to the reactants for the aromatic amine systems by charge delocalization. In comparison of aniline with NMA, the higher value of k_{-1} for the latter is due to the relief of steric compression in PH on reversion to the reactants. In the second stage, deprotonation of PH by an aromatic amine is strongly disfavored compared to an aliphatic amine due to the loss in resonance stabilization in the resulting conjugate acid.

For aliphatic amine systems in Me_2SO, a change in mechanism results, from formation of PH being rate-determining to its deprotonation being rate-limiting, by a change in the basicity of the reacting amine, from less to more strongly basic; for the weaker bases the solvent-catalyzed reaction becomes the more favorable pathway.

For a weakly basic nucleophile such as TFE a change in mechanism also occurs on switching from Me_2SO to the much less basic acetonitrile, from an uncatalyzed pathway (formation of PH rate-limiting) to a catalyzed pathway (deprotonation of PH rate-limiting).

Experimental Section

Materials. TNB was recrystallized from ethanol and dried in vacuo, mp 123 °C. NMA was purified via the *N*-nitroso derivative,[21] and the resulting amine was fractionated three times under reduced pressure and stored under nitrogen in the dark. A solution of DABCO in benzene was refluxed over potassium hydroxide pellets, the solvent was distilled off, and the DABCO was recrystallized twice from a mixture of benzene–hexane (1:1 v/v) and dried in vacuo. The resulting material was sublimed to yield white crystals, mp 157 °C. Et_4NCl was recrystallized twice from a mixture of benzene–acetonitrile (1:1 v/v) and dried in vacuo. Me_2SO (Fisher Certified Reagent) was distilled from barium oxide under nitrogen and stored in the dark under nitrogen. All solutions were made up in a drybox and protected from light.

Kinetic Measurements. The reactions were followed spectrophotometrically by monitoring the increase in absorbance due to the product, $TNB{\cdot}NMePh^-$, as a function of time on a Beckman Acta IV spectrophotometer at 442 nm, the λ_{max} of the σ-complex. Solutions of DABCO in Me_2SO at a given electrolyte concentration were introduced into a 1-cm cuvette placed in the cell compartment of the spectrophotometer thermostated at 25.0 ± 0.2 °C. Reaction was initiated by injecting 5 μL of a stock solution of TNB in Me_2SO (6.01×10^{-2} M) into 3 mL of the DABCO solution, and the cuvette was shaken to ensure homogeneity. Data were collected at 442 nm. The pseudo-first-order rate constants were calculated by application of eq 5. The plot for a typical run in which $[TNB]_0 = 1.00 \times 10^{-4}$ M, $[NMA]_0 = 5.09 \times 10^{-3}$ M, $[DABCO] = 0.100$ M, and $[Et_4NCl] = 0.101$ M is given in Figure 1.

The molar extinction coefficient for the $TNB{\cdot}NMePh^-$ complex was obtained by increasing the concentrations of NMA and DABCO until conversion of TNB to the σ-complex was complete. The value $\epsilon = 3.04 \times 10^4\ M^{-1}\ cm^{-1}$ at λ_{max} 442 nm obtained in this study is in good agreement with a previously reported value.[4a]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for a grant in aid of this research (E.B.) and for a CIDA/NSERC Fellowship (I.O.). Discussions with Prof. J. Hirst are also acknowledged.

Registry No. TNB, 99-35-4; NMA, 100-61-8; DABCO, 280-57-9.

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Products and Mechanism of the Oxidation of 9-Methylanthracene by Peroxydisulfate. Proton Loss and Nucleophile Addition Reactions of the 9-Methylanthracene Radical Cation[1]

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Received March 25, 1986

The $Cu(II)-S_2O_8^{2-}$ oxidation of 9-methylanthracene (**1**) was studied in refluxing CH_3CN/acetic acid and aqueous CH_3CN. Side-chain and nuclear oxidation products and the dimeric compound lepidopterene (**7**) were produced. The lepidopterene was determined to be formed by the reaction of intermediate anthracenylmethyl cation with **1**. In CH_3CN/H_2O nuclear oxidation products, 10-hydroxy-10-methyl-9-anthrone (**2**) and 10-methylene-9-anthrone (**3**) and dimer **7** were produced, with the nuclear products predominating. In CH_3CN/HOAc the dimer and side-chain substitution products, 1–OAc (**5a**) and 1–NHAc (**5c**), were predominant over the nuclear products, which consisted mainly of **3** and 10-acetoxy-9-methylanthracene (**4a**). A mechanism is proposed where the initially formed radical cation undergoes competing proton loss and reversible nucleophile addition reactions to form respectively the anthracenylmethyl radical and nucleophile adduct radicals. Oxidation of the radicals by Cu(II) or $S_2O_8^{2-}$ yield the corresponding cations that react to form the products **4**, **5**, and **7**. Compounds **2** and **3** form by subsequent oxidation of the nuclear oxidation product, 10-methyl-9-anthrol. The results suggest that nucleophile addition is faster than proton loss and that it is more reversible in CH_3CN/HOAc than in CH_3CN/H_2O.

Radical cations have come under intense study due to a growing realization that they are intermediates in many organic reactions.[2-4] Since the early 1970s the oxidations of aromatic substrates by peroxydisulfate have been understood to occur via radical-cation intermediates,[5-8] and the oxidations have proven useful for studying the reactions of aromatic radical cations in solution.[9-13] A large number of functionally substituted alkylbenzene com-

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[†] University of Washington—Northwest College and University Association for Science (NORCUS) Postdoctoral Research Associates.

[1] This work supported by the Gas Research Institute, Basic Coal Science Program, Contracts 5081-260-0536 and 5084-260-1087.

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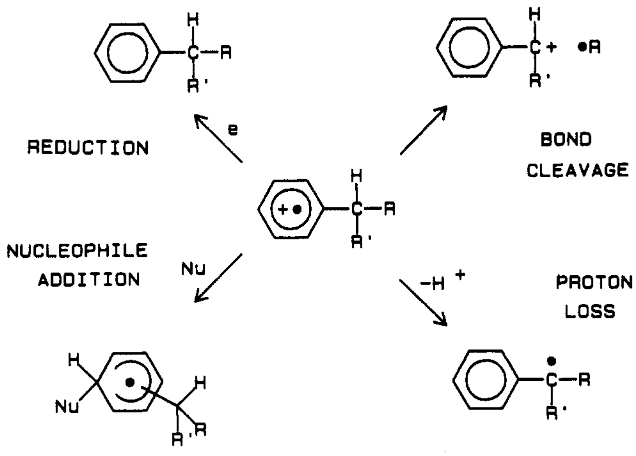
Table I. Low-Conversion Oxidation of 9-Methylanthracene in 0.03 M $Cu(ClO_4)_2$ in Aqueous CH_3CN at 83 °C[a] (Yields of Products[b] Based on Peroxydisulfate Used)

run	$[HClO_4]$	[NaOAc]	% CH_3CN	$[S_2O_8^{2-}]$	time, min	2	3	others
1			70		15	11	4	
2			70	0.01	15	36	12	
3			70	0.01	30	49	27	
4	0.1		70	0.01	40	30	16	
5[c]		0.15	70	0.01	30	5	4	**5a** (9), **4a** (1), **5b** (6), **6** (1)
6			95	0.01	15	12	20	
7	0.1		95	0.01	15	tr	16	

[a] 0.1 M methylanthracene. [b] **2**, 10-hydroxy-10-methyl-9-anthrone; **3**, 10-methylene-9-anthrone; 4a, 9-acetoxy-10-methylanthracene; **5a**, 9-anthracenylmethyl acetate; **5b**, 9-anthracenemethanol; **6**, 9-anthraldehyde. [c] 0.03 M copper(II) acetate.

Scheme I. Reactions of Alkyl Aromatic Radical Cations in Solution



pounds have now been oxidized. General structure/reactivity relationships are emerging,[7-12] and complex solvent dependencies have been noted.[9,11] Scheme I depicts the general types of reactions that are understood to occur for these radical cations.

Rather few studies of the oxidations of polycyclic aromatic compounds (PAC) by $S_2O_8^{2-}$ have been conducted such that the extrapolation of structure/reactivity relationships to PAC systems is uncertain. Therefore, we became interested in studying the reactions of polycyclic aromatic radical cations formed by $S_2O_8^{2-}$ oxidation for comparison with the results of monocyclic analogues. Knowledge of how polycyclic aromatic radical cations react may be of importance for understanding the metabolic fate of PAC's in cells.[14] Further, efficient processes for the conversion of coal (an ensemble of functionalized aromatic macromolecules)[15,16] may develop from this knowledge since bond cleavage reactions of aromatic radical cations require considerably less activation energy than do reactions of neutral molecules.[9b,10,17,18] To our knowledge, naphthalene[19,20] is the only PAC reported to have been oxidized by $S_2O_8^{2-}$ prior to our interest in these systems. Recently we reported the oxidation of 9-acylanthracenes that underwent nuclear oxidation in CH_3CN/H_2O to product acylanthrones and acylhydroxyanthrones.[13]

This paper reports a detailed study of the oxidation of 9-methylanthracene (1) in $H_2O/CH_3CN/HOAc$ mixtures. The results show a pattern of reactivity that is analogous to and yet significantly different from that of toluene, the monocyclic analogue of 1. We have found that nuclear oxidation is generally favored for 1; however, conditions can be selected that favor proton loss. The reactivity differences between 1 and toluene that were observed apparently are due to differences in the rates of reactions of $1^{•+}$ and of the nucleophile–adduct radicals, caused, in part, by the extra stability of the anthracene ring.

Results

Oxidations of 9-Methylanthracene with Low Conversion in CH_3CN/H_2O. Oxidations of 9-methylanthracene (1) with copper(II) peroxydisulfate were first performed with low conversions ($S_2O_8^{2-}$ approximately 10% of 1) in CH_3CN/H_2O. The results for these oxidations are presented in Table I. Reactions conducted in 70/30 (v/v) CH_3CN/H_2O without added acid yielded 10-methyl-10-hydroxy-9-anthrone (**2**) and its dehydration product, 10-methylene-9-anthrone (**3**). Compound **2** is assumed to be a nuclear oxidation product formed via subsequent oxidation of 9-methyl-10-hydroxyanthracene. The yields of products **2** and **3** in runs 2–4 approached or exceeded that which was theoretically possible on the basis of $S_2O_8^{2-}$ used, assuming 2 equiv of $S_2O_8^{2-}$/equiv of **2** or **3**. Control experiments conducted without $S_2O_8^{2-}$ present showed that Cu(II) could effect the oxidation of 1 to these same products. Thus, the excess product is attributed to concurrent oxidation by Cu(II), presumably via electron transfer since the products are formed in the same ratio as in the $S_2O_8^{2-}$ oxidations. When reactions were carried out in 95/5 (v/v) CH_3CN/H_2O or with 1.0 M $HClO_4$ present (runs 6 and 7), the product distributions were shifted toward compound **3**. Total yields in some cases were significantly below that theoretically possible based on $S_2O_8^{2-}$.

In run 5 conditions were made basic by adding sodium acetate. Here, in addition to compounds **2** and **3**, the nuclear acetate, 10-acetoxy-9-methylanthracene (**4a**), and

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Table II. Low-Conversion Oxidation of 9-Methylanthracene in 70/30 (v/v) $CH_3CN/HOAc$ at 83 °C[a] (Yields of Products[b] Based on Peroxydisulfate Used)

run	$[Cu(OAc)_2]$	[NaOAc]	$[S_2O_8^{2-}]$	5a	4a	5a/4a	comments
1	0.03	0.03	0.01	28	9.2	3.0	
2	0.03	0.03	0.01	23	6.9	3.3	70 min
3	0.03	0.03		2.9	0.7	4.1	
4	0.1	0.03	0.01	23	12	1.9	
5	0.1	0.03		3.0	1.0	3.0	
6	0.03	0.15	0.01	34	3.3	10	
7	0.20	0.15	0.01	31	5.2	5.3	2 (9.5), 3 (6.0)
8	0.03		0.01	14	18	0.8	
9	0.20		0.01	17	28	0.6	2 (9.0), 3 (5.0)
10	0.03	0.15	0.01	0.9	0.8	1.1	neat CH_3CN
11	0.03		0.01	7.6	1.7	4.5	neat CH_3COOH

[a]0.1 M methylanthracene, 30-min [b]**2**, 10-hydroxy-10-methylanthrone; **3**, 10-methylene-9-anthrone; **4a**, 9-acetoxy-10-methylantracene; **5a**, 9-anthracenylmethyl acetate; **5b**, 9-anthracenemethanol; **6**, 9-anthraldehyde.

Table III. Oxidation of 9-Methylanthracene with 0.9 equiv of Peroxydisulfate in 70/30 (v/v) $CH_3CN/HOAc$ at 91 °C[a] (Yields in Percent, Based on 1 Oxidized)

run	[Cu(II)]	[NaOAc]	7	5c	5a	4a	(2 + 3)	PL	N	FS	MB	conv
1	0.03	0.02	40	4.0	2.7	1.3	14	47	15	76	102	63
2	0.03	0.15	22	0.7	41	4.6	5.7	64	10	86	96	87
3	0.03	0.45	22	0.0	41	3.3	1.5	63	4.8	93	90	51
4	0.0	0.0	44	5.7	0.9	0.7	6.8	51	7.5	87	102	44
5	0.2	0.02	26	0.0	26	11	20	52	31	63	109	78
6[b]	0.2	0.02	<1	0.0	15	20	8.2	15	28	35	45	6.8
7	0.0	0.5	32	0.0	11	1.9	0.0	43	1.9	96	76	12
8[c]	0.03	0.15	23	0.0	35	8.0	2.5	58	11	84	92	37

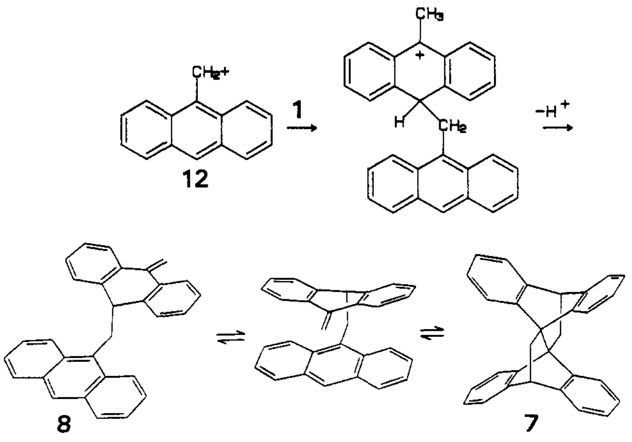
[a]0.1 M methylanthracene, one-hour reaction times. **2**, 10-hydroxy-10-methyl-9-anthrone; **3**, 10-methylene-9-anthrone; **4a**, 9-acetoxy-10-methylanthracene; **5a**, 9-anthracenylmethyl acetate; **5c**, *N*-(9-anthracenylmethyl)acetamide; **7**, lepidopterene. PL, proton loss; N, nuclear oxidation; FS, fraction side-chain oxidation; MB, mass balance; conv, percent conversion of starting material. [b]No peroxydisulfate. [c]Neat acetic acid.

Table IV. Oxidation of 9-Methylanthracene with 0.9 equiv of Peroxydisulfate in 0.03 M $Cu(ClO_4)_2$ in Aqueous CH_3CN at 91 ± 1 °C[a] (Yields in Percent of 1 Oxidized)

run	% CH_3CN	$[HClO_4]$	7	2	3	PL	N	FS	MB	conv
1[b]	70		17	54	8.5	17	63	21	97	61
2	70	0.1	20	48	7.6	20	56	26	96	68
3	70	1.0	13	1.5	3.5	13	5	72	31	52
4	95	0.1	28	0.0	3.3	28	3.3	89	59	49

[a]0.1 M methylanthracene, one-hour M methylanthracene, one-hour reaction times; column headings same as Table III. [b]0.4% 9-anthraldehyde (**6**) and 0.7% 9-anthracenemethanol (**5b**) were also produced.

Scheme II



side-chain oxidation products, 9-anthracenylmethyl acetate (**5a**), 9-anthracenemethanol (**5b**), and 9-anthraldehyde (**6**), were formed. Total yields of products in this reaction also were significantly less than theoretically possible.

Oxidations with Low Conversion in $CH_3CN/HOAc$. Results of oxidations conducted with low conversions in $CH_3CN/HOAc$ are presented in Table II. In addition to **2** and **3**, side-chain and nuclear acetates **5a** and **4a** were produced, with the side-chain acetate predominating. Interestingly, the yields of the side-chain acetate increased with added sodium acetate while the yields of the nuclear acetate correspondingly decreased.

These oxidations characteristically gave less than theoretical yields based on $S_2O_8^{2-}$. This phenomenon of less than theoretical accounting of products in the oxidations listed in Tables I and II may be due to either incomplete reaction of the $S_2O_8^{2-}$ during the allotted reaction time or production of undetected products such as dimeric species that may not have been eluted from the gas chromatograph. The latter possibility was suspected to be the case since increased reaction times did not improve the yields of products. Confirmation of this explanation was gained from GC analyses on a short column that showed a broad irregularly shaped peak eluting after programming to 300 °C. GC–MS analysis of this peak gave a molecular ion of *m/e* 382 and a base ion of *m/e* 191, indicating a structural dimer of 1. A crystalline compound with matching GC and MS properties was then isolated from one of the reaction mixtures. Spectral analyses showed it to be the known compound lepidopterene[21] (**7**), and control reactions (see the Experimental Section and ref 22) showed that the

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compound was formed via attack of the 9-anthracenylmethyl cation on **1** (Scheme II).[23] This mechanism is similar to that proposed by Becker et al.[21] except that adduct **8** was derived from carbanions in their case.

Oxidations with High Conversions. Oxidations were then conducted with high conversions in order to obtain material balances and yields based on the amount of **1** that reacted. Oxidations were performed with ca. 0.9 mol equiv of peroxydisulfate. Under these conditions, the yield of lepidopterene could be determined by ^{1}H NMR spectroscopy. Tables III and IV present the results for the oxidations in $CH_3CN/HOAc$ and CH_3CN/H_2O.

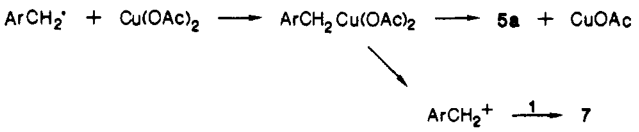
Products identical with those formed in the low-conversion oxidations were generally observed in these oxidations. The tables report product yields, conversion and material balance data, total yields of side-chain and nuclear oxidation products, and the fraction of products that are derived from side-chain oxidation. The acetate **5a**, the amide **5c**, and the dimer **7** are considered to be side-chain oxidation products, whereas anthrones **2** and **3** and acetate **4a** are considered nuclear oxidation products. Conversions usually ranged from 40 to 65% for the 1-h reactions, and material balances generally ranged from 90 to 110%. Exceptions were observed for oxidation runs 6 and 7 of Table III, which gave poor material balances perhaps due to 12% or less conversion of **1** to products. Runs 3 and 4 in Table IV also gave poor material balances possibly due to the instability of the products to the very acidic conditions of these runs.

For the oxidations conducted in $CH_3CN/HOAc$, significant yields of compound **7** ranging from 20 to 45% were observed and side-chain oxidation products were predominant. Even with 0.2 M Cu(II), 63% of the products was from side-chain oxidation. Lowering the Cu(II) concentration to 0.03 M increased the fraction of side-chain oxidation to 75%, and when 0.15 and 0.45 M NaOAc were present, the fractions of side-chain oxidation were further increased to 87% and 93%, respectively. In the absence of Cu(II) and added NaOAc, good conversions and very high fractions of side-chain oxidation were still observed, suggesting that $S_2O_8^{2-}$ was effective at oxidizing the radical intermediates to products. Repeating this oxidation with 0.5 M acetate present (run 7, Table III) resulted in proton loss products (**5a**, **7**) accounting for 96% of the products (ca. 70% dimer). The low conversions reported for this run (7%) were probably due to solubility problems. It was observed that whenever high concentrations of either copper(II) acetate or sodium acetate were used, a water-soluble, white solid precipitated during the reaction, indicating that the reaction mixture became saturated with salts (i.e., acetates and sulfates).

Results of oxidations in neat HOAc were essentially the same as in 70/30 (v/v) $CH_3CN/HOAc$ (compare runs 8 and 2). Lower conversions were obtained, which we attribute to the lower solubility of the $S_2O_8^{2-}$ in neat acetic acid.

For oxidations in CH_3CN/H_2O (Table IV), yields of **7** of up to 28% were produced but nuclear oxidation products were predominant. In 70/30 (v/v) CH_3CN/H_2O and 0.1 M $HClO_4$ yields of **7** were approximately 20%. Higher acidities gave material balances that were low, and only small amounts of nuclear products were observed, suggesting that they may have been unstable to the strong acid conditions. The methyleneanthrone (**3**) is reported to undergo decomposition in acidic media.[24] Addition of NaOAc appeared to produce compound **5a** at the expense of **7** and increase the fraction of side-chain oxidation.

Scheme III



Reactions conducted in 95/5 (v/v) CH_3CN/H_2O increased the yield of **7** to 28%, signaling an increased participation of the side-chain oxidation path. Material balances for these runs averaged 60%. As in the reactions that were conducted in 1 M acid and 70/30 (v/v) CH_3CN/H_2O, few nuclear oxidation products were found. Although only 0.1 M $HClO_4$ was present in these reactions, the low water content makes the 95/5 (v/v) CH_3CN/H_2O medium much more acidic. Nonetheless, even if all the missing products (40%) are attributed to the nuclear path, the fraction of side-chain oxidation is 38%, compared to 26% in the 70/30 media.

The distribution of side-chain oxidation products showed considerable variation with changes in the concentrations of Cu(II) and NaOAc. When Cu(II) and NaOAc were low in concentration, compound **7** was produced in its highest yields (runs 1 and 4, Table III). The ratios of **7**/**5a** were 15 and 52, and the ratios of **5c**/**5a** were 1.5 and 6, for these respective runs. Increasing the amount of NaOAc to 0.15 M or higher while keeping Cu(II) at 0.03 M (see runs 2 and 3, Table III) caused **5a** to be formed in maximum yield (41%), exceeding the yield of **7** by approximately 2-fold. These latter runs also produced negligible amounts of the amide **5c**. These variations in the yields of **7**, **5a**, and **5c** with added NaOAc when little or no Cu(II) was present indicate that anthracenylmethyl cations are intermediately formed perhaps via oxidation of anthracenylmethyl radicals by $S_2O_8^{2-}$.[5,25]

$$R\bullet + S_2O_8^{2-} \rightarrow R^+ + SO_4^{\bullet -} + SO_4^{2-}$$

When the Cu(II) concentration was 0.2 M, roughly equal amounts of **7** and **5a** were formed (see run 5, Table III). Here, anthracenylmethyl radicals may be preferentially oxidized by Cu(II) via an organocopper intermediate that then partitions between ligand-transfer and solvolytic decomposition pathways[11] (Scheme III).

Discussion

Origin of Side-Chain Oxidation Products. The yields of side-chain oxidation products that are observed in these oxidations and the production of lepidopterene **7** are unprecedented for radical-cation-mediated oxidations of **1**. Our control experiments suggest that the production of lepidopterene requires the intermediacy of the anthracenylmethyl cation, and therefore it too qualifies as a side-chain oxidation product of **1**. Taken together, the fraction of side-chain oxidation products ranges from 26 to 90% in aqueous CH_3CN and 63 to 90% in $CH_3CN/HOAc$. While some side-chain oxidation product may be formed via the nuclear oxidation pathway (to be discussed below), the distribution of the products observed here suggests that proton loss from $1^{\bullet +}$ must have been occurring as well, provided that no other routes to side-chain oxidation were operable. Side-chain oxidation products could have been formed, for instance, by solvent-derived

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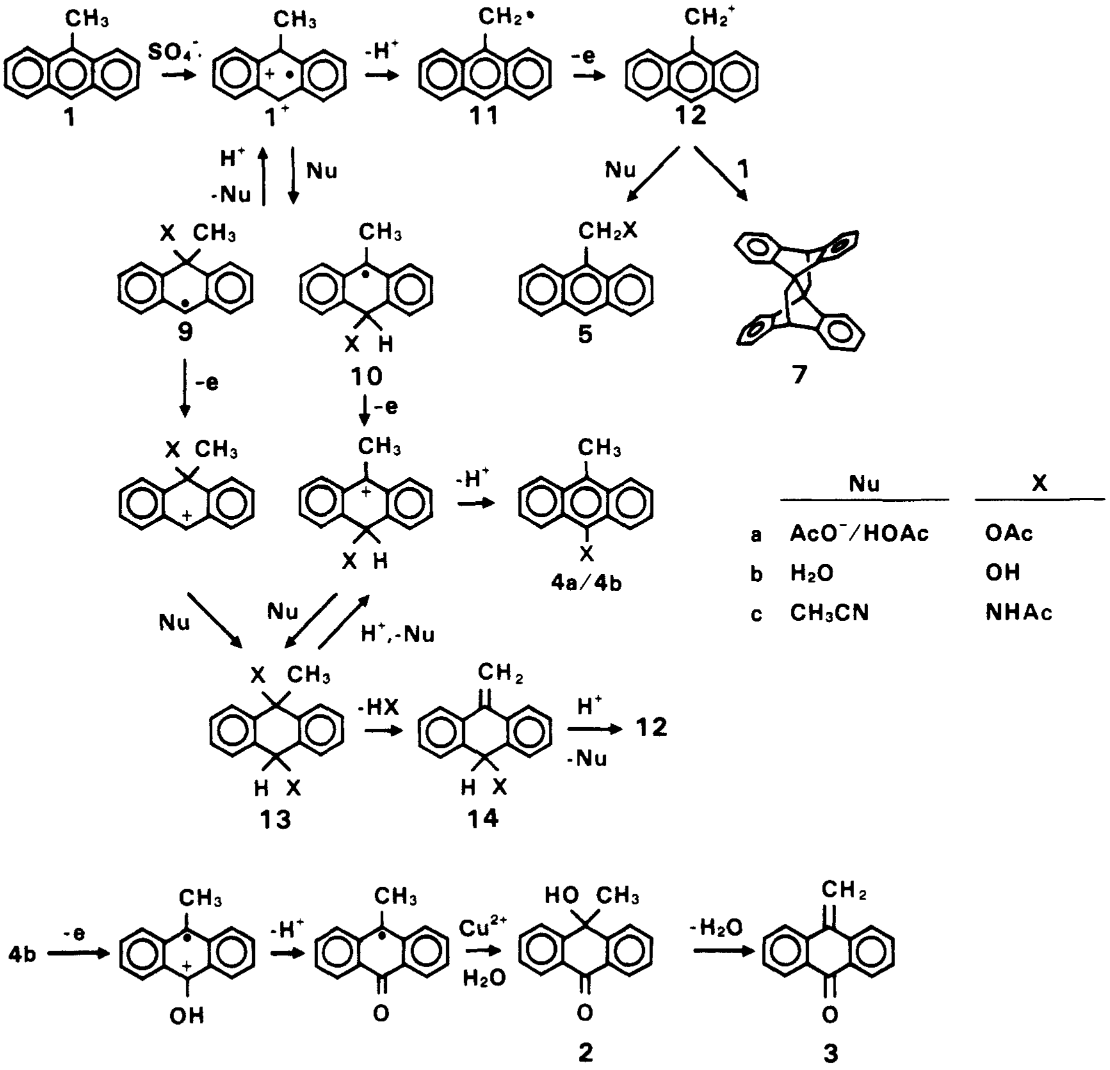
(23) *An alternative mechanism that may operate during the oxidation* would involve attack of anthracenylmethyl radical on **1** followed by oxidation to the cation **8H**$^+$.

(24) Hirakawa, K.; Nakazawa, S. *J. Org. Chem.* **1978**, *43*, 1804.

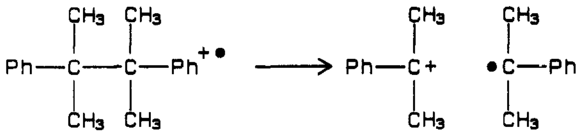
(25) Norman, R. O. C.; Storey, P. M.; West, D. R. *J. Chem. Soc. B* **1970**, 1087.

Scheme IV



	Nu	X
a	$AcO^-/HOAc$	OAc
b	H_2O	OH
c	CH_3CN	NHAc

radicals that abstract hydrogen from the methyl group of 1. The following considerations, however, tend to rule out the intermediacy of radicals derived from CH_3CN, HOAc, or AcO^-. We have previously argued that in CH_3CN/H_2O the $SO_4^{\bullet -}$ reacts preferentially with aromatic compounds to form radical cations.[10] These arguments were based on the ability to obtain good yields of nuclear oxidation products from toluene and bibenzyl and nearly quantitative amounts of radical-cation cleavage products from bicumyl (cumyl alcohol and α-methylstyrene).



$$Ph-C(CH_3)_2-C(CH_3)_2-Ph^{+\bullet} \longrightarrow Ph-C^+(CH_3)_2 \quad {}^{\bullet}C(CH_3)_2-Ph$$

More recently, we have observed good yields of nuclear oxidation products from 9-acylanthracenes.[13] These products are not consistent with cyanomethyl radicals being an intermediate in the oxidations. With regard to intermediate formation of $HO_2CCH_2^{\bullet}$, the rate of attack by $SO_4^{\bullet -}$ on acetic acid is relatively slow.[26] Thus, attack by $SO_4^{\bullet -}$ on acetic acid should not compete with attack on 1, which is expected to be near the diffusion-controlled limit.[27] Evidence for the intermediacy of methyl radicals produced by the oxidation of acetate ion was observed for the oxidation of naphthalene in acetic acid,[19] but when Cu(II) was present, the methyl radicals, instead of adding to naphthalenes, were oxidized. Control experiments were, nonetheless, conducted here to test for the oxidation of acetate ion to methyl radical and CO_2. When the gas phase above the reaction mixtures was analyzed, only exceedingly small yields of CO_2 and methane were detected (see the Experimental Section). Thus, we conclude that essentially all the $SO_4^{\bullet -}$ attack 1 to form $1^{\bullet +}$ and that side-chain oxidation products result from subsequent reactions of $1^{\bullet +}$.

Oxidation Mechanism. A mechanism consistent with the results of this work is depicted in Scheme IV. The initially formed radical cation undergoes nucleophile addition and proton loss reactions, respectively, to product adduct radicals 9 and 10 and the anthracenylmethyl radical 11. Since compound 4c, nuclear amide, was not observed, we presume that nucleophilic attack on $1^{\bullet +}$ by CH_3CN was negligible.

The pathways by which the radicals are converted to products is rather complex. Apparently, they may be oxidized by either $S_2O_8^{2-}$ or Cu(II). In the first case, the corresponding cations are probably formed, and in the latter case, an organocopper(III) species may be intermediately formed (Scheme III). For simplicity, Scheme IV

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[26] (a) Davies, M. J.; Gilbert, B. C.; Thomas, B.; Young, J. J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1199. (b) Dogliotti, L.; Hayon, E. *J. Phys. Chem.* **1967**, *71*, 2511, 3802.

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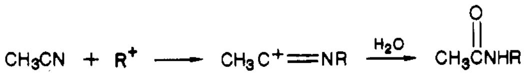
only depicts the oxidation of the radicals to cations. The anthracenylmethyl cation, **12** reacts with **1** to product **7**, or with nucleophilic solvent components to produce **5a** and **5c**. Compound **5c** forms by attack of acetonitrile and hydration of the intermediate nitrilium ion.



$$CH_3CN + R^+ \longrightarrow CH_3C^+{=}NR \xrightarrow{H_2O} CH_3\overset{O}{\overset{\|}{C}}NHR$$

5c

The cations formed by oxidation of the nucleophile adduct radicals **9** and **10** may add nucleophiles to produce the dinucleophile addition product **13**. The cation from **10** also may eliminate a proton to produce the nuclear substitution product **4**. Compound **13**, if formed, may be expected to undergo E1 elimination of HX to produce **4**. For oxidations in acetic acid where Nu = OAc, compound **13a** undergoes a competing Ei elimination reaction[28,29b] to yield **14**, which solvolyzes to produce the cation **12**.

To the extent that the diacetate **13a** is formed, some side-chain oxidation may be attributable to the nucleophile addition path. Parker[29b] reported that when **13a** was decomposed in refluxing acetic acid, the ratio of side-chain and nuclear acetates **5a** and **4a** was 0.67. When we solvolyzed **13a** in media representative of our oxidations, a maximum ratio of 0.28 was observed. Thus, the maximum contribution to side-chain oxidation products by the nuclear oxidation path can only be 28% of the nuclear products. Run 5 of Table III yielded the maximum nuclear oxidation products, 25%; therefore, at most only 8% out of the 63% of the side-chain product could have come from the nuclear oxidation path. For reactions conducted in aqueous CH_3CN it is not clear that any side-chain oxidation products may be formed via the nuclear oxidation path. The 1,2-elimination of the analogous dihydrodiol **13b** may not be important.

The nuclear oxidation product **4b** is unstable in the oxidation media and undergoes subsequent oxidation to compounds **2** and **3** as depicted at the bottom of Scheme IV. Since the concentration of **4b** does not build up even at low conversions, we presume it was oxidized by electron-transfer reactions with $\mathbf{1}^{\bullet+}$ or Cu(II). In CH_3CN/HOAc, the production of **2** and **3** may arise by subsequent oxidation of either **4a** or **4b**. Compound **4b** could have been intermediately formed in the CH_3CN/HOAc media since approximately 1 M water was present in the reaction media, having been adventitiously added via the acetic acid and copper(II) acetate monohydrate. That added sodium acetate tended to disfavor production of **2** and **3** is consistent with their formation via nucleophilic addition of water to $\mathbf{1}^{\bullet+}$.

Comparisons with Monocyclic Systems. The oxidation of toluene, the monocyclic analogue of **1**, has been well studied.[7–9,20,30–32] In acidic aqueous solutions, benzyl alcohol and cresols are formed in distributions that are dependent on acidity and Cu(II) concentration.[7,8,10,30] This behavior is taken to be indicative of the nucleophilic addition of water to the toluene radical cation being reversible. Spectroscopic and kinetic studies[33] of the pulse radiolysis of toluene in water have confirmed this fact. Oxidations of toluene in acetic acid gave primarily benzyl acetate.[9a,32] However, the mechanistic details are less clear. Whether the lack of nuclear acetates is due to proton loss being more competitive with nucleophilic attack by acetic acid/acetate ion or if nucleophilic attack is just more readily reversed in acetic acid is not clear.[11]

We find that nuclear oxidation is more favored for **1** compared to toluene. This is probably due to differences in the relative rates with which the respective radical cations undergo proton loss and nucleophile addition reactions and in the relative rates with which the respective nucleophile adduct radicals undergo elimination and oxidation reactions. The outcomes of these competing reactions are understandably both substrate and solvent dependent.

Some rate data are available to illustrate the effect of radical-cation structure and stability on reaction rates. Pulse-radiolysis studies by Sehested and Holcman of methylated benzenes in water have provided rates for proton loss from and rates for hydration of the radical cations as well as rates for acid-catalyzed dehydration of hydroxyl adduct radicals.[33] For toluene, the rate constant (s^{-1}) for proton loss is $>10^7$, and the rate constant for hydration is $>5 \times 10^8$. The rate constants for proton loss from methylated benzenes dropped by 10^3 on going from toluene to pentamethylbenzene, and rates of hydration decreased by 10^7. These trends suggest that rate constants for proton loss and hydration reactions decrease with increasing stability of the radical cations. The rate constants for dehydration of the hydroxyl adduct radicals of methylated benzenes remained relatively constant at 10^9 M^{-1} s^{-1}, but rates of 10^6 M^{-1} s^{-1} for biphenyl[34a] and 10^5 M^{-1} s^{-1} for naphthalene[34b] have been measured. These findings suggest that the rates of dehydration are decreased by structural changes that increase the stability of the HO adduct radical. Solvation may also affect rates of dehydration, since transition states for forming larger, more delocalized radical cations may be less well solvated.

The above trends when extrapolated to **1** suggest that the rates of proton loss, hydration, and dehydration should all be slowed down relative to toluene. If dehydration of the hydroxyl adducts of **1** is much slower than dehydration of hydroxyl adducts of naphthalene, then the reaction may not compete well with oxidation by Cu(II). Our observations of the oxidation of **1** in aqueous media are consistent with this view. The side-chain/nuclear product ratio (side/nuc) was relatively insensitive to acid concentration and was only increased by decreasing the water content of the reaction medium, the effect of which would be to slow down the hydration reaction and speed up dehydration (the medium having the same amount of $HClO_4$ but less water would be more acidic). That nuclear oxidation predominates for oxidations in CH_3CN/H_2O suggests that the rate constant for hydration is faster than the rate constant for proton loss, as is the case for the toluene system.[33]

For the reactions in acetic acid media, little quantitative data are available on which to base speculations about the effect of aromatic structure on the reaction rates. Our observations of a shift in the side/nuc product ratios in favor of side-chain products upon changing from water to HOAc are generally consistent with observations of monocyclic aromatic systems.[7,9–11] The observed preponderance of side-chain product may indicate that proton loss is faster than nucleophile addition. However, this

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[28] March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; pp 917.

[29] (a) Parker, V. D. *Acta Chem. Scand.* **1970**, *24*, 3151. (b) Parker, V. D. *Acta Chem. Scand.* **1970**, *24*, 3455. (c) Parker, V. D. *Acta Chem. Scand.* **1970**, *24*, 3171. (d) Parker, V. D. *Acta Chem. Scand.* **1970**, *24*, 2757. (e) *Parker*, V. D. *Acta Chem. Scand.* **1970**, *24*, 3162.

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[34] (a) Sehested, K.; Hart, E. J. *J. Phys. Chem.* **1975**, *79*, 1639. (b) Zevos, N.; Sehested, K. *J. Phys. Chem.* **1978**, *82*, 138–141.

proposal is disfavored by electrochemical oxidations of **1** in acetic acid, which are not known to produce side-chain products by proton loss.[29b] Alternatively, nucleophile addition may be faster than proton loss and more reversible than in the aqueous media. Our observations that nuclear products are increased with high Cu(II) concentrations are consistent with nucleophile addition being reversible in acetic acid media. We also observed that the addition of sodium acetate to reactions in $CH_3CN/HOAc$ increased the fraction of side-chain oxidation, mainly at the expense of **2** and **3** (see Table III). This trend may be due to (1) acetate ion competing more effectively with water in the nucleophile addition reaction, (2) increased rates of proton loss in the buffered medium, and (3) an ionic strength effect that stabilizes $\mathbf{1}^{\bullet+}$ relative to **9** and **10** and makes nucleophile addition more reversible.

Comparison to Other Oxidations of PAC's. The production of side-chain oxidation products from alkylated PAC's has not generally been observed. Indeed, electrochemical oxidations of PAC's are reported not to yield side-chain-substituted products.[4b,35-37] Proton loss apparently does occur from electrochemically generated radical cations of 9,10-dimethylanthracene[36] and 9-methyl-10-methoxyanthracene,[37] but only dimeric products are formed. An ESR study of the thallium(III) oxidation of **1** in trifluoroacetic acid only showed the radical cation to undergo nucleophilic addition.[38] An early study of the oxidation of 7,12-dimethylbenz[*a*]anthracene by one-electron oxidants reports a variety of nuclear and side-chain oxidation products.[38] The oxidation of 1-methylnaphthalene in acetic acid by cerium(IV) has been reported to yield 70% side-chain oxidation,[39] and no nuclear oxidation products were reported from Ce(IV) oxidation of 1-ethyl- and 1-ethyl-4-methylnaphthalene.[39] These products indicate that proton loss was occurring from these radical cations. Clearly, structure and medium effects are important in determining the reaction paths of polycyclic aromatic radical cations.

The distinct differences that exist between the electrochemical oxidation of **1** and the results reported here may possibly be reconciled. Parker[29b] reported that anodic oxidation of **1** in $CH_3CN/HOAc$ (3/1) gave the diacetate **13a** as the sole product at 25 °C. In a very similar solvent (7/3 $CH_3CN/HOAc$), we observed mainly proton loss products **7** and **5a**. Our reactions were conducted in refluxing solvent, so the results may not be comparable due to the difference in temperature. Alternatively, the addition of acetate to $\mathbf{1}^{\bullet+}$ might not have been reversible in the electrochemical experiment since the acetoxy adduct radicals having been formed at the electrode would have been rapidly oxidized. This explanation requires that nucleophile addition to the radical cation be faster than proton loss from the radical cation, a situation that is consistent with our observations here and known to exist for the toluene radical cation in water.[33] For our $S_2O_8^{2-}$ oxidations, the adduct radicals may undergo elimination faster than oxidation such that equilibration of the adduct radicals with the radical cations occurred and thereby permitted the proton loss reaction to compete.

Experimental Section

General Procedures. All solvents were HPLC/GC grade and obtained from Baker, Burdick & Jackson, or Fischer Scientific. Ammonium peroxydisulfate, copper(II) acetate, copper(II) perchlorate (Alfa), and phenanthrene (Aldrich) were used without further purification. 9-Methylanthracene (Alfa) and 9-anthracenemethanol (Aldrich) were recrystallized from benzene/hexane prior to use. NMR spectra were recorded on a Varian FT-80 or a XL-300 spectrometer. Chemical shifts are reported (ppm) downfield from internal tetramethylsilane. GC analyses were obtained on a Hewlett-Packard Model 5880A (Level Four microprocessor) or a Model 5890 (with Model 3392A integrator) instrument. Either a 6-m (for dimer analysis) or a 30-m × 0.53-mm i.d. DB-5 column (J&W Scientific) was used with the latter instrument. Both splitless and on-column injection techniques were employed. GC/MS analyses were performed on an HP 5890 GC interfaced to the HP 5970 series mass selective detector.

9,10-Diacetoxy-9,10-dihydro-9-methylanthracene (13a). 9-Methylanthracene was oxidized with lead tetraacetate for 4 h according to the procedure of Parker.[29a] The oil obtained was crystallized in a minimum amount of ethanol to yield 0.24 g (0.77 mmol, 30%) of **13a**: mp 142–145 °C; ^1H NMR (80 MHz, $CDCl_3$) δ 7.25–7.65 (nm, 13 H, ArH), 2.09 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 1.87 (s, 3 H, CH_3Ar). Recrystallization from hexane was accompanied by some decomposition.

9-Acetoxy-10-methylanthracene (4a). A portion of recrystallized **13a** was heated in hexane for 3 h. The hexane solution was allowed to cool in a freezer. The resultant solid was recrystallized from benzene/ethanol to yield 2.5 mg of **4a**: mp 169–172 °C (lit.[29b] mp 166–167 °C); ^1H NMR (80 MHz, $CDCl_3$) δ 7.4–8.4 (m, 10 H, ArH), 3.09 (s, 3 H, CCH_3).

Lepidopterene (7). The compound was isolated from the reaction mixture described by entry 1, Table III. After solvent removal, addition of benzene to the residue and filtration gave **7** as a white solid: mp 330–335 °C (lit.[21] mp 317–323 °C); HRMS, *m/e* calcd for $C_{30}H_{22}$ (M^+) 382.17215, found 382.1731; ^1H NMR (300 MHz, $CDCl_3$) matched the published spectrum;[21] ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.40, 143.15, 125.48, 125.22, 122.64, 122.25, 54.01, 45.58, 28.93; IR (KBr) 3080, 3020, 2990, 2980, 2950, 1460, 990, 760, 740, 635, 585 cm^{-1}; UV-vis [cyclohexane; λ_{max}, nm ($\epsilon \times 10^{-3}$)] 272 (2), 264 (1.9), 257 (1.7), 235 (1.7).

Procedure for the Peroxydisulfate–Cu(II) Oxidations. Procedures for conducting the oxidations in aqueous CH_3CN have been previously described.[13] Typical procedures for oxidations conducted in $CH_3CN/HOAc$ were as follows: 0.060 g (0.30 mmol) of $Cu(OAc)_2$, 0.124 g (1.51 mmol) of NaOAc, 0.0228 g (0.1 mmol) of $(NH_4)_2S_2O_8$, and 1 mmol of substrate were added to a 25-mL flask equipped with reflux condenser and argon inlet. After the mixture was purged with argon for 10 min, 10 mL of degassed solvent was added. The resultant suspension was heated at 83 ± 1 °C for the prescribed time (see Table I). A 1-mL aliquot of 0.05 M phenanthrene was added as internal GC standard. The reaction mixture was poured into 75 mL of water and extracted three times with methylene chloride. The combined extracts (50 mL) were dried over $MgSO_4$ and analyzed by GC techniques. The reactions that were done with high conversion utilized ca. 0.9 mol equiv of peroxydisulfate and only 0.096 g (0.5 mmol) of **1** in 5 mL of solvent. The copper(II) and sodium acetate concentrations used are listed in the tables.

Analyses for CO_2 and methane were performed on some reactions that were conducted in media containing $HOAc/AcO^-$. In these cases, the reflux condenser was replaced with a serum cap, and 1.0 mmol each of peroxydisulfate and **1** were used. After the reaction was over, 0.5 mL of ethane gas was added as internal GC standard. The gas phase was then sampled and analyzed on a Carle gas chromatograph (Model 311 H, series S) with integration and data reduction by a Spectrophysics SP 4000 integrating recorder. For reactions such as entries 6 and 7 of Table II, 0.036% CO_2 and a trace amount of CH_4 were detected. In the absence of methylanthracene 3.1% CO_2 and 0.8% CH_4 were detected.

Product Identification and Yields. Components of the reaction mixture were identified by comparing their GC retention times and mass spectra to authentic material. In some cases GC/MS was used to identify peaks in the chromatogram. Quantitative analysis was obtained by reference to phenanthrene internal standard. Response factors obtained were linear over a (2–20) × 10^{-4} M concentration range. If authentic material was not available, response factors were estimated from similar com-

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(35) Fried, J.; Schumm, D. E. *J. Am. Chem. Soc.* **1967**, 5508.

(36) Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1969**, 848.

(37) Parker, V. D. *Tetrahedron Lett.* **1972**, 1450.

(38) Sullivan, P. D.; Menger, E. M.; Reddoch, A. H.; Paskovich, D. H. *J. Phys. Chem.* **1978**, *82*, 1158.

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pounds. Lepidopterene (**7**) yields were determined from ^{1}H NMR spectra of the reaction mixture (high-conversion runs).

Control Experiments. Treatment of 9-anthracenemethanol with 2 equiv or more of 9-methylanthracene and heating at reflux in 0.1 M $HClO_4$ (70/30 (v/v) CH_3CN/H_2O) resulted in quantitative formation of **7** (70% isolated).[22] If only a trace of acid was present or the solvent was changed to $CH_3CN/HOAc$ (70/30 v/v), then no dimer was formed. The acetate **5a** when heated under the same conditions as entry 3 in Table II underwent no reaction. If **5a** and a 10-fold molar excess of **1** were heated together under these same conditions (except without peroxydisulfate present), then a trace of **7** was detected. The diacetate **13a**, when heated under the conditions discussed above, resulted in only formation of **4a** and **5a**. No dimer was detected. If a 10-fold excess of **1** was present, and the conditions of entry 4, Table VI were employed, then the dimer **7** was formed along with **5a** and **4a**. These results appear consistent with the dimer arising from the reaction of 9-anthracenylmethyl cation with **1**. See Scheme II.

Registry No. **1**, 779-02-2; **2**, 17104-31-3; **3**, 4159-04-0; **4a**, 31688-72-9; **5a**, 16430-32-3; **5c**, 72169-49-4; **7**, 55614-27-2; $(NH_4)_2S_2O_8$, 7727-54-0; $Cu(OAc)_2$, 142-71-2; $Cu(ClO_4)_2$, 13770-18-8.

Notes

A New Synthesis of Lepidopterenes[1]

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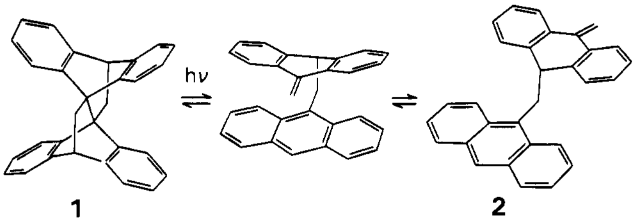
Received March 4, 1986

The recent interest in lepidopterene (**1**) and its derivatives for their ability to undergo adiabatic photoinduced cycloreversion reactions[3,4] has prompted us to report a new synthesis of these compounds. This new method should facilitate the preparation of a wider variety of substituted derivatives.

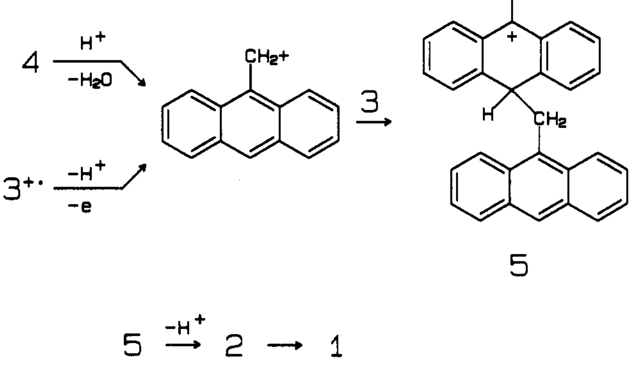


1 **2**

During the study[5] of the oxidation of 9-methylanthracene (**3**) with copper(II) peroxydisulfate, a "dimeric" compound identified as lepidopterene[6–8] (**1**) was formed. Depending on the conditions employed, **1** could be either a minor or the major product of oxidation. Thus, treatment of **3** with 0.9 mol equiv of peroxydisulfate in 0.03 M Cu(II) and 0.02 M sodium acetate in acetonitrile/acetic acid (7/3, v/v) at 90 °C gave an 80% yield of **1**. The same reaction performed in acetonitrile/water (7/3, v/v) without added sodium acetate produced **1** in 30% yield.

Since we are interested in the fate of the intermediate radical cations formed in these oxidations,[9] studies were undertaken to determine the mechanism for the formation of **1**. We suspected that subsequent reactions of **3**$^{\bullet+}$ could lead to the 9-anthracenylmethyl cation. Thus, control experiments were designed to test whether the cation would react with **3** to produce **1**. It was found by ^{1}H NMR spectroscopy that **1** was formed in quantitative yield (70% isolated) when 9-anthracenemethanol (**4**) and 2 equiv of **3** were heated in 0.1 M perchloric acid in acetonitrile/water (7/3, v/v). Thus, we suggest the mechanism shown in Scheme I. The anthracenylmethyl cation forms and adds to **3**, giving **5** which due to steric factors preferentially loses a proton from the methyl group to form the *exo*-methylene compound **2**. Intramolecular [2 + 4] cycloaddition of compound **2** yields compound **1**. Becker et al.[6] have shown that **1** is favored in its equilibrium with **2** (K_{eq} = 630).

Scheme I



Previous synthetic approaches[3,6,7] have mainly yielded symmetrical lepidopterenes. Our observations suggest that solvolysis of substituted anthracenemethanols in the presence of substituted 9-methylanthracenes can provide a convenient general approach to unsymmetrical and ring-substituted derivatives. For example, the new derivative 9-methyllepidopterene (**6**) was produced in ca. 33% yield (by ^{1}H NMR) when 1 equiv of 9-anthracenemethanol and 2 equiv of 9,10-dimethylanthracene (**7**) were heated at reflux in benzene with a catalytic amount of *p*-toluenesulfonic acid. (Benzene was used as a solvent to enhance the solubility of dimethylanthracene.) Since isolation of **6** from unreacted **7** proved difficult, an excess of 10-methyl-9-anthracenemethanol and **3** were allowed to

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(1) This work was supported by the Gas Research Institute, Basis Coal Science Program, Contract No. 5081-260-0536.

(2) University of Washington—Northwest College and University Association for Science (NORCUS) Postdoctoral Research Associate.

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