FORMATION OF MONOALDEHYDES BY CERIUM(IV) AMMONIUM NITRATE OXIDATION OF UNSYMMETRIC DIMETHYLNAPHTHALENES

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Abstract... When 1,2-, 1,3- and 1,6-dimethylnaphthalene are oxidized by Ce^{4+} in acetic acid the corresponding monoaldehydes are formed in better than 80% yield. In each case aldehyde formation takes place with a high degree of selectivity as the methyl-1- to methyl-2-naphthaldehyde ratio is better than 11:1. The selectivity may be explained from differences in reactivity as calculated within the frontier orbital method.

In a previous paper we have described the synthesis of naphthaldehydes by cerium(IV) ammonium nitrate (CAN) oxidation of methylnaphthalenes and symmetrically substituted dimethylnaphthalenes.¹ Generally it was found that 1-naphthaldehydes were formed in considerably higher yields than 2-naphthaldehydes. This suggests that a methyl group attached C-1 in the naphthalene nucleus is more easily oxidized than a methyl group connected to C-2. To test this hypothesis we have carried out competition experiments by treating dimethylnaphthalenes with a methyl group in both α and β positions with CAN; the results of this investigation are reported here.

RESULTS AND DISCUSSIONS

Preparative aspects

Three of the four possible unsymmetric dimethylnaphthalenes (DMNs) (1), viz. 1,2-, 1,3- and 1,6-DMN, were reacted with CAN in 50% acetic acid at 85° until the starting material had been consumed (2 hr). All the substrates gave a reaction mixture that consisted mainly (>80%) of the isomeric aldehydes 2 and 3 (Scheme 1). In addition various minor by-products were formed. The predominant one, formed in approximately 6% yield in each case, was probably the corresponding 1-naphthylmethyl acetate (4); the identification is based on characteristic IR absorptions around 1745 and 1215 cm⁻¹ and NMR resonances at 2.1 and 5.5 ppm.¹

When 1,2-DMN was treated with CAN 2-methyl-1naphthaldehyde (2a) and 1-methyl-2-naphthaldehyde (3a) were formed in 78 and 5% yield, respectively, according to GLC and NMR analyses. The aldehyde structures were easily deduced on the basis of the spectroscopic properties of authentic samples of the compounds.^{2,3} Oxidation of 1,3-DMN gave a product mixture which contained 79% of 3-methyl-1-naphthaldehyde (**2b**) and 7% of 4-methyl-2-naphthaldehyde (**3b**).

The aldehyde structures were most easily differentiated by proton NMR spectroscopy. Thus, 3b gives rise to a complex multiplet at 7.4-7.8 ppm for the aromatic protons whereas the same protons of 2b appear as a 5H multiplet in the same region and a 1H multiplet, due to H-8, at 9.14 ppm (Table 1). The downfield shift of H-8 is caused by a significant peri interaction between this proton and the formyl group which therefore has to be attached to C-1. This interaction will of course be mutual and influence the formyl group in the same way; it is therefore not surprising that the aldehyde proton appears at a lower field in the spectrum of 2b than in that of 3b (Table 1). The structure of the more abundant aldehyde was confirmed by converting 2b into 1-(3-methylnaphthyl)methanol which has been prepared by an independent route.4

Treatment of 1,6-DMN with CAN gave a reaction mixture which consisted of 89% of 6-methyl-1naphthaldehyde (2c) and 2% of 5-methyl-2naphthaldehyde (3c). Their structures were mainly assigned on the basis of proton NMR spectra which were significantly different for the two compounds because of *peri* interactions in 2c (Table 1). The structure of the main product was also supported by the conversion of 2c into the corresponding alcohol, 1-(6methylnaphthyl)methanol.⁵

From Table 1 and the discussion above it is evident that the proton NMR spectra of 1-naphthaldehydes



Compound	СНО	Aromatic protons	С <u>Н</u> 3	Ref.
1-NA	10.14	6.08-7.84 (6H, m), 9.11 (1H, d)	_	18
2-Mc-1-NA (2a)	10.90	7.0-8.0 (5H, m), 9.0 (1H, d)	2.59	2
3-Me-1-NA (2b)	10.32	7.42-7.79 (5H, m), 9.14 (1H, m)	2.53	This work
4-Me-1-NA	10.32	7.35-8.10 (5H, m), 9.30 (1H, m)	2.74	1
5-Me-1-NA	10.41	7.35-8.27 (5H, m), 9.09 (1H, d)	2.72	1
6-Mc-1-NA (2c)	10.35	7.44-8.03 (5H, m), 9.10 (1H, d)	2.51	This work
8-Me-1-NA	10.88	7.35-8.09 (6H, m)	2.79	1
2-NA	10.38	7.38-8.20 (7H, m)	_	18
1-Me-2-NA (3a)	10.6	7.48-8.28 (6H, m)	2.94	3
3-Me-2-NA	10.3	7.30-8.25 (6H, m)	2.77	19
4-Mc-2-NA (3b)	10.07	7.4-7.8 (6H, m)	2.68	This work
5-Me-2-NA (3c)	10.12	7.44-8.03 (6H, m)	2.72	This work
6-Me-2-NA	10.11	7.32–8.25 (6H, m)	2.54	1

Table 1. The proton NMR spectra of various naphthaldehydes (NAs) in ppm relative to internal TMS

Table 2. Characteristic mass spectrometric fragments of various methyl-1-naphthaldehydes (Me-1-NA) and methyl-2-naphthaldehydes (Me-2-NA) in % of the base peak

Compound	М	M-H	M-CH ₃	M-CHO	M-CHO/C ₂ H ₂	Reference
2-Me-1-NA (2a)	80	54	10	100	42	This work
3-Me-1-NA (2b)	90	51	5	100	40	This work
4-Me-1-NA	100	76	15	79	33	1
5-Me-1-NA	86	23	40	100	43	1
6-Mc-1-NA (2c)	82	41	22	100	44	This work
8-Me-1-NA	76	35	6	100	40	1
1-Me-2-NA (3a)	100	65	0	86	47	This work
3-Me-2-NA	100	83	1	96	48	1
4-Mc-2-NA (3b)	100	70	1	92	40	This work
5-Me-2-NA (3c)	100	62	10	87	37	This work
6-Me-2-NA	100	91	0	85	41	1

Table 3. Atom reactivity indices, $S_i(LUMO)$, and net charge, Q_i , for the methyl hydrogen atoms of the radical cation $(ArCH_3)^+$. The numbers refer in each case to the atom with the greatest index

	S _t (LUMO)		Qı	
ArCH ₃	С <u>Н</u> 3-С1	CH ₃ -C ₂	С <u>Н</u> 3-С1	С <u>Н</u> ₃ —С ₂
1-MN*	0.116		0.032	
2-MN		0.074		0.027
1,2-DMN ^b (1a)	0.126	0.084	0.033	0.021
1,3-DMN (1b)	0.108	0.072	0.028	0.023
1,4-DMN	0.128		0.031	
1,5-DMN	0.090		0.023	
1,6-DMN (1c)	0.106	0.054	0.028	0.020
1,8-DMN	0.108		0.024	
2,3-DMN		0.046		0.016
2,6-DMN		0.076		0.026

* MN = Methylnaphthalene.

^bDMN = Dimethylnaphthalene.

and 2-naphthaldehydes show characteristic and useful differences. The methylnaphthaldehydes can therefore be divided into two classes on the basis of their proton NMR spectra. Interestingly, it turns out that the same compounds can be divided into the same two groups by comparing their mass spectra. Although all mass spectra show characteristic peaks due to loss of H, CH₃, CHO and CHO/ $C_2H_2^6$ the relative intensity of the various peaks depends on the position of the formyl group. Generally, the base peak in the mass spectra of methyl-1-naphthaldehydes is due to M-CHOfragments whereas the intensity of the molecular ion is 80-90% (Table 3). On the other hand, methylnaphthaldehydes with the formyl group in β position give rise to mass spectra with the molecular ion as the base peak and the M-CHO fragment with a 85-90% intensity. It is also interesting to note that loss of a methyl group takes place much more frequently from methyl-1- than from methyl-2-naphthaldehydes. Elimination of acetylene, however, occurs ap-



Scheme 2.

proximately to the same extent irrespective of the position of the formyl group, indicating that this fragmentation process succeeds CHO cleavage.

Quantum chemical calculations

The compounds investigated, 1a-1c, can conceivably be oxidized in two different benzylic positions, but in spite of this the one attached to C-1, giving rise to 1-naphthaldehydes, is almost exclusively attacked. This clearly suggests that the first irreversible step in the oxidation of 1a-1c, involving proton abstraction from a methyl group (Scheme 2),^{7,8} takes place with a very high degree of selectivity at the CH₃ group attached to C-1. In order to sort out the basis for this selectivity we have carried out quantum chemical calculations of LUMO electron densities,9,10 parameters which have been used successfully to predict the selectivity in analogous reactions.¹¹ We have used the method to compare the proton abstraction from the two different methyl groups of the species involved in the first irreversible step, i.e. cation radical 5 (Scheme 2). This is done by comparing the atom reactivity indices, S_i (LUMO), and the net charge, Q_i , for the H-atoms in the methyl groups. From the results compiled in Table 3 it is evident that the positive charge of 5 is delocalized in such a way that the hydrogen atoms of the α -methyl groups are more positively charged and have a higher atom reactivity index than those belonging to the β -methyl groups. Proton transfer will therefore mainly take place from α -CH₃, resulting ultimately in formation of 1naphthaldehydes. This conclusion is supported by calculations of the total energy of the intermediate cations 6 that 1a-1c form in a subsequent electrontransfer reaction (Scheme 2). In all cases the 1naphthylmethyl cation is more stable than the corresponding 2-naphthylmethyl cation; the energy difference is 4.8, 3.4 and 5.5 kcal mol^{-1} for the corresponding cations resulting from 1,2-DMN, 1,3-DMN and 1,6-DMN, respectively.

Table 3 also includes $S_i(LUMO)$ and Q_i values for various symmetric dimethylnaphthalenes. Both values are considerably lower for β -methylated than for α methylated naphthalenes, suggesting that the latter group of compounds should be oxidized with Ce⁴⁺ more rapidly than the former group. This is in accordance with previous observations.¹

EXPERIMENTAL

The equipment employed has been described elsewhere.¹ The dimethylnaphthalenes used were commercially available with a purity of better than 98% and were used without further purification.

CAN oxidation, general procedure. A soln of ceric ammonium nitrate (1.400 g, 2.40 mmol) in 50% AcOH (200 ml)was added dropwise to a stirred, warm (85°) soln of dimethylnaphthalene(0.100 g, 0.65 mmol). After 2 hr of stirring at 85° the mixture was cooled and extracted (CH_2Cl_2) . The combined extracts were washed (H_2O) and dried $(MgSO_4)$. Work-up in the usual way gave a residue which was analyzed by GC, GC/MS and NMR prior to isolation.¹

Oxidation of 1,2-DMN (1a) gave 0.103 g of a product mixture which contained 78% of $2a^2$ and 5% of $3a^{2.3}$ In addition a compound, supposed to be 4a on the basis of spectroscopic evidence, ¹IR: 1747, 1218 cm⁻¹; NMR δ :2.12(s) and 5.59(s) in a ratio of 3:2, was formed in 6% yield.

Oxidation of 1,3-DMN (1b) gave a crude product (0.105 g) which consisted of 79% of 2b, IR: 2730, 2720, 1704 cm⁻¹; NMR: see Table 1; MS: see Table 2; mol. weight: cale for $C_{12}H_{10}O$ 170.0732, found 170.0730, and 7% of 3b, IR: 2720, 1704 cm⁻¹; NMR: see Table 1; MS: see Table 2. A by-product, tentatively assigned the structure 4b based on spectroscopic data,¹ IR: 1741, 1222 cm⁻¹; NMR δ : 2.13 (s) and 5.55 (s) in a ratio of 3:2, was formed in 6% yield.

Oxidation of 1,6-DMN (1c) gave 0.102 g of a product mixture, which contained 89% of 2c, IR: 2750, 2720, 1695 cm⁻¹; NMR: see Table 1; MS: see Table 2; mol. weight: calc for $C_{12}H_{10}O$ 170.0732, found 170.0730, and 2% of 3c, IR: 2720, 1698 cm⁻¹; NMR: see Table 1; MS: see Table 2. The major by-product, probably 4c according to spectroscopic evidence,¹ IR: 1745, 1213 cm⁻¹; NMR δ : 2.09(s) and 5.53(s) in a ratio of 3: 2, was formed in 6% yield.

Methods of calculations

Quantum chemical calculations were carried out using the frontier electron method^{9,10} which is based on the assumption that nucleophilic reactions take place at the atom with largest electron density in the lowest unoccupied molecular orbital (LUMO). In order to compare different naphthalene derivatives, atomic reactivity indices, S_i (LUMO), were calculated as approximate superdelocalizabilities: 9,12

$$S_i(LUMO) = 2C_i^2(LUMO) / - E(LUMO).$$

 C_t (LUMO) is the coefficient of atom *i* in the LUMO, and E(LUMO) the energy of this MO. In our study the E(LUMO) values were all negative, and -E(LUMO) was used in order to get positive values for S_t (LUMO). The units of the indices are electron charge per au.

The experimental results were also compared with the conventional net charge, Q_i . For hydrogen atoms

$$Q_i = 1 - 2\sum_{k}^{\text{occ}} C_{ik}^2$$

where C_{ik} is the coefficient of atom *i* in the *k*th occupied MO. The atomic reactivities and charge were calculated from eigenvectors using the semiempirical INDO-UHF MO method.^{13,14}

Input geometries for the naphthalenes were taken from the crystal structure of naphthalene itself.¹⁵ The methyl groups were assumed to have tetrahedral geometries with one H-atom in the ring plane and with C—H bonds equal to 1.09 Å. The position and orientation of the methyl groups were either taken from the crystal structure of 1,5-DMN¹⁶ or 1,8-DMN.¹⁷ In cases where different configurations were possible, the configuration with lowest total energy was chosen. For the CH₂-group in the naphthylmethyl cation bond angles were set to 120° with the hydrogen atoms in the ring plane.

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