(5 mL) was added to a suspension of $LiAlH_4$ (10.0 mg, 0.26 mM) in dry ether (5 mL) and cooled to −78 °C with a dry ice–acetone bath. The mixture was stirred for 2 h and then allowed to warm up to 25 °C for 1 more h. The reaction was then successively treated with water (0.1 mL), 15% sodium hydroxide (0.1 mL), and the granular precipitate was filtered and washed with ether. The combined ethereal solutions were evaporated, and the residue was methylated as above producing a yellow oil (5.0 mg, 68%) identical (IR, ^1H NMR) with **7g** produced as above.

4a-Methyl-3,4,4a,9,10,10aβ-hexahydrophenanthrene (9) and 1α-Azido-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (7c). The same procedure was used as in **7f** starting with tosylate **7e** (0.280 g, 0.75 mL). A higher temperature (120 °C) was required to cause the disappearance of the starting tosylate. After workup and column chromatography, 0.120 g (80%) of olefin **9** and 0.013 g (7%) of azide **7c** were isolated.

Olefin 9: ^1H NMR ($CDCl_3$) δ 7.50–6.80 (m, 4 H, Ar H), 5.60 (br s, 2 H, olefinic H), 2.90–2.56 (m, 2 H, benzylic), 2.5–1.30 (m, 8 H, aliphatic), 1.32 (s, 3 H, C-4a-CH_3); MS, m/z 198 (M^+), 185, 183, 157, 141, 129 (bp), 115, 91, 77.

Azide 7c: IR 2095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 3 H, C-4a-CH_3).

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (2a). Olefin **9** (0.1 g, 0.505 mmol) in (30 mL) was hydrogenated (30 psi H_2) in the presence of 10% Pd on charcoal (0.030 g) for 3 h. The catalyst was filtered, and the filtrate was concentrated in vacuo to yield 0.090 g (90%) of pure **2a** (GC). The ^1H NMR shows only one C-4a-CH_3 singlet for 3 H at δ ($CDCl_3$) 1.23 coincident with that reported by E. Wenkert and co-workers[11] for **2a**.

Registry No. 1, 22139-44-2; **2**, 22139-45-3; **2a**, 79297-74-8; **2b**, 70561-39-6; **3**, 98304-41-7; **4**, 98330-23-5; **5**, 98392-71-3; **6**, 41487-66-5; **7a**, 98304-44-0; **7b**, 98304-54-2; **7c**, 98304-57-5; **7d**, 98304-50-8; **7e**, 98304-42-8; **7f**, 98304-55-3; **7g**, 98304-49-5; **7h**, 98304-46-2; **8a**, 98304-45-1; **8b**, 98304-53-1; **8c**, 98304-51-9; **8d**, 98304-43-9; **8e**, 98304-52-0; **8f**, 98304-47-3; **9**, 98304-56-4; **10**, 98330-24-6; 1β-amino-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene, 98304-48-4.

Aromatic Hydroxylation and Deacylation of 9-Acylanthracenes by Copper(II)–Peroxydisulfate[1]

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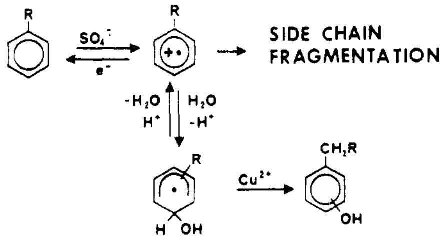
Received February 11, 1985

The Cu^{2+}–$S_2O_8^{2-}$ oxidations of 9-acylanthracenes (**1**) and 9-acyl-10-methylanthracenes (**10**) having formyl (**a**), acetyl (**b**), or benzoyl (**c**) groups were studied in refluxing acidic acetonitrile–water. Radical cations **1a–c**, **10a**, and **10c** reacted with water to produce 10-hydroxyl adduct radicals which were oxidized by Cu^{2+} to produce the corresponding hydroxylated products: 10-acylanthrols (**5**) from **1** and 9-acyl-10-methyl-9,10-dihydroxy-9,10-dihydroanthracenes (**15**) from **10**. Compounds **5** and **15** were unstable to reaction conditions and underwent subsequent reactions. Compound **5** underwent tautomerization competitive with oxidation to respectively produce 10-acyl-9-anthrones (**6**) and 10-acyl-10-hydroxy-9-anthrones (**8**). Compounds **6** and **8** were hydrolytically unstable, yielding respectively anthrone and 9,10-dihydroxyanthracene, at rates dependent on acidity (**6a**, **6b**, and **6c** exhibited 2.6, 44, and 45 min half-lives, respectively, in 0.1 M $HClO_4$). Compounds **15a** and **15c** solvolyzed in the acidic media to give 10-methylanthrol which was further oxidized to produce 10-methyl-10-hydroxy-9-anthrone (**12**). Partial dehydration of **12** produced 10-methylene-9-anthrone. Little product was formed by proton loss from the radical cations of **1a**, **10a**, and **10c**.

Aromatic hydroxylation and side chain oxidation reactions of aromatic compounds are known for peroxydisulfate oxidations.[2-8] These reactions are understood to derive from the reactions of initially formed radical cation intermediates. Attack by water and oxidation of the hydroxyl adduct radical by metal ion catalysts lead to the production of phenols (aromatic hydroxylation), whereas fragmentation of side chain functional groups to produce cations and radicals results in side chain oxidation products.

$$S_2O_8^{2-} \rightarrow 2SO_4^{-}\cdot \qquad (1)$$

$$Cu^+ + S_2O_8^{2-} \rightarrow Cu^{2+} + SO_4^{-}\cdot + SO_4^{2-} \qquad (2)$$



(3)

(4)

Most examples of these reactions have been provided by oxidation of monocyclic aromatic compounds with much emphasis on the study of functionalized alkyl side chain systems.[2-8] Few studies of $S_2O_8^{2-}$ oxidation of polycyclic aromatic compounds have been conducted. At least two studies of naphthalene oxidation have been reported,[9,10] but no oxidation of anthracenes are known. One reason for the limited study of polycyclic systems may be due to poor solubility in the aqueous medium normally employed for $S_2O_8^{2-}$ oxidations. Recent studies of peroxydisulfate oxidations of alkylaromatic compounds in

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(1) (a) This work supported by the Gas Research Institute, Basic Coal Science Program: Contract 5081-260-0536. (b) Portions of this work presented at the 34th Northwest Regional Meeting of the American Chemical Society (Pullman, WA, June 15, 1984) and at the 1984 International Chemical Congress of the Pacific Basin Societies (Honolulu, HI, Dec 16–21, 1984).

(2) Norman, R. O. C.; Storey, P. M. *J. Chem. Soc. B* **1970**, 1099.

(3) Snook, M. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 860.

(4) Walling, C.; Camaioni, D. M.; Kim, S. S. *J. Am. Chem. Soc.* **1978**, *100*, 4814. Walling, C.; Camaioni, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 1603.

(5) Walling, C.; Zhao, C.; El-Taliawi, G. M. *J. Org. Chem.* **1983**, *48*, 4910, 4914.

(6) Camaioni, D. M.; Franz, J. A. *J. Org. Chem.* **1984**, *49*, 1607.

(7) Walling, C.; El-Taliawi, G. M.; Amarnath, K. *J. Am. Chem. Soc.* **1984**, *106*, 7573–7578.

(8) Minisci, F.; Citterio, A.; Giordano, C. *Acc. Chem. Res.* **1983**, *16*, 27–32.

(9) Giordano, C.; Belli, A.; Citterio, A.; Minisci, F. *J. Org. Chem.* **1979**, *44*, 2314.

(10) Nyberg, K.; Wistrand, L. G. *J. Org. Chem.* **1978**, *43*, 2613.

0022-3263/85/1950-4456$01.50/0

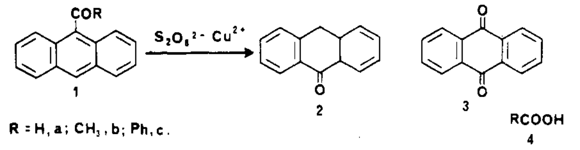
Table I. Oxidation of 9-Acylanthracenes by Cu^{2+}–$S_2O_8^{2-}$ in Acetonitrile–Water[a]

					products[b]						
expt	ACO–R	time, min	$HClO_4$, M	Cu^{2+}, M	anthrone	anthraquinone	acylanthrone	acylhydroxyanthrone	RCO_2H	fraction of deacylated products	% conversion[c]
1	CH_3	15		0.02	1.5	4	25	35	D[d]	0.084	107
2	CH_3	15		0.05	1.4	9	11	32	D	0.20	103
3	CH_3	15	0.10	0.05	2.5	9.9	7.8	21	D	0.30	82
4	CH_3	40		0.05	0.7	15	5	14	D	0.45	79
5	CH_3	40	0.10	0.05	2.4	22	3.2	0.9	D	0.86	73
6	Ph[e]	15		0.02	2.1	6.6	8.5	7	D	0.36	44
7	Ph	15		0.05	0.4	11	2.6	0.8	11	0.77	38
8	Ph	40		0.05	3.9	31	2.8	0.4	28	0.92	101
9	Ph	40	0.10	0.05	1.9	29	0.2	0	26	0.99	89
10	H	15	0.10	0.05	9.8	20			ND[f]		70
11	H	15		0.02	4.5	29	0.3		ND[f]		92

[a] 1.0 mmol of substrate, 0.010 M peroxydisulfate, and other reagents in 10 mL of 70% acetonitrile–water at reflux (83 °C) under argon; reaction extracts silylated for GC analyses. [b] Percent yield based on peroxydisulfate. [c] Percent peroxydisulfate converted to products assuming 1 equiv of peroxydisulfate to produce anthrone and acylanthrone, 2 equiv for acylhydroxyanthrone, and 3 equiv for anthraquinone. [d] Compound detected but not quantified. [e] Substrate only partly soluble in reaction medium. [f] Analyses for formic acid not conducted.

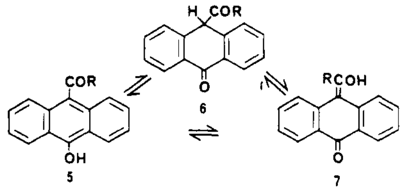
acetonitrile or acetic acid alone or as cosolvents with water have now demonstrated that the oxidation system can be successfully applied to oxidize substrates of low water solubility.[5-7] Therefore, we are conducting studies of the oxidation of substituted polycyclic aromatic systems in order to determine the relative importance and controlling factors of aromatic hydroxylation and side chain oxidation in these systems.[1] This information will provide a useful basis of knowledge for understanding the radical cation mediated oxidations of more complex aromatic materials. The metabolic chemistry of polycyclic aromatic compounds and coal conversion chemistry are just two diverse areas that stand to benefit from this work.

As part of a survey of the Cu^{2+}–$S_2O_8^{2-}$ oxidation of 9-substituted anthracenes, the oxidation of 9-anthracenecarboxaldehyde (**1a**) was conducted and found to yield mainly anthrone and anthraquinone with little anthroic acid being produced. This result contrasts with its monocyclic analogue, benzaldehyde, which was oxidized to benzoic acid.[11] Acetyl- and benzoylanthracenes (**1b**, **1c**) also were deacylated, producing the same products along with acetic and benzoic acids, respectively.



(5)

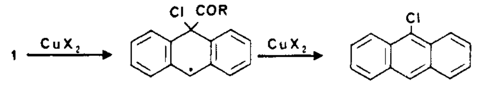
If the aromatic hydroxylation reaction were operable for these systems then formyl- and acylanthrols (**5a**–**5c**) would be initial products. Observations in the literature show that these compounds may exist with other more stable tautomeric forms (**6a**–**6c**, **7a**) and that they hydrolyze to anthrone and carboxylic acids.[12-14]



(6)

$$5,\ 6 \text{ or } 7 + H_2O \xrightarrow{H^+} 2 + 4 \qquad (7)$$

Thus, deacylated products may be consistent with an aromatic hydroxylation pathway. On the other hand, deacylation reactions may occur via other pathways or intermediates not leading to initial formation of acylanthrols. For example, heterogeneous oxidation of acylanthracenes by copper(II) halides reportedly results in deacylation via the intermediate formation of 9-Cl adduct radicals.[15]



(8)

To determine the reaction sequences operating in the oxidations, detailed product studies and control reactions were conducted. This paper reports our findings and conclusions.

Results

9-Acylanthracenes. Oxidations of 9-acylanthracenes by Cu^{2+}–$S_2O_8^{2-}$ conducted in refluxing acidic acetonitrile–water led to the production of acylated and deacylated products: 10-acyl-9-anthrones (**6**), 10-acyl-10-hydroxy-9-anthrones (**8**), anthrone (**2**), anthraquinone (**3**), and carboxylic acids (**4**). Table I reports the results for the oxidations of formyl-, acetyl-, and benzoyl-substituted anthracenes (**1a**–**1c**). Although total yields based on $S_2O_8^{2-}$ were variable,[16] trends in the data are discernible on the basis of comparisons of the fractions of deacylated products (Table I). The distribution of products for the reactions of acetylanthracene (**1b**) showed a marked dependence on reaction time, acidity, and Cu(II) concentrations. Increased reaction times or added acid yielded higher fractions of deacylated products (compare experiment 4 to experiment 2 and experiment 2 to experiment 1). In-

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(11) Benzaldehyde, *p*-tolualdehyde, and *p*-chlorobenzaldehyde oxidized according to the conditions of Table I, experiment 3, all yielded the corresponding benzoic acids.

(12) Nédélec, L.; Rigaudy, J. *Bull. Soc. Chem. Fr.* **1960**, 1204–1216. Structure 7 is only important when R = H.

(13) Wolfbeis, O. S.; Junek, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1979, *34B*, 283–289.

(14) Krollpfeiffer, F.; Branscheid, F.; Thorn, F.; Schneider, K. J. L. *Ann.* **1928**, *462*, 46–72.

(15) Nonhebel, D. C.; Russell, J. A. *Tetrahedron* **1970**, *26*, 2781–2786.

(16) Possible reasons for variation in the conversion yields are many. The oxidation is a chain reaction, and rates of reaction may differ with reaction conditions. This might explain the low conversions for 15-min reactions of the partly soluble benzoylanthracene. Longer reaction times gave better yields. The products may undergo further reaction to produce undetected products. For instance, dimeric or coupling products would not have been detected by our GC analyses. Response factors were estimated and the discrepancies may arise from cumulative errors (see ref 18).

Table II. Pseudo-First-Order Rate Constants for Reactions of Anthrones with Acid and Cu^{2+} in 70% Acetonitrile-Water (83 °C)

expt	substrate	$HClO_4$, M	Cu^{2+}, M	$10^{-2}k$, min^{-1}	t, min
1	formylanthrone	0.1		26.6 ± 0.9	2.6
2	acetylanthrone	0.1		1.56 ± 0.08	44.4
3	acetylanthrone	0.2		2.94 ± 0.02	23.4
4	acetylanthrone[a]	0.1	0.05	1.73 ± 0.09	40.1
5	benzoylanthrone	0.1		1.54 ± 0.03	45.0
6	anthrone[b]	0.1	0.05	8.67 ± 0.23	8.0
7	anthrone[b]	0.05	0.05	4.42 ± 0.21	15.7

[a] No acetylhydroxyanthrone was produced. [b] 9,10-Dihydroxyanthracene initially formed and then disappeared, producing anthraquinone.

creasing Cu(II) above 0.02 M also increased deacylation. Small yields (<2%) of 9-acetoxy-10-anthrol (**9b**) accompanied the production of acetylanthrones.[17] Reactions of benzoylanthracene (**1c**) reproduced these trends, although fractions of deacylated products were generally greater. This observation may be an artifact due to low conversions to products for 15-min reactions, possibly caused by the poorer solubility of benzoylanthracene. As observed for acetylanthracene, short reaction times favored benzoylanthrones. Better recoveries were observed for long reaction times where anthraquinone was the major product.[18] Acetic and benzoic acids (**4b** and **4c**) were detected from the respective acetyl- and benzoyl anthracenes. Yields of acetic acid were not quantified; however, benzoic acid yields were in all cases close to the sum of the yields of anthrone plus anthraquinone. For the anthracenecarboxaldehyde (**1a**), mainly anthrone and anthraquinone were produced. Trace quantities of a compound having a GC–MS spectrum consistent with the 9-formyl-10-anthrone (**6a**) structure were detected. That little formylanthrone (**6a**) and formylhydroxyanthrone (**8a**) were detected in the oxidations is apparently due to the relatively fast deformylation reactions of these compounds (see below).

Control experiments showed that acylanthracenes (**1**) were stable to the reaction conditions in the absence of $S_2O_8^{2-}$; however, anthrone (**2**) and acylanthrones (**6**) were observed to be labile (see Table II). The acylanthrones (**6a–6c**) reacted in acidic acetonitrile–water to form anthrone with rates of disappearance that were first order in acidity and concentration of acylanthrones. The 9-formylanthrone hydrolyzed at the fastest rate ($t_{1/2}$ = 2.6 min in 0.1 M $HClO_4$), while the acetyl- and benzoylanthrones hydrolyzed more slowly ($t_{1/2}$ = 45 min in 0.1 $HClO_4$). The acylhydroxyanthrones, though not separately studied, were similarly unstable to acidic conditions, as their yields were decreased in the longer reaction time experiments (Table I).

Scheme I

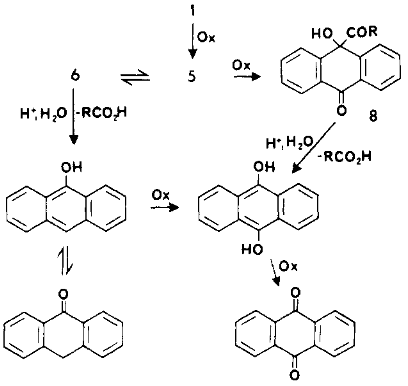


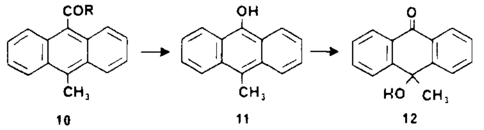
Table III. Oxidation of 9-Acyl-10-methylanthracenes[a]

			products[b]		
expt	ArCO-R	$HClO_4$, M	methylhydroxyanthrone	methylene-anthrone	carboxylic acid
1	H		43.7	4.7	ND[c]
2	H	0.10	34.1	5.5	ND[c]
3	Ph		43.4	7.9	47.5
4	Ph	0.10	30.4	8	46.7

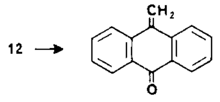
[a] Reaction conditions similar to those of Table I. [b] Yields based on $S_2O_8^{2-}$. [c] Analysis for formic acid was not conducted.

These control experiments together with the results of Table I are consistent with the reaction sequence depicted in Scheme I where acylanthrols are initial products of the oxidation of acylanthracenes. The acylanthrols undergo tautomerization and oxidation reactions to respectively produce acylanthrones (**6**) and acylhydroxyanthrones (**8**). These compounds are then subsequently deacylated. The resulting anthrone and 9,10-dihydroxyanthracene are oxidized to anthraquinone (Table II, experiments 6 and 7).

9-Acyl-10-methylanthracenes (10a and 10c). A study of these compounds was initiated to determine if deacylation might occur when the 10-position is substituted with a methyl group. For both systems, deacylated products, 10-hydroxy-10-methyl-9-anthrone (**12**) and 10-methylene-9-anthrone (**13**), are formed (see Table III). Control experiments showed that the methyleneanthrone was produced by dehydration of the 10-hydroxy-10-methyl-9-anthrone which was likely formed by the oxidation of methylanthrol (**11**).[19]



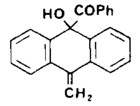
(9)



13

(10)

For the benzoylmethylanthracene (**10c**), benzoic acid was observed to be formed in yields comparable with the deacylated product. Silylation of the reaction mixture enabled the detection of a product identified by GC–MS as the trimethylsilyl ether of **14c**.



14c

Discussion

In a previous study,[6] radical cations of diarylethanes were demonstrated to be formed by $S_2O_8^{2-}$ oxidations in

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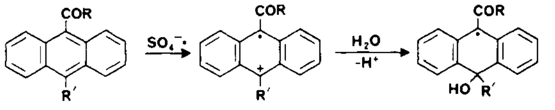
[17] Product identified by GC–MS of silylated reaction extract.

[18] Since response factors were estimated, actual yields of benzoylanthrones **6c** and **8c** may have been higher for short reaction times, because the trimethylsilyl derivatives were long retained by the GC column, eluting as broad peaks during the 300 °C isothermal portion of the chromatogram, whereas the internal standard (phenanthrene) eluted at 240 °C as a narrow peak. Lower precision and systematic errors are to be expected for this situation.

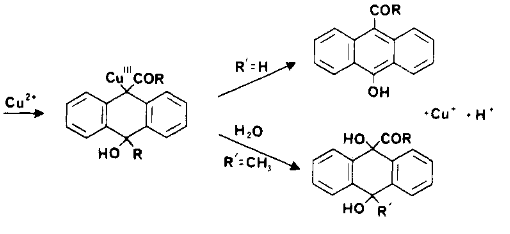
[19] 10-Hydroxy-10-methyl-9-anthrone is the major product of the oxidation of 9-methylanthracene by Cu^{2+}–$S_2O_8^{2-}$ in acetonitrile–water (to be published).

acetonitrile–water. Thus it is logical to assume that radical cations of acylanthracenes were formed in these oxidations as well. The results of this study then are most consistent with deacylation occurring subsequent to the aromatic hydroxylation reaction. The observation of acylanthrones that are tautomers of acylanthrols favors this conclusion. Attack of water on the radical cations at the 10-position probably predominates since substituent electronic effects favor greater charge density at the 10-position.



(11)

The follow-up reaction of the hydroxyl adducts with Cu(II) ions likely occurs to produce organocopper(III) species which decompose by elimination (eq 12) and ligand transfer (eq 13) reactions[7,20,21] to give acylanthrols and 9,10-dihydroxy-9,10-dihydroanthracenes (15). For the acylanthracenes (R′ = H), the elimination path forming acylanthrols appears dominant since acylanthrone products were observed.[22] For the 9-acyl-10-methylanthracenes (R′ = CH_3), the ligand transfer path forming 15 is consistent with the production of 10-methyl-9-anthrol (11) and compound 14c. Solvolysis of 15 would produce the carbonium ion 16 which can eliminate the acylium ion or a methyl proton.



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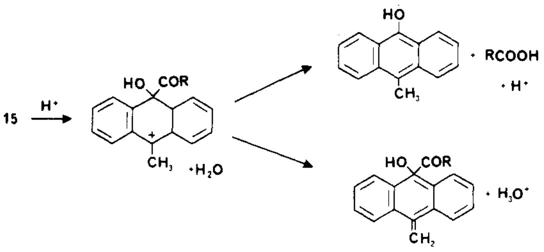
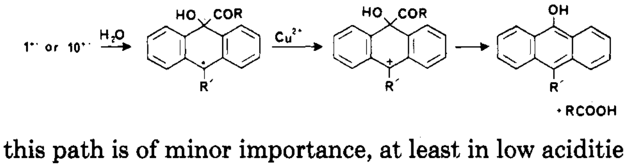


(14)

(15)

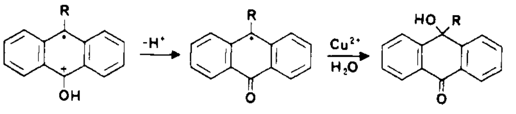
Attack of water at the 9-position (carbon attached to the acyl group) of the radical cations can give deacylated products directly, but this pathway is probably of lesser importance. The results on acetylanthracene show that this path is of minor importance, at least in low acidities, since only small fractions of deacylated products were produced (experiment 1, Table I). Nonetheless, the production of some portion of the deacylated products by this route cannot be totally ruled out.



(16)

The acylanthrols from 1 and methylanthrols from 10 produced via reactions 11–15 are labile and undergo subsequent reactions. Tautomerization of acylanthrols to acylanthrones occurs rapidly; although the reaction is reversible so that subsequent oxidation to acylhydroxyanthrones and deacylation of acylanthrone consumes these initial products. The subsequent oxidations of acylanthrols and methylanthrols to the corresponding hydroxy-anthrones are probably radical cation mediated. The oxidations likely occur by deprotonation of the anthrol radical cations which are formed by electron-exchange reactions[23] between reactant radical cations and the anthrols.[24]

$$\mathrm{ArH^{+\cdot} + ArOH \rightarrow ArH + ArOH^{+\cdot}} \qquad (17)$$



(18)

Electron-exchange reactions are now well documented in radical cation mediated reactions[23] and have been invoked to explain selectivities observed in $S_2O_8^{2-}$ oxidations.[5-8] The anthrol, 10-methylanthrol and 9,10-dihydroxyanthracene would also have been oxidized by Cu(II), since we observed anthrone to be oxidized by Cu(II) to anthraquinone in acidic acetonitrile–water. The oxidation of acylanthrols by Cu(II) is apparently noncompetitive with deacylation, for acetylanthrone was not oxidized to acetylhydroxyanthrone by Cu(II) in experiment 4 of Table II.

One noteworthy observation is the finding that when methyl or formyl groups were present in the 9- or 10-positions, little proton loss from the radical cations occured. These results contrast with those for the analogous monocyclic radical cations where the proton loss reaction occurred in preference to the aromatic hydroxylation reaction.[6,11] Similar differences for mono- and polycyclic alkylaromatic compounds have been noted in anodic oxidations.[25] That little proton loss occurred in these anthracene systems suggests that perhaps proton loss is much slower and/or that hydration is less reversible than for the monocyclic systems. In a separate paper on the oxidation of alkylanthracenes by Cu(II)–$S_2O_8^{2-}$ we will report experiments that elaborate on this supposition.[26]

$$\mathrm{[ArCH_3]^{+\cdot} \rightarrow Ar\dot{C}H_2 + H^+} \qquad (19)$$

$$\mathrm{[ArCH{=}O]^{+\cdot} \rightarrow Ar\dot{C}{=}O + H^+} \qquad (20)$$

Summary

Our results seem most consistent with aromatic hydroxylation of acylanthracenes and 9-acyl-10-methylanthracenes having occurred to produce acylanthrols and 9,10-dihydroxy-9,10-dihydroanthracenes which were deacylated via subsequent acid-catalyzed heterolytic reactions. In contrast to monocyclic aromatic radical cations, proton

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[20] Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

[21] Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, pp 595–623.

[22] 9,10-Dihydroxy-9-acyl-9,10-dihydroanthracenes would likely undergo deacylation instead of dehydration. The acid-catalyzed dehydration of 9,10-dihydro-9-anthrols occurs via the E1 mechanism (Miller, B.; Marhevka, V. C. *Tetrahedron Lett.* **1981**, *22*, 895).

[23] (a) Bard, A. J.; Ledwith, A.; Shine, H. J. In "Advances in Physical Organic Chemistry"; Gold, V., Ed.; Academic Press: New York, 1976; Vol. 13, pp 218–222. (b) Hammerlich, O.; Parker, V. D. "Advances in Physical Organic Chemistry"; Gold, V., Ed.; Academic Press: New ork, 1984; Vol. 20, pp 99–108. (c) Yoshida, K. "Electrooxidation in Organic Chemistry: The Role of Cation Radicals as Synthetic Intermediates"; Wiley: New York, 1984; pp 73–76.

[24] The sulfate radical anions are not expected to be the primary oxidant of anthrols since the acylanthracenes were usually present in >10-fold excess and rates of attack of $SO_4^{-\cdot}$ on the compounds should be near the diffusion limit. See: Neta, P.; Madhaven, V.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 163.

[25] Reference 23c, pp 162–165, 200, 201.

[26] Camaioni, D. M.; Alnajjar, M. S.; Deardurff, L. A., manuscript in preparation.

Table IV. GC-MS (EI) Spectral Data

compound	*m/e* (relative intensity)
anthrone	195 (15), 194 (100, M^+), 193 (13), 166 (13), 165 (77), 164 (11), 163 (11), 82 (26)
9-anthrol, trimethylsilyl ether	267 (22), 266 (100, M^+), 221 (4), 193 (4), 177 (3), 165 (6), 151 (16), 73 (92)
9,10-dihydroxyanthracene, bis(trimethylsilyl) ether	356 (12), 355 (32), 354 (100, M^+), 339 (6), 265 (6), 250 (3), 235 (6), 73 (58)
9,10-anthraquinone	209 (15), 208 (100, M^+), 180 (85), 152 (67), 151 (39), 76 (67), 75 (27), 63 (18), 50 (20)
9-anthracenecarboxaldehyde	207 (16), 206 (100, M^+), 205 (61), 178 (87), 177 (48), 176 (59), 151 (20), 150 (16), 89 (31)
10-methyl-9-anthracenecarboxaldehyde	221 (16), 220 (100, M^+), 219 (56), 205 (45), 192 (31), 191 (68), 190 (28), 189 (60), 165 (21), 95 (25), 83 (15)
10-formylanthrone[a]	226 (26, M^+), 194 (100), 193 (31), 165 (79), 164 (13), 163 (16), 82 (25)
9-acetylanthracene	221 (9), 220 (54, M^+), 206 (16), 205 (100), 177 (77), 176 (69), 151 (22), 150 (20), 88 (29), 75 (15), 43 (14)
10-acetylanthrone	236 (0.2, M^+), 195 (15), 194 (100), 193 (19), 165 (29), 164 (8), 163 (9), 43 (5)
10-hydroxy-10-acetylanthrone[a]	252 (0.0, M^+), 211 (14), 210 (100), 209 (76), 181 (15), 152 (39), 105 (10), 77 (12)
10-hydroxy-10-acetylanthrone trimethylsilyl ether	324 (0.0, M^+), 309 (6), 283 (11), 282 (55), 281 (70), 235 (8), 74 (8), 73 (100)
10-acetyl-9-anthrol, trimethylsilyl ether[a]	309 (15), 308 (58, M^+), 294 (25), 293 (100), 235 (7), 220 (6), 73 (49)
10-acetoxy-9-anthrol, trimethylsilyl ether	324 (9, M^+), 309 (2), 284 (6), 283 (24), 282 (100), 235 (7), 73 (47)
10-benzoylanthrone	298 (3, M^+), 193 (7), 165 (7), 164 (3), 163 (4), 106 (8), 105 (100), 77 (32)
10-benzoyl-9-anthrol, trimethylsilyl ether	371 (24), 370 (71, M^+), 294 (10), 293 (38), 105 (21), 77 (18), 73 (100)
10-hydroxy-10-benzoylanthrone, trimethylsilyl ether[a]	387 (5), 386 (14, M^+), 282 (17), 281 (67), 105 (49), 77 (18), 73 (100)
10-methyl-10-hydroxyanthrone	224 (0.5, M^+), 210 (15), 209 (100), 207 (1), 152 (19), 151 (6), 77 (12), 76 (13)
10-methyleneanthrone	207 (17), 206 (100, M^+), 178 (65), 177 (17), 176 (28), 152 (14), 89 (22), 88 (23), 76 (35), 75 (12)
10-hydroxy-10-benzoyl-9-methylene (**14c**)[a]	385 (14), 384 (49, M^+), 355 (16), 279 (29), 267 (22), 265 (21), 252 (19), 189 (30), 105 (27), 77 (24), 73 (100)

[a] Identification not corroborated with authentic sample.

loss from methyl or formyl groups was not a competing reaction path for these anthracene radical cations.

Experimental Section

General. Proton nuclear magnetic resonance spectra were obtained with a Varian FT-80 spectrometer. Chemical shifts (δ) are reported in parts per million downfield from internal tetramethylsilane followed in parentheses by the multiplicity and number of protons. Infrared spectra were recorded on a Perkin-Elmer Model 283 IR spectrophotometer. Carbon-hydrogen analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN.

Analytical gas chromatographic (GC) analyses were performed on a Hewlett-Packard Model HP-5880A instrument equipped with capillary inlet system, flame ionization detector, Level 4 microprocessor and 30 m × 0.32 mm i.d. (J&W Scientific) DB-5 capillary column (1-μm film thickness). The direct injection mode and temperature programming from 100–300 °C were routinely employed with injection port and detector maintained at temperatures of 300 and 315 °C, respectively. Gas chromatographic–mass spectrometric (GC–MS) analyses were carried out on a Hewlett-Packard Model 5985 system.

All reactions with ammonium peroxydisulfate and cupric perchlorate were conducted under argon. Reagents were obtained from commercial sources or were synthesized and purified as required. Stock solutions of ammonium peroxydisulfate were used or discarded within 5 days after preparation.

9-Benzoylanthracene (1c). This ketone was prepared according to Bachman and Barton by the addition of anthracene to a mixture of benzoyl chloride/aluminum chloride[27] in CS_2. Recrystallization from benzene/hexane gave yellow crystals: mp 148–150 °C; ^1H NMR ($CDCl_3$) 7.23–8.0 (br m, 13 H), 8.55 (s, 1 H).

9-Anthrol, Trimethylsilyl Ether. To a solution of anthrone (20.0 g, 103 mmol) in 300 mL of pyridine/CH_2Cl_2 (50/50 v/v) was added 12.5 g (123.5 mmol) of triethylamine under argon. To the yellow solution was added 18 g (165.7 mmol) of chlorotrimethylsilane and the mixture was stirred for 2 h at room temperature. The reaction mixture was hydrolyzed by dilute hydrochloric acid and extracted with CH_2Cl_2. The extracts were combined, dried over $MgSO_4$, and concentrated. The residue was recrystallized from hexane to give 36% yield of the trimethylsilyl ether contaminated with small amounts of anthrone and anthraquinone: mp 101–103 °C; MS, see Table IV.

10-Formylanthrone (6a). The procedure described by Nêdêlec and Rigaudy[12] was used: mp 170–175 °C, turning red and evolving gas (203 °C reported). The material was approximately 80% pure by GC. Anthrone and anthraquinone were the main impurities. Silylation produced two products in a 10/1 ratio by GC. The larger one eluted first on the DB-5 column. The IR spectrum in $CHCl_3$ [1725 (C=O, aliphatic aldehyde), 1668 (C=O, aromatic ketone), 1605 cm^{-1} (aromatic C=C)] was identical with that published by Nêdêlec and Rigaudy, and the NMR in $CHCl_3$ was consistent with the formylanthrone structure: ^1H NMR ($CDCl_3$) 9.14 (d, 1 H, J = 4 Hz), 8.39 (m, 2 H), 7.62 (m, 6 H), 5.08 (d, 1 H, J = 4 Hz).

10-Acetylanthrone (6b). The trimethylsilyl ether of 9-anthrol (2.0 g, 7.5 mmol) and acetyl chloride (0.6 g, 7.6 mmol) were mixed in carbon disulfide (40 mL) under argon, and the resulting suspension was stirred while cooling to 0–5 °C with an ice bath. Aluminum chloride (3 g, 22.5 mmol) was then added and the reaction mixture was stirred for 45 min. The dark brown reaction mixture was filtered, and the black precipitate was stirred in dilute hydrochloric acid. Yellow solid 10-acetylanthrone was collected, air-dried, and purified by HPLC: mp 87–89 °C; ^1H NMR ($CDCl_3$) 1.61 (s, 3 H), 5.19 (s, 1 H), 7.45–7.68 (m, 6 H), 8.35–8.45 (m, 2 H); MS, see Table IV; IR ($CHCl_3$) 3120, 1765, 1720, 1655, 1510 cm^{-1}.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.60; H, 5.26.

10-Benzoylanthrone (6c). The trimethylsilyl ether of 9-anthrol was added to a mixture of benzoyl chloride/aluminum chloride in carbon disulfide. The solution was filtered, and the black precipitate was stirred in dilute hydrochloric acid to give a yellow solid. Repeated recrystallization from benzene/hexane gave 10-benzoylanthrone (82% pure) contaminated with anthrone and anthraquinone. The compound was purified by forward-phase high-performance liquid chromatography (HPLC) on silica, using 20% *tert*-butyl methyl ether/hexane mobile phase: mp 145 °C dec; ^1H NMR ($CDCl_3$) 6.02 (s, 1 H), 7.25–7.57 (m, 11 H), 8.25–8.43 (m, 2 H); MS, see Table IV.

Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.24; H, 4.84.

10-Methyl-9-benzoylanthracene (12c). The method for preparing benzoylanthracene was followed using 9-methyl-

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(27) Bachmann, W. E.; Sister Barton, M. X. *J. Org. Chem.* **1938**, *3*, 300.

anthracene. Recrystallization from benzene/hexane mixture produced yellow crystals: mp 180–182 °C; ^{1}H NMR ($CDCl_3$) 3.15 (s, 3 H), 7.23–7.77 (m, 7 H), 7.82–7.87 (m, 4 H), 8.31–8.40 (m, 2 H); MS, see Table IV.

10-Hydroxy-10-methyl-9-anthrone (13). The procedure of Julian, Cole, and Diemer was used.[28] A solution of methylmagnesium iodide in ether (100 mmol) was added to a suspension of anthraquinone (200 mmol) in 300 mL of benzene under argon. After the workup, yellow crystals were obtained upon recrystallization from benzene/hexane: mp 159–161 °C; ^{1}H NMR ($CDCl_3$) 1.66 (s, 3 H), 2.72 (s, 1 H), 7.2–8.2 (m, 8 H); MS, see Table IV.

10-Methyleneanthrone (14). This compound prepared by stirring 9-hydroxy-9-methyl-10-anthrone in a boiling mixture of oxalic and acetic acids for 45 s:[29] mp 147–149 °C; ^{1}H NMR ($CDCl_3$) 6.33 (s, 2 H), 7.25–7.67 (m, 4 H), 7.95–7.99 (m, 2 H), 8.05–8.41 (m, 2 H); MS, see Table IV.

9,10-Dihydroxyanthracene. This compound was prepared according to the method of Dimmel et al.:[30] MS of the bis(trimethylsilyl) ether, see Table IV.

General Procedure for Oxidations. In a typical reaction appropriate amounts of the acylanthracene and perchloric acid were added to an acetonitrile/water (70/30) mixture to form solutions of desired concentrations. After refluxing for 10 min under argon, stock solutions of copper(II) perchlorate and peroxydisulfate were added respectively to the rapidly stirred reactants. At the chosen time, reactions were quenched with water, internal standard was added, and the mixtures were extracted with three 15-mL volumes of CH_2Cl_2. The extracts were combined and dried over $MgSO_4$. When silylation was employed to derivatize anthrols and hydroxyanthrones, 3–5 drops of the above solutions were mixed with 1 drop of pyridine followed by the addition of 100 μL of *N,O*-bis(trimethylsilyl)acetamide (BSA). Analyses of the samples were accomplished within 1 h of silylation as storage for long periods of time caused decomposition.

Kinetic Determinations. Reactions (Table II) were initiated by addition of a 0.2-mL aliquot of a solution, 0.02–0.05 M acylanthrone or anthrone, and 0.05 M phenanthrene to a 20-mL volume of reactants at specific concentrations (Table III) and at reflux under Ar. At periodic intervals 1-mL aliquots of the reacting solution were withdrawn, diluted with 2 mL of water and shaken with 2–5-mL portions of methylene chloride. The extracts were dried over anhydrous sodium sulfate and analyzed by GC. A natural log plot of the area ratios of reactants to phenanthrene vs. time yielded pseudo-first-order rate constants for the reactions. The decrease in reactant was usually followed for two or more half-lives.

Product Identifications and Analyses. Products were usually identified by matching capillary GC retention times and capillary GC–MS spectra with authentic standards. For instances when authentic standards could not be obtained identifications were based on interpretations of the GC–MS spectra (see Table IV). GC response factors to phenanthrene internal standard were determined for anthracene, anthrone, anthraquinone, acetylanthracene, benzoylanthracene, anthracenecarboxaldehyde, 10-hydroxy-10-methylanthrone, and the trimethylsilyl ether of anthrol. Response factors for the other products were estimated from the response factors of these compounds.

Registry No. **1a**, 642-31-9; **1b**, 784-04-3; **1c**, 1564-53-0; **2**, 90-44-8; **3**, 84-65-1; **6** (R = CH_3), 98540-92-2; **6** (R = Ph), 53010-87-0; **6a**, 85090-11-5; **8** (R = CH_3), 98540-93-3; **8** (R = Ph), 98540-94-4; **10** (R = H), 7072-00-6; **10** (R = Ph), 24451-23-8; **12**, 17104-31-3; **13**, 4159-04-0; **14c** (trimethylsilyl deriv), 98540-99-9; PhCOCl, 98-88-4; CH_3CO_2H, 64-19-7; $PhCO_2H$, 65-85-0; $NH_3\cdot(OSO_2OH)_2$, 7727-54-0; anthracene, 120-12-7; 9-anthrol trimethylsilyl ether, 28871-54-7; 9-methylanthracene, 779-02-2; 9,10-dihydroxyanthracene bis(trimethylsilyl ether), 28871-52-5; 10-hydroxy-10-acetyl-9-anthrone trimethylsilyl ether, 98540-95-5; 10-acetoxy-9-anthrol trimethylsilyl ether, 98540-96-6; 10-benzoyl-9-anthrol trimethylsilyl ether, 98540-97-7; 10-hydroxy-10-benzoylanthrone trimethylsilyl ether, 98540-98-8.

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[28] Julian, P. L.; Cole, W.; Diemer, G. *J. Am. Chem. Soc.* **1945**, *67*, 1721. Bhattacharya, A. K.; Miller, B. *J. Org. Chem.* **1983**, *48*, 2412.

[29] Heymann, H.; Trowbridge, L. *J. Am. Chem. Soc.* **1950**, *72*, 84.

[30] Dimmel, D. R.; Shepard, D. *J. Org. Chem.* **1982**, *47*, 22.

Alkylation of Ambident Anions Derived from 2-Aryl-1,3,4-oxadiazol-5(4*H*)-ones. 1. Crystal Structures of the Silver and Rubidium Salts of 2-Phenyl-1,3,4-oxadiazol-5(4*H*)-one

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The analyses of crystal structures of two 2-phenyl-1,3,4-oxadiazol-5(4*H*)-one salts (Rb^+ and Ag^+) indicate an excellent agreement between the steric influence of the cation and the chemical behavior of the salts upon heterogeneous alkylation. This provides the first experimental structural evidence of a shielding effect induced by the cation over the possible alkylation sites of the anion. This effect controls the regioselectivity of the O- vs. N-alkylation and explains the different behavior of silver salt vs. alkaline salts under heterogeneous conditions.

The alkylation of anionic species derived from amide salts (termed "ambident anions" thereafter[1]) are known to follow different pathways depending on now quite well-defined factors.[2] Two of them are known to play a key role in the reaction: (1) the nature of the counterion and (2) the homogeneous or heterogeneous state of the reaction, in connection with the solvent used.

These factors have been widely investigated in the case of alkylation of 2-pyridone,[3] 2- and 4-hydroxypyrimidine,[4] and formanilide[5] salts. All these salts are true ambident anions with two possible alkylation sites. In the present

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[1] Kornblum, N.; Smiley, R. A.; Blackwood, R. K.; Iffland, D. C. *J. Am. Chem. Soc.* **1955**, *77*, 6269–6280.

[2] (a) Gompper, R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 560–570. (b) Gompper, R.; Wagner, H. U. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 321–331. (c) LeNoble, W. J. *Synthesis* **1970**, 1–6.

[3] (a) Hopkins, G. C.; Jonak, J. P.; Minnemeyer, H. J.; Tieckelmann, H. *J. Org. Chem.* **1967**, *32*, 4040–4044. (b) Chung, N. M.; Tieckelmann, H. *J. Org. Chem.* **1970**, *35*, 2517–2520.

[4] (a) Hopkins, G. C.; Jonak, J. P.; Tieckelmann, H.; Minnemeyer, H. J. *J. Org. Chem.* **1966**, *31*, 3969–3973. (b) Jonak, J. P.; Hopkins, G. C.; Minnemeyer, H. J.; Tieckelmann, H. *J. Org. Chem.* **1970**, *35*, 2512–2516.