

Short Communication

Methylphenanthrenecarbaldehydes by Selective Cerium(IV) Oxidation of Dimethylphenanthrenes

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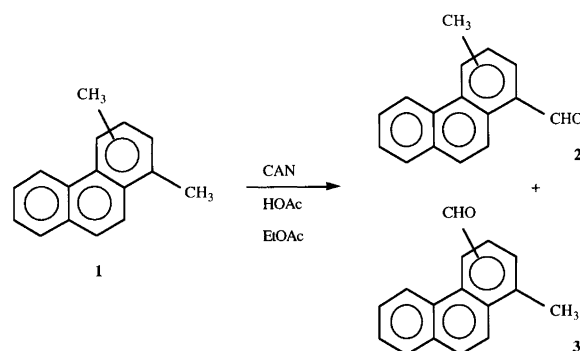
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The strong oxidizing power of cerium(IV) ammonium nitrate (CAN) has been recognized for many years.^{1–4} Particularly striking is the reagent's ability to transform aromatic hydrocarbons containing a methyl or a methylene group into the corresponding aldehydes or ketones. This is generally an efficient transformation for benzene derivatives^{1,4} and the same is true for methyl-substituted naphthalenes under the right conditions.^{5,6} We therefore expected that CAN would also react selectively with dimethylphenanthrenes (DMPs) and afford the corresponding methylphenanthrenecarbaldehydes in spite of the fact that phenanthrene itself gives a complex reaction mixture when treated with ceric ion.^{7,8}

In order to find the best conditions for conversion of DMPs into monoaldehydes, exploratory experiments were carried out with several phenanthrenes. Under the conditions most favourable for conversion of dimethylnaphthalenes into monoaldehydes^{5,6} the DMPs were only slightly soluble and gave methylphenanthrenecarbaldehydes in rather low yields; furthermore, significant amounts of dialdehyde, quinone and unreacted starting material were obtained. However, after addition of ethyl acetate as a cosolvent and lowering of the reaction time from 2 h to 1 h, far less complex reaction mixtures were obtained.

When the measures outlined above were taken, the six 1,*x*-DMPs (**1**) at hand reacted satisfactorily and gave reaction mixtures containing mainly the isomeric aldehydes *x*-methylphenanthrene-1-carbaldehyde (**2**) and 1-methylphenanthrene-*x*-carbaldehyde (**3**) (Scheme 1), which have not previously been described. In addition various by-products, **4–7** (Scheme 2), were obtained, the

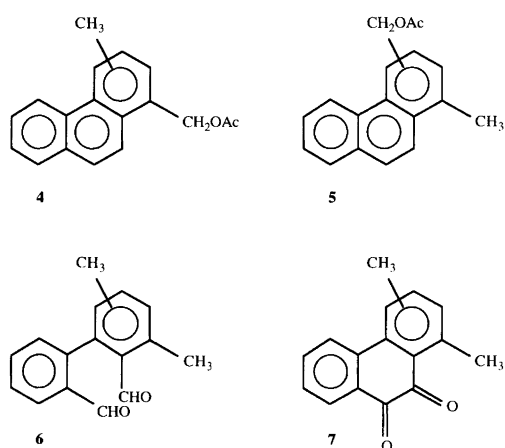


Scheme 1.

formation of which can be accounted for on the basis of the accepted mechanism for CAN oxidation of alkyl-substituted aromatic hydrocarbons.⁹ The most consistent by-products were the corresponding (methylphenanthryl)methyl acetates (**4** and **5**) which showed characteristic IR absorptions around 1745 and 1215 cm^{-1} and NMR resonances around 2.1 and 5.5 ppm. The combined yield of acetates **4** and **5** was almost constant. Another by-product was the C-9, C-10 cleavage product **6**, whose yield was substrate-dependent. Formation of quinone **7**, which takes place to a considerable extent when phenanthrene itself is oxidized with CAN,⁷ was barely observed.

Oxidation of **1a–1f** under the optimum conditions afforded the aldehyde distribution summarized in Table 1. Both the efficiency and the selectivity of the reactions leading to **2** and **3** depend on the position of the methyl groups. Thus, the combined contents of the aldehydes varied from 61% in the case of 1,6-DMP to 93% which was obtained when 1,9-DMP was reacted. Furthermore, the *x*-carbaldehyde:1-carbaldehyde ratio

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Scheme 2.

Table 1. *x*-Methylphenanthrene-1-carbaldehyde (**2**) and 1-methylphenanthrene-*x*-carbaldehyde (**3**) obtained by CAN oxidation of 1,*x*-dimethylphenanthrenes (**1**) according to the general procedure.

1, <i>x</i> -DMP (1)	Amount ^a	
	2	3
1,2-DMP (1a)	59	7
1,3-DMP (1b)	26	45
1,4-DMP (1c)	43	22
1,6-DMP (1d)	25	36
1,8-DMP (1e)	^b	^b
1,9-DMP (1f)	1	92

^aAs a percentage of the crude reaction mixture as determined by GLC and ¹H NMR spectroscopy. For isolated yields, see Experimental. ^b**2f** and **3f** are identical.

(**3**:**2**) dropped from 92 to 0.12 when the position of the second methyl group changed from C-9 to C-2. Dimethylphenanthrenes therefore resemble dimethylnaphthalenes in that aldehyde formation is sensitive to the point of attachment to the aromatic moiety. However, whereas dimethylnaphthalenes are oxidized at the methyl group attached to C-1 irrespective of the position of the second methyl group, the selectivity of the oxidation of the DMPs appears to depend on the position of both methyl groups.

The observation above is substantiated by quantum-chemical calculations using the frontier electron method.^{10,11} It is assumed that the first irreversible step in the oxidation process involves proton abstraction from a methyl group of the DMP radical cation (DMP^{•+}),^{9,12} and that the nucleophilic attack takes place at the hydrogen atom with the highest coefficient of the lowest unoccupied molecular orbital (LUMO).^{10,11} Calculated atomic reactivity indices, *S_i*(LUMO),^{10,13} have been used successfully to predict the selectivity in analogous naphthalene reactions.⁵ When the method was used to compare the proton abstraction from the two methyl groups, the data compiled in Table 2 were obtained. Table 2 also

Table 2. Atomic reactivity indices, *S_i*(LUMO), for the hydrogen atoms of the methyl groups of the radical cation DMP^{•+}.

1, <i>x</i> -DMP	<i>S_i</i> (LUMO)	
	CH ₃ at C-1	CH ₃ at C- <i>x</i>
1,2-DMP	0.044	0.002
1,3-DMP	0.060	0.071
1,4-DMP	0.063	0.055
1,5-DMP	0.038	0.025
1,6-DMP	0.030	0.045
1,7-DMP	0.063	0.001
1,8-DMP	0.032	0.032
1,9-DMP	0.037	0.104
1,10-DMP	0.043	0.120

includes reactivities for 1,5-DMP, 1,7-DMP and 1,10-DMP, which have not yet been investigated.

Attempts were also made to correlate the regioselectivity with different acidities of the methyl CH bonds in the radical cation assumed to be an intermediate in the reaction, i.e. relative energy differences for the process ArCH₃^{•+} → ArCH₂[•] + H⁺. However, the calculated energy differences are small (generally less than 1 kcal mol⁻¹), and although the selectivity in most cases is correctly predicted by the acidities, they correlate well with neither the experiments nor the calculated *S_i*(LUMO) values.

From the calculated *S_i*(LUMO) data in Table 2, it is evident that proton abstraction from the radical cation is influenced by *x*, i.e. the position of the methyl group attached to C-*x*. The calculated reactivities are highest for methyl groups at C-9 and C-10, and lowest for those at C-2 and C-7. Furthermore, when the methyl group is attached to C-2, C-4, C-5 or C-7, oxidation of the methyl group at C-1 is predicted to predominate. However, when *x* is 3, 6, 9 or 10, formation of the corresponding 1-methylphenanthrene-*x*-carbaldehydes is expected to be favoured. Indeed, these predictions are verified for the investigated molecules (Table 1). Consequently, the atomic reactivity indices seem to be useful parameters in predicting the primary site of methyl-group oxidation of dimethylphenanthrenes and perhaps also of other methylated aromatic hydrocarbons.

Experimental

General. In addition to the equipment described elsewhere⁶ a Jeol JNM-EX 400 spectrometer was used to run ¹H NMR spectra.

Chemicals. Dimethylphenanthrenes **1a**–**1f**, synthesized by oxidative photocyclization^{14,15} of the corresponding dimethylstilbenes,¹⁶ were known from the literature.^{17–19}

CAN oxidation, general procedure. A solution of ceric ammonium nitrate (1.06 g, 1.96 mmol) in 50% acetic acid (200 ml) was added dropwise to a stirred, warm (85 °C) solution of dimethylphenanthrene (DMP)

(0.100 g, 0.49 mmol) in ethyl acetate (100 ml). After 1 h the mixture was cooled and extracted with CH_2Cl_2 . The combined extracts were washed with water and dried (MgSO_4). Evaporation of the solvent left a residue which was analysed by GLC and ^1H NMR spectroscopy prior to final purification by gravity flow-circular TLC using ethyl acetate–hexane 2:5 as mobile phase.

Oxidation of 1,2-DMP (1a) gave **2a** and **3a** which were separated and showed the following spectroscopic properties. **2a** was isolated in 37% yield.

2a: IR (CCl_4): 3080, 2970, 2910, 2850, 2760, 1740, 1690 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.81 (3 H, s), 7.49 (1 H, d, J 8.8 Hz), 7.62–7.89 (5 H, m), 8.62–8.65 (1 H, m), 8.78 (1 H, d, J 9.3 Hz), 10.99 (1 H, s). MS [m/z (rel. int. %)]: 220 (100, M^+), 219 (42), 205 (13), 192 (61), 191 (73), 190 (23), 189 (51), 187 (7), 176 (5), 165 (19), 163 (6), 152 (4), 110 (11), 95 (24). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.088.

3a: IR (CCl_4): 3070, 1740, 1690 cm^{-1} . ^1H NMR (90 MHz, CDCl_3): δ 2.78 (3 H, s), 7.4–8.9 (8 H, m), 10.63 (1 H, s). MS [m/z (rel. int. %)]: 220 (100, M^+), 219 (51), 192 (13), 191 (53), 190 (18), 189 (38), 176 (4), 165 (10), 163 (5), 110 (10), 95 (16). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.090.

Oxidation of 1,3-DMP (1b) gave **2b** and **3b** which were inseparable on a preparative scale. The aldehydes were isolated as a mixture in 69% yield. A mixture of the products gave the following spectra: IR (CCl_4): 3060, 2930, 2860, 2710, 1735, 1695 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.69 (**2b**) and 2.80 (**3b**) (3 H, 2 s), 7.55–9.06 (8 H, m), 10.22 (**2b**) and 10.49 (**3b**) (1 H, 2 s).

2b: GC–MS [m/z (rel. int. %)]: 220 (100, M^+), 219 (25), 205 (5), 192 (62), 191 (71), 190 (24), 189 (51), 187 (7), 165 (14), 163 (5), 110 (12), 96 (4), 95 (24). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.088.

3b: GC–MS [m/z (rel. int. %)]: 220 (100, M^+), 219 (44), 192 (12), 191 (44), 190 (19), 189 (38), 187 (4), 176 (5), 165 (8), 163 (4), 110 (2), 97 (7), 95 (6), 94 (12). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.088.

Oxidation of 1,4-DMP (1c) gave **2c** and **3c** which were inseparable on a preparative scale. A mixture of the products gave the following spectra: IR (CCl_4): 3050, 2910, 2850, 2730, 1725, 1695 cm^{-1} . ^1H NMR (90 MHz, CDCl_3): δ 2.83 (**3c**) and 2.90 (**2c**) (3 H, 2 s), 7.55–8.05 (7 H, m), 8.56 (**3c**) and 9.19 (**2c**) (1 H, 2 d, J 7.8 and 9.3 Hz, respectively), 10.49 (**2c**) and 10.58 (**3c**) (1 H, 2 s).

2c: GC–MS [m/z (rel. int. %)]: 220 (100, M^+), 219 (39), 205 (16), 192 (32), 191 (56), 190 (27), 189 (52), 176 (5), 165 (13), 163 (5), 152 (3), 139 (2), 110 (7), 109 (6), 95 (10), 94 (19). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.090.

3c: GC–MS [m/z (rel. int. %)]: 220 (64, M^+), 219 (100), 205 (67), 192 (13), 191 (38), 190 (27), 189 (52), 176 (6), 165 (9), 163 (5), 152 (2), 139 (2), 109 (8), 102

(5), 95 (6), 94 (13). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.088.

Oxidation of 1,6-DMP (1d) gave **2d** and **3d** which were inseparable on a preparative scale. A mixture of the products, isolated in 45% yield, gave the following spectra: IR (CCl_4): 3060, 2960, 2920, 2850, 2710, 1735, 1700 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.65 (**2d**) and 2.79 (**3d**) (3 H, 2 s), 7.42–9.10 (8 H, m), 10.28 (**3d**) and 10.53 (**2d**) (1 H, 2 s).

2d: GC–MS [m/z (rel. int. %)]: 220 (92, M^+), 219 (14), 205 (11), 192 (70), 191 (100), 190 (28), 189 (66), 176 (19), 165 (15), 163 (8), 152 (4), 139 (3), 110 (5), 109 (20), 95 (20), 94 (20). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.088.

3d: GC–MS [m/z (rel. int. %)]: 220 (100, M^+), 219 (54), 206 (2), 192 (16), 191 (49), 190 (27), 189 (49), 176 (12), 165 (10), 163 (6), 152 (4), 139 (3), 109 (5), 96 (8), 95 (24), 94 (9). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.088.

Oxidation of 1,8-DMP (1e) gave **2e** (identical with **3e**) which was isolated as a solid in 71% yield, m.p. 132–135 °C; IR (CCl_4): 3070, 2950, 2920, 2855, 2720, 1740, 1700 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.80 (3 H, s), 7.52 (1 H, d, J 7.3 Hz), 7.60–8.12 (3 H, m), 8.19 (1 H, d, J 9.3 Hz), 8.61 (1 H, d, J 8.3 Hz), 9.02 (1 H, m), 9.20 (1 H, m), 10.53 (1 H, s). MS [m/z (rel. int. %)]: 220 (100, M^+), 219 (23), 205 (15), 192 (64), 191 (73), 190 (10), 189 (50), 176 (16), 165 (16), 163 (8), 152 (3), 139 (3), 109 (19), 95 (17). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.090.

Oxidation of 1,9-DMP (1f) gave **2f** and **3f**. Aldehyde **3f** was isolated as a solid in 75% yield, m.p. 89–91 °C. A mixture of the products gave the following spectra: IR (CCl_4): 3060, 2955, 2915, 2850, 2720, 1738, 1695 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.80 (**2f**) and 2.82 (**3f**) (3 H, 2 s), 7.50–9.45 (8 H, m), 10.39 (**3f**) and 10.48 (**2f**) (1 H, 2 s).

2f: GC–MS [m/z (rel. int. %)]: 220 (100, M^+), 219 (34), 205 (12), 192 (36), 191 (54), 190 (14), 189 (38), 187 (6), 176 (5), 165 (15), 163 (5), 152 (3), 139 (3), 110 (7), 109 (6), 95 (11). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.088.

3f: MS [m/z (rel. int. %)]: 220 (100, M^+), 219 (45), 205 (12), 192 (46), 191 (96), 190 (34), 189 (72), 187 (12), 176 (7), 165 (29), 163 (10), 152 (4), 139 (3), 110 (4), 109 (11), 95 (22). Mol. wt: calc. for $\text{C}_{16}\text{H}_{12}\text{O}$ 220.089, found 220.089.

Quantum chemical calculations. The calculations were carried out using the semiempirical AM1 (UHF) method²⁰ as implemented in GAUSSIAN 94. Atomic reactivity indices were calculated as approximate superdelocalizabilities,^{10,13} eqn. (1),

$$S_i(\text{LUMO}) = \sum_{\alpha} \frac{C_{i,k}^2(\text{LUMO})}{-\epsilon_k(\text{LUMO})} \quad (1)$$

where $C_{i,k}$ (LUMO) is the coefficient of the s-orbital of hydrogen atom i in LUMO k of α and β spin, and ϵ_k (LUMO) is the energy of these MOs. In our study the ϵ (LUMO) values were all negative and $-\epsilon$ (LUMO) was used in order to obtain positive values for S_i (LUMO). The molecular structure for each of the radical cations was obtained from geometry optimizations assuming C_s symmetry. In cases where different orientations of the methyl groups were possible, the configuration with lowest energy was chosen. Test calculations on unsubstituted phenanthrene show good agreement with bond lengths and angles as determined by neutron diffraction.²¹

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