis[5,6] acids). Under analogous conditions, phenyl-containing secondary carbocation **1b** gave only symmetrical spiro compound **3b**,[8] whereas its α-methyl-containing analog **1c** was converted into the 4-vinyl derivative of the "proton sponge," apparently, as a result of E1 elimination.[7] Spiro compounds are formed due to strong resonance stabilization of carbocations **1a—c** resulting in an increase in the contribution of the extreme structures **1'a—c** with the essentially multiple exocyclic C=C bond to the ground state. Carbocations in this form exhibit simultaneously the pronounced properties of both dienophiles and 1,3-dienes and undergo [4+2] cyclodimerization. Taking into account the aforesaid, it was of interest to study the reactivity of tertiary carbocations containing the 4,5-bis(dimethylamino)-1-naphthyl group as one of the substituents. In this work, we sum up the results of these studies.

Scheme 1



R = H (**a**), Ph (**b**), or Me (**c**)

Alcohols **6a—c** were prepared by the reactions of MeMgI or PhMgBr with the 4-acetyl (**5a**) or 4-benzoyl (**5b**) derivatives of the "proton sponge" in 46, 38, and 16% yields, respectively. Low yields of alcohols **6b,c** are partly attributable to the fact that the reactions of ketone **5b** are accompanied by competitive 1,4-addition to form

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[*] For Part 26, see Ref. 1; this paper simultaneously presents Part 5 of the series "Resonance-stabilized α-naphthylmethyl carbocations and derived spiro compounds;" for Part 4, see Ref. 2.

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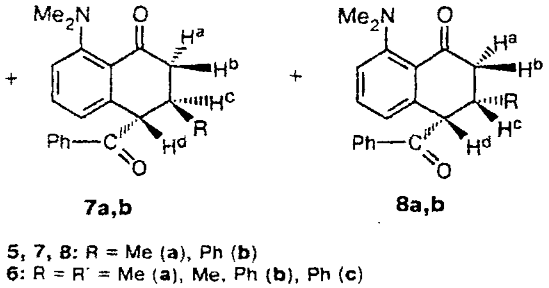
the *trans* (**7a,b**) and *cis* isomers (**8a,b**) of 3-R-4-benzoyl-8-dimethylamino-1,2,3,4-tetrahydronaphthalen-1-one (Scheme 2) (analogous reactions for compounds of the arene series are known; see the review[9]) due, apparently, to the fact that the direct addition of the Grignard reagent at the C=O group is sterically hindered. In our case, the enamine was, evidently, formed as an intermediate 1,4-addition product, and hence, subsequent hydrolysis led to the replacement of the dimethylamino group by the carbonyl group. Owing to the difference in the solubility in CCl_4, we succeeded in separating *trans* and *cis* isomers **7b** and **8b**, which were obtained in 16.5 and 21% yields, respectively. Diastereomers **7a** and **8a** were not separated. According to the data from ^{1}H NMR spectroscopy, these compounds were formed in a ratio of 5.5 : 1 in a total yield of 9%. The structures of the resulting stereoisomers were established based on the characteristic spin-spin coupling constants of the vicinal protons at the C(3) and C(4) atoms. Thus the spin-spin coupling constant for *trans* isomer **7b** is ~9 Hz, whereas this constant for *cis* isomer **8b** is ~5 Hz (*cf.* Ref. 10). Later on, we found that the reactions of benzophenone with the 4-lithio or 4-bromomagnesio derivatives of the "proton sponge" are more convenient procedures for the preparation of alcohol **6c** (these data will be published elsewhere).

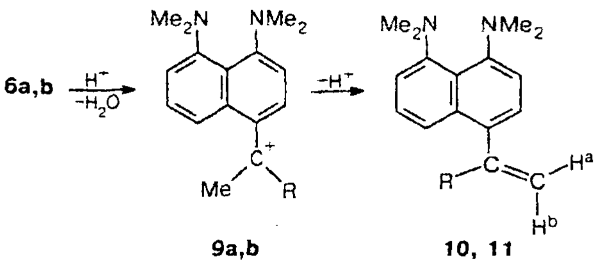
When treated with hydrochloric acid, alcohols **6a,b** containing the α-methyl group were converted into alkenes **10** and **11**, respectively, in ~40% yields, the reactions being accompanied by substantial resinification. Similar results were obtained upon heating of benzene solutions of compounds **6a,b** with Al_2O_3. Therefore, when treated with protic or Lewis acids, both alcohols behave analogously to the secondary alcohol, *viz.*, 4-(α-hydroxyethyl)-1,8-bis(dimethylamino)naphthalene,[7] *i.e.*, all these alcohols are prone to E1 elimination (Scheme 3).

Scheme 2



5, 7, 8: R = Me (**a**), Ph (**b**)
6: R = R' = Me (**a**), Me, Ph (**b**), Ph (**c**)

Scheme 3



R = Me (**9a**, **10**) or Ph (**9b**, **11**)

Under the same conditions, the behavior of 4-(α-hydroxybenzhydryl)-1,8-bis(dimethylamino)naphthalene (**6c**) is quite different. This alcohol remains virtually unchanged upon prolonged stirring of its benzene solution with Al_2O_3. In dilute hydrochloric acid, compound **6c** is dissolved to form a colorless solution in which it remains unchanged even upon storage for several days and can be precipitated with an alkali. Apparently, chelated cation **6cH**$^+$ typical of "proton sponges" is formed under these conditions as a result of protonation of the NMe_2 group. However, when alcohol **6c** was treated with concentrated HCl, the solution turned dark-red. Probably, this color is associated with carbocation **12**. When heated,* the color of the solution changed to dark-yellow. It appeared that partially hydrogenated benzo[*a*]fluorene derivative **15** was formed as the only reaction product (the yield was 66%; Scheme 4). The structure of the resulting compound was established based on the data of X-ray diffraction analysis and NMR spectroscopy. In the ^{1}H NMR spectrum of compound **15**, the most characteristic signals are those of the CH_2—CH group that form an AMX spin system. The magnetically nonequivalent protons of the methylene unit, *viz.*, H^a and H^b, are observed as doublets of doublets at δ 2.40 and 3.42, respectively, J_{gem} = 16.3 Hz. The methine proton H^c gives a signal as a doublet of doublets at δ 4.13 with ${}^3J_{cis}$ = 6.1 Hz and ${}^3J_{trans}$=13.7 Hz.

First attempts to grow crystals of compound **15** suitable for X-ray diffraction study failed. However, in one of the runs, alcohol **6c** containing an impurity of 1,1,2,2-tetraphenylethanediol was accidentally used in the reaction with concentrated HCl for the preparation of compound **15**. Apparently, 1,1,2,2-tetraphenylethanediol was formed as a by-product upon dimerization of benzophenone when alcohol **6c** was prepared from 4,5-bis(dimethylamino)-1-naphthylmagnesium bro-

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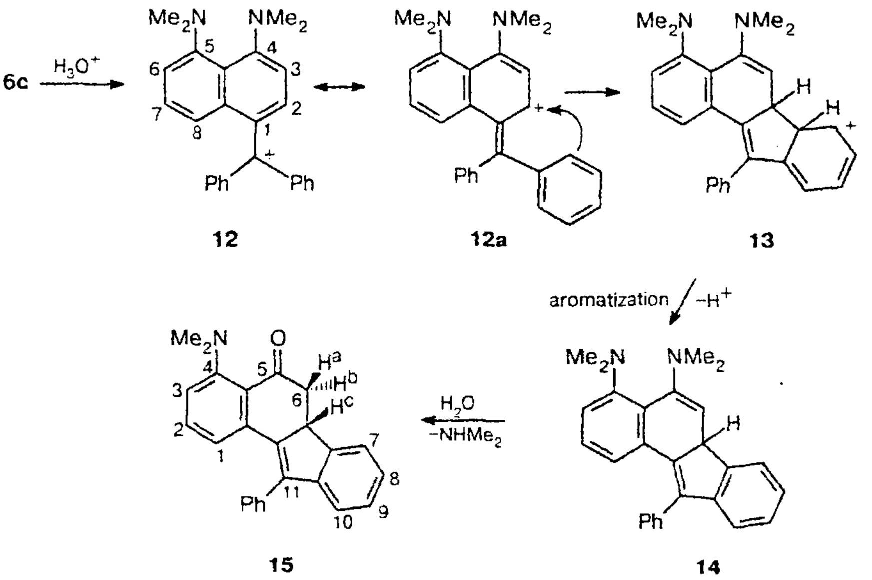
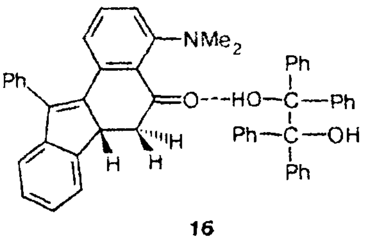
* Even after storage of the red solution for 2—3 days and neutralization with sodium bicarbonate, the initial alcohol **6c** precipitated from the reaction mixture. Regeneration of alcohol **6c** (as the N cation), which was accompanied by decoloration, occurred also upon dilution of the red solution with water. All the aforesaid indicate that carbocation **12** is very stable under these conditions. The possibility of its isolation in the individual state is being studied.

Scheme 4



mide and benzophenone. Benzo[*a*]fluorenone **15**, which was prepared from crude alcohol **6c**, was isolated as a 1 : 1 molecular complex with 1,1,2,2-tetraphenylethanediol (**16**). This complex gave well-faceted crystals and their crystallographic characteristics were determined. For convenience, the overall views of both components of complex **16** are given separately in Figs. 1 and 2. The components are linked through a hydrogen bond between the O(1) atom of the carbonyl group and the O(2)H hydroxy group. This hydrogen bond is characterized by the following parameters: the O(1)...O(2) and O(1)...HO(2) distances are 2.867(4) and 2.00(5) Å, respectively, and the O(1)...H—O(2) angle is 155(4)°. The hydrogen atom of the O(3)H hydroxyl group is disordered over two positions with equal occupancies and is not involved in hydrogen bonding. The ^{1}H NMR spectrum of the benzofluorene fragment of complex **16** is virtually identical with the spectrum of the individual sample of **15**, except for a slight broadening of the peaks.



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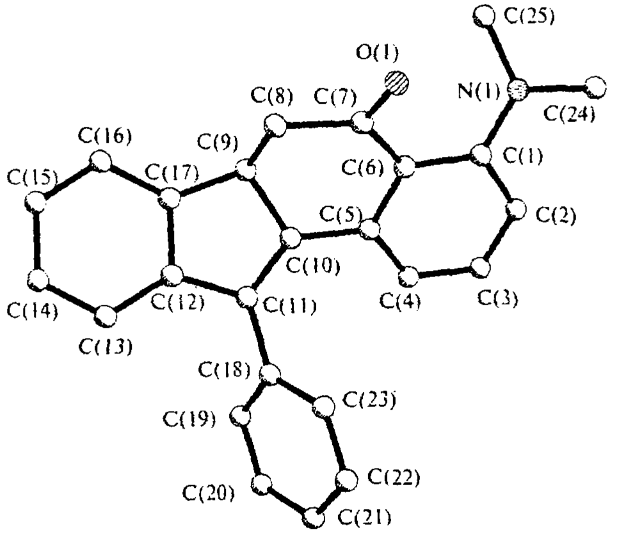


Fig. 1. Overall view of molecule **15** in the molecular complex with 1,1,2,2-tetraphenylethane-1,2-diol.

Some characteristic features of the molecular structure of compound **15** are of interest. The N(1) atom is weakly pyramidal. This atom deviates from the plane formed by the surrounding C(1), C(24), and C(25) atoms by 0.131 Å, and the sum of the bond angles about this atom is 357.1°. This indicates that the N(1) atom has the sp^2 hybridization due, apparently, to very efficient conjugation between its lone electron pair and the carbonyl group through the π system of the ring. This conclusion is supported by the bright yellow color of compound **15**. The dihedral angle between the N(1)C(24)C(25) and C(1)C(2)C(3)C(4)C(5)C(6) planes is 27.6°. The dihedral angle between the plane of the phenyl ring at the C(11) atom and the plane of the five-membered ring is 54.1°. The O(1) atom deviates from the plane passing through the surrounding atoms by only 0.074 Å. The selected bond lengths and bond angles are given in Tables 1 and 2, respectively.

The key stage of formation of compound **15** can be considered as the Friedel—Crafts-type intramolecular electrophilic substitution in cation **12** (in this case, it is more convenient to represent the cation as the reso-

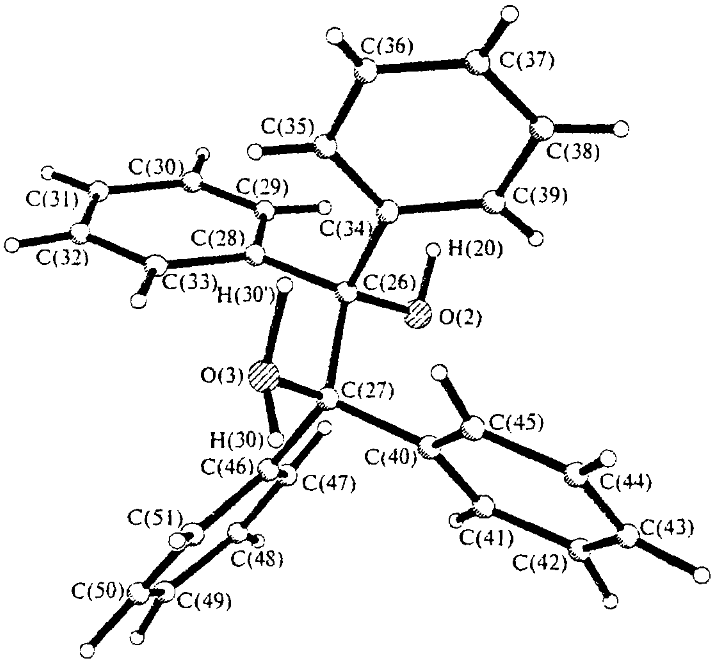


Fig. 2. Overall view of the 1,1,2,2-tetraphenylethane-1,2-diol molecule in the molecular complex with compound **15**.

nance structure **12a**). Analogous cyclization to form the corresponding fluorene derivatives has been observed recently for the tris(1-naphthyl)- and tris(2-naphthyl)-methyl cations[11] and earlier for the triphenylmethyl cation.[12] Apparently, the peculiarity of the process under consideration is associated with subsequent hydrolytic replacement of one of the dimethylamio groups by the carbonyl group in intermediate **14** as well as with the fact that the 1,3-sigmatropic shift of the proton of the CH group is hindered in the case of conversion of compound **15** into **17**.

Compound **15** is a tautomer of a more stable aromatic form **17**, which is additionally stabilized through an intramolecular hydrogen bond between the hydroxy group of the phenol ring and the NMe_2 group. Actually, in attempting to determine the melting point of benzo[*a*]fluorenone **15**, we found that this compound was quantitatively isomerized to form phenol **17** upon heating above 135 °C, *i.e.*, tautomerization was accompanied by simultaneous 1,3-sigmatropic shifts of two H atoms. In the ^1H NMR spectrum of compound **17**, the signal for the proton of the OH groups is observed at even lower field (at δ 14.83, $CDCl_3$) than that in 8-dimethylamino-1-naphthol (at δ 14.39, $CDCl_3$),[13] which is indicative of the formation of a rather strong intramolecular hydrogen bond. The fact that conversion **15** → **17** is rather hindered can be explained by the

Table 1. Bond lengths (*d*) in the components of molecular complex **16**

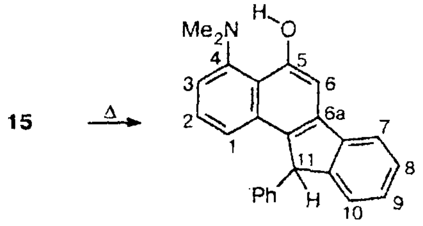
Bond	*d*/Å	Bond	*d*/Å
O(1)—C(7)	1.240(4)	N(1)—C(25)	1.443(6)
O(3)—C(27)	1.437(4)	C(5)—C(6)	1.437(4)
N(1)—C(24)	1.432(7)	C(6)—C(7)	1.479(5)
C(5)—C(10)	1.452(5)	C(8)—C(9)	1.536(5)
C(7)—C(8)	1.495(5)	C(9)—C(17)	1.497(5)
C(9)—C(10)	1.496(5)	C(11)—C(12)	1.459(5)
C(26)—C(28)	1.532(6)	C(26)—C(34)	1.529(6)
C(27)—C(46)	1.533(5)	C(26)—C(27)	1.598(6)
O(2)—C(26)	1.436(4)	C(27)—C(40)	1.547(5)
N(1)—C(1)	1379(5)		

Table 2. Bond angles (θ) in the components of molecular complex **16**

Angle	θ/deg	Angle	θ/deg
C(1)—N(1)—C(24)	119.7(4)	C(45)—C(40)—C(27)	119.6(4)
C(24)—N(1)—C(25)	114.9(5)	C(51)—C(46)—C(27)	120.1(3)
N(1)—C(1)—C(6)	122.8(3)	C(1)—N(1)—C(25)	122.9(3)
C(4)—C(5)—C(10)	123.1(3)	N(1)—C(1)—C(2)	118.2(3)
C(5)—C(6)—C(7)	116.5(3)	C(6)—C(5)—C(10)	117.6(3)
O(1)—C(7)—C(8)	118.2(3)	C(1)—C(6)—C(7)	123.1(3)
C(7)—C(8)—C(9)	114.1(3)	O(1)—C(7)—C(6)	121.0(3)
C(10)—C(9)—C(8)	107.3(3)	C(6)—C(7)—C(8)	120.7(3)
C(11)—C(10)—C(5)	131.6(3)	C(17)—C(9)—C(8)	115.4(3)
C(5)—C(10)—C(9)	117.9(3)	C(11)—C(10)—C(9)	110.5(3)
C(10)—C(11)—C(18)	128.0(3)	O(2)—C(26)—C(28)	109.6(3)
C(16)—C(17)—C(9)	131.6(3)	O(2)—C(26)—C(27)	104.0(3)
O(2)—C(26)—C(34)	109.5(3)	C(28)—C(26)—C(27)	112.2(3)
C(34)—C(26)—C(28)	111.4(3)	O(3)—C(27)—C(40)	108.6(3)
C(34)—C(26)—C(27)	109.8(3)	O(3)—C(27)—C(26)	104.9(3)
O(3)—C(27)—C(46)	108.4(3)	C(40)—C(27)—C(26)	110.4(3)
C(46)—C(27)—C(40)	111.7(3)	C(35)—C(34)—C(26)	122.7(4)
C(46)—C(27)—C(26)	112.5(3)	C(41)—C(40)—C(27)	122.4(4)
C(33)—C(28)—C(26)	123.2(4)	C(47)—C(46)—C(27)	123.7(3)
C(39)—C(34)—C(26)	120.4(4)		

necessity of cleaving simultaneously two C—H bonds, which are characterized by the lower tendency to undergo acidic dissociation compared to the O—H and N—H bonds.

In the chemistry of naphthalene "proton sponges," conversion **6c** → **15** along with the formation of compounds **7** and **8** is, to our knowledge, the first example of reactions occurring at the *meta* position with respect to the NMe_2 group.



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The atomic coordinates, bond lengths, and bond angles for the structures of **15** and **16** were deposited with the Cambridge Structural Database.

Experimental

The ^1H NMR spectra of all compounds were recorded at 25 °C on a Unity-300 spectrometer operating at 300 MHz. The IR spectra were measured on a UR-20 instrument. The UV spectrum of compound **15** was obtained on a Specord M-40 instrument in acetonitrile. The melting points were determined in sealed capillaries on a PTP instrument and were not corrected. Chromatography was carried out on Al_2O_3 (Brockmann III).

Dark-yellow crystals of molecular complex **16** suitable for X-ray diffraction analysis were grown by slow evaporation of its solution in toluene at room temperature. The X-ray data were collected from a single crystal of dimensions 0.5×0.3×0.2 mm. The crystals of the complex ($C_{51}H_{43}NO_3$, M = 717.86) are triclinic, at 298 K: a = 11.266(2) Å, b = 12.778(3) Å, c = 14.912(3) Å, α = 90.41(3)°, β = 102.81(3)°, γ = 111.52(3)°, V = 1938.0(7) Å^3, Z = 2, d_{calc} = 1.230 g cm^{-3}, $F(000)$ = 1208, μ = 0.75 cm^{-1}, space group $P\bar{1}$. The intensities were measured on an automated four-circle CAD4 Enraf-Nonius diffractometer at room temperature. The structure was solved by direct methods and refined by the least-squares method based on F^2_{hkl}. The coordinates and the thermal parameters of the nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were located from difference electron density syntheses and refined isotropically. A total of 6508 reflections were measured of which 6196 reflections were independent. The final values of the R factors were as follows: R_1 = 0.0658 (calculated based on F_{hkl} for 3200 independent reflections with $I > 2\sigma(I)$), wR_2 = 0.1607 (calculated based on F^2_{hkl} for all 6154 reflections included in the refinement at the final stage); the number of the refinable parameters was 672, GOOF = 1.007. All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[14]

2-[4,5-Bis(dimethylamino)-1-naphthyl]propan-2-ol (6a). A solution of 4-acetyl-1,8-bis(dimethylamino)naphthalene (**5a**)[15] (0.32 g, 1.2 mmol) in dry THF (1.5 mL) was added dropwise with stirring to a solution of methylmagnesium iodide, which was prepared from Mg (0.11 g, 4.6 mg-at.) and MeI (0.71 g, 5 mmol), in dry THF (1.5 mL). The reaction mixture was refluxed with stirring until the initial compound was consumed (~1.5 h) and then decomposed with a saturated solution of NH_4Cl (~4 mL) upon cooling. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (3×5 mL). The combined layers were concentrated and reaction product **6a** was isolated by preparative TLC on Al_2O_3 ($CHCl_3$ as the eluent), R_f 0.21. The yield was 0.15 g (46%). Colorless crystals, m.p. 110—111 °C (from EtOH). Found (%): C, 74.85; H, 8.71; N, 10.39. $C_{17}H_{24}N_2O$. Calculated (%): C, 74.96; H, 8.88; N, 10.28. IR (CCl_4), ν/cm^{-1}: 3598 (OH); 1570 (ring). ^1H NMR ($CDCl_3$), δ: 1.83 (s, 6 H, 2 Me), 1.96 (br.s, 1 H, OH); 2.79 (s, 12 H, 2 NMe_2); 6.80 (d, 1 H, H(3), $J_{3,2}$ = 8.1 Hz); 6.93 (dd, 1 H, H(6), $J_{6,7}$ = 7.5 Hz, $J_{6,8}$ = 0.8 Hz); 7.33 (dd, 1 H, H(7), $J_{7,6}$ = 7.5 Hz, $J_{7,8}$ = 8.6 Hz); 7.40 (d, 1 H, H(2), $J_{2,3}$ = 8.1 Hz); 8.37 (dd, 1 H, H(8), $J_{8,7}$ = 8.6 Hz, $J_{8,6}$ = 0.9 Hz).

1-[4,5-Bis(dimethylamino)naphthyl]-1-phenylethanol (6b). The reaction of 4-benzoyl-1,8-bis(dimethylamino)naphthalene (**5b**)[15] (0.64 g, 2 mmol) in dry THF (4 mL) with a solution of MeMgI, which was prepared from Mg (0.36 g, 15 mg-at.) and MeI (1.42 g, 9.8 mmol), in dry THF (6 mL) was carried out as described above (refluxing for ~2 h) and treated analogously. The bright-yellow reaction product was isolated by preparative TLC on Al_2O_3 ($CHCl_3$ as the eluent), R_f 0.94. The total yield of the mixture of stereoisomeric *trans* (**7a**) and *cis* ketones (**8a**) was 0.056 g (9%). The ^1H NMR spectrum of this mixture has two signals for the H(4) protons of the *trans* and *cis* forms as characteristic doublets at δ 5.13 and 5.20 with the spin-spin coupling constants 9.1 and 5.6 Hz, respectively. Judging from their relative intensities, the isomer ratio **7a** : **8a** was 5.5 : 1.

Alcohol **6b** was isolated from the zone with R_f 0.27 in a yield of 0.26 g (38%) as colorless crystals, m.p. 141—142 °C (decomp., from ethanol). Found (%): C, 79.12; H, 7.87; N, 8.12. $C_{22}H_{26}N_2O$. Calculated (%): C, 79.01; H, 7.84; N, 8.38. IR (CCl_4), ν/cm^{-1}: 3610 (OH); 1580 (aromatic ring). ^1H NMR ($CDCl_3$), δ: 1.99 (s, 3 H, Me); 2.55 (br.s, 1 H, OH); 2.78 and 2.83 (both s, 6 H each, 2 NMe_2); 6.81 (dd, 1 H, H(6), $J_{6,7}$ = 7.5 Hz, $J_{6,8}$ = 0.9 Hz); 6.89 (d, 1 H, H(3), $J_{3,2}$ = 8.0 Hz); 7.04 (dd, 1 H, H(7), $J_{7,8}$ = 8.4 Hz, $J_{7,6}$ = 7.5 Hz); 7.14—7.39 (m, 6 H, H(8) and C_6H_5); 7.65 (d, 1 H, H(2), $J_{2,3}$ = 8.0 Hz).

[4,5-Bis(dimethylamino)-1-naphthyl]diphenylmethanol (6c). The reaction of a solution of ketone (**5b**) (0.636 g, 2 mmol) in dry THF (3 mL) with a solution of PhMgBr, which was prepared from Mg (0.36 g, 15 mg-at.) and PhBr (1.56 g, 9.9 mmol), in dry THF (4 mL) was carried out as described above. After evaporation of the extracts, the reaction products were triturated with CCl_4 (6 mL), and *trans*-4-benzoyl-8-dimethylamino-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-one (**7b**) was filtered off. The yield was 0.14 g (16.5%); soft yellow needle-like crystals, m.p. 196.5—198 °C (from ethanol) or 199—200 °C (from toluene). Found (%): C, 81.21; H, 6.31; N, 3.70. $C_{25}H_{23}NO_2$. Calculated (%): C, 81.27; H, 6.27; N, 3.79. R_f 0.73. ^1H NMR ($CDCl_3$), δ: 2.89 (dd, 1 H, CH_2 (H^b), J_{gem} = 17.3 Hz, $J_{2,3(trans)}$ = 10.5 Hz); 2.94 (s, 6 H, NMe_2); 3.02 (dd, 1 H, CH_2 (H^a), J_{gem} = 17.3 Hz, $J_{2,3(cis)}$ = 5.3 Hz); 3.87 (ddd, 1 H, H(3), $J_{3,2(trans)}$ = 10.5 Hz, $J_{3,2(cis)}$ = 5.3 Hz, $J_{3,4(trans)}$ = 8.9 Hz); 5.14 (d, 1 H, H(4), $J_{4,3(trans)}$ = 8.9 Hz); 6.37 (br.d, 1 H, H(7), $J_{7,6}$ = 7.3 Hz); 6.87 (br.d, 1 H, H(5), $J_{5,6}$ = 8.7 Hz); 7.16 (m, 6 H, H(6) and 3-C_6H_5); 7.39 (m, 2 H, C_6H_5CO, H-*o*); 7.52 (m, 1 H, C_6H_5CO, H-*p*); 7.80 (m, 2 H, C_6H_5CO, H-*m*).

CCl_4 was distilled off from the filtrate, and *cis*-isomer **8b** with R_f 0.53 and alcohol **6c** with R_f 0.26 were isolated by preparative TLC on Al_2O_3 ($CHCl_3$ as the eluent) in yields of 0.18 g (21%) and 0.1 g (16.3%), respectively. ***cis*-4-Benzoyl-8-dimethylamino-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-one (8b)** was obtained as small yellow-orange crystals, m.p. 130—132 °C (from octane). Found (%): C, 81.30; H, 6.29; N, 3.35. $C_{25}H_{23}NO_2$. Calculated (%): C, 81.27; H, 6.27; N, 3.79. ^1H NMR ($CDCl_3$), δ: 2.79 (dd, 1 H, CH_2, H^b, J_{gem} =

16.9 Hz, $J_{2,3\,(cis)}$ = 5.1 Hz); 2.95 (s, 6 H, NMe_2); 3.68 (dd, 1 H, CH_2, H^a, J_{gem} = 16.9 Hz, $J_{2,3\,(trans)}$ = 14.1 Hz); 3.93 (m, 1 H, H(3), $J_{3,2\,(trans)}$ = 14.1 Hz, $J_{3,2\,(cis)}$ = 5.1 Hz, $J_{3,4\,(cis)}$ = 4.9 Hz); 5.20 (d, 1 H, H(4), $J_{4,3\,(cis)}$ = 4.5 Hz); 6.46 (br.d, 1 H, H(7), $J_{7,6}$ = 7.1 Hz); 6.90 (br.d, 1 H, H(5), $J_{5,6}$ = 8.6 Hz); 7.13 (m, 8 H, H(6)+3-C_6H_5+C_6H_5CO, H-*o*); 7.38 (tt, 1 H, C_6H_5CO, H-*p*, J_o = 8.4 Hz, J_m = 1.3 Hz); 7.50 (m, 2 H, C_6H_5CO, H-*m*).

Compound **6c** was obtained as colorless crystals, m.p. 141 °C (from ethanol). Found (%): C, 81.48; H, 7.20; N, 7.10. $C_{27}H_{28}N_2O$. Calculated (%): C, 81.78; H, 7.12; N, 7.06. IR (CCl_4), ν/cm^{-1}: 3596 (OH); 1565 (ring). ^1H NMR ($CDCl_3$), δ: 2.79 (s, 12 H, 2 NMe_2); 3.42 (s, 1 H, OH); 6.58 (d, 1 H, H(3), $J_{3,2}$ = 8.1 Hz); 6.64 (br.d, 1 H, H(2), $J_{2,3}$ = 8.2 Hz); 6.85 (br.d, 1 H, H(6), $J_{6,7}$ = 7.4 Hz); 7.09 (dd, 1 H, H(7), $J_{7,8}$ = 8.5 Hz, $J_{7,6}$ = 7.4 Hz); 7.22–7.38 (m, 10 H, 2 C_6H_5); 7.55 (br.d, 1 H, H(8), $J_{8,7}$ = 8.5 Hz).

General procedure for the preparation of alkenes 10 and 11. A. Alcohol **6a** or **6b** (0.1 mmol) was dissolved in concentrated hydrochloric acid (5 mL). The yellowish solution was kept at room temperature for 1 h. Then the reaction mixture was alkalized with 20% NaOH to pH 12. The precipitate that formed was extracted with $CHCl_3$ (3×4 mL). After evaporation of the solvent, the products were purified by passing through a column with Al_2O_3 (*d* = 1.5 cm, *l* = 3 cm) in $CHCl_3$.

B. Alcohol **6a** or **6b** (40 mg) was dissolved in benzene (5 mL) and the solution was vigorously shaken with Al_2O_3 (1 g). Then the reaction mixture was kept at 80 °C for 6 h, the mixture being shaken occasionally. After completion of the reaction, Al_2O_3 was filtered off and washed with acetone. The solvents were evaporated and the residue was crystallized from hexane. Compounds **10** and **11** were obtained in 38% and 40% yields, respectively.

2-[4,5-Bis(dimethylamino)-1-naphthyl]propene (10). A yellowish caramel-like compound, R_f 0.23. Found (%): C, 80.23; H, 8.90; N, 10.04. $C_{17}H_{22}N_2$. Calculated (%): C, 80.27; H, 8.72; N, 11.01. ^1H NMR ($CDCl_3$), δ: 2.15 (s, 3 H, Me); 2.78 (s, 6 H, 5-NMe_2); 2.79 (s, 6 H, 4-NMe_2); 4.99 (br.s, 1 H, H^a, J_{H^a-Me} = 0.9 Hz); 5.30 (br.s, 1 H, H^b, J_{H^b-Me}=1.5 Hz); 6.87 (d, 1 H, H(3), $J_{3,2}$ = 7.6 Hz); 6.9 (br.d, 1 H, H(6), $J_{6,7}$ = 7.5 Hz, $J_{6,8}$ = 0.9 Hz); 7.12 (d, 1 H, H(2), $J_{2,3}$ = 7.9 Hz); 7.28 (dd, 1 H, H(7), $J_{7,6}$ = 8.2 Hz, $J_{7,8}$ = 8.6 Hz); 7.54 (dd, 1 H, H(8), $J_{8,7}$ = 8.4 Hz, $J_{8,6}$ = 0.88 Hz).

α-[4,5-Bis(dimethylamino)-1-naphthyl]styrene (11). A yellow-brown caramel-like compound with R_f 0.26. Found (%): C, 83.58; H, 7.70; N, 8.89. $C_{22}H_{24}N_2$. Calculated (%): C, 83.50; H, 7.64; N, 8.85. ^1H NMR ($CDCl_3$), δ: 2.79 (br.s, 6 H, NMe_2); 2.82 (br.s, 6 H, NMe_2); 5.32 (d, 1 H, H^a, J_{gem} = 1.6 Hz); 5.87 (br.d, 1 H, H^b, J_{gem} = 1.5 Hz); 6.85 (br.d, 1 H, H(6)); 6.91 (br.d, 1 H, H(3)); 7.12 (br.dd, 1 H, H(7)); 7.20-7.33 (m, 7 H, H(2), H(8), C_6H_5). Due to slow dynamics, the peaks of the protons of the naphthalene ring are noticeably broadened.

4-Dimethylamino-11-phenyl-6*H*,6a*H*-benzo[*a*]fluoren-5-one (15). Alcohol **6c** (100 mg, 0.25 mmol) was dissolved in concentrated HCl (35 mL). The dark-red solution was refluxed for 1 h, cooled, and neutralized with dry Na_2CO_3. The yellow-green precipitate that formed was extracted with $CHCl_3$ (3×5 mL). The extract was concentrated and reaction product **15** was purified from impurities by preparative TLC on Al_2O_3 ($CHCl_3$ as the eluent). R_f 0.86. The yield was 62 mg (71%). The color of the crystals gradually changed from dark-yellow to grey upon heating above 135 °C and the crystals melted at 210 °C, which corresponds to the melting point of phenol **17** (see below). Found (%): C, 85.42; H, 6.01; N, 3.98. $C_{25}H_{21}NO$. Calculated (%): C, 85.44; H, 6.02; N, 3.99. UV (MeCN), λ_{max}/nm (log ε): 245 (4.48), 279 (4.31), 328, broad shoulder (3.97), 414 (3.67) with terminal adsorption to ~460 nm. IR (CCl_4), ν/cm^{-1}: 1670 (C=O); 1590 (C—$C_{arom.}$). ^1H NMR ($CDCl_3$), δ: 2.40 (dd, 1 H, CH_2, H^b, J_{gem} = 16.3 Hz, $J_{b,c}$ = 13.7 Hz); 2.91 (s, 1 H, 6 H, NMe_2); 3.42 (dd, 1 H, H^a, J_{gem} = 16.3 Hz, $J_{a,c}$ = 6.1 Hz); 4.13 (dd, 1 H, H(6a), $J_{c,a}$ = 6.1 Hz, $J_{c,b}$ = 13.7 Hz); 6.57 (dd, 1 H, H(6´), $J_{6',5'}$ = 7.9 Hz, $J_{6',4'}$ = 0.9 Hz); 6.81 (dd, 1 H, H(4´), $J_{4',5'}$ = 8.6 Hz, $J_{4',6'}$ = 0.9 Hz); 7.06 (dd, 1 H, H(5´), $J_{5',4'}$ = 8.5 Hz, $J_{5',6'}$ = 7.6 Hz); 7.16—7.50 (m, 9 H, C_6H_5, H(7)—H(10)).

4-Dimethylamino-5-hydroxy-11-phenylbenzo[*a*]fluorene (17). Compound **15** (60 mg, 0.17 mmol) was kept in a sealed tube at 135 °C for 0.5 h. The color of the compound changed from dark-yellow to grey. Isomerization product **17** was purified by recrystallization from toluene. The yield was 45 mg (75%). Colorless crystals, m.p. 213 °C; R_f 0.98. Found (%): C, 85.41; H, 5.98; N, 3.96. $C_{25}H_{21}NO$. Calculated (%): C, 85.44; H, 6.02; N, 3.99. ^1H NMR ($CDCl_3$), δ: 2.85 (s, 6 H, NMe_2); 5.20 (s, 1 H, H(11)); 7.08—7.28 (m, 9 H, H(2), H(7), H(8), H(10), C_6H_5); 7.33 (s, 1 H, H(6)); 7.34 (ddd, 1 H, H(9), *J* = 7.4, $J_{9,7}$ = 1.0 Hz); 7.46 (dd, 1 H, H(3), $J_{3,2}$ = 7.0 Hz, $J_{3,1}$ = 2.4 Hz); 7.76 (br.d, 1 H, H(1), $J_{1,2}$ = 7.6 Hz); 14.83 (s, 1 H, OH).

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