

peri-Naphthylenediamines

18.* 1,8-Bis(dimethylamino)-4-vinylnaphthalene

*N. V. Vistorobskii and A. F. Pozharskii**

*Rostov State University,
7 ul. Zorge, 344090 Rostov-on-Don, Russian Federation.
Fax: 007 (863 2) 28 5667*

The 1-[1,8-bis(dimethylamino)-4-naphthyl]ethyl carbocation generated from the corresponding alcohol in benzene in the presence of Al_2O_3 undergoes elimination according to the *E1* mechanism to give previously unknown 1,8-bis(dimethylamino)-4-vinylnaphthalene in a good yield. This compound was also synthesized from 1,8-bis(dimethylamino)-4-formylnaphthalene by the Wittig reaction. Polymerization of the vinylic derivative obtained was studied.

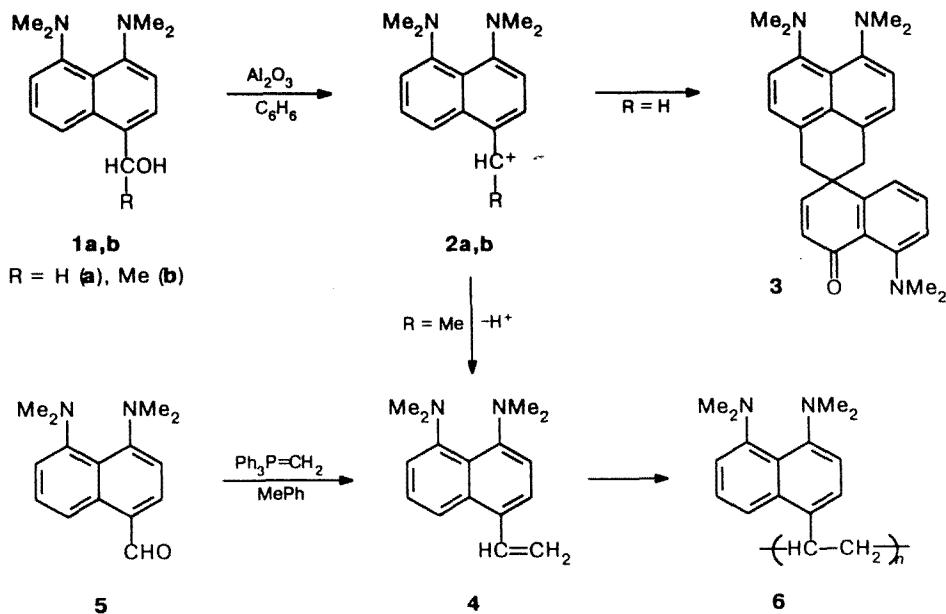
Key words: naphthalene, naphthylmethyl carbocations, vinyl derivatives, "proton sponge"; Wittig reaction; polymerization.

Recently we found^{2,3} that heating 4-hydroxymethyl-1,8-bis(dimethylamino)naphthalene (**1a**) in benzene with Al_2O_3 (Scheme 1) affords spiro-compound **3**. The reaction is assumed to occur as two-step electrophilic cyclodimerization of the intermediate carbocation **2a**. It has been of interest to study the behavior of 1,8-bis(dimethylamino)-4-(1-hydroxyethyl)naphthalene (**1b**) under similar conditions.

Prolonged heating of compound **1b** in benzene with anhydrous Al_2O_3 afforded the previously unknown 1,8-bis(dimethylamino)-4-vinylnaphthalene (**4**), a derivative of a "proton sponge", as the main reaction product in 73% yield. In addition to compound **4**, 4-acetyl-1,8-bis(dimethylamino)naphthalene⁴ was isolated in 9% yield; this apparently resulted from dehydration of alcohol **1b** with carbocation **2b**. Thus, it is energetically more favorable for carbocation **2b** to be converted into the vinylic compound, *i.e.*, to undergo *E1* elimination, than to undergo cyclodimerization to the corresponding spiro-derivative.

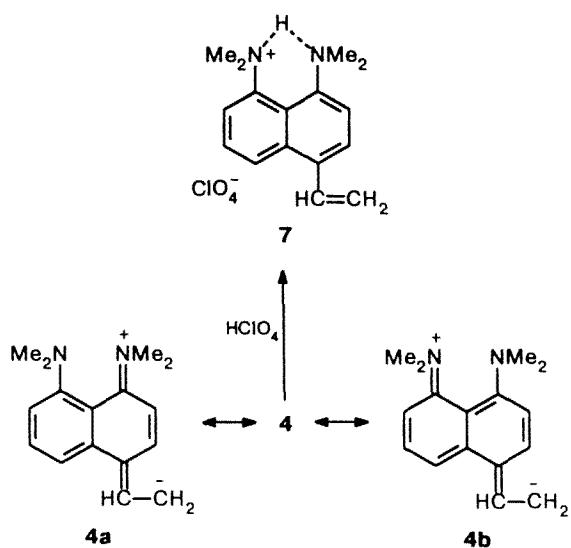
* For Part 17, see Ref. 1.

Scheme 1



We also synthesized⁵ compound **4** from aldehyde **5** by the Wittig reaction (yield 81%). It is of interest that we were not able to convert 1,8-bis(dimethylamino)naphthalene-4,5-dicarbaldehyde⁵ into the 4,5-divinyl "proton sponge" derivative under similar conditions: the reaction led to a complex mixture of compounds that were difficult to identify.

The dimethylamino groups and the vinyl group in molecule **4** are probably conjugated, which results in an increase in the contribution of bipolar structures **4a** and **4b** to the resonance hybrid. This is indicated by the bathochromic shift of the long-wavelength absorption band in the electronic spectrum of compound **4** from 338 nm, where this band is located in the spectrum of the "proton sponge", to 353 nm. The vinylic derivative **4** reacts with perchloric acid to give salt **7**, whose molecule contains a strong intramolecular hydrogen bond typical of cations derived from a "proton sponge".⁶ The hydrogen bond is somewhat asymmetrical, and thus the proton belongs to the N(8) atom to a somewhat greater extent. This is indicated by the fact that the signal for the H(7) atom in the ¹H NMR spectrum of perchlorate **7** (δ 8.12) is located somewhat downfield from the doublet for the H(2) proton (δ 8.07). The signal for the chelated proton in the NH group is a multiplet at δ 18.66 with a spin-spin coupling constant typical of salts of this type,⁷ $J_{\text{NH}-\text{CH}_3} = 2.30$ Hz.

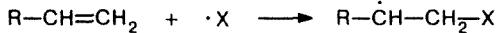


It was enticing to convert monomer **4** into the polymeric "proton sponge" **6**, the use of which as a strong low-nucleophilicity base could in some cases be more convenient. For this purpose, we studied some procedures for polymerization of compound **4**. 1-Vinyl- and 1,8-divinylnaphthalenes are known to polymerize by a radical mechanism.⁸ The former affords a high-molecular-weight polymer, while the latter yields readily soluble oligomers with molecular weights ranging from 1620 to 1760. We attempted to polymerize monomer **4** in the presence of an initiator of radical polymerization,

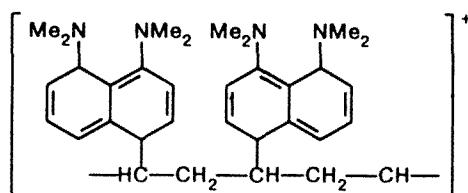
viz., azobisisobutyronitrile (AIBN). The experiments were carried out in sealed tubes, which were degassed beforehand. Copolymerization of compound **4** with methyl methacrylate (MMA) was studied under similar conditions. In order to obtain copolymers of the polysulfone type, we attempted to copolymerize compound **5** with sulfur dioxide.

We found that polymerization of vinylic derivative **4** in the presence of AIBN did not occur either upon photoinitiation in the bulk or in hexane or upon thermal initiation (70 °C). The copolymerization experiments were also unsuccessful. When the **4** : MMA ratio was equal to 1 : 1 (w/w) (AIBN, 80 °C, 20 h), a high-molecular-weight compound was isolated, which contained a vanishingly small proportion of monomer **4** (this was established by comparing the IR spectra of poly(methyl methacrylate), of the polymer obtained, and of 1,8-bis(dimethylamino)-4-vinylnaphthalene). Copolymerization in a mixture of MMA with compound **4**, containing a higher amount of the latter, did not lead to the formation of a polymer; in the case in which a higher amount of MMA was taken, the process yielded poly(methyl methacrylate).

When sulfur dioxide is introduced into a preliminarily degassed tube containing a 20% solution of compound **4** in hexane and cooled to the temperature of liquid nitrogen, a bright-red colored product is immediately formed, which is apparently a π -complex or a σ -complex. As soon as cooling with liquid nitrogen is discontinued, resinification and spontaneous warming-up of the mixture begin; consequently, the tube bursts within a few seconds. The fact that the polymerization of compound **4** presents difficulties can be explained by the strong electron-donating effect of the dimethylamino groups,⁹ which results in an increase in the activation energy of the initiation, in particular, of the interaction between the radical derived from the initiator and the double bond of the monomer.



Taking the foregoing into account, it might be suggested that the protonated form of compound **4** would polymerize more readily. This hypothesis was borne out to some extent. Polymerization of the vinylic derivative in concentrated orthophosphoric acid (AIBN, 75 °C, 20 h) gave a solid product, whose reprecipitation with methanol from a solution in benzene afforded a polymer as a white powder. Its IR spectrum exhibits an absorption band at 1585 cm^{-1} typical of a "proton sponge" and its derivatives and corresponding to the stretching vibrations of the ring C—C bonds. The mass spectrum contains peaks with m/z of 493 (24%) and 494 (8%), which can be assigned to dimeric fragments like **8**. However, the yield of the polymer is as low as 5%. The fact that much material is lost during reprecipitation indicates that the crude product contains a large proportion of low-molecular-weight oligomers.



Experimental

¹H NMR spectra were recorded on a Unity-300 instrument (300 MHz) at 30 °C with SiMe₄ as the internal standard. UV spectra were measured on a Specord M40 spectrophotometer, and mass spectra were obtained on a Finnigan 4021 mass spectrometer. Chromatography was carried out using Al₂O₃ of Brockman activity II. Anhydrous Al₂O₃ for the dehydration of alcohol **1b** was obtained by calcining Al₂O₃ of Brockman activity III at 250 °C for 20 min.

1,8-Bis(dimethylamino)-4-vinylnaphthalene (4). *A.* Compound **1b** (0.3 g, 1.16 mmol) was stirred with 30 g of anhydrous Al₂O₃ in 40 mL of benzene for ~30 h at 80 °C (until the spot corresponding to the initial substance was no longer found on the chromatogram). Then the Al₂O₃ was filtered off and washed with chloroform (3×20 mL). The combined filtrates were concentrated to a small volume and chromatographed on a column with Al₂O₃ (*h* = 10 cm, *d* = 2 cm, hexane as the eluent), and compound **4** was isolated as a colorless fraction with *R*_f 0.08. Yield 0.204 g (73%). After that, the only yellow fraction, 4-acetyl-1,8-bis(dimethylamino)naphthalene, was washed out with benzene from the same column. Yield 0.027 g (9%), yellow plates, m.p. 65–66 °C (from hexane). All physicochemical parameters of the product were identical to those of an authentic sample.⁴

1,8-Bis(dimethylamino)-4-vinylnaphthalene (4) is a pale yellow thick oil, readily soluble in most common organic solvents and insoluble in water. The material exhibited no clear signs of polymerization after it was stored in a sealed tube for several months. Found (%): C, 79.79; H, 8.34; N, 11.59. C₁₆H₂₀N₂. Calculated (%): C, 79.96; H, 8.38; N, 11.66. UV (MeOH), $\lambda_{\text{max}}/\text{nm}$ (log_e): 248 (4.11), 353 (3.62). IR (film), ν/cm^{-1} : 3080, 3050, 3000, 2970, 2930, 2870, 2830, 2780 (C–H); 1615, 1570, 1510 (C–C(Ar)). ¹H NMR (acetone-d₆), δ : 2.80 (s, 6 H, 8-NMe₂); 2.82 (s, 6 H, 1-NMe₂); 5.28 (dd, 1 H, CH=CH₂ (A), $J_{\text{gem}} = 1.83$ Hz, $J_{\text{cis}} = 10.84$ Hz); 5.64 (dd, 1 H, CH=CH₂ (B), $J_{\text{gem}} = 1.83$ Hz, $J_{\text{trans}} = 17.20$ Hz); 6.98 (m, 2 H, H(2), H(7)); 7.35 (dd, 1 H, H(6), $J_{6,5} = J_{6,7} = 8.20$ Hz); 7.41 (dd, 1 H, CH=CH₂, $J_{\text{cis}} = 10.84$ Hz, $J_{\text{trans}} = 17.20$ Hz); 7.51 (d, 1 H, H(3), $J_{3,2} = 7.98$ Hz); 7.64 (dd, 1 H, H(5), $J_{5,6} = 8.20$ Hz, $J_{5,7} < 1$ Hz).

B. Triphenylphosphonium iodide (6.06 g, 0.015 mol) was added with stirring to sodium amide prepared from metallic Na (0.35 g, 0.0152 g-at.) in 30 mL of liquid ammonia. Stirring was continued until the ammonia completely evaporated; after that, 70 mL of anhydrous toluene was carefully added under argon, and 30 min later, a solution of aldehyde **5** (2.42 g, 0.010 mol) in 10 mL of toluene was added dropwise. The reaction mixture was stirred for 1 h, the toluene was decanted, and the precipitate was washed with toluene (3×15 mL). The solvent from the combined toluene solutions was evaporated under reduced pressure, and the residue was chromatographed on a column with Al₂O₃ (*h* = 12 cm, *d* = 2.5 cm, hexane as the eluent). The first pale yellow fraction was collected; this contained the vinylic derivative **4**. Yield 1.95 g (81%).

Perchlorate 7 was obtained by adding 0.2 mL of 60% perchloric acid to a solution of compound **4** in 10 mL of ethanol

cooled to 0 °C. The white crystals that precipitated were filtered off, washed with cold ethanol (~3 mL), and dried in a vacuum desiccator. Yield 0.295 g (94%), m.p. 197–199 °C. ¹H NMR (DMSO-d₆), δ : 3.12, 3.13 (both as.d, 12 H, 1-NMe₂, 8-NMe₂, $J_{\text{CH}_3-\text{NH}} = 2.30$ Hz); 5.59 (dd, 1 H, CH=CH₂ (A), $J_{\text{gem}} = 1.36$ Hz, $J_{\text{cis}} = 10.90$ Hz); 5.91 (dd, 1 H, CH=CH₂ (B), $J_{\text{gem}} = 1.36$ Hz, $J_{\text{trans}} = 17.25$ Hz); 7.56 (dd, 1 H, CH=CH₂, $J_{\text{cis}} = 10.90$ Hz, $J_{\text{trans}} = 17.25$ Hz); 7.77 (dd, 1 H, H(6), $J_{6,5} = 8.35$ Hz, $J_{6,7} = 7.80$ Hz); 7.87 (d, 1 H, H(3), $J_{3,2} = 8.02$ Hz); 8.07 (d, 1 H, H(2), $J_{2,3} = 8.02$ Hz); 8.12 (dd, 1 H, H(7), $J_{7,6} = 7.47$ Hz, $J_{7,5} < 1$ Hz); 8.31 (dd, 1 H, H(5), $J_{5,6} = 8.57$ Hz, $J_{5,7} < 1$ Hz); 18.66 (m, 1 H, NH, $J_{\text{NH}-\text{CH}_3} = 2.30$ Hz).

Radical polymerization of compound 4. The vinylic derivative **4** (1.5 g) was dissolved in 4.5 mL of 94.5% phosphoric acid in a 20-mL tube cooled to –10 °C. When the compound had completely dissolved, 0.04 g of azobisisobutyronitrile was added. The contents of the tube were degassed by freezing to the liquid-nitrogen temperature followed by evacuation (10^{–3} Torr). The procedure was repeated 3 times, and then the tube was sealed, kept for 20 h at 75 °C, cooled to –30 °C, and opened. The contents were dissolved in 200 mL of ice water and made alkaline with a 10% solution of KOH to pH 12. The plentiful clotted precipitate was separated, washed with water, and dried over alkali to give 1.5 g of a cream-colored powder, which was dissolved in 12 mL of benzene. This solution was filtered and diluted with 85 mL of methanol. A polymer coagulated; the coagulate was kept for 24 h at –20 °C, and the precipitate was separated by decanting, washed with methanol (2×2 mL), and dried over KOH to give 0.10 g of the polymer as a white powder, yield 6.7%. IR (Vaseline oil), ν/cm^{-1} : 2980, 2940, 2870, 2830, 2790 (C–H); 1585 (C–C(Ar)).

The authors wish to thank V. B. Golubev (M. V. Lomonosov Moscow State University) for consultations concerning the polymerization of the 4-vinylic "proton sponge" derivative.

The work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 96-03-32153a).

References

1. A. F. Pozharskii, G. G. Aleksandrov, and N. V. Vistorobskii, *Zh. Org. Khim.*, 1996, **32**, in press [*Russ. J. Org. Chem.*, 1996, **32** (Engl. Transl.)].
2. A. F. Pozharskii and N. V. Vistorobskii, *Izv. Akad. Nauk, Ser. Khim.*, 1996, **1016** [*Russ. Chem. Bull.*, 1996, **45**, 971 (Engl. Transl.)].
3. A. F. Pozharskii, N. V. Vistorobskii, A. I. Chernyshev, and M. I. Rudnev, *Izv. Akad. Nauk, Ser. Khim.*, 1996, **2039** [*Russ. Chem. Bull.*, 1996, **45**, No. 8 (Engl. Transl.)].
4. N. V. Vistorobskii and A. F. Pozharskii, *Zh. Org. Khim.*, 1991, **27**, 1543 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
5. N. V. Vistorobskii and A. F. Pozharskii, *Zh. Org. Khim.*, 1989, **25**, 2154 [*J. Org. Chem. USSR*, 1989, **25** (Engl. Transl.)].
6. H. A. Staab and T. Saupe, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 865.
7. A. F. Pozharskii, V. V. Kuz'menko, G. G. Aleksandrov, and D. V. Dmitrienko, *Zh. Org. Khim.*, 1995, **31**, 570 [*Russ. J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
8. J. K. Stille and R. T. Foster, *J. Org. Chem.*, 1963, **28**, 2703.
9. A. F. Pozharskii, A. N. Suslov, N. M. Starshikov, L. L. Popova, N. A. Klyuev, and V. A. Adanin, *Zh. Org. Khim.*, 1980, **16**, 2216 [*J. Org. Chem. USSR*, 1980, **16** (Engl. Transl.)].

Received March 29, 1996