Organic Chemistry

Resonance-stabilized α-naphthylmethyl carbocations and derived spiro compounds

4.* Transformations of 4-dimethylamino-5-methoxynaphthylmethyl carbocation in the presence of protic and Lewis acids. The formation of an asymmetrical spiro compound

A. F. Pozharskii, N. V. Vistorobskii, M. I. Rudnev, and A. I. Chernyshev*

Rostov State University,
7 ul. Zorge, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 (863 2) 28 5667

4-Dimethylamino-5-methoxynaphthylmethyl carbocation generated from 1-hydroxymethyl-4-dimethylamino-5-methoxynaphthalene in trifluoroacetic acid behaves as both diene and dienophile and undergoes (4π + 2π) cycloaddition to give an asymmetrical spiro compound. The other reaction product is 4,4′-bis(dimethylamino)-5,5′-dimethoxy-1,1′-dinaphthylmethane, which is formed *via ipso*-substitution of the hydroxymethyl group in the initial alcohol. When this cation is generated on Al_2O_3, 4-dimethylamino-5-methoxy-1-naphthaldehyde is formed along with the substituted dinaphthylmethane.

Key words: 8-amino-1-naphthols, formylation, naphthylmethyl carbocations, (4π + 2π) cycloaddition, electrophilic *ipso*-substitution, spiro compounds.

Recently we have discovered the two essentially different types of cyclodimerization of 4,5-bis(dimethylamino)naphthylmethyl carbocation (**2a**) formed from 1-hydroxymethyl-4,5-bis(dimethylamino)naphthalene (**1a**) (Scheme 1). When this cation is generated in strong protic acids, the only product of the transformation is spiro compound (**3**) of a "head-to-head" type that is formed in a high yield.[2,3] However, the treatment of alcohol **1a** with alumina affords an isomeric spiro compound **4** in a moderate yield, in which naphthylmethyl carbocation fragments are connected following "head-to-tail".[4] It has been suggested that in the first case the reaction mixture contains only the alcohol protonated at the nitrogen atom and cation **2a** due to the high basicity (pK_a 12.1) of 1,8-bis(dimethylamino)naphthalene ("proton sponge"). Due to the strong resonance stabilization of the latter, the contribution of structures of the **2′a**

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* For Part 3, see Ref. 1.

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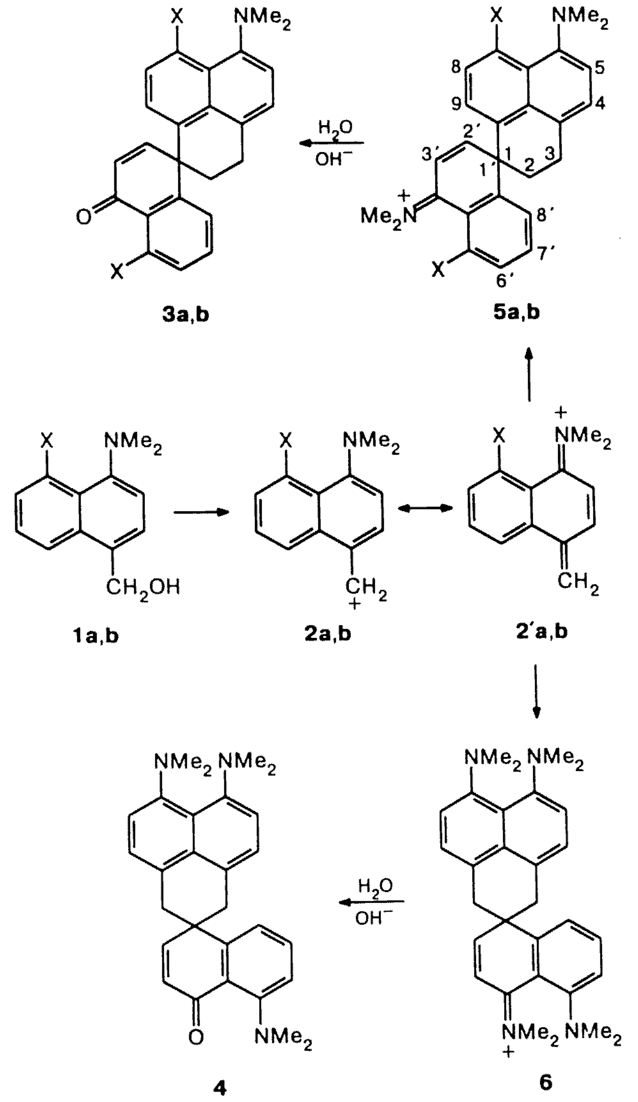
type, which have a 1,3-diene fragment and can undergo cycloaddition with another similar molecule acting as the dienophile, to the resonance hybrid of **2a** is rather high. The regioselectivity of the process is determined by the properties of boundary orbitals of the diene, which has been confirmed by quantum-chemical calculations.[2,3,5] Cation **2a** is probably formed on alumina in a low equilibrium concentration, and therefore it coexists with nonprotonated alcohol **1a** and attacks it as an electrophile at the free *peri*-position 5. Compound **4** is formed as a result of the two-step electrophilic substitution, the second step being the intramolecular process. In both cases, the direct product of the cyclodimerization is immonium salt **5** or **6**, which further undergo hydrolysis to the carbonyl-containing compound.

Scheme 1

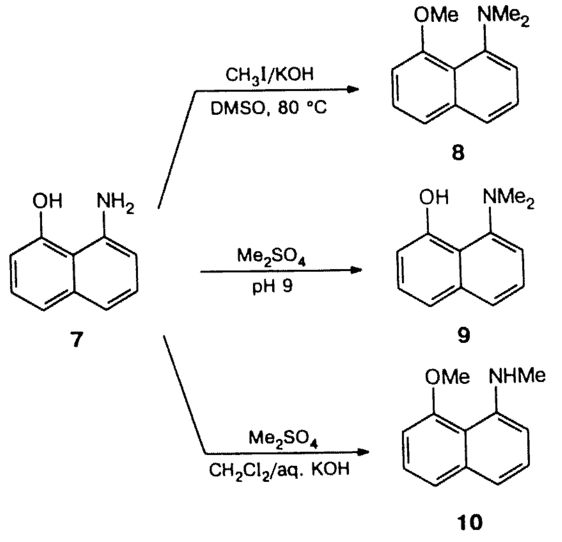


X = NMe2 (**a**), OMe (**b**)

The dimethoxy analog of compound **1a** behaves similarly on Al_2O_3 affording the symmetrical spiro compound of type **4** with three MeO groups instead of NMe_2.[4] However, 1-hydroxymethyl-4,5-dimethoxynaphthalene in an acidic medium undergoes only oligomerization; this is quite understandable since 1,8-dimethoxynaphthalene does not possess any noticeable basicity. Therefore, this alcohol and its oligomerization products exist in neutral forms even in an acidic medium and can easily react with carbocations. From the aforesaid, it was of interest to study the behavior of 1-hydroxymethyl-4-dimethylamino-5-methoxynaphthalene (**1b**) under similar conditions. The results of this study are discussed in this work.

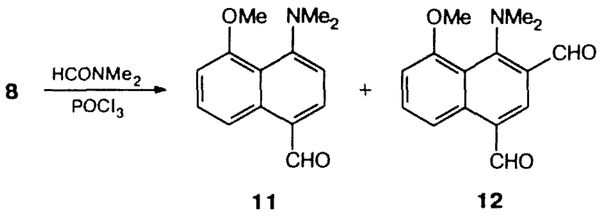
8-Dimethylamino-1-methoxynaphthalene (**8**) was obtained by methylation of 8-amino-1-naphthol (**7**).[6,7] The direction of this reaction depends strongly on the reaction conditions (Scheme 2). According to the published data,[6] treatment of an aqueous solution of compound **7** with dimethyl sulfoxide at pH 8—9 affords only 8-dimethylamino-1-naphthol (**9**). Three methyl groups could be introduced to give compound **8** only by using 20 equiv. of dimethyl sulfate and by the addition of a 10 *M* solution of NaOH into the reaction mixture.[6] We have studied two other variants of methylation of aminonaphthol **7**. With phase-transfer catalysis (tetrabutylammonium bromide as the catalyst), the previously unknown 8-methylamino-1-methoxynaphthalene (**10**) (yield 35 %) was the only reaction product. Methylation of an alkaline melt of aminonaphthol **7** with methyl iodide in DMSO afforded the target product **8** in a 52 % yield. Two equivalents of the methylating agent were used in both cases.

Scheme 2



Under formylation conditions, compound **8** is as reactive as the "proton sponge".[8] The process is accompanied by the formation of dialdehyde (**12**) along with 4-dimethylamino-5-methoxy-1-naphthaldehyde (**11**) (Scheme 3); therefore, to obtain monoaldehyde **11** in the highest yield, it is reasonable to carry out the reaction at low temperatures. For example, the mono- and dialdehydes are formed in a ~3 : 1 ratio at −10 °C, whereas at −45 °C this ratio is already 97 : 3 (the reaction does not proceed at a noticeable rate at lower temperatures). It should be noted that approximately one half of the initial compound is transformed into hydrochloride under the reaction conditions and is further recovered.

Scheme 3



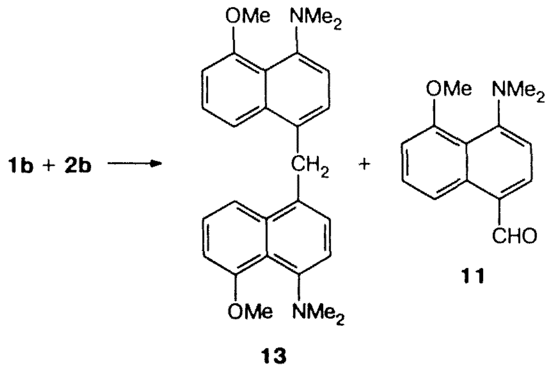
The fact that the formyl group entered into the ring with the dimethylamino group is confirmed by the ^{1}H NMR spectra. The chemical shift of the protons of the MeO group remains practically unchanged for a series of compounds **8**, **1b**, and **11** (δ is 4.01, 3.98, and 3.97, respectively), whereas a noticeable downfield shift of the signal of the protons of the NMe$_2$ group is observed for the same series on passing to the aldehyde (2.87, 2.82, and 2.98 ppm). In addition, the presence in the spectrum of the high-field signals of the H(6) and H(3) protons at δ 6.91 and 6.87 indicates that the formyl group was introduced into the *para*- rather than into the *ortho*-position. Additional evidence is the noticeable downfield shift of the signal of the H(8) proton due to the deshielding effect of the *peri*-aldehyde group.[8] In dialdehyde **12**, the signal of the NMe$_2$ group is shifted even more downfield (δ 3.26), whereas the chemical shift of the MeO group (δ 3.93) again remains almost unchanged. This fact, together with the appearance of the signal of the H(2) proton as a singlet, indicates the location of the two aldehyde groups in the same ring. In this connection it is noteworthy that diformylation of the "proton sponge" occurs at different nuclei.[8] These data altogether allow one to suggest that both the first route and, even more, the second route of formylation of compound **8** occur through the formation of a neutral molecule. Reduction of aldehyde **11** with sodium alumohydride yielded alcohol **1b**.

Prolonged refluxing of alcohol **1b** in trifluoroacetic acid yielded a complex mixture of products, from which spiro compound **3b** (yield 38 %) and the derivative of dinaphthylmethane **13** (yield 14 %) were isolated by column chromatography. The structures of both compounds are confirmed by the NMR and mass spectrometry data. In particular, in the ^{1}H NMR spectrum of spiro product **3b**, the signals of the protons of the CH$_2$CH$_2$ bridge appear practically in the same region as in the case of the analog **3a** [2] as two complex multiplets (due to nonequivalence of the geminal protons) at δ 2.20 (2-CH$_2$) and 3.16 (3-CH$_2$). The protons of methylene groups in the spiro compounds of type **4** manifest themselves quite differently, as two doublets at δ 2.95 and 3.75 with geminal coupling constant ≈ 14.7 Hz.[4]

A very strong resinification is observed upon heating of alcohol **1b** in conc. HCl, which makes isolation of individual reaction products difficult. According to the TLC data, compound **13** is absent in the reaction mixture, although some amount of spiro product **3b** is present. Thus, the behavior of carbocation **2b** in protic media resembles that of carbocation **2a**. The rather high basicity of 8-dimethylamino-1-methoxynaphthalene (pK_a 7.75),[6] although it is significantly lower than the basicity of the "proton sponge," allows one to suggest that alcohol **1b**, like **1a**, can exist in a strongly acidic medium primarily in protonated form. As mentioned above, this suppresses the oligomerization processes and increases the probability of dimerization of the carbocation according to the (4π + 2π) cycloaddition mechanism. In addition, cyclodimerization of cation **2b** proceeds noticeably slower than that of cation **2a**. It seems likely that a small amount of alcohol **1b** still remains unprotonated and is subjected to the attack with carbocation **2b** at position 5 resulting in the formation of compound **13** through the *ipso*-substitution of the hydroxymethyl group. In fact, as has been shown by formylation of naphthalene **8** (see above), the *para*-position in the ring containing dimethylamino group is significantly more reactive than position 4 in the ring with the MeO group.

The data on the action of alumina on alcohol **1b** also agree with these concepts. Heating of **1b** with anhydrous Al$_2$O$_3$ in benzene yielded two products, dinaphthylmethane **13** (yield 35 %) and aldehyde **11** (yield 20 %) (Scheme 4). The formation of even traces of spiro compounds of the type **4** was not observed. This is quite understandable since in this case the attack of the

Scheme 4



carbocation at a relatively low reactive position 8 of the initial alcohol would be necessary. As can be seen, position 1 is preferable for this attack under these conditions. As for aldehyde **11**, it is probably synthesized upon dehydrogenation of alcohol **1b** with carbocation **2b**. This process has been earlier observed by us for alcohol **1a** under similar conditions.[4]

Thus, we have shown in this study that cation **2b**, along with some similarity with analogous carbocations based on 1,8-bis(dimethylamino)- and 1,8-dimethoxynaphthalenes, possesses significant differences. The nature of these differences is mainly related to the nonequivalence of substituents in positions 1 and 8 and, as a consequence, to different activation of the corresponding *para*-positions.

Experimental

^{1}H NMR spectra were recorded on a Unity-300 instrument (300 MHz) at 30 °C using $SiMe_4$ as the internal standard. ^{13}C NMR spectra were obtained on a Unity-300 instrument (75.4 MHz). IR spectra were obtained on an IKS-40 instrument. Mass spectra were recorded on an MKh-1321A mass spectrometer; the sample was introduced directly into the ionization chamber of the vaporizer at 50—100 °C. The electron ionizing energy was 70 eV. The course of the reaction and the purity of compounds obtained were monitored by TLC on UV-254 Silufol plates with chloroform as the eluent; the detection was performed by treating the plates with iodine vapor. Unless otherwise specified, alumina had Brockmann grade-II activity. Anhydrous alumina for the generation of carbocations from alcohols **1a,b** was obtained by calcination of Al_2O_3 of grade-III activity at 250 °C for 20 min. Melting points were measured in sealed capillaries on a PTP instrument and were not corrected.

8-Dimethylamino-1-methoxynaphthalene (8). 1-Amino-8-naphthalenesulfonic acid (30 g) was melted with NaOH (70 g) and NaOH (70 g) at 255 °C for 30 min. Black foam was collected, cooled to room temperature, triturated in a mortar, and dissolved in DMSO (170 mL) in an argon atmosphere with vigorous stirring. Methyl iodide (76.7 g) was added dropwise over ~1 h to the solution obtained at 5—7 °C. The reaction mixture was stirred for 1 h at 20 °C and 30 min at 80 °C, cooled to room temperature, and poured into 1.5 L of cold water. The reaction product was extracted with ether (2×100 mL), the extract was dried with anhydrous Na_2SO_4 and applied on a short column with Al_2O_3 (d = 4 cm, h = 5 cm) for the separation from resins; the reaction product was eluted with ether (~200 mL). The resulting light-yellow eluate was concentrated, and the residue was distilled *in vacuo*. Only one fraction with b.p. 161—166 °C (2 Torr) was collected as a yellowish oil, which was gradually crystallized on storage. The yield was 14.1 g (52 %), m.p. 29—30 °C (methanol—water, 9 : 1), *cf.* Refs. 6 and 7: m.p. 30 °C.

1-Methoxy-8-methylaminonaphthalene (10). 1-Amino-8-naphtalenesulfonic acid (15 g) was melted with KOH (30 g) and NaOH (30 g) at 250 °C for 20 min. Black foam was collected, cooled to room temperature, and dissolved in water (170 mL). Tetrabutylammonium bromide (3 g) and dichloromethane (120 mL) were added to the solution with vigorous stirring in an argon atmosphere, and then dimethyl sulfate (50.4 g) was added over 1 h at 5—10 °C. The reaction mixture was stirred for 3 h at the same temperature, poured into 0.5 mL of water, and acidified with conc. HCl to pH 1. The resulting emulsion was filtered to remove a small amount of black precipitate, and the aqueous layer was separated and alkalified with a 40 % solution of NaOH to pH 12. The resulting dark oil was extracted with dichloromethane (2×30 mL), and the extract was dried with Na_2SO_4. The solvent was distilled off, and the residue was distilled *in vacuo*. The fraction with b.p. 156—162 °C (1 Torr) was collected as a light yellow oil, which was gradually crystallized upon cooling, and crystallized from methanol with activated carbon to afford 4.36 g (35 %) of compound **10** as white lamellar crystals, m.p. 126—127 °C, R_f 0.78 (Al_2O_3, benzene). Found (%): C, 76.81; H, 7.08; N, 7.34. $C_{12}H_{13}NO$. Calculated (%): C, 76.98; H, 7.00; N, 7.48. ^{1}H NMR ($CDCl_3$), δ: 2.96 (s, 3 H, NHMe); 3.97 (s, 3 H, MeO); 6.45 (dd, 1 H, 7-H, $J_{7,6}$ = 7.91 Hz, $J_{7,5}$ = 1.17 Hz); 6.72 (dd, 1 H, 2-H, $J_{2,3}$ = 7.32 Hz, $J_{2,4}$ < 1 Hz); 7.03 (br.s, 1 H, NH); 7.08 (dd, 1 H, 5-H, $J_{5,6}$ = 7.91 Hz, $J_{5,7}$ = 1.17 Hz); 7.25—7.38 (m, 3 H, 3-H, 4-H, and 6-H).

4-Dimethylamino-5-methoxy-1-naphthaldehyde (11) and 4-dimethylamino-5-methoxynaphthalene-1,3-dicarbaldehyde (12). A solution of compound **8** (7.85 g) in dry toluene (30 mL) was cooled to −60 °C, and a formylating complex, prepared from anhydrous DMF (10 mL) and freshly distilled phosphorus oxychloride (3.37 g) at −15 °C, was added dropwise. The color of the homogeneous solution changed from pale-yellow to orange as the temperature rose to −45 °C. The mixture was stirred for 1 h at −45 °C, then cooling was discontinued. After the temperature in the reaction vessel reached 0 °C, water (100 mL) was added. The toluene layer was removed, the aqueous layer was neutralized with solid sodium bicarbonate to pH 5 and extracted with toluene (3×15 mL), and the extract was dried with anhydrous Na_2SO_4. Toluene was distilled off, and the oily residue was distilled *in vacuo* using a 10-cm long Vigreaux column. Two fractions were collected. The first fraction, b.p. 142—146 °C (1 Torr), was the starting compound **8**, the yield was 3.38 g (43 %), and the second fraction, b.p. 189—190 °C (1 Torr), was monoaldehyde **11** as a light-orange oil, which crystallized into bright yellow crystals on cooling. The yield of **11** was 3.67 g (82 % with respect to the initial compound consumed), m.p. 67—68 °C (from 80 % aqueous ethanol), R_f 0.46 (Al_2O_3, benzene). Found (%): C, 73.18; H, 6.67; N, 6.24. $C_{14}H_{15}NO_2$. Calculated (%): C, 73.34; H, 6.59; N, 6.11. ^{1}H NMR ($CDCl_3$), δ: 2.98 (s, 6 H, NMe_2); 3.97 (s, 3 H, MeO); 6.87 (d, 1 H, 3-H, $J_{2,3}$ = 8.49 Hz); 6.91 (dd, 1 H, 6-H, $J_{6,7}$ = 7.62 Hz, $J_{6,8}$ = 0.88 Hz); 7.53 (dd, 1 H, 7-H, $J_{6,7}$ = 7.62 Hz, $J_{7,8}$ = 8.50 Hz); 7.75 (d, 1 H, 2-H, $J_{2,3}$ = 8.49 Hz); 8.99 (dd, 1 H, 8-H, $J_{7,8}$ = 8.50 Hz, $J_{6,8}$ = 0.88 Hz); 10.06 (s, 1 H, CHO).

The aqueous layer remaining after the extraction with toluene was alkalifed to pH 10 with a saturated solution of K_2CO_3 and again extracted with toluene (3×10 mL). The extract was concentrated to ~2 mL and applied to an Al_2O_3 column (d = 1.5 cm, h = 4 cm), chloroform was used as the eluent. The yellow fraction of dialdehyde **12** was collected. The yield of **12** was 0.13 g (2.5 %, orange crystals), m.p. 103—104 °C (CCl_4), R_f 0.12 (Al_2O_3, benzene). Found (%): C, 69.89; H, 5.94; N, 5.41. $C_{15}H_{15}NO_3$. Calculated (%): C, 70.02; H, 5.88; N, 5.44. ^{1}H NMR ($CDCl_3$), δ: 3.26 (s, 6 H, NMe_2); 3.93 (s, 3 H, MeO); 6.86 (dd, 1 H, 6-H, $J_{6,7}$ = 8.20 Hz, $J_{6,8}$ = 0.59 Hz); 7.56 (dd, 1 H, 7-H, $J_{6,7}$ = $J_{7,8}$ = 8.20 Hz); 7.97 (s, 1 H, 2-H); 8.72 (dd, 1 H, 8-H, $J_{7,8}$ = 8.20 Hz, $J_{6,8}$ = 0.59 Hz); 9.77 (s, 1 H, 7-CHO); 9.90 (s, 1 H, 5-CHO).

When the synthesis was carried out at −10 °C with the same amounts of reagents, the ratio of mono- and dialdehydes was ~3 : 1.

1-Hydroxymethyl-4-dimethylamino-5-methoxynaphthalene (1b). Sodium alumohydride (0.081 g) was added in one portion to a solution of aldehyde **11** (1.00 g) in abs. THF (10 mL). The mixture was stirred for 15 min at 40 °C, cooled, and water (0.2 mL) was added dropwise. The solution of the reaction product in THF was separated from the aqueous suspension of sodium and aluminum hydroxides by decantation. THF was distilled off, and the light-grey crystalline residue was recrystallized from benzene using Al_2O_3 (0.2 g) for clarification, to afford 0.97 g (96 %) of **1b** as white crystals, m.p. 78—79 °C, R_f 0.36 (Al_2O_3, $CHCl_3$). Found (%): C, 72.83; H, 7.44; N, 5.98. $C_{14}H_{17}NO_2$. Calculated (%): C, 72.70; H, 7.41; N, 6.06. ^1H NMR ($CDCl_3$), δ: 1.95 (br.s, 1 H, OH); 2.82 (s, 6 H, NMe_2); 3.98 (s, 3 H, MeO); 4.99 (s, 2 H, $\underline{CH_2}OH$); 6.85 (dd, 1 H, 6-H, $J_{6,7}$ = 7.91 Hz, $J_{6,8}$ = 0.88 Hz); 6.89 (d, 1 H, 3-H, $J_{2,3}$ = 7.62 Hz); 7.31 (d, 1 H, 2-H, $J_{2,3}$ = 7.62 Hz); 7.43 (dd, 1 H, 7-H, $J_{6,7} = J_{7,8}$ = 8.20 Hz); 7.72 (dd, 1 H, 8-H, $J_{7,8}$ = 8.20 Hz, $J_{6,8}$ = 0.88 Hz). IR (CCl_4), ν/cm^{-1}: 3620 (O—H_{free}); 3480 (O—H_{ass}); 1570 (C—C_{ar}).

Transformations of 1-hydroxymethyl-4-dimethylamino-5-methoxynaphthalene. *A.* In trifluoroacetic acid. A solution of alcohol **1b** (0.200 g, 0.87 mmol) in freshly distilled trifluoroacetic acid (10 mL) was refluxed for 35 h. The reaction mixture was cooled, diluted with water (20 mL), alkalifed with a 20 % solution of NaOH to pH 13, and extracted with chloroform (3×10 mL). The combined extracts were concentrated and chromatographed on a column with Al_2O_3 of Brockmann grade III activity (*h* = 45 cm, *d* = 2 cm, eluent chloroform). The colorless fraction of 4,4′-bis(dimethylamino)-8,8′-dimethoxy-1,1′-dinaphthylmethane (**13**) was collected, R_f 0.88, the yield was 0.025 g (14 %); pale cream-colored amorphous powder, m.p. 107—109 °C (from a 1 : 1 toluene—hexane mixture). Found (%): C, 77.85; H, 7.20; N, 6.18. $C_{27}H_{30}N_2O_2$. Calculated (%): C, 78.23; H, 7.29; N, 6.76. ^1H NMR ($CDCl_3$), δ: 2.82 (s, 12 H, 2 NMe_2); 4.02 (s, 6 H, 2 MeO); 4.63 (s, 2 H, CH_2); 6.87 (d, 2 H, 7-H, and 7′-H, $J_{7,6}$ = 7.90 Hz); 6.92 (dd, 2 H, 2-H, and 2′-H, $J_{2,3}$ = 8.10 Hz, $J_{2,4}$ < 1 Hz); 6.94 (d, 2 H, 6-H, and 6′-H, $J_{6,7}$ = 7.90 Hz); 7.37 (dd, 2 H, 3-H, and 3′-H, $J_{3,2} \approx J_{3,4}$ = 8.10 Hz); 7.62 (dd, 2 H, 4-H, and 4′-H, $J_{4,3}$ = 8.10 Hz, $J_{4,2}$ < 1 Hz). MS, *m/z* (*I* (%)): 414 [M$^+$] (27), 259 (18), 229 (13), 214 (40), 170 (13), 71 (13), 57 (54), 43 (100).

Several overlapping minor intermediate fractions were discarded, then a yellow fraction with R_f 0.50 was collected (appeared as a grey spot at TLC in iodine vapor) and rechromatographed on a column with Al_2O_3 of grade II activity (*h* = 35 cm, *d* = 2 cm, eluent chloroform) to afford 0.066 g (38 %) of spiro[7,5′-dimethoxy-6-dimethylamino-2,3,1′,4′-tetrahydro-4′-oxophenalene-1,1′-naphthalene] (**3b**) as fine pale-yellow crystals, m.p. 105—107 °C (from hexane). Found (%): C, 78.23; H, 6.29, N, 3.55. $C_{26}H_{25}NO_3$. Calculated (%): C, 78.19; H, 6.27; N, 3.51. ^1H NMR ($CDCl_3$), δ: 2.20 (m, 2 H, 2-CH_2); 2.84 (s, 6 H, NMe_2); 3.16 (m, 2 H, 3-CH_2); 3.94 (s, 3 H, 5′-MeO); 3.98 (s, 3 H, 7-MeO); 6.34 (d, 1 H, 3′-H, $J_{3',2'}$ = 10.03 Hz); 6.56 (dd, 1 H, 6′-H, $J_{6',7'}$ = 7.91 Hz, $J_{6',8'}$ = 0.81 Hz); 6.73 (d, 1 H, 8-H, $J_{8,9}$ = 8.28 Hz); 6.89 (dd, 1 H, 8′-H, $J_{8',7'}$ = 7.76 Hz, $J_{8',6'}$ = 0.81 Hz); 7.02 (br.d, 1 H, 4-H, $J_{4,5}$ = 7.76 Hz); 7.06 (d, 1 H, 2′-H, $J_{2',3'}$ = 10.03 Hz); 7.27 (m, 1 H, 7′-H); 7.32 (d, 1 H, 9-H, $J_{9,8}$ = 8.20 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ: 27.13 (C-2); 38.32 (C-3); 45.59 (NMe_2); 46.96 (C-1); 56.20, 56.48 (7-MeO, 5′-MeO); 106.60 (C-8); 109.95 (C-6); 113.07 (C-5); 120.31 (C-6a); 121.26 (C-4′a); 121.87 (C-8′); 125.75 (C-4); 126.81 (C-9); 127.47 (C-3′); 130.16 (C-3a); 132.74 (C-7′); 133.03 (C-9a); 148.71 (C-9b); 149.77 (6-NMe_2); 151.51 (C-2′); 153.29 (C-8′a); 156.26 (7-MeO); 160.25 (5′-MeO); 184.81 (C=O). IR (vaseline oil), ν/cm^{-1}: 1645 (C=O). MS, *m/z* (*I* (%)): 399 [M$^+$] (100), 385 (9), 229 (5), 182 (8), 83 (16).

B.* On alumina. Anhydrous Al_2O_3 (20 g) was added to a solution of compound **1b** (0.200 g, 0.87 mmol) in benzene (30 mL), and the mixture was heated at 80 °C with reflux for 2 h. Alumina was filtered off, and the residue was washed with chloroform (3×15 mL). The filtrate was concentrated and chromatographed on a column with Al_2O_3 of grade-II activity (*h* = 35 cm, *d* = 2 cm, eluent chloroform). A yellow fraction of aldehyde **11** with R_f 0.81 was collected first; the yield of **11** was 0.04 g (20 %). The second colorless fraction with R_f 0.69 contained compound **13.** The yield of **13** was 0.063 g (35 %), m.p. 107—109 °C (from a 1 : 1 toluene—hexane mixture). Subsequent fractions have a very complex composition according to ^1H NMR spectral data and were most probably a mixture of oligomers. No fractions contained even traces of spiro compounds.

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* The procedure given below for the generation of carbocations from 1-hydroxymethylnaphthalenes is much more effective than that previously described by us, which involved the use of a chromatographic column.[4] For example, the transformation of alcohol **1a** into spiro compound **3a** under the present conditions was complete in 1 h, whereas it took 75—80 h on an Al_2O_3 column. In addition, the yield of compond **3a** in this case increased from 23 to 37 %.