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Mendeleev Commun., 1991, **1(1)**, 10–12

Mendeleev Communications

Unexpected Formation of Diels–Alder Spiro Adducts from 4-Hydroxymethyl Derivatives of 'Proton Sponge'

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Treatment of 4-hydroxymethyl derivatives of 1,8-bis(dimethylamino)naphthalenes **1a** and **1b** with concentrated hydrochloric acid leads to the formation of spiro compounds **7a** and **b** in high yield.

During our investigations of methods for the functionalization of 1,8-bis(dimethylamino)naphthalene ('proton sponge')[1–3] we needed to obtain its 4-chloromethyl derivative. 4-Hydroxymethyl-1,8-bis(dimethylamino)naphthalene **1a** was therefore treated with concentrated hydrochloric acid at 45 °C. ^{1}H NMR spectral data established that compound **1a** is rapidly and quantitatively transformed under these conditions to 4-chloromethyl-1,8-bis(dimethylamino)naphthalene **2a**. Thus, after as little as 20 min the signal due to the methylene protons of the CH_2OH group (δ 4.96), belonging to the cation form of **1a**, disappeared completely, and the proton signal of the CH_2Cl group appeared at δ 4.86 with the same intensity. The addition of potassium iodide to the solution of **2a** led to a rapid decrease in the intensity of the CH_2Cl signal and to an increase in the intensity of a new signal at δ 4.66. This signal is obviously, due to the CH_2I group and demonstrates the easy nucleophilic substitution of the chlorine atom in cation **2a**.

However, our attempt to isolate the base **3a** by treatment with alkali of a hydrochloric acid solution of **3a** unexpectedly led to the formation of a yellow amorphous substance in almost quantitative yield with a molecular mass of 425, that is evidence of the dimerization of the two fragments of the initial compound. Its spectral characteristics indicate a compound with three non-equivalent dimethylamino groups, a conjugated carbonyl group ($\nu_{C=O}$/cm^{-1} 1655) and a $CH_2{-}CH_2$ bridge attached to an sp^2- and an sp^3-hybridized carbon atom.

The spectral data leads us to conclude that the product obtained is 2,3-dihydro-6,7-bis(dimethylamino)phenalene-1-spiro-1′-naphthalene-5′-dimethylamino-4′-one **7a**.† A possible mechanism for its formation is proposed in Scheme 1. Since the ^{1}H NMR spectrum of cation **2a** remains unchanged for several days, one can conclude that **7a** is formed on treatment of the reaction mixture with alkali. We suppose that the base **3a**, formed on neutralization, loses the chloride ion very easily and is transformed to naphthylmethyl carbocation **4a**. The driving force for this process must be the high resonance stabilization

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† Satisfactory analyses were obtained for all new compounds. For **7a**: m.p. 98–100 °C (from 80% aq. ethanol); UV λ_{max}/nm (MeOH) 234 (log ϵ 4.33), 346 (3.71), 415 (3.36); IR ν_{max}/cm^{-1} (CCl_4) 1655 (C=O), 1625 ($C{=}C_{quin}$), 1580 ($C{-}C_{ar}$); ^{1}H NMR δ (400 MHz, $CDCl_3$, standard $SiMe_4$) 2.15–2.99 (m, 2H, 2-CH_2), 2.79 (s, 6H, 6-NMe_2), 2.82 (s, 6H, 7-NMe_2), 2.97 (s, 6H, 5′-NMe_2), 3.05–3.22 (m, 2H, 3-CH_2), 6.30 (d, 1H, $J_{2',3'}$ 10.0 Hz, 2′-H), 6.44 (dd, 1H, $J_{6',7'}$ 7.8, $J_{6',8'}$ 1.0 Hz, 6′-H), 6.79 (d, 1H, $J_{9,8}$ 8.0 Hz, 9-H), 6.83 (d, 1H, $J_{8,9}$ 8.0 Hz, 8-H), 6.89 (dd, 1H, $J_{8',7'}$ 8.4, $J_{8',6'}$ 1.0 Hz, 8′-H), 6.95 (d, 1H, $J_{5,4}$ 7.7 Hz, 5-H), 7.01 (d, 1H, $J_{3',2'}$ 10.0 Hz, 3′-H), 7.19 (dd, 1H, $J_{7',8'}$ 8.4, $J_{7',6'}$ 7.8 Hz, 7′-H), 7.22 (d, 1H, $J_{4,5}$ 7.7 Hz, 4-H); ^{13}C NMR (22.62 MHz, $CDCl_3$) δ 27.26 (tm, ^1J 129.7 Hz, 3-CH_2), 38.82 (tm, ^1J 131.3 Hz, 2-CH_2), 44.12, 44.19, 44.33 (all qq, ^1J 134.2 Hz, $^3J_{Me}$ 2.3 Hz, NMe), 47.38 (m, C-1), 112.72 (d, ^1J 157.4 Hz, C-5), 113.21 (d, ^1J 157.8 Hz, C-8), 114.70 (dd, ^1J 158.9 Hz, $^3J_{H\text{-}6'}$ 7.4 Hz, C-8′), 120.42 (dd, ^1J 161.5, $^3J_{H\text{-}8'}$ 7.4 Hz, C-6′), 120.56 (m, C-6a), 121.60 (m, C-4′a), 125.16 (dt, ^1J 156.4, $^3J_{3\text{-}CH_2}$ 3.7 Hz, C-4), 127.05 (d, ^1J 157.3 Hz, C-9), 127.61 (m, C-9a), 127.65 (br d, ^1J 165.7 Hz, C-3′), 131.61 (m, C-3a), 133.96 (m, C-9b), 149.77 (m, C-8′a), 149.94 (dt, ^1J 162.7, $^3J_{2\text{-}CH_2}$ 3.4 Hz, C-2′), 150.12 (m, C-5′), 153.47 (m, C-7), 154.22 (m, C-6), 183.48 (dd, $^2J_{H\text{-}3'}$ 1.0, $^3J_{H\text{-}2'}$ 10.0 Hz, C-4′); *m/z* 425 (M^+).

7b: yellow crystals; 87% yield; m.p. 255–257 °C (from hexane–chloroform, 10: 1); UV λ_{max}/nm (MeOH) 237 (log ϵ 4.32), 289sh (3.71), 304(3.75), 319sh (3.65), 430 (3.27); IR ν_{max}/cm^{-1} (CCl_4) 1660 (C=O), 1625 ($C{=}C_{quin}$), 1580 cm^{-1} ($C{-}C_{ar}$); ^{1}H NMR δ (90 MHz, $CDCl_3$) 2.37 (s, 6H, NMe_2), 2.81 (s, 12H, 2NMe_2), 5.37 (m, 2H, 2-H, 3-H), 6.24 (d, 1H, $J_{3',2'}$ 10.4 Hz, H-3′), 6.64 (dd, 1H, $J_{6',7'}$ 7.9, $J_{6',8'}$ 1.3 Hz, 6′-H), 6.64 (dd, 1H, $J_{4,5}$ 8.0, $J_{4,3}$ 1.3 Hz, 4-H), 6.64 (d, 1H, $J_{8,9}$ 8.0 Hz, 8-H), 6.87 (d, 2H, $J_{5,4}$ and $J_{9,8}$ 8.0 Hz, 5-H, 9-H), 6.90–7.30 (m, 10H, 2Ph), 7.03 (d, 1H, $J_{2',3'}$ 10.4 Hz, 2′-H), 7.37 (dd, 1H, $J_{7',6'}$ and $J_{7',8'}$ 7.9 Hz, 7′-H), 7.57 (dd, 1H, $J_{8',7'}$ 7.9, $J_{8',6'}$ 1.3 Hz, 8′-H); the ^{1}H NMR data do not permit a conclusion about the stereochemistry of this compound; *m/z* 577 (M^+).

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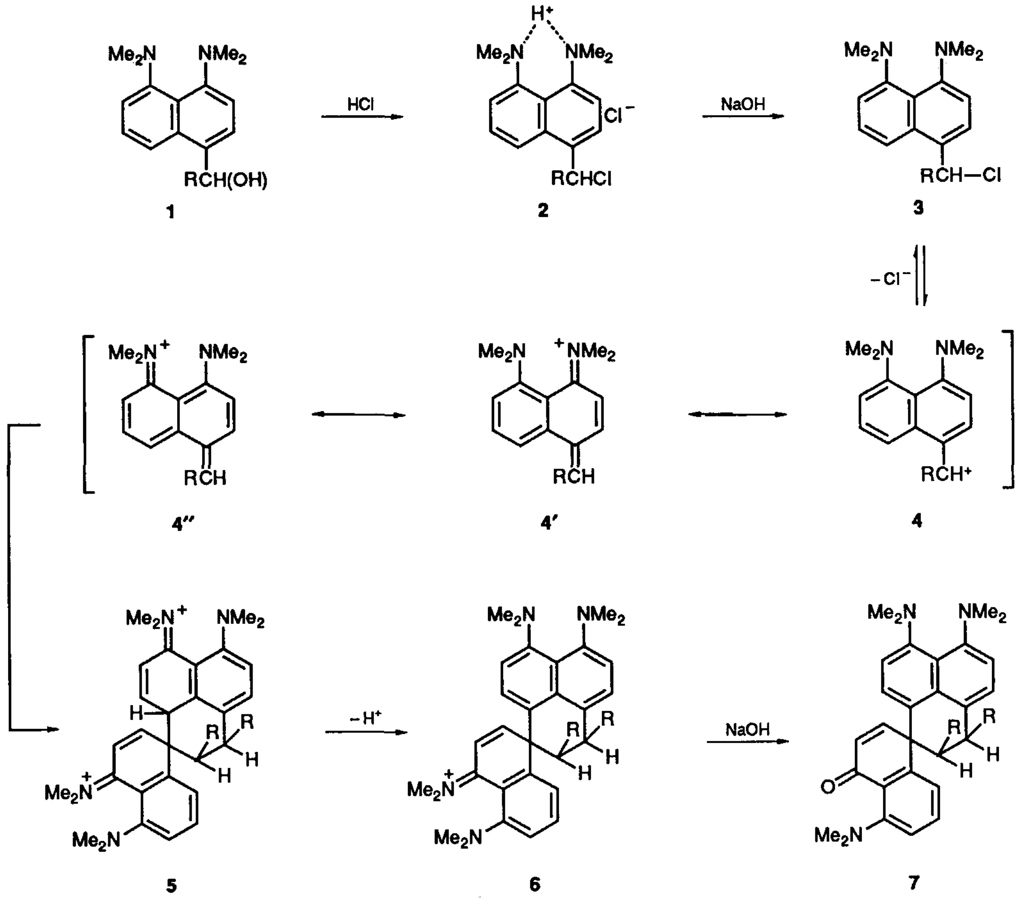

Scheme 1 **a**, R = H; **b**, R = Ph; **c**, R = Me; **d**, R = CF_3

of the cation **4a**, in which both dimethylamino groups participate in the delocalization of the positive charge. The large contribution of structures **4**′ and **4**″ makes cation **4a** both an active diene (the ends of the diene fragment being the methylene carbon atom and C-5) and also a good dienophile (through the $C{=}CH_2$ double bond). This fact enables two molecules of cation **4a** to react with each other in a Diels–Alder reaction yielding spiro adduct **5a**, which is aromatized to the cation **6a** with the loss of a proton. Subsequent alkaline hydrolysis of the immonium group leads to **7a**.

The Diels–Alder reaction proceeds very rapidly, judging from the ^{1}H NMR spectral data (appearance of the characteristic proton signals of the CH_2CH_2 bridge and the H-2′ doublet of the quinone ring at δ 6.3). The high rate is also apparent visually: when treatment with alkali starts, at pH $\leq$ 1 in the originally pale-yellow mixture, an orange–red colour rapidly appears, and at pH $<$ 10 an orange precipitate is formed evidently **6a**, which is transformed on grinding to the yellow spiro compound **7a**.

Quantum chemical calculations support the diene character of cation **4a** and show the dependence of the reaction on symmetry (Fig. 1). The direction of this reaction shows that the highest occupied molecular orbital (HOMO) of the dienophile and the lowest unoccupied molecular orbital (LUMO) of diene participate to reach the transition state, *i.e.* this is a $(4\pi + 2\pi)$ cycloaddition process with inverse electron demand.

4-(α-Hydroxybenzyl)-1,8-bis(dimethylamino)naphthalene **1b** undergoes an analogous reaction, although the process is

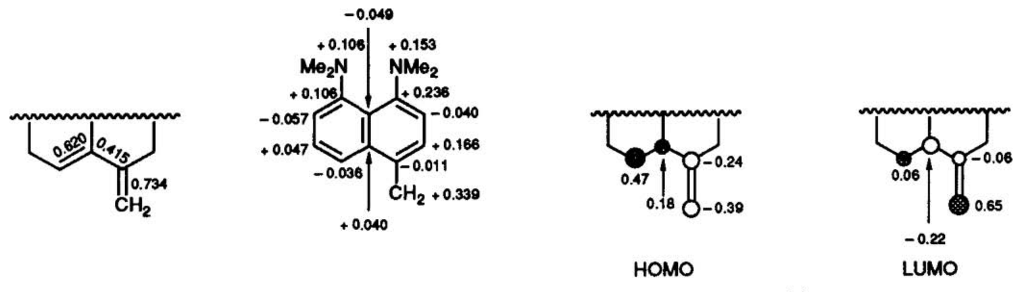

Fig. 1 (a) π-Bond orders, (b) π-charge value and (c) coefficients of the boundary orbitals in cation **4a** (Hückel MO method on parametrization;[4] the methyl groups were not considered)

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more difficult. At the same time, attempts to carry out such a conversion with compounds **1c** and **1d** were unsuccessful.‡

Dimerization by this type of Diels–Alder reaction has been described for methyleneanthrones[5,6] and for some other quinone methides.[7] The conversion reported here is probably the first example of such dimerization for a series of quinone methide imines.

Received in USSR, 21st November 1990
Received in UK, 27th November 1990; Com. 0/05325B

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‡ Compounds **1a–d** were obtained in quantitative yield on reduction of the corresponding 4-formyl-[2] and 4-acyl-[3] derivatives of 'proton sponge' with lithium aluminium hydride. Compounds **1a–d** are caramel-like, pale yellow substances which were purified by column chromatography on Al_2O_3. Their spectral data fully support the proposed structures.

References

1 L. A. Kurasov, A. F. Pozharskii, V. V. Kuz'menko, N. A. Klyuev, A. I. Chernyshev, S. S. Goryaev and N. L. Chikina, *Zh. Org. Khim.*, 1983, **19**, 590 (English translation in *J. Org. Chem. USSR*, 1983, **19**, 520).
2 N. V. Vistorobskii and A. F. Pozharskii, *Zh. Org. Khim.*, 1989, **25**, 2154 (English translation in *J. Org. Chem. USSR*, 1989, **25**, 1946).
3 N. V. Vistorobskii and A. F. Pozharskii, *Zh. Org. Khim.*, 1991, **27**, to be published.
4 A. Streitwieser, *Molecular orbital theory*, Wiley, New York, London, 1961.
5 W. H. Starnes, *J. Org. Chem.*, 1970, **35**, 1974.
6 H. D. Becker and D. Sanchez, *J. Org. Chem.*, 1979, **44**, 1787.
7 M. A. Chauncey, M. F. Grundon and M. J. Rutherford, *J. Chem. Soc., Chem. Commun.*, 1988, **8**, 527.