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PREPARATION OF NAPHTHALDEHYDES BY CERIUM(IV) AMMONIUM NITRATE OXIDATION OF METHYLNAPHTHALENES

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Abstract—Naphthalenes with an Me group in the 1-position gave aldehydes in good to excellent yields when oxidized with cerium(IV) ammonium nitrate (CAN) in 50% HOAc at 85°. Under the same conditions methylnaphthalenes with no Me group in a *peri* position gave aldehydes in fair yields but also significant amounts of 1,4-naphthoquinone.

In connection with another project we needed fair amounts of a variety of naphthaldehydes. Numerous methods exist for the preparation of aliphatic and aromatic aldehydes,[1] but it turned out that no simple and general route to this particular class of aldehydes has been described. On the contrary, scattered reports on the synthesis of various naphthaldehydes seem to indicate that such compounds are difficult to prepare by any method even in fair yield.[2–6] This has turned out to be the case also when cerium(IV) ammonium nitrate (CAN) is used in spite of the fact that this reagent probably is the most versatile for the synthesis of aromatic aldehydes.[2,7] Thus, Syper[2] was unable to isolate any aldehyde when 1-methyl- and 2-methylnaphthalene were treated with CAN in acidic media whereas Trahanovsky *et al.*[4] obtained 1-naphthaldehyde only in 28% yield when 1-naphthylmethanol was treated with the same reagent under similar conditions. Nevertheless we hoped that CAN, under the right reaction conditions, would transform Me-substituted naphthalenes into the corresponding formyl-substituted naphthalenes and this expectation was certainly met.

RESULTS AND DISCUSSION

The first compounds reacted were 1,4-dimethylnaphthalene (1,4-DMN) (**1b**) and 1,8-dimethylnaphthalene (1,8-DMN) (**1d**) which gave the corresponding aldehydes **2b** and **d** (Scheme 1) in 46 and 5% yield, respectively, when the reactions were performed with 8 M excess of CAN at 85° (Table 1). The rest of each reaction mixture consisted of at least 12 products, the structures of which were not elucidated. These reactions as well as all the others were carried out in 50% acetic acid which turned out to be the best of the solvents tried (50% acetic acid, 45% formic acid and 3.5 M nitric acid).[2,4]

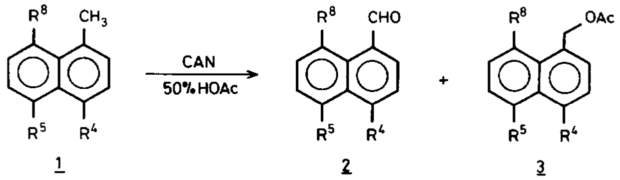
Table 1. Formation of 4-methyl-1-naphthaldehyde (**2b**) and 8-methyl-1-naphthaldehyde (**2d**) from reactions of 0.10 g of 1,4-DMN (**1b**) and 1,8-DMN (**1d**), respectively, with CAN in 35 ml of 50% HOAc for 2 hr

Starting material	Molar ratio CAN/DMN	Reaction temperature (°)	Yield[a] Starting material	Aldehyde
1b	8.0	50	9	53
1b	8.0	85	0	46
1d	8.0	50	60	11
1d	8.0	85	0	5
1b	4.0	85	0	82
1b	2.0	85	18	39
1d	4.0	85	0	70
1d	2.0	85	30	23

[a] In percentage of the crude reaction mixture.

In order to find the optimum conditions for aldehyde formation a variety of experiments were carried out, varying the reaction parameters which have been reported to influence the transformation of methylbenzene derivatives into benzaldehyde derivatives.[2,4,8,9] From the results compiled in Table 1 it is evident that the starting material is consumed faster at 85° than at 50°. At the higher temperature, however, the aldehydes are further oxidized[7] so that the chemical yield of these products is only slightly higher at 85°. Nevertheless, we decided to carry out the reactions at 85°.

Aldehyde formation is most significantly influenced by the relative amount of ceric salt employed (Table 1). The optimum CAN/methylnaphthalene molar ratio turned out to be 4.0 which is the theoretical ratio for the transformation of an Me group to a formyl group by



Scheme 1. **a** $R^4 = R^5 = R^8 = H$; **b** $R^4 = CH_3$, $R^5 = R^8 = H$; **c** $R^4 = R^8 = H$, $R^5 = CH_3$; **d** $R^4 = R^5 = H$, $R^8 = CH_3$.

one-electron oxidizing agents. Finally, the reactant concentrations and the reaction time also influence the aldehyde formation to some extent; the highest yields were obtained when the oxidation was carried out in dilute solutions for 2 hr.

A variety of Me-substituted naphthalenes were reacted with CAN under the optimum conditions outlined above. The substrates with an Me group in a *peri* position gave the corresponding 1-naphthaldehydes (Scheme 1) in excellent yields (Table 2). In addition these naphthalenes gave various by-products of which the corresponding 1-naphthylmethyl acetate **3**, formed in very low yield (2–6%), was the predominant one in most cases. Nitrates[8] were not observed in any reaction, but when 1,8-DMN (**1d**) was reacted under the optimum conditions a nitronaphthalene derivative was formed in 11% yield. The nature of the compound is evident from its IR spectrum which exhibits absorptions around 1340 and 1520 cm^{-1}, typical for nitro derivatives of aromatic compounds.[10,11] Furthermore, the mass spectrum shows significant peaks due to loss of O, NO, HNO, NO_2, HNO_2, and NOCO which is a characteristic fragmentation pattern for this class of compounds.[12] However, no peak in the mass spectrum can be ascribed to $M-OH]^{+}$, a fragment generally present, due to the *ortho* effect, in high abundance in spectra of aromatic compounds containing an *o*-nitromethyl moiety.[13] The nitro group can therefore not be attached to C-2. This conclusion is also borne out by the ^{1}H-NMR spectrum which contains a 6H singlet at 2.83 ppm for the two Me groups; if the product had been 1,8-dimethyl-2-nitronaphthalene the Me group attached to C-1 ought to appear as a singlet at a much lower field (around 3.7 ppm).[14,15] The remaining alternative structures are therefore the 3-nitro and 4-nitro derivatives of 1,8-DMN. In order to determine which one is correct, the chemical shifts of the H atoms of the naphthalene moiety of the alternative structures were calculated (Table 3)[12,16–18] and compared with the experimental data (Fig. 1). This comparison clearly reveals that only the latter alternative will give doublets at low field with *ortho* coupling constants (J > 7.5 Hz); the nitro compound is therefore 1,8-dimethyl-4-nitro-naphthalene.

Oxidation of the methylnaphthalenes lacking a substituent in a *peri* position, on the other hand, gave the corresponding naphthaldehydes **5** in low to moderate yields (Scheme 2, Table 2). These substrates gave in addition significant amounts (24–33%) of the corresponding 1,4-naphthoquinones **7** as well as small quantities (1–4%) of the corresponding 2-naphthylmethyl acetate **6**. The naphthoquinones were easily recognized from their mass spectra which exhibited the fragmentation pattern characteristic for this class of compounds.[19,20] The latter group of products was easily detected based on their specific IR and NMR absorptions (*vide supra*).

Table 3. Chemical shifts in ppm, relative to internal TMS, of the H atoms in the naphthalene moiety as observed for 1,8-dimethylnaphthalene (1,8-DMN) and calculated for 1,8-dimethyl-3-nitronaphthalene (3-NO_2-1,8-DMN) and 1,8-dimethyl-4-nitronaphthalene (4-NO_2-1,8-DMN)

Proton	1,8-DMN[a]	3-NO_2-1,8-DMN[b]	4-NO_2-1,8-DMN[b]
H-2	7.13	7.91	7.31
H-3	7.18	—	8.01
H-4	7.54	8.47	—
H-5	7.54	7.74	8.33
H-6	7.18	7.35	7.53
H-7	7.13	7.35	7.33

[a] From Ref. 16.

[b] These values have been calculated from the observed values of 1,8-dimethylnaphthalene by using the deshielding parameters of Wells.[17]

Both the quinones and the other by-products were troublesome to remove by chromatography and recrystallization. The aldehydes were therefore difficult to isolate pure without significant amounts of the corresponding 1,4-naphthoquinone. However, they could be converted into the corresponding 2,4-dinitrophenylhydrazones which were formed essentially in quantitative yields and obtained pure by recrystallization from toluene.

Most of the products formed to any extent can be accounted for on the basis of the accepted reaction scheme for cerium(IV) oxidation of alkyl-substituted aromatic hydrocarbons (Scheme 3).[9] Initial one-electron transfer from **1** and **4** yield the radical cation **8** which can suffer (a) side-chain oxidation and (b) oxidation of the aromatic nucleus. The former reaction gives rise to **3** and **6** as well as intermediate alcohols which are further oxidized to the corresponding aldehydes **2** and **5**.[4,21,22] When the naphthalenes have no Me group in a *peri* position (**4a–c**) path b becomes important and gives rise to acetoxylated (X = OAc) and/or hydroxylated (X = OH) naphthalenes **9**. These products are not stable under the experimental

Table 2. Major products obtained by oxidation of methylated naphthalenes with CAN according to the general procedure

Starting material	Products (yield[a])		
1a	**2a** (95%)	**3a** (3%)	
1b	**2b** (91%)	**3b** (6%)	
1c	**2c** (94%)	**3c** (2%)	
1d	**2d** (76%)	**3d** (6%)	
4a	**5a** (37%)	**6a** (4%)	**7a** (27%)
4b	**5b** (52%)	**6b** (2%)	**7b** (33%)
4c	**5c** (73%)	**6c** (1%)	**7c** (24%)

[a] In percentage of the crude reaction mixture.

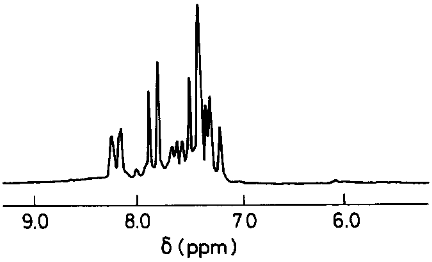
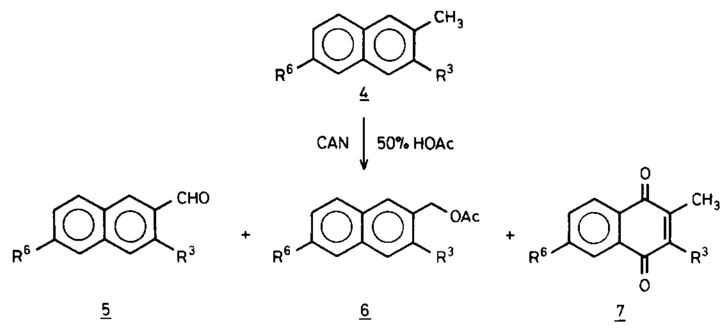


Fig. 1. The low-field part of the ^{1}H-NMR spectrum of 1,8-dimethyl-4-nitronaphthalene.



Scheme 2. **a** $R^3 = R^6 = H$; **b** $R^3 = CH_3$, $R^6 = H$; **c** $R^3 = H$, $R^6 = CH_3$.

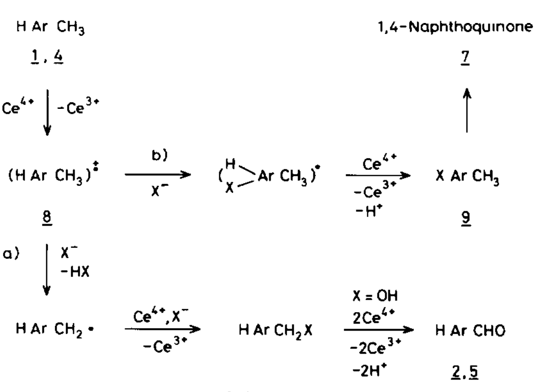
conditions but are further oxidized to 1,4-naphthoquinones **7**.[23]

EXPERIMENTAL

IR spectra were recorded in CCl_4 unless stated otherwise, on a Shimadzu IR-420 spectrophotometer. ^{1}H-NMR spectra were measured at 90 MHz on a Jeol 90Q FT spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Chemical shifts are reported in ppm downfield from TMS. Mass spectra were obtained on a VG Micromass 7070H spectrometer operated in the EI mode at 70 eV. A Hewlett–Packard 5710 gas chromatograph equipped with a Varian OV 17 column (3 m, ID 2 mm) and connected to the spectrometer was employed when GC/MS analyses were carried out. Otherwise GLC analysis was performed on a Carlo Erba Fractovap 4160 equipped with FID and a Chrompack SE 54 fused silica capillary column (25 m, ID 0.32 mm). Helium was used as carrier gas. M.ps and decomposition temps, determined by an Electrothermal m.p. apparatus, are uncorrected. The naphthalenes used were commercially available with a purity of better than 98% and were used without further purification.

CAN oxidation of methylnaphthalenes. Oxidations were carried out with 0.10–1.00 g of starting material. When small quantities (< 0.5 g) were used, the reactions were carried out according to the general procedure which represents the optimum conditions. On a larger scale the reactions were performed in more concentrated solns but otherwise under identical conditions. This reduced the yield of aldehyde to some extent.

General oxidation procedure. A soln of ceric ammonium nitrate (2.40 mmol) in 200 ml of 50% AcOH was added dropwise to a stirred, warm (85°) soln of the naphthalene (0.60 mmol) in 150 ml of the same solvent. The mixture was stirred for 2 hr at 85°, then cooled and extracted quantitatively with CH_2Cl_2. The combined extracts were washed with water and dried ($MgSO_4$). Evaporation of the solvent left a residue which was analyzed by GLC prior to, if necessary, further work-up.



Scheme 3.

Aldehydes **2a–d** were pure enough for most synthetic purposes, but could be further purified, with some loss of material, by column chromatography (silica gel (70–230 mesh), 3% EtOAc in hexane). The compounds could also be isolated as the corresponding 2,4-dinitrophenylhydrazones and recrystallized from toluene. The latter method was the most efficient for isolation of **5a–c**.

Oxidation of **1a** (0.100 g) gave **2a** in 95% yield; the physical properties were identical with those of an authentic sample (Aldrich). The major by-product (3%) was **3a**.[24]

Oxidation of **1b** (0.100 g) gave a crude product (0.107 g) which contained 91% of **2b**, IR: 2830, 2720, 1695 cm^{-1}; NMR δ: 2.74 (3H, d, J = 0.6 Hz, CH_3), 7.35–8.10 (5H, m), 9.23–9.36 (1H, m, H-8), 10.30 (1H, s, CHO); mol weight: calc for $C_{12}H_{10}O$ 170.0732, found 170.0729; MS *m/e* (rel intensity): 170 (100), 169 (76), 141 (79), 139 (21), 115 (33). The compound was precipitated quantitatively as 2,4-dinitrophenylhydrazone, m.p. 259–260° (dec). The major by-product (6%) was probably **3b**, IR: 1747, 1217 cm^{-1}; NMR δ: 2.05 (s) and 5.50 (s) in a ratio of 3:2.

Oxidation of **1c** (0.100 g) gave a product mixture (0.105 g) which consisted of 94% of **2c**, IR: 2810, 2770, 2710, 1697 cm^{-1}; NMR δ: 2.72 (3H, s, CH_3), 7.35–8.03 (3H, m), 7.97 (1H, d × d, J = 1.5, 7.0 Hz), 8.27 (1H, d, J = 8.5 Hz), 9.09 (1H, d, J = 8.2, H-8), 10.41 (1H, s, CHO); mol weight: calc for $C_{12}H_{10}O$ 170.0732, found 170.0728; MS *m/e* (rel intensity): 170 (86), 169 (23), 141 (100), 139 (19), 115 (43). The compound was precipitated quantitatively as 2,4-dinitrophenylhydrazone, m.p. 245–246° (dec). The major by-product (2%) was **3c**.[25]

Oxidation of **1d** (0.100 g) gave a crude product (0.104 g) which consisted essentially of three products. The main product (76%) was **2d**, IR: 2840, 2790, 2715 cm^{-1}; NMR δ: 2.79 (3H, s, CH_3), 7.35–8.09 (6H, m), 10.88 (1H, s, CHO); mol weight: calc for $C_{12}H_{10}O$ 170.0732, found 170.0731; MS *m/e* (rel intensity): 170 (76), 169 (35), 141 (100), 139 (18), 115 (40). The compound was precipitated quantitatively as 2,4-dinitrophenylhydrazone, m.p. 270–272° (dec). The main by-product (11%) was 1,8-dimethyl-4-nitronaphthalene, IR: 1519, 1349, 1334 cm^{-1}; NMR δ: 2.83 (6H, s), 7.24–7.62 (3H, m), 7.75 (1H, d, J = 7.9 Hz, H-3), 8.11 (1H, d × d, J = 1.5, 8.5 Hz, H-5); MS *m/e* (rel intensity): 201 (66), 186 (7), 185 (7), 171 (9), 170 (18), 155 (19), 154 (26), 152 (43), 144 (32), 143 (19), 128 (100), 115 (54). A minor by-product (6%) was **3d**, IR: 1741, 1210 cm^{-1}; NMR δ: 2.08 (3H, s, $COCH_3$), 2.87 (3H, s, CH_3), 5.63 (2H, s, CH_2), 7.25–7.85 (6H, m); MS *m/e* (rel intensity): 214 (17), 172 (2), 169 (3), 154 (95), 153 (100), 143 (7), 141 (9), 128 (15), 115 (12).

Oxidation of **4a** (0.100 g) gave a product mixture (0.086 g) which consisted of 28% unreacted starting material and three major products. The main product (37%) was **5a** whose physical properties were identical to those of an authentic sample (Aldrich). Compound **7a** was obtained in 27% yield; the compound was identical to an authentic sample (Aldrich). The third product, formed in 4% yield, was acetate **6a** according to spectroscopic data of an impure sample of the compound, IR: 1739, 1220 cm^{-1}; NMR δ: 2.13 (3H, s, $COCH_3$), 5.26 (2H, s, CH_2), 7.35–7.70 (7H, m).

Oxidation of **4b** (0.100 g) yielded a crude product (0.109 g) which consisted essentially of two products. The main product (52%) was **5b**[26] which was precipitated quantitatively as 2,4-dinitrophenylhydrazone, m.p. 233–235° (dec). The minor product, formed in 33% yield, was **7b**, IR: 1661 cm^{-1}; NMR δ: 2.16 (6H, s, $2CH_3$), 7.50–8.15 (4H, m); MS.[20]

Oxidation of **4c** (0.100 g) gave 0.103 g of crude product which essentially was a mixture of two compounds. The main product (73%) was aldehyde **5c**, IR: 2805, 2790, 2750, 2705, 1700 cm^{-1}; NMR δ: 2.54 (3H, s, CH_3), 7.32–8.05 (5H, m), 8.25 (1H, broad s, H-1), 10.11 (1H, s, CHO); MS *m/e* (rel intensity): 170 (100), 169 (91), 141 (85), 139 (20), 115 (41); mol weight: calc for $C_{12}H_{10}O$ 170.0732, found 170.0730. The compound was precipitated as 2,4-dinitrophenylhydrazone, m.p. 285–286° (dec). The other product, formed in 24% yield, was **7c** according to analyses performed on an impure sample of the compound, IR: 1663 cm^{-1}; NMR δ: 2.15 (3H, d, J = 1.4 Hz, $COCCH_3$), 2.46 (3H, s, CH_3), 6.76 (1H, d, J = 1.4 Hz, H-3), 7.30–7.95 (3H, m); MS *m/e* (rel intensity): 186 (100), 169 (6), 158 (40), 141 (7), 129 (27), 115 (35).

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