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Structure of Protonated Products of Potassium 1-(Dimethylamino)naphthylide

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Synopsis. Potassium 1-(dimethylamino)naphthylide ($\mathrm{K^+DMAN^{\overline{\cdot}}}$) was protonated by aqueous THF and the structures of protonated products (overall yield of three isomeric products was almost quantitative) were analyzed by ^{1}H NMR and their 2D-NOE correlation. Products were 1-(dimethylamino)-5,8-dihydronaphthalene (major product, 88%), 7,8-dihydro- (9%), and 5,6-dihydro-isomer (3%). Deducing from the structures, the protonation pathway as well as the spin distribution in $\mathrm{K^+DMAN^{\overline{\cdot}}}$ is discussed.

Potassium 1-(dimethylamino)naphthylide radical anion (abbreviated as $\mathrm{K^+DMAN^{\overline{\cdot}}}$) has recently been appearing in literatures as a useful reductant instead of parent naphthylide[1,2] because of the ease with which DMAN and its derivatives can be removed from the reaction mixture by the workup with aqueous acid, and which enables easy product analysis as well as the accomplishment of synthetic purposes. Although $\mathrm{DMAN^{\overline{\cdot}}}$ can be used in diverse ways,[3–6] it seemed strange to us that the structure of the most common workup products from $\mathrm{DMAN^{\overline{\cdot}}}$, i.e., dihydro-DMAN (abbreviated as DMAN-$\mathrm{H_2}$), has not yet been elucidated. Since $\mathrm{DMAN^{\overline{\cdot}}}$ is an unsymmetrically substituted naphthalene radical anion, the structural analysis of its protonated products will also afford information for the spin distribution in this radical anion. We report here the structural elucidation of protonated products of $\mathrm{DMAN^{\overline{\cdot}}}$.

When a THF solution of $\mathrm{K^+DMAN^{\overline{\cdot}}}$, prepared from potassium metal and DMAN in THF under a nitrogen atmosphere (60% of the initially charged DMAN was active), was treated at −70 °C with aqueous THF, a mixture of isomeric 1-(dimethylamino)dihydronaphthalenes (DMAN-$\mathrm{H_2}$) was obtained besides DMAN. The most likely protonation mechanism is:[7]

$$[\mathrm{DMAN^{\overline{\cdot}}}] + \mathrm{H_2O} \longrightarrow [\mathrm{DMAN\text{-}H_1}]^{\cdot} + \mathrm{OH^-} \qquad (1)$$

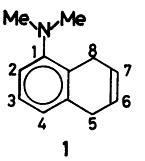
$$[\mathrm{DMAN\text{-}H_1}]^{\cdot} + [\mathrm{DMAN^{\overline{\cdot}}}] \longrightarrow [\mathrm{DMAN\text{-}H_1}]^- + \mathrm{DMAN} \qquad (2)$$

$$[\mathrm{DMAN\text{-}H_1}]^- + \mathrm{H_2O} \longrightarrow \mathrm{DMAN\text{-}H_2} + \mathrm{OH^-} \qquad (3)$$

$$2[\mathrm{K^+DMAN^{\overline{\cdot}}}] + 2\mathrm{H_2O} \longrightarrow 2\mathrm{DMAN} + 2\mathrm{KOH} + \mathrm{H_2}. \qquad (4)$$

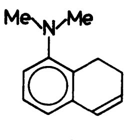
According to Eqs. 1—3, one mol each of DMAN and DMAN-$\mathrm{H_2}$ should be produced from two moles of $\mathrm{DMAN^{\overline{\cdot}}}$. In fact, the protonation mixture was analyzed by VPC to be consisting of DMAN (retention time, t_r=23.74 min) and three other products **1** (t_r=22.87 min), **2** and **3** (t_r=21.27 min) in the ratio DMAN/**1**/**2**/**3**=67/29/3/1.[8] Taking into account that the titrated concentration of active $\mathrm{K^+DMAN^{\overline{\cdot}}}$ before protonation was 60% based on the initially charged DMAN, the calculated (theoretical) product distribution based upon this correction should be DMAN/DMAN-$\mathrm{H_2}$=70/30,[9] which agrees well with the observed distribution DMAN/(**1**+**2**+**3**)=67/33. Consequently, it is concluded that active $\mathrm{K^+DMAN^{\overline{\cdot}}}$ was transformed almost quantitatively into dihydronaphthalenes **1**, **2**, and **3** (corrected yields: **1**=88%, **2**=9%, **3**=3%). The participation of a reduction process (Eq. 4)[10] which may partially account for the production of DMAN is thus negligible.

Product **1** and a mixture of **2** and **3** were separated and purified by column as well as by VPC. The mass spectral analysis of both **1** and the mixture of **2** and **3** showed $\mathrm{M^+}$ (m/z)=173 which agrees with DMAN-$\mathrm{H_2}$. The ^{1}H NMR spectra of these products showed the same proton ratio of N-methyl/Ar-H/(aliphatic+olefinic)=6/3/6, indicating that the protonation took place mainly on the unsubstituted ring. Three structures which agree with the above observations are shown below.



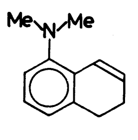
1

88%



2

9%



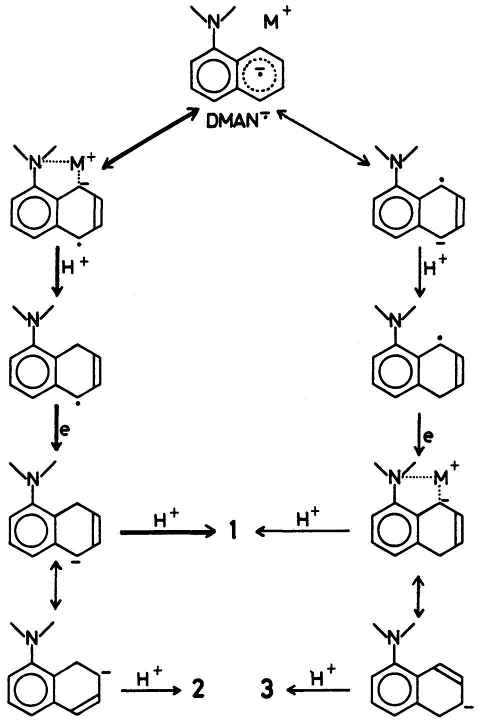
3

3%

The structure of the major product was determined to be **1** by its ^{1}H NMR spectrum: Two sets of methylene protons with roughly the same chemical shift are appearing at δ 3.26 as doublets, and two olefinic protons at δ 5.93 as a doublet.

Structural determination of **2** and **3** was somewhat complicated because their separation was possible only by the use of a capillary column (OV-101 30 m, ΔR_f=0.03, isomer ratio=3/1) and their ^{1}H NMR spectra are almost identical: N-Methyl protons are appearing as two singlets at δ 2.61 and 2.65 (ratio 1 : 3), and β-methylene protons between 2.16—2.33, benzylic α-methylene protons at δ 2.68 (partially overlapping N-methyls), β-olefinic methines at δ 6.0, α-olefinic methines at δ 7.0 (overlapping aromatic protons, identified by the irradiation at δ 6.06).

To determine which isomer predominates in the mixture of **2** and **3**, a two-dimensional Nuclear Overhauser Effect (2D-NOE) correlation diagram was taken.[11] The expected NOE between N-methyl (δ 2.65) and α-methylene protons (δ 2.68) of **2** was indecipherable due to the mutual overlapping of their signals. However, an appreciable correlation between N-methyl (δ 2.65) and β-methylene protons (δ 2.20) was observed. By a molecular model analysis it is shown that protons of N-methyls and 7-methylene group of **2** stay within the interproton distance of 2.4—2.6 Å, whereas those of N-methyls and 6-



Scheme 1.

methylene group of **3** stay more apart. This observation supports at least the presence of isomer **2**. In addition, the anticipated strong correlation between methyls (δ 2.61) and 8-methine proton (δ 7.0) of **3** appeared only weakly. Although 2D-NOE measurements are generally considered not so reliable for quantitative analysis, yet the above results reasonably lead us to conclude that isomer **2** predominates over the other isomer **3** (isomer ratio **2**/**3**=3 by VPC).

Structures and the product distribution both provide information for solving the major channel of the protonation mechanism (Scheme 1). First of all, the protonation takes place exclusively on the unsubstituted ring of DMAN$^{\cdot -}$. This may be due to the spin distribution which is greatly shifted toward the unsubstituted half of the molecule. Second, the peri-position spatially adjacent to the dimethylamino group in DMAN$^{\cdot -}$ is predominantly protonated. This selectivity can be explained in terms of both the stability of benzylic carbanion intermediates and the coordination effect between the alkali metal cation and the nitrogen atom.

Experimental

General. 1-(Dimethylamino)naphthalene (DMAN) was commercially available and was purified by distillation before use. ^{1}H NMR spectra and homonuclear NOE correlated 2D-NMR were taken on Varian XL 200 spectrometer equipped with a 2D-NOE program. Mass spectra were taken on Hitachi M-80A spectrometer. For the VPC analysis Shimazu GC-9A was used.

Preparation and Determination of K$^+$DMAN$^{\cdot -}$. A THF solution of K$^+$DMAN$^{\cdot -}$ was prepared under a nitrogen atmosphere by mixing 2.0 g (0.05 gram atom) of potassium metal and 8.6 g (0.05 mol) of DMAN in 100 mL of THF at 0 °C. The concentration of active radical anion was determined to be 0.30 dm^{-3} according to the titration method reported previously.[12]

Reaction and Workup Procedures. The radical anion solution prepared above was cooled to 0 °C, to which was slowly added dropwise a 5:1 mixture (20 cm^3) of THF and water. The reaction mixture was warmed up to 20 °C and was extracted with diethyl ether. After drying over anhydrous Na_2SO_4 and concentrating the ethereal solution, the product mixture was analyzed by VPC (packed column Apiezon Grease-L 2 m; fused silica capillary column OV-101 0.5 mm×30 m). Results are described in the main text.

^{1}H NMR Spectra of 1-(Dimethylamino)-5,8-dihydronaphthalene (5,8-Dihydro-DMAN, 1). δ=2.67 (6H, s, 2Me); 3.26 (4H, d, CH_2, $J(5,6)=J(8,7)=1.0$ Hz); 5.93 (2H, bs, –CH=, $J(6,5)=J(7,8)=1.0$ Hz); 6.85 (1H, dd, ArH(4), $J(4,3)=7.6$, $J(4,2)=1.0$ Hz); 6.95 (1H, dd, ArH(2), $J(2,3)=7.6$, $J(2,4)=1.0$ Hz); 7.14 (1H, t, ArH(3), $J(3,2)=J(3,4)=7.6$ Hz). Mass spectrum M$^+$ (m/z)=173. Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08%. Found: C, 83.03; H, 8.98; N, 7.87%.

^{1}H NMR Spectra of a Mixture of 7,8-Dihydro-DMAN (2) and 5,6-Dihydro-DMAN (3). δ=2.20 (2H, m, 7-CH_2 of **2** and 6-CH_2 of **3**, $J(7,8)=8.0$ Hz); 2.61 (s, Me's of **3**) and 2.65 (s, Me's of **2**), total integration of 2.61 plus 2.65 is equivalent to 6H; 2.68 (2H, bt, 8-CH_2 of **2** and 5-CH_2 of **3**, $J(8,7)$ of **2**=$J(5,6)$ of **3**=8.0 Hz); 6.00 (1H, dt, 6-CH= of **2** and 7-CH= of **3**, $J(6,7)$ of **2**=$J(7,6)$ of **3**=4.4 Hz, $J(6,5)$ of **2**=$J(7,8)$ of **3**=10.0 Hz); 6.74 (1H, d, 5-CH= of **2**, $J(5,6)$ of **2**=10.0 Hz); 6.73 (1H, d, ArH(4) of **2** and **3**, $J(4,3)$ of **2** and **3**=7.6 Hz); 6.81 (1H, d, ArH(2) of **2** and **3**, $J(2,3)=7.6$ Hz); 7.00 (1H, t, ArH(3) of **2** and **3**, $J(3,4)=J(3,2)=7.6$ Hz); 8-CH= of **3** may be hidden near 7.0. Mass spectrum M$^+$ (m/z)=173. Anal. Found: C, 83.07; H, 9.05; N, 7.78%.

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9) The ratio corresponds to [(100-60)+1/2(60)]/[1/2(60)].

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11) Varian XL-200 NMR spectrometer equipped with a 2D-NOE program was used. A supplementary material for the NOE correlated 2D-^{1}H NMR spectra of the mixture (**2**+**3**) is available.

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