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Rearrangement of carbocations derived from 1,8-bis(dimethylamino)naphthyl-2-methanols into 4-R-1,1,3-trimethyl-2,3-dihydroperimidinium salts

Oksana V. Ryabtsova, Alexander F. Pozharskii,* Alexander V. Degtyarev and Valery A. Ozeryanskii

Department of Chemistry, Rostov State University, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 863 297 5146; e-mail: apozharskii@rsu.ru

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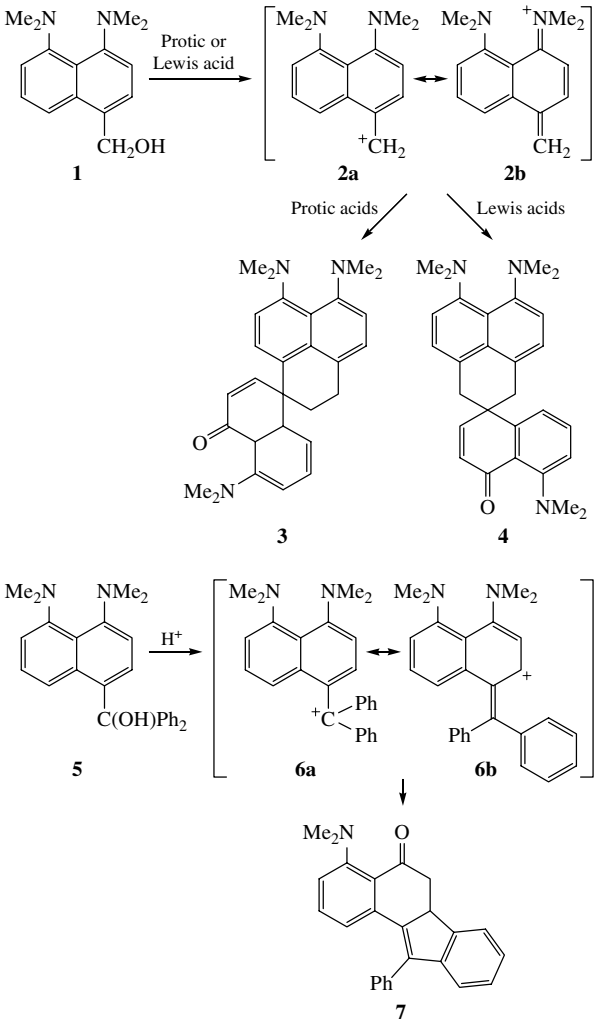
α-Phenylated 1,8-bis(dimethylamino)-2-naphthylmethyl carbocations have been shown to rearrange into 4-R-1,1,3-trimethyl-2,3-dihydroperimidinium cations through an intramolecular hydride shift from the 1-NMe_2 group.

Recent studies have demonstrated diverse and spectacular reactivity of naphthylmethyl carbocations,[1–5] including those based on 1,8-bis(dimethylamino)naphthalene (proton sponge). Thus, primary alcohol **1** at treatment with strong protic acids quantitatively produces spiro-compound **3**.[6,7] The latter resulted from the [4 + 2]-cyclodimerization of resonance-stabilised 4,5-bis(dimethylamino)-1-naphthylmethyl cation **2**, which behaves both as a 1,3-diene and a dienophile (Scheme 1). Contrary to this, the generation of cation **2** in the presence of Lewis acids (Al_2O_3, TiO_2 and SiO_2) leads to isomeric spiro-compound **4**

forming through stepwise electrophilic substitution.[8,9] Secondary and tertiary proton sponge alcohols react differently. For example, 4-α-hydroxybenzhydryl-1,8-bis(dimethylamino)naphthalene **5** transforms in protic acids into benzofluorenone derivative **7**, presumably *via* intramolecular arylation in intermediate carbocation **6** (Scheme 1).[10] Compounds with the α-Me group in alcoholic function smoothly underwent E1 elimination to furnish the corresponding alkene.[10] In the light of these observations, it seemed interesting to examine the reactivity of 1,8-bis(dimethylamino)-2-naphthylmethyl carbocations. One could expect that owing to proximity of the carbenium centre and the NMe_2 groups they will display somewhat different and not easily predictable behaviours.

Alcohols **8a–d** were used as starting materials for the generation of corresponding 2-naphthylmethyl carbocations.† At treatment of **8a** with concentrated hydrochloric acid, an orange-red colour, typical of triarylmethyl cations, immediately developed followed by fast discolouration and precipitation of 4-benzhydryl-2,3-dihydroperimidinium salt **14a**‡ as colourless crystals in quantitative yield. Similarly, secondary alcohol **8b** gave chloride **14b**‡ with the 4-benzyl group (70%). The structures of these salts were confirmed by NMR spectra; for **14b**, X-ray measurements were also conducted (Figure 1).§

The most probable mechanism of this transformation is shown in Scheme 2. It starts with the formation of chelated cation **9** equilibrating with hydroxonium salt **10**, which serves as the precursor of carbocation **12**. The latter is stabilised by intramolecular hydride ion transfer from the nearest NMe_2 group to the carbenium centre. Methyleneimmonium intermediate **13** thus formed is then cyclised into 2,3-dihydroperimidinium salt **14**. Such a kind of cyclization with the participation of an internal oxidising group has been never observed before and was only reported for the parent proton sponge at its treatment with some rhodium or ruthenium complexes for hydride abstrac-



Scheme 1

† Synthesis of compound **8a** has been reported in ref. 11. Alcohols **8b–d** will be described elsewhere.

‡ All new structures gave correct analytical and spectral data. Habit and selected spectral data [^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), MS EI (70 eV)] are as follows.

14a: colourless leaflets with mp 182.5–183 °C (decomp., H_2O). ^{1}H NMR ($CDCl_3$) δ: 3.48 (s, 3H, NMe), 3.98 (br. s, 6H, $^+NMe_2$), 6.01 (s, 1H, C*H*Ph_2), 7.00–7.97 (m, 15H, 2Ph, H-5, H-6, H-7, H-8, H-9). ^{1}H NMR ([$^2H_6$]DMSO) δ: 3.29 (s, 3H, NMe), 3.61 (br. s, 6H, $^+NMe_2$), 5.33 (br. s, 2H, CH_2), 6.08 (s, 1H, $CHPh_2$), 7.10–7.40 (m, 11H, 2Ph, H-5), 7.72 (dd, 1H, H-8, ^3J 7.5 Hz, ^3J 8.3 Hz), 7.79 (d, 1H, H-6, ^3J 9.1 Hz), 8.08 (br. d, 1H, H-7, ^3J 8.3 Hz), 8.15 (br. d, 1H, H-9, ^3J 7.8 Hz). MS, *m*/*z* (%): 364 [M – MeCl]$^+$ (47), 349 (23), 182 [M – MeCl – Me – $CHPh_2$]$^+$ (20), 167 [Ph_2CH]$^+$ (15), 91 (20), 50 [MeCl]$^+$ (100).

14b: ^{1}H NMR ($CDCl_3$) δ: 3.64 (s, 3H, NMe_2), 4.03 (br. s, 6H, $^+NMe_2$), 4.24 (br. s, 2H, CH_2Ph), 7.13 (m, 2H, Ph), 7.28 (m, 3H, Ph), 7.36 (d, 1H, H-5, ^3J 8.5 Hz), 7.61 (m, 2H, H-6, H-8), 7.93 (br. d, 1H, H-7, ^3J 8.2 Hz), 8.04 (br. d, 1H, H-9, ^3J 7.6 Hz). ^{1}H NMR ([$^2H_6$]DMSO) δ: 3.44 (s, 3H, NMe), 3.62 (br. s, 6H, $^+NMe_2$), 4.24 (br. s, 2H, CH_2Ph), 5.29 (br. s, 2H, CH_2), 7.19–7.32 (m, 5H, Ph), 7.38 (d, 1H, H-5, ^3J 8.4 Hz), 7.68 (t, 1H, H-8, ^3J 8.1 Hz), 7.78 (d, 1H, H-6, ^3J 8.4 Hz), 8.09 (br. d, 1H, H-7, ^3J 8.1 Hz), 8.14 (br. d, 1H, H-9, ^3J 7.7 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$) δ: 37.9 (CH_2Ph), 44.4 (NMe), 52.6 ($^+NMe_2$), 82.2 (NCH_2N), 117.49 (C-2), 117.9 (C-5), 123.6 (C-3), 125.5 (C-7), 126.5 (C-10), 128.7 (C-17, C-18, C-20, C-21), 130.2 (C-16), 130.3 (C-19), 131.5 (C-6), 133.4 (C-8), 137.2 (C-9), 139.4 (C-4), 139.8 (C-1).

17: oil-like substance. ^{1}H NMR ($CDCl_3$) δ: 2.07 (s, 3H, C–Me), 2.79 (s, 6H, 8-NMe_2), 2.92 (s, 6H, 1-NMe_2), 4.91 (m, 1H, H^b), 5.19 (m, 1H, H^a), 7.01 (d, 1H, H-5, ^3J 7.7 Hz), 7.16 (d, 1H, H-3, ^3J 8.4 Hz), 7.31–7.44 (m, 3H, H-4, H-6, H-7).

18: colourless crystals with mp 207–210 °C (H_2O). ^{1}H NMR (CD_3CN) δ: 3.25 (d, 6H, 8-NMe_2, ^3J 1.6 Hz), 3.28 (d, 6H, 1-NMe_2, ^3J 3.7 Hz), 4.92 (s, 2H, CH_2OH), 7.68 (d, 1H, H-3, ^3J 8.6 Hz), 7.34 (t, 1H, H-6, ^3J 7.8 Hz, ^3J 8.1 Hz), 7.97 (dd, 1H, H-7, ^3J 7.6 Hz, ^4J 1.1 Hz), 8.04 (m, 2H, H-4, H-5), 18.90 (br. s, 1H, NH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 3.20 (br. s, 6H, 8-NMe_2), 3.30 (d, 6H, 1-NMe_2, ^3J 3.5 Hz), 5.06 (s, 2H, CH_2Br), 7.68 (dd, 1H, H-5, ^3J 8.6 Hz, ^4J 2.5 Hz), 7.77 (td, 1H, H-6, ^3J 8.1 Hz, ^4J 2.5 Hz), 8.09 (m, 2H, H-3, H-7), 8.18 (d, 1H, H-4, ^3J 7.5 Hz), 18.47 (br. s, 1H, NH).

19a: light-beige crystals with mp 111.5–112 °C (*n*-hexane). ^{1}H NMR ($CDCl_3$) δ: 2.73 (s, 6H, 1-NMe_2), 2.85 (s, 6H, 8-NMe_2), 6.11 (s, 1H, $CHPh_2$), 7.04 (d, 1H, H-3, ^3J 8.3 Hz), 7.07–7.42 (m, 14H, H-4, H-5, H-6, H-7, 2Ph).

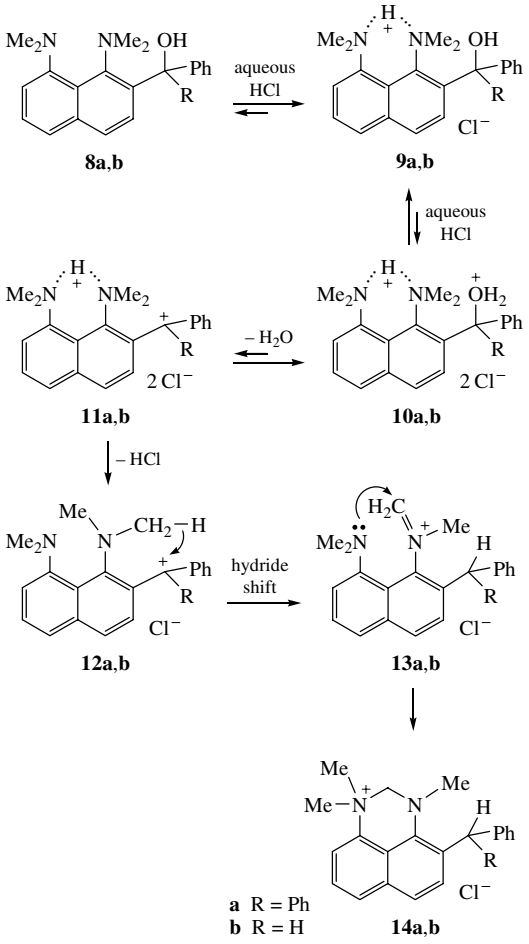
19b: colourless caramel. ^{1}H NMR ($CDCl_3$) δ: 2.76 (s, 6H, 1-NMe_2), 2.88 (s, 6H, 8-NMe_2), 4.17 (s, 2H, CH_2Ph), 7.07–7.31 (m, 8H, H-3, H-6, H-7, Ph), 7.43 (m, 2H, H-4, H-5).

20: yellowish crystals with mp 169–171 °C (MeOH). ^{1}H NMR ($CDCl_3$) δ: 2.65 (s, 3H, NMe), 2.81 (s, 6H, NMe_2), 6.22 (s, 1H, $CHPh_2$), 7.13–7.35 (m, 14H, H-3, H-4, H-5, H-6, 2Ph), 7.52 (br. d, H-7, ^3J 7.8 Hz), 8.71 (br. s, 1H, NH).

21: beige caramel. ^{1}H NMR ($CDCl_3$) δ: 2.59 (s, 3H, 3-NMe), 2.99 (s, 3H, 1-NMe), 4.20 (s, 2H, CH_2), 6.36 (br. s, 1H, $CHPh_2$), 6.54 (d, 1H, H-9, ^3J 7.7 Hz), 7.10–7.28 (m, 13H, 2Ph, H-5, H-6), 7.33 (t, 1H, H-8, ^3J 8.1 Hz), 7.45 (d, 1H, H-7, ^3J 8.5 Hz).

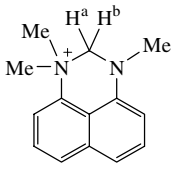
§ Crystals of chloride **14b** (as monohydrate) were obtained as colourless plates upon slow evaporation of saturated acetonitrile solution, mp 173–176 °C (decomp.). *Crystallographic data*: crystals of **14b** ($C_{21}H_{25}ClN_2O$, M = 356.88) are triclinic, space group $P\bar{1}$, at 293 K, a = 7.116(2), b = 8.3801(16) and c = 16.688(4) Å, V = 929.4(4) Å^3, Z = 2, d_{calc} = 1.275 g cm^{-3}, μ(MoKα) = 2.17 cm^{-1}, F(000) = 380. Intensities of 4923 reflections were measured with a CAD4 Enraf-Nonius diffractometer [λ(MoKα) = 0.71072 Å, $\theta/2\theta$-scans, $2\theta_{max}$ = 27.99°] and 4420 independent reflections [R_{int} = 0.0294] were used in a further refinement. The refinement converged to wR_2 = 0.0911 and GOF = 1.014 for all independent reflections [R_1 = 0.0480 was calculated against F for 2959 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 611180. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.



Scheme 2

tion; this produced cation **15** *via* related methyleneimmonium intermediate.[12,13]



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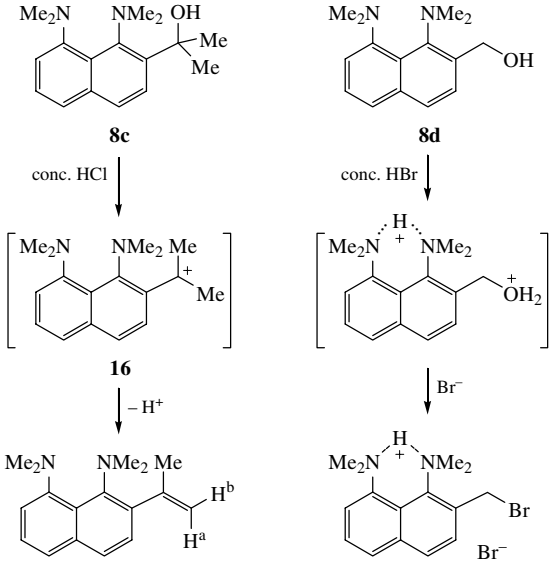
Interestingly, at attempt to monitor the reaction in an NMR ampoule by the treatment of a solution of **8a** in [$^2H_6$]DMSO with 1–10 equiv. of $HClO_4$, the formation of N-protonated cation **9a**, which remained unchanged for a long time, was only observed. One can assume that dimethylsulfoxide being significantly more basic than water (pK_a 0.0 against –1.7 for water[14]) gives no chance for oxonium salt **10a** to be formed.

Unlike alcohols **8a**,**b**, their analogue **8c** with the α-Me groups being treated with conc. HCl forms carbocation **16**, which undergoes E1 elimination to produce after basification 1,8-bis(dimethylamino)-2-isopropenylnaphthalene **17**‡ in 96% yield (Scheme 3). Primary alcohol **8d** at heating with acids, *e.g.*, conc. HBr, exchanges the hydroxylic group with the formation of a 2-bromomethyl derivative isolated as hydrobromide **18**.‡ Apparently, this reaction reflects relatively low stability of the corresponding 2-naphthylmethyl carbenium ion.

Note that the intramolecular hydride shift–cyclization sequence with participation of *ortho*- or *peri*-$NAlk_2$ group closely reminds the so-called '*t*-amino effect'.[15] Several examples of the latter involving electron-deficient multiple bonds have been reported in the naphthalene series.[16,17] However, to our knowledge it is realised for the first time *via* a carbocation intermediate under mild conditions and with the participation of the third functional group. Obviously, all these originate from specificity of the



Scheme 3

proton sponge moiety, namely, its low ionization potential and closeness of *peri*-NMe_2 groups.[18,19]

The appearance of μ-CH_2 protons in the ^{1}H NMR spectra of salts **14a**,**b** deserves special comments. In [$^2H_6$]DMSO, they give a broadened two-proton singlet at δ 5.3 ppm, whereas in $CDCl_3$ the signal is not seen at all. This observation testifies that in [$^2H_6$]DMSO the protons H^a and H^b, which are unequal in the solid (Figure 1), rapidly exchange and become magnetically equivalent. At the same time, in a $CDCl_3$ solution, their exchange sharply slows down and results in strong broadening or even disappearance of the signal. In the ^{1}H NMR spectrum of iodide **15**·I^-,¶ which we also measured for comparison, the peaks of the CH_2 protons in $CDCl_3$ at 25 °C are also strongly diffused at δ 4.71 and 6.25 ppm, whereas in [$^2H_6$]DMSO they give again two-proton singlet at δ 5.05 ppm.[20]

Dihydroperimidinium salts **14** can be used for preparation of other 1,8-diaminonaphthalene derivatives in accordance with known procedures.[20] Thus, their reductive cleavage with $LiAlH_4$ gives earlier undescribed 2-benzhydryl- or 2-benzyl-1,8-bis-(dimethylamino)naphthalenes **19a**,**b**.‡ The short heating of **14a** with conc. aqueous KOH results in heterocycle ring opening with the formation of *N*,*N*,*N*′-trimethyl-1,8-diaminonaphthalene derivative **20**‡ (68%). At heating above 183 °C, **14a** loses the CH_3Cl molecule to produce quantitatively 2,3-dihydroperimidine **21**‡ (Scheme 4).

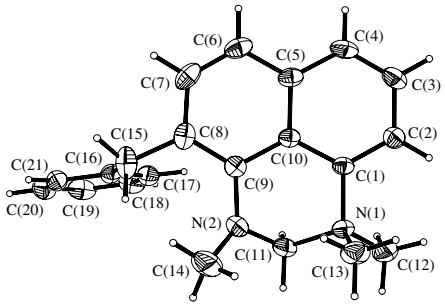
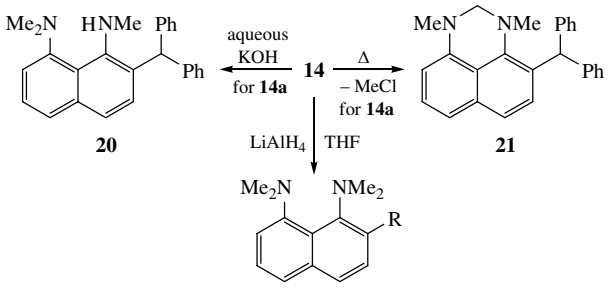


Figure 1 General view of **14b** (chloride anion and water molecule are not shown). Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å): N(1)–C(1) 1.486(2), N(1)–C(11) 1.540(2), N(2)–C(11) 1.404(2), N(2)–C(9) 1.407(2), C(8)–C(15) 1.505(3); selected bond angles (°): C(1)–N(1)–C(11) 107.87(13), N(1)–C(11)–N(2) 112.76(15), C(11)–N(2)–C(9) 114.51(15), C(9)–N(2)–C(14) 121.84(18), C(9)–C(8)–C(15) 123.7(2).

¶ Iodide **15**·I^- was synthesised according to ref. 20. ^{1}H NMR ($CDCl_3$) δ: 3.47 (s, 3H, NMe), 3.98 (br. s, 6H, $^+NMe_2$), 4.71 (br. s, 1H, CH_2), 6.25 (br. s, 1H, CH_2), 6.94 (d, 1H, H-4, ^3J 7.5 Hz), 7.48 (d, 1H, H-6, ^3J 8.4 Hz), 7.60 (dd, 2H, H-5, H-8), 7.94 (d, 1H, H-7, ^3J 8.4 Hz), 8.02 (d, 1H, H-9, ^3J 7.6 Hz).



19a R = $CHPh_2$, 56%
19b R = CH_2Ph, 49%

Scheme 4

In summary, we have observed three kinds of reactivity of 2-naphthylmethanols based on the proton sponge at their treatment with strong protic acids. The nature of the final product in each case seems to be mainly determined by the relative stability of the primarily formed 2-naphthylmethyl carbocation. When this stability is lowered [1,8-bis(dimethylamino)-2-naphthylmethyl carbenium ion], ordinary nucleophilic substitution of a hydroxylic group occurs. The carbocations with the α-Me group to carbenium atom, in the result of E1 elimination, produce the corresponding alkene derivative as a single product. On the other hand, the related diaryl- and triarylcarbinols under acidic treatment generate resonance-stabilised carbocations which undergo rearrangement into 4-R-1,1,3-trimethyl-2,3-dihydroperimidinium salts. This transformation represents earlier unknown modification of the *t*-amino effect.

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