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Anodic Oxidation of Active Methylene Groups in the Presence of Excess Carboxylic Acid

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Synopsis. The anodic oxidation of anthrone, (9,(10*H*)-anthracenone), 9,10-dihydroanthracene and 1-tetralone in acetonitrile was studied under the presence of excess carboxylic acids. The oxidation of anthrone with acetic acid gave anthraquinone, 10-acetoxyanthrone and 10-methyl-10-acetoxyanthrone. A similar reaction of anthrone with propionic acid yielded 10-propionyloxyanthrone. The electronic oxidation of 9,10-dihydroanthracene yielded anthraquinone, anthrone, and 9-acetoxyanthrone under the same conditions. Also, 1-tetralone reacted with acetic acid and propionic acid at the 4 position of the carbonyl group, giving 4-acetoxy- and 4-propionyloxy-1-tetralone, respectively.

In a series of papers concerning the reactions of anthrone with trivalent phosphorus compounds[1,2] and organometallic compounds[3—5] we have demonstrated that under the presence of alkanethiol, the cathodic reactions of carbonyl compounds took place, giving various reduced products: e.g., anthrone was reduced to anthracene in 65% yield.[6] Anthrone was proved to react with nucleophiles at the carbonyl group and, through its enol form, with electrophiles at the methylene group to give many interesting derivatives.

The electrolytic acetoxylation of arenes in acetic acid has been extensively studied during these twenty years, and the mechanism of this reaction seems to be well established.[7] In the reaction of the arenes that have alkyl substituents as side-chain, it is common to obtain products that result from substitution on both the aromatic nucleus and the aliphatic side-chain. An anodic acetoxylation of toluene and ethylbenzene in acetic acid containing sodium acetate yielded both nuclear and side-chain substitution products, in contrast to a reaction in the presence of sodium perchlorate or tetraethylammonium tosylate that produced exclusively the side chain-acetate.[8] Ross and co-workers observed that the anodic reaction of toluene with acetic acid in the presence of tetraethylammonium tosylate gave benzyl acetate as the main products along with ethylbenzene.[9] The minor product, ethylbenzene results from a coupling between a benzyl radical and a methyl radical. This result indicates the fact that, although the anodic acetoxylation of aromatic compounds proceeds through an initial two-electron transfer from the aromatic nucleus to the anode, there is still a possibility of a Kolbe reaction producing a methyl radical. This paper reports on the anodic oxidation of anthrone, 9,10-dihydroanthracene and 1-tetralone in a carboxylic acid–acetonitrile mixed solvent containing both sodium salts of the corresponding carboxylic acid and lithium perchlorate as electrolytes.

Experimental

The melting points determined with a Yanagimoto micro-melting point apparatus are uncorrected. IR and NMR spectra were recorded on Perkin–Elmer 1600 series FTIR and JEOL FX 60 FT NMR spectrometers, respectively. UV spectra were taken on a Hitachi 200-10 spectrophotometer. The mass spectra (70 eV) were measured using a Hitachi RMU-6L spectrometer. HPLC measurements were recorded on a JASCO UVIDEC-100 using a column of Uniseer Inertsil ODS-2 and 70% methanol as an eluent. The electrolyses were carried out by using a Nikko Keisoku NOGFZ-2501A potentiogalvanostat attached to a Nikko Keisoku Digital NDCM-1 Coulomb meter. Column chromatography was performed using Mallinckrodt silicic acid (100 mesh) with benzene as an eluent.

Materials. Commercially available acetonitrile, methanol, acetic acid, and propionic acid were distilled before use. Sodium acetate, sodium propionate, 1-tetralone, and 9,10-dihydroanthracene were used as purchased. Anthrone was prepared from anthraquinone according to the reported procedure.[7]

Electrolysis Apparatus. An undivided cell was equipped with two platinum plates (2×2 cm^2, 10 mm apart), inert gas inlet and outlet tubes and a thermometer. The cell was dipped in a water bath at 25 °C.

10-Acetoxyanthrone (Ia) and 10-Methyl-10-acetoxyanthrone (Ib) from Anthrone. A mixture of anthrone (300 mg, 1.55 mmol) and sodium acetate (310 mg, 3.7 mmol) was dissolved in 40 ml of solvent (acetonitrile–acetic acid 1/1 vol.) containing 0.1 equiv lithium perchlorate as a supporting electrolyte. A constant voltage of 2.3 V vs. SCE (the applied voltage between two terminal electrodes was 7 V) was applied until 5 Faraday mol^{-1} of electricity was passed under a nitrogen atmosphere. The reaction mixture was concentrated and taken up in benzene (50 ml) and washed with water. After removal of the solvent, the residue was chromatographed on silica gel to give three fractions: The first eluent contained 30 mg (9.3% yield based on anthrone) of anthraquinone.

The second fraction consisted of 123 mg (31% yield) of **Ia**: Dark-yellow crystals; mp 232—235 °C; MS *m/z* 252 (M$^+$); IR (KBr) 1756 (m), 1676 (s), 1595 (m), 1460 (w), 1373 (w), 1315 (s), 1283 (s), 1210 (m), 1170 (w), 1090 (w), 1072 (w), 930 (m), 810 (w), 796 (w), and 694 cm^{-1} (s); ^{1}H NMR (CDCl$_3$) δ=8.66—7.19 (m, 8H), 2.16 (s, 1H), and 0.09 (s, 3H); ^{13}C NMR (CDCl$_3$) δ=128.10 (C-1), 128.95 (C-2), 133.37 (C-3), 127.26 (C-4), 182.97 (C-9), 66.49 (C-10), 131.48 (C-9a), 138.69 (C-4a), 170.96 (C=O), 21.10 (Me); UV (MeOH) 206 (log ε 4.32), 252 (4.21), and 272 (4.00). Found: C, 75.88; H, 4.65%. Calcd for C$_{16}$H$_{12}$O$_3$: C, 76.18; H, 4.80%.

The third run involved 160 mg (39% yield) of **Ib** as yellow crystals; mp 54—56 °C; MS m/z 266 (M^+); IR (KBr) 2930 (m), 1742 (s), 1667 (s), 1602 (s), 1463 (s), 1372 (m), 1320 (s), 1298 (s), 1233 (s), 1160 (w), 1070 (s), 1015 (w), 931 (m), 863 (w), 766 (s), 684 (s), 666 (w), and 628 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.36—7.27 (m, 8H), and 2.07—0.92 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=127.45 (C-1), 127.85 (C-2), 133.63 (C-3), 123.76 (C-4), 182.77 (C-9), 75.77 (C-10), 129.60 (C-9a), 145.89 (C-4a), 168.43 (C=O), 21.49 (acetyl), and 35.26 (10-Me); UV (MeOH) 208 ($\log\varepsilon$ 4.34), 268 (4.15). Found: C, 76.56; H, 5.53%. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%.

10-Propionyloxyanthrone (Ic) from Anthrone. In a similar manner, the electrolysis of anthrone under the presence of propionic acid, gave **Ic** as pale-yellow crystals; mp 160—162 °C; MS m/z 266 (M^+); IR (KBr) 2940 (w), 1730 (s), 1680 (s), 1596 (m), 1462 (m), 1310 (s), 1285 (s), 1190 (s), 1081 (w), 1018 (w), 935 (m), 810 (m), 762 (m), 715 (m), 697 (s), 678 (m), and 623 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ=7.71—7.51 (m, 8H), 3.71 (s, 1H), 2.25—1.62 (q, 2H), and 1.48—1.04 (t, 3H); ^{13}C NMR ($CDCl_3$) δ=126.47 (C-1), 127.85 (C-2), 128.11 (C-3), 125.83 (C-4), 182.25 (C-9), 73.94 (C-10), 128.37 (C-9a), 133.50 (C-4a), 151.87 (C=O), 29.61, 9.03 (Et). Found: C, 77.06; H, 5.35%. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%.

10-Acetoxyanthrone (Ia) from 9,10-Dihydroanthracene. In an undivided cell, 9,10-dihydroanthracene (320 mg, 1.75 mmol) and sodium acetate (150 mg, 1.75 mmol) were dissolved in a mixed solvent of acetonitrile–acetic acid (1/1 vol.). The solution was treated electrolytically, as mentioned before. After passing 3 Faraday mol^{-1}, anthraquinone (55 mg, 15%), anthrone (24 mg, 7%), and **Ia** (212 mg, 48%) was separated by column chromatographic treatments.

4-Acetoxy-1-tetralone (IIa) from 1-Tetralone. A solution of 500 mg (3.4 mmol) of 1-tetralone and 300 mg (3.5 mmol) of sodium acetate in the mixed solvent of 20 ml acetonitrile and 20 ml of acetic acid was electrolyzed in a similar way under a constant voltage (2.3 V vs. SCE). After passing 5 Faraday mol^{-1} of electricity, the reaction mixture was worked up using the same procedure and chromatographed (benzene–AcOEt 10 : 1) to give 390 mg (54% yield) of **IIa**.

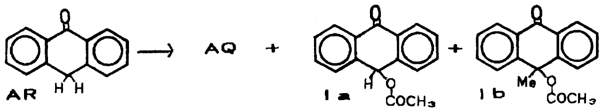
IIa: Brown oil; MS m/z 204 (M^+); IR (neat) 2930 (w), 1670 (s), 1598 (m), 1370 (w), 1320 (w), 1282 (m), 1229 (w), 1032 (w), 935 (w), and 766 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ= 7.94—7.68 (m, 4H), 2.45—1.62 (m, 8H); ^{13}C NMR ($CDCl_3$) δ=196.35 (C-1), 28.18 (C-2), 34.09 (C-3), 68.94 (C-4), 126.81 (C-5), 133.56 (C-6), 128.63 (C-7), 127.98 (C-8), 131.61 (C-8a), 169.99 (C=O), and 20.91 (Me); UV (MeOH) 209 ($\log\varepsilon$ 4.91), 219 (4.83), 242 (4.65), and 289 (4.05). Found: C, 70.21; H, 5.65%. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92%.

4-Propionyloxy-1-tetralone (IIb) from 1-Tetralone. In a similar way, by using propionic acid and sodium propionate, 1-tetralone gave 4-propionyloxy-1-tetralone **IIb** in 33% yield (250 mg).

IIb: Brown oil; MS m/z 218 (M^+); IR (neat) 2920 (m), 1730 (s), 1692 (s), 1598 (s), 1455 (m), 1415 (w), 1327 (w), 1283 (w), 1175 (m), 1115 (w), 1078 (m), 1020 (m), 938 (m), and 765 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ=8.40—7.06 (m, 4H), 2.78—2.27 (m, 7H), and 1.73—0.69 (m, 3H); ^{13}C NMR ($CDCl_3$) δ=196.41 (C-1), 28.24 (C-2), 34.15 (C-3), 68.63 (C-4), 126.03 (C-5), 133.56 (C-6), 127.98 (C-7), 126.81 (C-8), 128.63 (C-8a), 138.30 (C-4a), 173.50 (C=O), 27.53, 8.83 (Et); UV (MeOH) 207 ($\log\varepsilon$ 4.41), 246 (4.32), and 285 (3.42). Found: C, 71.01; H, 6.07%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.46%.

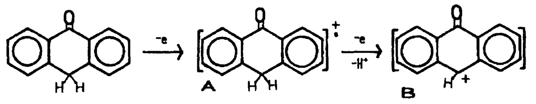
Results and Discussion

Previous reports in this series have dealt with the anodic alkoxylation[10] and cathodic reduction of anthrone.[6] The anodic reaction of anthrone with methanol and ethanol in the presence of lithium perchlorate as an electrolyte yielded each 10-alkoxyanthrones in low yields (24 and 41%, respectively). The oxidation potentials of the compounds chosen for investigation in this paper do not differ widely from those of other aromatic compounds.[11] Anthrone has an oxidation peak at 2.3 V in its cyclic voltammogram; those of 9,10-dihydroanthracene and 1-tetralone appeared at 1.9 and 1.7 V, respectively. When anthrone is oxidized anodically in an acetonitrile–acetic acid mixed solvent containing lithium perchlorate and acetate ion, anthraquinone and two other products were detected by HPLC analysis. The isolated yield of anthraquinone was 9.3%. The other products were separated by column chromatography on silica gel, and were proved to be 10-acetoxyanthrone (**Ia**, 31%) and 10-methyl-10-acetoxyanthrone (**Ib**, 39%). The products were identified by elemental analyses and their IR, mass, NMR, and UV spectral data.



(1)

The formation of quinone was reported to proceed through the anodic transacylation to water or to the acetate anion.[12,13] However, anthraquinone is always formed from anthrone in the solution when exposed to air, and accelerated upon electrolysis considerably.[14] Clearly, the formation of anthraquinone in this case proceeds through cation radical **A** or cation **B** followed by auto-oxidation.



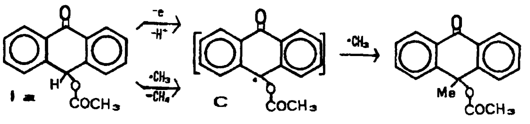
(2)

Acetoxylation at the 10-position of anthrone could be explained by the same intermediate **B** followed by a reaction with acetate anion to form **Ia**.

The formation of **Ib** implies a Kolbe decomposition of the acetate anion to a methyl radical via an acetoxy radical:

$$CH_3COO^- \xrightarrow{-e} CH_3COO\cdot \longrightarrow \cdot CH_3 + CO_2 \qquad (3)$$

The methyl radical would couple with intermediate cation radical **C** derived from by either an anodic electron transfer or by hydrogen abstraction by the methyl radical from **Ia**.



(4)

The replacement of acetic acid to propionic acid leads to the formation of 10-propionyloxyanthrone alone, and no alkylation product was found. This result might be explained by the fact that the discharge of the propionate anion does not occur at the potential used in this experiment.

The anodic oxidation of 9,10-dihydroanthracene was reported to give anthrone and anthraquinone upon electrolysis in acetonitrile in the presence of lithium perchlorate.[14] The presence of the acetate anion as a nucleophile leads to the formation of 10-acetoxyanthrone (**Ia**, 48%) along with anthrone (7%) and anthraquinone (15%). **Ia** in this reaction might originate from the anodic acetoxylation of anthrone formed as a first oxidation product from 9,10-dihydroanthracene. The reaction mechanism is the same as that described above.

Under a similar oxidation condition, 1-tetralone was oxidized at the 4-position to gave 4-acetoxy-1-tetralone **IIa** in 54% yield. The reaction of 1-tetralone with propionic acid gave 4-propionyloxy-1-tetralone **IIb** through the cation radical formed at the 4-position. Although the α-position to the carbonyl group is also activated by a strong electron-withdrawing effect of the carbonyl group, an electrolytic reaction needs the presence of an aromatic group as the first oxidized part in the molecule.

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