Radical Ion Probes. 9. The Chemistry of Radical Cations Derived from 9-Cyclopropylanthracene and 9-Bromo-10-cyclopropylanthracene

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Reactions of radical cations generated from 9-cyclopropylanthracene (**1**) and 9-bromo-10-cyclopropylanthracene (**2**) in the presence of methanol have been investigated electrochemically. The major products arising from oxidation of both substrates are attributable to CH$_3$OH attack at the aromatic ring (occurring at the radical cation stage for **2** and the dication stage for **1**) rather than CH$_3$OH-induced cyclopropane ring opening, which is estimated to be exothermic by 20 kcal/mol. Although ring-opened products *are* detected in some instances, these are found to arise from subsequent reaction of the primary oxidation products. These observations are consistent with a proposed product-like transition state for the nucleophile-induced ring opening of cyclopropylarene radical cations in which the positive charge is localized on the cyclopropyl group and nucleophile, and thus unable to derive stabilization from the aromatic ring.

Introduction

Cyclopropyl-containing substrates have frequently been utilized to "probe" for radical cation intermediates in a number of important chemical and biochemical oxidations.,[1-4] It is frequently assumed that incorporation of a cyclopropyl group into a substrate will result in ring-opened products if a radical cation is an important reactive intermediate in the reaction pathway. A difficulty associated with this approach is that there is surprisingly little actually known about the chemistry of these cyclopropane radical cations.

In a series of papers,[5-8] Dinnocenzo et al. have demonstrated that ring opening of a phenylcyclopropane radical cation occurs via a bimolecular, S$_N$2-type process (eq 1).[9] The rate constant for reaction of phenylcyclopropane radical cation and methanol has been determined to be 9.5×10^7 M^{-1} s^{-1} in CH$_3$CN.[7]

Recently, we reported results pertaining to the reactivity of radical cations derived from α- and β-cyclopropyl-naphthalene.[10] While oxidation of these substrates in the presence of methanol leads to cyclopropane ring-opened products, the rate constant for ring opening was exceptionally slow (<20 M^{-1} s^{-1} for α-cyclopropylnaphthalene radical cation) despite the fact that the ring-opening reaction is exothermic by nearly 30 kcal/mol. These observations were interpreted on the basis of a late, product-like transition state for ring opening in which the positive charge is effectively localized on the cyclopropyl group and thus unable to enjoy stabilization by the aromatic ring.[10]

To further test this hypothesis, utilizing electrochemical methods, the chemistry of radical cations generated from 9-cyclopropylanthracene (**1**) and 9-bromo-10-cyclopropylanthracene (**2**) was examined. The results of these experiments are described herein.
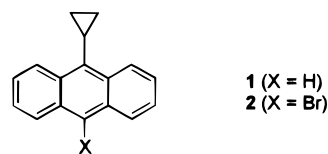
Radical cations have been shown to be reactive intermediates produced during the anodic oxidation of anthracene and related compounds.[11-13] The follow-up chemistry of anthracene radical cations, which generally involves dimerization and/or reaction with nucleophiles, has been the subject of numerous investigations.[14-16]

(1) Silverman, R. B.; Hoffman, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 884. Silverman, R. B.; Hoffman, S. J.; Catus, W. B., III. *J. Am. Chem. Soc.* **1980**, *102*, 7126.

(2) Hanzlik, R. P.; Tullman, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2048. Riley, P.; Hanzlik, R. P. *Tetrahedron Lett.* **1989**, *30*, 3015.

(3) Macdonald, T. L.; Zirvi, K.; Burke, L. T.; Peyman, P.; Guengerich, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2050.

(4) Castellino, A. J.; Bruice, T. C.; *J. Am. Chem. Soc.* **1988**, *110*, 1313. Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7512.

(5) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462.

(6) Dinnocenzo, J. P.; Simpson, T. R.; Zuilhof, H.; Todd, W. P.; Heinrich, T. *J. Am. Chem. Soc.* **1997**, *119*, 987.

(7) Dinnocenzo, J. P.; Lieberman, D. R.; Simpson, T. R. *J. Am. Chem. Soc.* **1993**, *115*, 366.

(8) Dinnocenzo, J. P.; Zuilhof, H.; Lieberman, D. R.; Simpson, T. R.; McKechney, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 994.

(9) This bimolecular mechanism for cyclopropane ring opening was originally proposed by Rao and Hixson. See: Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458.

(10) Wang, Y.; Tanko, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 8201.

(11) Marcoux, L. S.; Fritsch, J. M.; Adams, R. N. *J. Am. Chem. Soc.* **1967**, *89*, 5766.

(12) Phelps, J.; Santhanam, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1967**, *89*, 1752.

(13) Peover, M. E.; White, B. S. *J. Electroanal. Chem.* **1967**, *13*, 93.

(14) Parker, V. D. *Acc. Chem. Res* **1984**, *17*, 243.

(15) Hammerich, O.; Parker, V. D. In *Advances in Physical Organic Chemistry, Vol. 20*; Academic Press: London 1984; pp 55−189.

(16) Eberson, L.; Utley, J. H. P.; Hammerich, O. In *Organic Electrochemistry, An Introduction and a Guide, Third Edition, Revised and Expanded*; Lund, H., Baizer, M. M., Eds.; Marcel Dekker, Inc.: New York, 1990; pp 505−533.
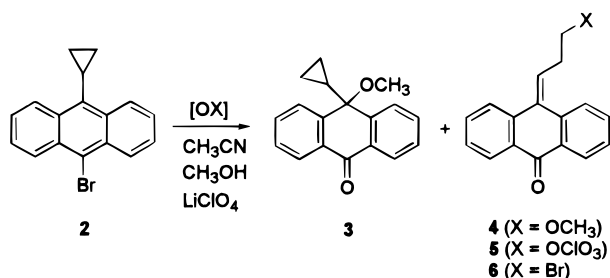
Scheme 1

2   **3**   **4** (X = OCH$_3$)
                              5 (X = OClO$_3$)
                              6 (X = Br)

Table 1. Yields of Products Produced in the Controlled-Current Oxidation of 9-Bromo-10-cyclopropylanthracene (2)

[CH$_3$OH], M	electrons, equiv	workup method	yield (%)			
			3	**4**	**5**	**6**
4.1	2.8	aqueous	62^a	b	b	b
2.5	2.7	aqueous	68^c	b	b	b
4.1	2.5	nonaqueous	0.0	7.4^a	21.8^a	23.2^a
2.5	2.7	nonaqueous	0.0	9.3^c	41.0^c	12.3^c
0.25	2.5	nonaqueous	0.0	5.8^c	12.6^c	4.3^c

^{a} Isolated yield. ^{b} Trace. ^{c} Yield determined by ^{1}H NMR.

Results

1. Preparative Electrolyses. 9-Bromo-10-cyclopropylanthracene (2). The preparative (constant current) electrolysis of **2** was conducted in CH$_3$CN/CH$_3$OH with 0.1 M LiClO$_4$ as the supporting electrolyte. The products isolated from this electrolysis (Scheme 1) varied dramatically as a function of the workup procedure employed. Aqueous workup (extraction with H$_2$O/ether) yielded exclusively 9-cyclopropyl-9-methoxyanthracene (**3**). In contrast, nonaqueous workup (removing solvent by rotary evaporation followed by extraction with CH$_2$-Cl$_2$) yielded mainly cyclopropyl ring-opened products (**4**, **5**, and **6**). The yields of several representative runs are shown in Table 1.

Although substantially different products resulted, the mass balances observed for both the aqueous and nonaqueous workup procedures were similar (60−70%), leading to the suspicion that the reaction products might be interconverting during workup. Indeed, monitoring of the electrolysis *prior* to workup by either GC or TLC revealed that only **3** was produced during the electrolysis, suggesting that this compound was the precursor to **4**, **5**, and **6**.

In separate experiments this hypothesis was validated by subjecting **3** to conditions designed to emulate the conditions of the nonaqueous workup procedure. For example, treatment of **3** with HBr in CH$_3$CN led to formation of ring-opened bromide **6** in 80% yield (unoptimized). Similarly, treatment of **3** with HClO$_4$ in CH$_3$-CN yielded perchlorate ester **5** in 46% yield (unoptimized). These results substantiate the contention that cyclopropyl ring-opened products **4**, **5**, and **6** are produced during workup.

9-Cyclopropylanthracene (1). Controlled-current electrolysis of **1** in CH$_3$CN/CH$_3$OH followed by a nonaqueous workup resulted in the formation of cyclopropane ring-opened products (in analogy to the results observed in the oxidation of **2**). However, ring-opened products were also found when an aqueous workup was employed (Table 2). Periodic monitoring of the reaction mixture during the electrolysis by TLC and GC revealed that 9-cyclopropyl-10-methoxyanthracene (**7**) was formed

**Table 2. Yields of Products Produced in the Controlled-Current Oxidation of 9-Cyclopropylanthracene (1)**

[CH$_3$OH], M	electrons, equiv	workup method	yield, %^{a}						
			7	**3**	**4**	**5**	**8**	**9**	**1**
4.1	2.0	aqueous	37.0	19.8	1.2	0.0	13.9	b	20.4
2.5	3.0	aqueous	3.6	27.6	32.0	0.0	3.6	b	17.8
2.5	3.0	nonaqueous	0.0	2.8	41.4	20.4	13.0	b	6.2
0.25	2.5	nonaqueous	0.0	b	12.8	16.7	b	8.0	b

^{a} Yield determined by GC or ^{1}H NMR. ^{b} Trace.

Scheme 2

A $\longrightarrow$ B + e$^-$

a A + b B + x X $\xrightarrow{k}$ product(s)

$$\frac{-d[B]}{dt} = k [A]^a [B]^b [X]^x$$
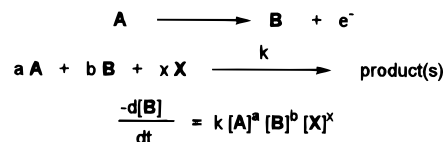
early in the electrolysis but was converted to other products upon further electrolysis. (The yield of **7** reached a maximum of 37% after 2 equiv of electrons was transferred). A small quantity of anthraquinone (**8**) was detected, even at the early stages of the electrolysis. Bianthrone (**9**) was also detected in runs at low methanol concentration.

7   **8**   **9**
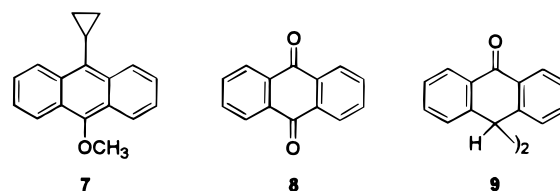
2. Linear Sweep, Cyclic, and Derivative Cyclic Voltammetry. The mechanism and kinetics of decay of radical cations generated from **1** and **2** were studied electrochemically. Voltammetric techniques such as cyclic voltammetry, derivative cyclic voltammetry (CV, DCV), or linear sweep voltammetry (LSV) permit assignment of the rate law for the decay of species generated (reversibly) by heterogeneous electron transfer (Scheme 2), where **A** represents the neutral substrate, **B** the radical cation, and **X** another chemical entity in solution which may be involved in the reaction (e.g., nucleophile).

In cases where no reverse wave is observed in the cyclic voltammogram, linear sweep voltammetry (LSV) is a powerful technique for studying the follow-up chemistry of the electrogenerated intermediate.[17,18] Put briefly, the observed variation in the forward peak potential (E_p) as a function of sweep rate ν, substrate concentration [**A**], and auxiliary reagent (nucleophile) concentration [**X**] provides useful information regarding the rate law for decay of electrogenerated species **B**.

When a reverse wave *is* observed, cyclic and derivative cyclic voltammetry (CV, DCV) and the "reaction order approach" advocated by Parker et al. are applicable.[18] The reaction order approach provides a means of assessing the rate law for radical ion decay by observing the variation of the cathodic to anodic derivative peak current ratio (I_{pc}'/I_{pa}') as a function of [**A**], [**X**], and ν.[18]

(17) Nadjo, L.; Savéant, J. M. *Electroanal. Chem.* **1973**, *48*, 113.
(18) Parker, V. D. in *Topics in Organic Electrochemistry*; Fry, A. J., Britton, W., Eds.; Plenum Press: New York, 1986; pp 35−79. Parker, V. D. In *Comprehensive Chemical Kinetics, Vol. 26, Electrode Kinetics: Principles and Methodology*; Bamford, C. H., Compton, R. G., Eds.; Elsevier: New York, 1986; pp 145−202.
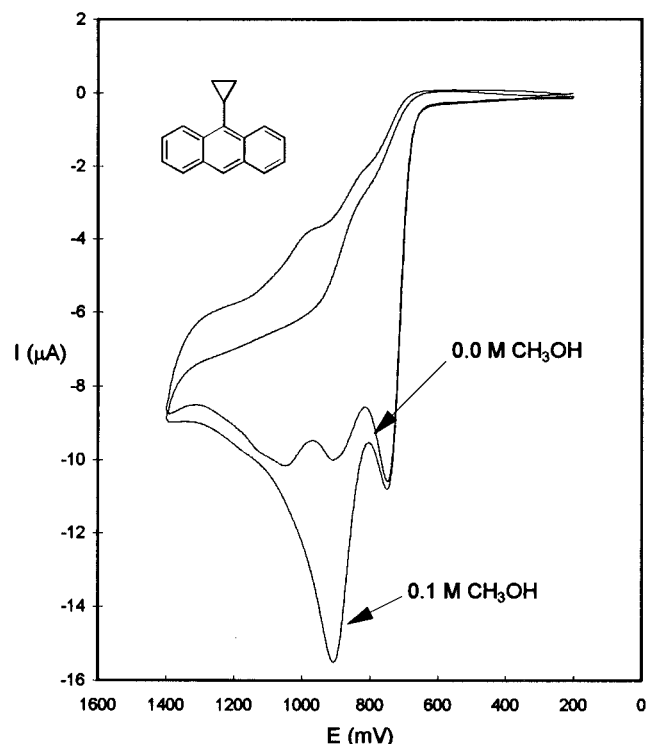
Figure 1. Cyclic voltammogram of 9-cyclopropylanthracene (**1**) at 200 mV/s (CH$_3$CN solvent, LiClO$_4$ supporting electrolyte, 0.1 M Ag$^+$/Ag reference).

Table 3. LSV Analysis of the Electrochemical Oxidation of 9-Cyclopropylanthracene (1)

rate law	$\partial E_p/\partial \log(\nu)$	$\partial E_p/\partial \log[\mathbf{A}]$	$\partial E_p/\partial \log[\mathbf{X}]^a$
$k[\mathbf{B}]$	29.6^b	0^b	0^b
$k[\mathbf{B}]^2$	19.7^b	-19.7^b	0^b
$k[\mathbf{B}]^2[\mathbf{X}]/[\mathbf{A}]$	19.7^b	0^b	-19.7^b
observed	21 ± 1	$-21 ± 1$	0 ± 1

^{a} X = CH$_3$OH. ^{b} Theoretical response, see refs 18 and 19.

9-Cyclopropylanthracene (1). The cyclic voltammogram of **1** (Figure 1) is characterized by an initial oxidation wave ($E_p \approx$ +780 mV at 500 mV/s) and several additional oxidation waves at more positive potentials. In the presence of CH$_3$OH the peaks at more positive potentials are perturbed but the initial oxidation wave is unaffected (i.e., the peak potential and current remain the same, Figure 1). The initial oxidation wave is irreversible at all accessible sweeprates (up to 50 V/s for our system). Consequently, LSV was an appropriate technique for studying this system.

E_p was found to vary both as a function of sweeprate and substrate concentration but was *independent* of the concentration of methanol (Table 3). These observations are in excellent agreement with a second-order mechanism for radical cation decay: $-\mathrm{d}[\mathbf{1}^{\bullet+}]/\mathrm{d}t = k[\mathbf{1}^{\bullet+}]^2$.

9-Bromo-10-cyclopropylanthracene (2). The cyclic voltammogram of **2** (Figure 2) reveals an initial oxidation wave ($E_p \approx$ +950 mV at 2000 mV/s) and subsequent oxidation waves at more positive potentials. However, unlike **1**, at higher sweeprates the initial oxidation wave becomes reversible (Figure 3). At the higher sweeprates, the initial wave corresponds to a one-electron process (**2** → **2**$^{\bullet+}$ + e$^-$). In the presence of methanol, the initial oxidation wave becomes irreversible and corresponds to a 2 e$^-$ process. (Details regarding electron stoichiometry are provided in the Supporting Information.)

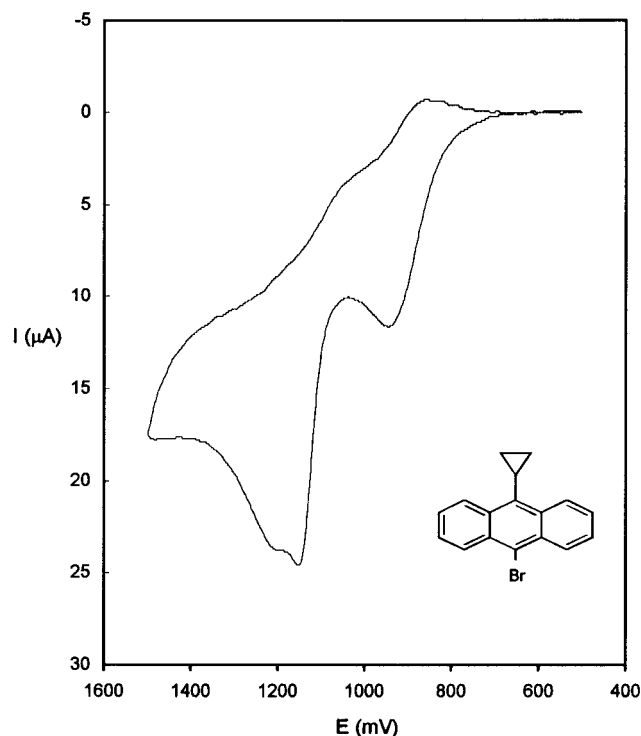At the higher sweeprates, the DCV reaction order approach is applicable. The results of these experiments

Figure 2. Cyclic voltammogram of 9-bromo-10-cyclopropyl-anthracene (**2**) at 2000 mV/s (CH$_3$CN solvent, LiClO$_4$ supporting electrolyte, 0.1 M Ag$^+$/Ag reference).
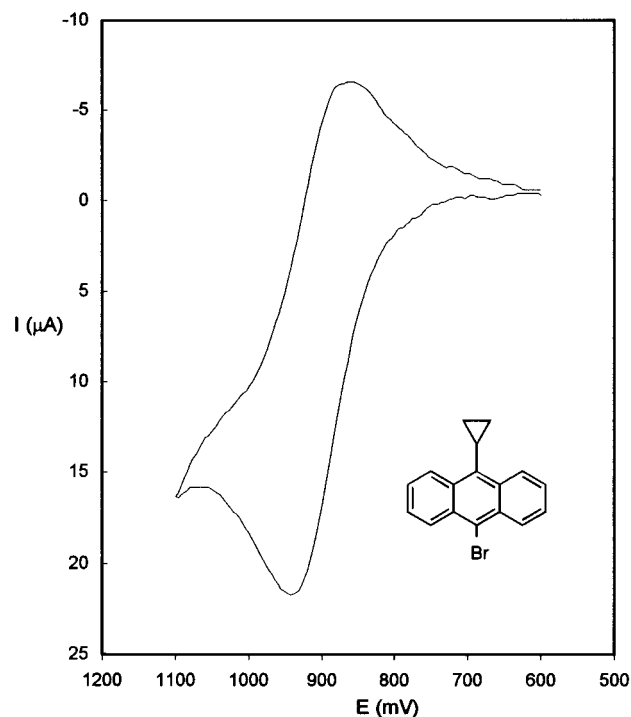

Figure 3. Cyclic voltammogram of 9-bromo-10-cyclopropyl-anthracene (**2**) at 8000 mV/s (CH$_3$CN solvent, LiClO$_4$ supporting electrolyte, 0.1 M Ag$^+$/Ag reference).

are summarized in Table 4. Two rate laws are consistent with the observed DCV results. (The DCV reaction order approach does not allow deconvolution of the individual reaction orders in **A** and **B**.[18]) However, both CV and LSV permit the separation of the individual reaction orders in **A** and **B**. LSV is applicable at lower scanrates where no reverse (cathodic) wave is observed. At low scan rates, E_p was found to vary as a function of

Table 4. DCV Analysis of the Electrochemical Oxidation of 9-Bromo-10-cyclopropylanthracene (2)

rate law	$\partial \log(\nu_C)/\partial \log[A]$	$\partial \log(\nu_C)/\partial \log[X]^a$	$R_{A/B}$	$R_X{}^a$
$k[B][X]$	0.0^b	1.0^b	1	1
$k[B]^2[X]$	1.0^b	1.0^b	2	1
$k[A][B][X]$	1.0^b	1.0^b	2	1
observed	1.1 ± 0.1	1.1 ± 0.1	2	1

[a] $X = CH_3OH$. [b] Theoretical response, see ref 18.

Table 5. LSV Analysis of the Electrochemical Oxidation of 9-Bromo-10-cyclopropylanthracene (2)

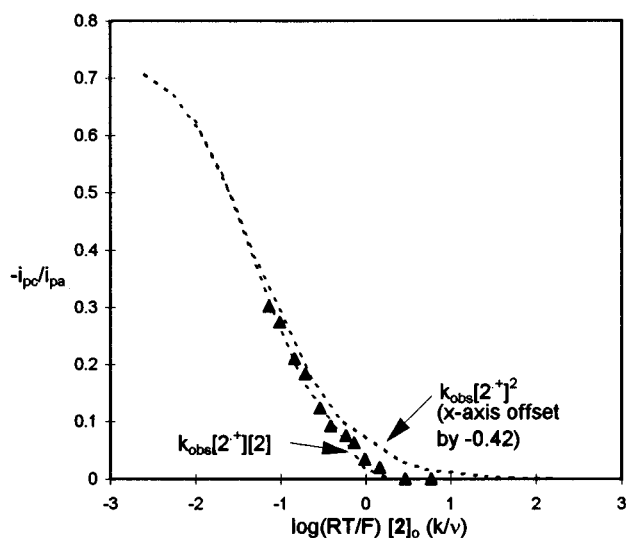| rate law	$\partial E_p/\partial \log(\nu)$	$\partial E_p/\partial \log[A]$	$\partial E_p/\partial \log[X]$
$k[A][X]$	29.6^a	0.0^a	-29.6^a
$k[A][B]$	29.6^a	-29.6^a	0.0^a
$k[A][B][X]$	29.6^a	-29.6^a	-29.6^a
observed	31 ± 1	-30 ± 1	-30 ± 1

[a] Theoretical response, see refs 18 and 19.

Figure 4. Variation of the cathodic to anodic current ratio $(-i_{pc}/i_{pa})$ with sweeprate for the oxidation of 9-bromo-10-cyclopropylanthracene (**2**, 0.25 M CH_3OH, CH_3CN solvent, $LiClO_4$ supporting electrolyte).

sweeprate and both the concentrations of **2** and CH_3OH (Table 5), supporting a rate law that is first order each in **2**[.]+, **2**, and CH_3OH: $-d[2^{•+}]/dt = k [2^{•+}] [2][CH_3OH]$.

At higher sweeprates where the CV becomes partly reversible, differentiation between the rate laws $k[A][B][X]$ vs $k[B]^2[X]$ can also be achieved by examining the variation of the cathodic to anodic current ratio (i_{pc}/i_{pa}) as a function of sweeprate.[19] In Figure 4, the theoretical response for these two rate laws[20] and the experimental results obtained at 0.25 M CH_3OH are compared.[21] A substantially better fit to the curve corresponding to the rate law first order each in A and B is observed.[22]

Discussion

1. Oxidation of 9-Cyclopropylanthracene (1).

LSV results for **1** show that decay of **1**[.]+ in CH_3CN/CH_3OH is second order in radical cation and zero order in CH_3OH. Consequently, CH_3OH attack must occur *after* the rate-limiting step. On the basis of these results, a disproportionation mechanism for decay of the radical cation from **1** is proposed (Scheme 3).[23] Because the dication will invariably be more reactive toward nucleophiles than the radical cation, it is reasonable to suppose that $k_2[CH_3OH] > k_{-1}[1]$ so that the overall rate law reduces to $k_1[1^{•+}]$.[2] A nearly identical mechanism for decay of 9-alkylanthracene radical cations in CH_3CN/H_2O, studied by stopped-flow kinetics, was recently

Scheme 3
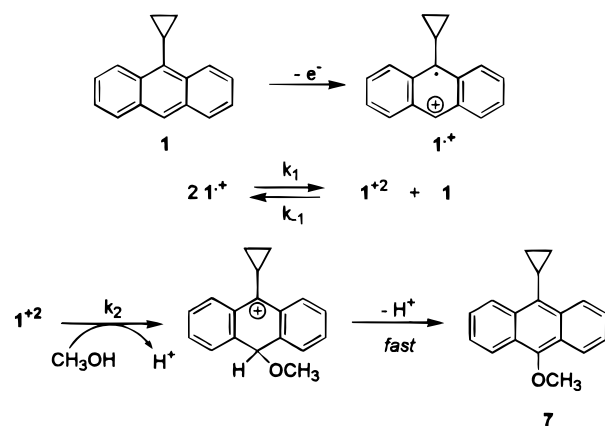
Scheme 4
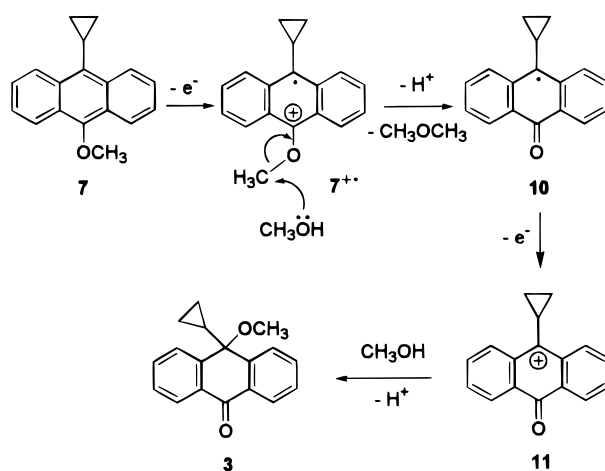
reported by Fujita and Fukuzumi.[24] This mechanism is further supported by the bulk electrolysis results which reveal that **7** is the product initially produced during the oxidation. The isolation of **7** and **3** as the only detectable products provides direct evidence that the cyclopropyl group survives both the radical cation and dication stages of oxidation.

Further oxidation of **7**[25] forms **7**[.]+ which likely undergoes oxidative methyl transfer (Scheme 4), as proposed in Parker's studies of the anodic oxidation of dimethoxydurene,[26] to form **10**. Further oxidation yields **11** which leads to the isolated product (**3**) after nucleophilic attack of methanol.

(19) Andrieux, C. P.; Savéant, J. M. In *Investigation of Rates and Mechanisms of Reactions, Part II*, 4th ed.; Bernasconi, C., Ed.; Wiley: New York, 1986; pp 305–390. See also: Andrieux, C. P.; Nadjo, L.; Savéant, J. M. *J. Electroanal. Chem.* **1970**, *26*, 147.

(20) Simulations were performed using DigiSim 2.0, (Bioanalytical Systems, Inc., W. Lafayette, IN) for the rate laws $k_{obs}[A][B]$ and $k_{obs}[B]^2$, where $k_{obs} = k[CH_3OH]$.

(21) For the data in Figure 4, the cathodic current (i_{pc}) is measured from the zero-current axis.

(22) Similar results were obtained at other concentrations of methanol (Supporting Information). The pseudo-second-order rate constant k_{obs} was found to vary with [CH_3OH]: $k_{obs} = 4.3 \times 10^3$, 1.1×10^4, and 2.6×10^4 M^{-1} s^{-1} at 0.25, 0.5, and 1.0 M CH_3OH, respectively. Thus, based upon CV analysis, the overall rate law is $k[A][B][X]$ with $k = 2.9 \times 10^4$ M^{-2} s^{-1}.

(23) The factors which affect whether radical cation decay might occur via disproportionation have been extensively discussed by Parker, see ref 14.

(24) Fujita, M.; Fukuzumi, S. *Chem Lett.* **1993**, 1911.

(25) As might be expected, the electron-donating methoxy in **7** causes the molecule to be more easily oxidized than starting compound **1**. The CV of **7** exhibits a peak potentail of +676 mV (0.69 mM in $CH_3CN/LiClO_4$). Under analogous conditions, E_p for **1** is ca. 750 mV.

Scheme 5
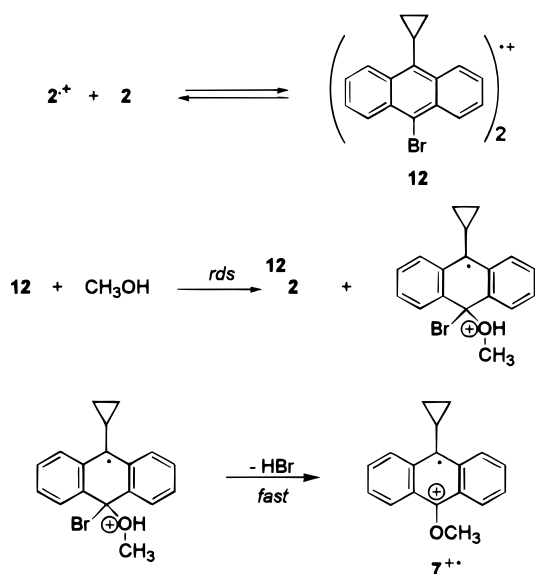
Because the anodic process produces H$^+$, some of **3** is converted to cyclopropyl-ring-opened products either during the electrolysis or upon workup.

2. Oxidation of 9-Bromo-10-cyclopropylanthracene (2). CV, DCV, and LSV results for **2** are all consistent with a rate law for decay of **2**$^{•+}$ which is first order each in radical cation, parent compound, and methanol ($-d[\mathbf{2}^{•+}]/dt = k[\mathbf{2}^{•+}][\mathbf{2}][CH_3OH]$). The reason **2**$^{•+}$ does not decay via a disproportionation mechanism (as was proposed for **1**$^{•+}$) may be due to the fact that the bromine substituent deactivates the aromatic ring, making the removal of a *second* electron from **2**$^{•+}$ energetically prohibitive. (Parker found that $E°$ for 9-bromoanthracene was more positive than anthracene by 90 mV).[27] As a consequence of having the disproportionation pathway effectively "turned-off," decay of the radical cation follows a different pathway, presumably involving nucleophilic attack of CH$_3$OH prior to or during the rate-limiting step. However, the appearance of **2** in the rate law was somewhat unexpected.

Two plausible mechanisms account for the presence of **2** in the rate law. The first involves formation of π-complex between **2** and **2**$^{•+}$ (**12**, Scheme 5). Radical cation/neutral molecule complexes involving aromatic radical cations have been characterized spectroscopically and are usually formulated as a π-dimer with the two molecules oriented face to face, with charge and spin delocalized into both rings.[28] (Radical cation **7**$^{•+}$ presumably undergoes the same follow-up chemistry outlined in Scheme 4.)

An alternative possibility is that CH$_3$OH attacks the radical cation directly (prior to the rate-limiting step)[29] and that the neutral substrate serves as a "shuttle" in a subsequent bromine atom or H$^+$ transfer step. Our results do not allow differentiation between these two possibilities.

3. Thermodynamic Considerations. It might be argued that the failure of **1**$^{•+}$ and **2**$^{•+}$ to undergo ring opening may be thermodynamic in origin, i.e., because

of the intrinsic stability of the anthracene radical cations, ring opening is thermodynamically (and thus kinetically) disfavored. Similar arguments have been advanced to explain the extremely low rate of ring opening of several cyclopropane-containing radical anions.[30]

Previously, we devised a thermodynamic cycle (Scheme 6) to estimate $\Delta G°$ for the CH$_3$OH-induced ring opening of a cyclopropylarene radical cation in CH$_3$CN.[10] The pertinent $\Delta G°$s for reactions i → vi were obtained as follows: (i) the oxidation potential of Ar-c-C$_3$H$_5$,[31] (ii) the C−C bond dissociation energy of cyclopropane (BDE$_{C-C}$ = 61 kcal/mol) corrected for the radical stabilization energy (RSE) of the different aryl groups,[32] (iii) the bond dissociation energy of a 1° R−OCH$_3$ bond (BDE$_{C-O}$ = 82 kcal/mol),[33] (iv) the H−O bond strength of methanol (BDE$_{O-H}$ = 104 kcal/mol), (v) the standard potential of the H$^+$/H$^•$ couple in CH$_3$CN (reported by Parker to be −1.88 V vs NHE),[34] and (vi) the difference in pK_a between CH$_3$CN and the ether oxygen (pK_a(CH$_3$CN) = −10.12;[35] pK_a(CH$_3$CH$_2$OCH$_2$CH$_3$) = −3.59).[36] The results of this analysis are summarized in Table 6.

As the data in Table 6 show, these ring-opening reactions are extremely exothermic for Ar = phenyl, α-naphthyl, or 9-anthryl. Thus the fact that 9-cyclopropylanthracene radical cations do not undergo ring opening is *not* because the ring opening is endothermic.

4. Nature of the Transition State for Ring Opening. Methanol-induced ring opening of Ar-c-C$_3$H$_5$$^{•+}$ is substantially exothermic for Ar = phenyl, α-naphthyl, and 9-anthryl (−39, −28, and −20 kcal/mol, respectively). For such exothermic reactions, an early (reactant-like) transition state would normally be anticipated on the basis of the Hammond postulate. However, the change from Ar = phenyl to naphthyl results in a 6 order of magnitude decrease in rate, corresponding to $\partial\Delta G^{\ddagger}/\partial\Delta G° \geq 0.77$ and thus suggesting a late (product like) transition state.[10]

There are two important contributors to $\Delta G°$ for ring opening of cyclopropylarene radical cations: (a) the ability of Ar to stabilize the ring-closed radical cation (i.e., $E°_{Ar^{•+}/Ar}$), and b) the ability of Ar to stabilize the radical portion of the ring-opened, distonic radical cation (RSE-(Ar)). Of these two, the former is far more important.

(26) Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1968**, 610.

(27) Norrsell, F.; Handoo, K. L.; Parker, V. D. *J. Org. Chem.* **1993**, *58*, 4929

(28) Eberson, L.; Hartshorn, M. P.; Persson, O. *J. Chem. Soc., Perkin Trans. 2* **1995**, 409 and references therein.

(29) Norrsell, F.; Handoo, K. L.; Parker, V. D. *J. Org. Chem.* **1993**, *58*, 4929.

(30) (a) Tanko, J. M.; Drumright, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 5362. (b) Tanko, J. M.; Drumright, R. E. *J. Am. Chem. Soc.* **1992**, *114*, 1844. (c) Tanko, J. M.; Drumright, R. E.; Suleman, N. K.; Brammer, L. E., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 1785. (d) Tanko, J. M.; Brammer, L. E., Jr.; Hervas', M.; Campos, K., *J. Chem. Soc., Perkin Trans. 2* **1994**, 1407.

(31) Because the CV of **1** is irreversible, it was not possible to determine $E°$ experimentally. However, ionization potentials derived from semiempirical MO theory (AM1) have been shown to accurately predict $E°$s for a series of aromatic hydrocarbons: $E°$ (V vs NHE) = 0.9121 × IP − 5.8255 (ref 10). For **1**, the AM1-calculated IP is 8.01 eV leading to an $E°$ of 1.48 V. For **2**, $E°$ is predicted to be 1.599 V (based upon a calculated IP of 8.14 eV). This calculated value compares very favorably to the experimentally determine value of 1.498 V. (Note: At higher sweeprates, the CV of **2** is reversible, permitting determination of $E°$.)

(32) RSEs for ArCH$_2$$^•$ were taken as the difference in the bond strength of ArCH$_2$−H (88.0, 85.1, and 81.8 kcal/mol for Ar = C$_6$H$_5$, α-C$_{10}$H$_7$, and 9-C$_{14}$H$_9$, respectively) and CH$_3$CH$_2$−H (98.2 kcal/mol). Bond strengths were taken from McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(33) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 309.

(34) Parker, V. D. *J. Am. Chem. Soc.* **1992**, *114*, 7458.

(35) Deno, N. C.; Gaugler, R. W.; Wisotsky, M. J. *J. Org. Chem.* **1966**, *31*, 1967.

(36) Deno, N. C.; Turner, J. O. *J. Org. Chem.* **1966**, *31*, 1969.

Scheme 6

Reaction	Free energy term
$Ar\text{-}c\text{-}C_3H_5^{\cdot+} + e^- \longrightarrow Ar\text{-}c\text{-}C_3H_5$	$-nFE_{Ar\cdot+/Ar}$
$Ar\text{-}c\text{-}C_3H_5 \longrightarrow Ar\diagdown\diagup^{\cdot}$	$BDE_{C\text{-}C} - RSE(Ar)$
$Ar\diagdown\diagup^{\cdot} + CH_3O\cdot \longrightarrow Ar\diagdown\diagup OCH_3$	$-BDE_{C\text{-}O}$
$CH_3OH \longrightarrow CH_3O\cdot + H\cdot$	$BDE_{O\text{-}H}$
$H\cdot \longrightarrow H^+ + e^-$	$nFE^o{}_{H+/H\cdot}$
$Ar\diagdown\diagup OCH_3 + H^+ \longrightarrow Ar\diagdown\diagup \overset{H}{\underset{\oplus}{O}}CH_3$	$2.303RT(pK_a[CH_3CNH^+] - pK_a[R_2OH^+])$
$Ar\text{-}c\text{-}C_3H_5^{\cdot+} + CH_3OH \longrightarrow Ar\diagdown\diagup \overset{H}{\underset{\oplus}{O}}CH_3$	ΔG^o

Table 6. ΔG^o for the Methanol-Induced Ring Opening of Cyclopropylarene Radical Cations in CH_3CN

aryl group	$E^o{}_{Ar\cdot+/Ar}$ (V vs NHE)	RSE (kcal/mol)	ΔG^o (kcal/mol)[a]
phenyl	2.58[b]	10.2[b]	−39.1[b]
α-naphthyl	1.99[b]	13.1[b]	−28.4[b]
9-anthryl	1.48	16.4	−20.0

[a] $\Delta G^o = 30.7 - 23.1 E_{Ar\cdot+/Ar} - RSE(Ar)$ in kcal/mol, see text and Scheme 8. [b] Reference 10.
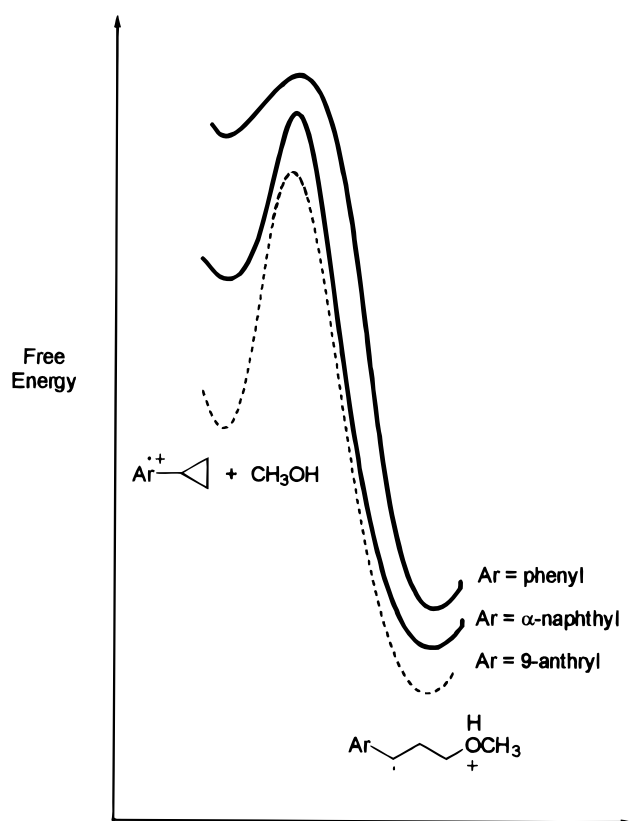

Figure 5. Effect of different aryl groups on the reaction coordinate diagram for the methanol-induced ring opening of $Ar\text{-}c\text{-}C_3H_5^{\cdot+}$

On this basis, the implication of a product-like transition state for ring opening is that the aromatic ring is expected to have little effect on the free energy of the transition state but a large effect on the free energy of the reactants (Figure 5). These arguments are reasonable in light of the mechanism associated with these ring-opening reactions. In the reacting radical cation, charge and spin are highly delocalized and able to enjoy the

stabilization afforded by the aromatic ring. In the transition state (**13**), however, although the radical portion of the developing distonic radical ion can still derive stabilization from the aromatic ring, the cation portion becomes highly localized at C-2 and at the oxygen of the attacking nucleophile.
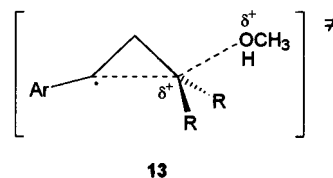
5. Stereoelectronic Considerations. Stereoelectronic factors may also contribute to the high barrier associated with the ring opening of 9-cyclopropylanthracene radical cations. Two conformational extremes are important for cyclopropane rings attached to a π-system, bisected ($\theta = 0°$) and perpendicular ($\theta = 90°$), where θ is the angle defined by the cyclopropyl methine C−H bond with respect to the atoms of the adjacent π-system. In general, the bisected conformation is preferred because overlap between the cyclopropyl HOMO and LUMO of the π-system is maximal in this conformation[37] and is thus expected to be the reactive conformation for the ring opening reaction.
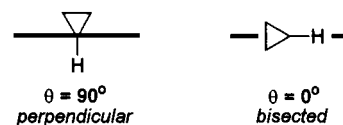
Earlier studies have found that 9-cyclopropylanthracene (neutral molecule) adopts the perpendicular conformation because the normally preferred bisected is destabilized by steric interactions between the cyclopropyl group and the peri-hydrogens.[38] The conformational preference(s) of 9-cyclopropylnaphthalene radical cation was explored using SCF-MO theory (AM1, C.I. = 1).[39] AM1 calculations suggest that for 9-cyclopropylanthracene the perpendicular conformation is preferred by 4.5 kcal/mol.

(37) For an excellent discussion of qualitative MO theory pertaining to arylcyclopropanes, see Takahashi, Y.; Ohaku, H.; Nishioka, N.; Ikeda, H.; Miyashi, T.; Gormin, D. A.; Hillinski, E. F. *J. Chem. Soc., Perkin Trans. 2* **1997**, 303.
(38) Drumright, R. E.; Mas, R. H.; Merola, J. S.; Tanko, J. M. *J. Org. Chem.* **1990**, *55*, 4098.

However, in 1969, Bauld, et al. reported the ambient temperature EPR spectrum of **1**[.+] (generated from treatment of **1** with H_2SO_4).[40] The observed hyperfine coupling constant to the cyclopropyl methine hydrogen ($a_H{}^\beta$) was reported to be 4.0 G, and the spectrum was interpreted on the basis of a freely rotating cyclopropyl group with a slight preference for the bisected conformation.[40] However, variable temperature experiments were not performed, and it is difficult to assess whether the EPR spectrum is more consistent with a time-averaged signal arising from both conformations or a single, discrete conformation (AM1 calcuations predict $a_H{}^\beta$ to be 0.7 and 7.0 G for the bisected and perpendicular conformations, respectively.)[41] At present, it is not possible to assess whether the transition state for ring opening is even *higher* than that depicted in Figure 5 because of unfavorable stereoelectronic factors. 9-Cyclopropylanthracene radical cations do not appear to be a good test case for ascertaining the role of stereoelectronic factors on the rate of these nucleophile-induced ring-opening reactions.

6. Implications Regarding the Use of Cyclopropyl-Containing Substrates as Probes for Radical Cation Intermediates. The fact that these radical cations do not undergo cyclopropane ring opening is especially significant because cyclopropyl-containing compounds are often utilized as probes for radical cation intermediates in a number of important chemical and biochemical oxidations (e.g. MAO-A, c-P450).[1–4] The assumption is that radical cation intermediacy can be inferred if ring-opened products are formed. These results demonstrate that for some substrates (a) ring-opened products might not be produced despite the fact that radical cations are bona fide intermediates of the oxidation and/or (b) that other intermediates or products produced during oxidation may lead to ring opening.

7. Note on the Formation of Perchlorate Ester 5. Suprisingly, perchlorate ester **5** was successfully isolated and characterized despite the unstable and extremely explosive nature of alkyl perchlorates. Because of the novelty of this compound,[42] some discussion of its characterization is warranted. The IR spectrum of **5** exhibited two peaks at 1230 and 1260 cm^{-1} (Cl−O asymmetric stretching) and a peak at 1040 cm^{-1} (Cl−O symmetric stretching), which are a characteristic of covalent organic perchlorates.[42] The ^{1}H NMR spectrum of **5** possesses a triplet shifted unusually downfield ($\delta = 4.8$ ppm vs TMS) corresponding to the CH$_2$ α to the perchlorate group. Finally, the molecular weight (and formula) were both confirmed using FAB-MS, HRMS, and elemental analysis.

Conclusions

Radical cations generated from 9-cyclopropylanthracene (and derivatives) do *not* undergo nucleophile-assisted ring opening, despite the fact that these reactions are highly exothermic. These results are consistent with a model for the transtion state for ring opening of cyclopropylarene radical cations, which in terms of the distribution of charge and spin is more product-like than reactant-like. Thus, the effect of the aromatic ring on reaction rate is mainly due to changes in the free energy of the reactant(s), with only a small effect on the free energy of the transtion state for ring opening. These results suggest that caution should be exercised when using cyclopropyl-containing substrates as probes for radical cation intermediates in that they demonstrate that a potent thermodynamic driving force for ring opening does not guarantee that ring opening will occur.

Experimental Section

General. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR were run at 270 and 400 MHz. All chemical shifts are reported in δ units relative to TMS in CDCl$_3$. LiClO$_4$ (Aldrich) was dried under vacuum before use. Acetonitrile (Mallinckrodt, HPLC grade, 99+%) was refluxed over calcium hydride for at least 1 h and then distilled slowly, discarding the first 5 and last 10% of distillate. Methanol (Baker Analyzed HPLC grade) was dried by stirring over calcium hydride, followed by distillation. 9-Cyclopropylanthracene was prepared according to published procedures.[40] 9-Bromo-10-cyclopropylanthracene was prepared from 9-cyclopropylanthracene via reaction with NBS.[43]

Electrochemical Experiments. Electrochemical measurements were performed on an EG&G Princeton Applied Research model 273 potentiostat/galvanostat interfaced to an MS-DOS computer. The details regarding this instrument and data collection software were described earlier.[30] Voltammetric measurements were performed on solutions which contained 0.5 M LiClO$_4$ in CH$_3$CN. The solutions were prepared by weighing LiClO$_4$ into an oven-dried 10 mL volumetric flask and then placing the volumetric flask, together with all voltammetry cell pieces, in a vacuum-drying oven under vacuum (30−40 mmHg) at 40 °C for at least 8 h CH$_3$CN and the desired amount of CH$_3$OH were added to the septum-sealed volumetric flask via syringe. The resulting solution was transferred to a vacuum oven-dried, argon-purged voltammetry cell. The electroactive substance was added, and the resulting solution was purged with argon. A three-electrode voltammetry cell was utilized: A Pt microdisk working electrode (0.32 mm diameter) was prepared for use by polish-

(39) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. F. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(40) Bauld, N. L.; McDermed, J. D.; Hudson, C. E.; Rim, Y. S.; Zoeller, J., Jr.; Gordon, R. D.; Hyde, J. S. *J. Am. Chem. Soc.* **1969**, *91*, 6666.

(41) Spin desnities for the H(1s) orbital were determined using the keywords UHF and ESR and converted to hyperfine coupling constants using the relationship: $a_H = \rho H$, 1s x 382 G. (The constant 382 G is derived from the experimentally observed $a_H{}^\alpha$ for the methyl radical (23.0 G) and the AM1-calculated spin density in H(1s) (0.0602). Hyperfine coupling constants calculated in this manner nicely duplicate experimental values for several cyclopropyl-containing radicals and radical ions. For example, the observed hyperfine couplings for the cyclopropylcarbinyl radical (which adopts the bisected conformation) are $a_H{}^\alpha = 20.74$ G, $a_H{}^\beta = 2.55$ G, $a_H{}^\chi = 2.01, 2.98$ G (Kochi, J. K.; Krusic, P. J.; Eaton, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 1877). The AM1-derived values are $a_H{}^\alpha = 21.8$ G, $a_H{}^\beta = 2.65$ G, $a_H{}^\chi = 0.68, 1.6$ G. For 9-cyclopropylanthracene radical anion (which adopts the perpendicular conformation), AM1 predicts $a_H{}^\beta = 5.9$ G (experimentally, $a_H{}^\beta = 6.64$ G.; ref 40).

(42) Recent studies have demonstrated that perchlorate ion can manifest nucleophilic properties in the presence of extraneous nucleophiles (e.g., halide ions). See: Zefirov, N. S.; Zhdankin, V. V.; Koz′min, A. S. *Russian Chem. Rev.* **1988**, *57*, 1041, and references therein.

(43) The following procedure was taken from Mas, R. H., Ph.D. dissertation, Virginia Polytechnic Institute and State University, 1989. A 20 mL carbon tetrachloride solution of bromine (35 μL, 0.69 mmol) was added dropwise to a mixture of 9-cyclopropylanthracene (0.30 g, 1.38 mmol) and NBS (0.12 g, 0.70 mmol) inside a 100 mL round-bottomed flask wrapped with Al foil and equipped with a magnetic stir bar. The reaction mixture was maintained at 15 °C with a water bath. After 1 h, 30 mL of saturated sodium bisulfite was added to quench the reaction. The organic layer was isolated, dried over anhydrous sodium sulfate, filtered, and evaporated. The resulting residue was dissolved in 40 mL of hexane, chilled in an ice bath, and filtered to remove any remaining NBS or succinimide. After column chromatography using neutral alumina and 1:30 benzene/hexane, 0.35 mg (85% yield) of 9-bromo-10-cyclopropylanthracene was obtained and subsequently recrystallized from ethanol: mp 113−114 °C; ^{1}H NMR δ 0.78 (2H, m), 1.48 (2H, m), 2.46 (1H, m), 7.50−7.61 (m, 4H), 8.56 (2H, m), 8.78 (2H, m); IR 2996, 2987, 1438, 1361, 1310, 1274, 1254, 1029, 1007, 954, 907, 865, 846, 817, 797, 757, 750, 699, 655, 612, 597, 578, 523; UV (C$_2$H$_5$OH) 399 (10, 243), 378 (10, 392), 359 (6, 176), 341 (1, 900), 257 (135 683); EI-MS *m/e* (%) 298 (11.8, M + 2), 296 (12.0, M$^+$), 217 (100), 215 (55), 202 (54), 189 (18), 176 (10), 108 (18).

ing with alumina slurry as outlined in the BAS electrode polishing kit (part no. MF-2056). An Ag/Ag$^+$ (0.10 M in CH$_3$-CN) electrode was used as a reference (+0.337 V vs SCE). A Pt wire (2 cm in length, 2 mm in diameter) was used as auxiliary electrode. The voltammetry cell was placed in a Fisher FS-14 solid state/ultrasonic bath filled with water. Between runs, the ultrasonic system was activated for 30 s to clean the working electrode surface and agitate the solution. Positive-feedback iR compensation was set as described previously (90% of oscillation value). All experiments were performed at ambient temperature (23 °C).

Preparative-scale electrolyses were performed on solutions which contained 0.1 M LiClO$_4$ in CH$_3$CN containing CH$_3$OH. The solutions were prepared as described for the voltammetry experiments. A conventional H-cell, with two compartments separated by a medium glass frit (22 mm in diameter), was utilized. The electrolyte solution (60 mL) was partitioned equally between the two compartments under argon. The electroactive substrate was added to the anodic compartment, and both anodic and cathodic compartments were purged for at least 10 min with argon before electrolysis. The working electrode was fabricated from Pt gauze (45 mesh, 30 mm × 20 mm). For the cathodic compartment, a coiled copper wire (2 mm in diameter, 5 dm in length) was utilized as the auxiliary electrode. The reference electrode was Ag/Ag$^+$. All electrolysis experiments were performed at ambient temperature (23 °C). Constant current electrolyses were performed at currents ranging from −25 to −40 mA. Both the anodic and cathodic compartments were purged with argon and agitated via ultrasound during electrolysis. GC and TLC were used to monitor the progress of the electrolyses.

Electroylsis of 9-Bromo-10-cyclopropylanthracene (2). **2** 56.0 mg (0.189 mmol) in CH$_3$CN containing 2.5 M methanol was electrolyzed at −30 mA for 27 min (2.7 equiv of electrons). The anodic solution (30 mL) was divided into two portions, and two workup procedures were employed. Aqueous work-up: one portion of electrolytic solution was extracted with H$_2$O/ ether for three times. The ether layers were combined, dried over anhydrous MgSO$_4$, and concentrated. Quantitative ^{1}H NMR analysis with [(CH$_3$)$_3$SiOSi(CH$_3$)$_3$] as internal standard was used to determine the yield of **3**. An analytical sample of **3** was obtained for characterization via flash column chromatography with CH$_2$Cl$_2$ as eluting solvent. Analogous procedures were followed for electrolyses in the presence of 4.1 and 0.25 M CH$_3$OH. The results are summarized in Table 1. Nonaqueous workup: The second portion of the electroytic solution was transferred into a 50 mL flask and evaporated. CH$_2$Cl$_2$ was added to extract the organic materials, and the resulting solution was filtered to remove LiClO$_4$. Yields of **4**, **5**, and **6** were determined by ^{1}H NMR analysis. Analytical samples of these compounds were obtained as follows: Flash column chromatography of the nonaqueous workup solution with CH$_2$Cl$_2$ as eluting solvent gave pure **4** and a mixture of **5** and **6**, which was subsequently separated via flash chromatography using a solvent gradient 5 → 20% EtOAc/hexane.

9-Cyclopropyl-9-methoxyanthrone (3): ^{1}H NMR δ 0.304 (m, 2H), 0.334 (m, 2H), 1.20 (m, 1H), 2.99 (s, 3H), 7.94 (t, 2H), 7.67 (t, 2H), 7.76 (d, 2H), 8.29 (d, 2H); ^{13}C NMR δ 2.44 (t), 28.1 (d), 52.3 (q), 77.6 (s), 126.7 (d), 127.3 (d), 127.9 (d), 132.1 (s), 133.1 (s), 144.2 (s), 183.4 (s); IR (cm^{-1}) 1665, 1601, 1458, 1319, 1272, 1072; EI-MS m/e (%) 265 (M + 1, 3.38), 264 (M$^+$, 18.7), 236 (M$^+$ − 28, 92), 223 (M$^+$ − C$_3$H$_5$, 100), 215 (17.8), 208 (15.3); HRMS (EI) for C$_{18}$H$_{16}$O$_2$, calcd 264.1150, found 264.1158, error 2.9 ppm.

Methoxy ether 4: ^{1}H NMR δ 2.95 (q, 2H, J = 7 Hz), 3.38 (s, 3H), 3.59 (t, 2H, J = 7 Hz), 6.62 (t, 1H, J = 7 Hz), 7.26− 7.50 (m, 2H), 7.53−7.64 (m, 2H), 7.76−7.85 (q, 2H), 8.21−8.32 (q, 2H); ^{13}C NMR δ 31.7 (t), 58.8 (q), 71.9 (t), 123.5 (d), 126.8 (d), 127.3 (d), 127.4 (d), 127.7 (d), 127.8 (d), 130.3 (s), 131.7 (d), 132.1 (s), 132.2 (s), 132.8 (d), 133 (d), 136.8 (d), 141.1 (s), 184.8 (s); IR (cm^{-1}) 1665, 1598, 1320, 1122; EI-MS m/e (%) 265 (M + 1, 7), 264 (M$^+$, 32.7), 249 (M − CH$_3$, 5.4), 219 (M − CH$_2$-OCH$_3$, 100), 45 (CH$_2$OCH$_3$$^+$, 91); HRMS (EI) for C$_{18}H_{16}O_2$, calcd 264.1150, found 264.1146, error −1.6 ppm.

Perchlorate ester 5: mp 98 °C; ^{1}H NMR δ 3.20 (q, 2H, J = 7 Hz), 4.73 (t, 2H, J = 7 Hz), 6.42 (t, 1H, J = 7 Hz), 7.50− 7.66 (m, 5H), 7.80 (d, 1H), 8.28 (q, 2H); ^{13}C NMR δ 29.2 (t), 74.4 (t), 123.4 (d), 127.0 (d), 127.3 (d), 127.7 (d), 128.1 (d), 128.5 (d), 130.5 (s), 131.9 (d), 132.3 (s), 133.1 (d), 134.6 (s), 136.1 (s), 140.4 (s), 184.5 (s); IR (cm^{-1}) 1664, 1598, 1474, 1382, 1317, 1289, 1269 (s, ν_s ClO$_3$), 1235 (s, ν_{as} ClO$_3$), 1098, 1037 (s, ν_s ClO$_3$); CI-MS m/e (%) 251 (MH$^+$ + 2 − ClO$_3$, 7.5), 249 (MH$^+$ − ClO$_3$, 5.4), 233 (MH$^+$ − ClO$_4$, 22.8), 231 (33.6), 195 (100), 194 (96.6); FAB-MS m/e (%) 335 (MH$^+$ + 2, 17.4), 333 (MH$^+$, 48.6), 251 (MH$^+$ + 2 − ClO$_3$, 16.5), 233 (MH$^+$ − ClO$_4$, 19.8), 231 (22.2), 220 (48.6), 219 (40.8), 83 (ClO$_3$$^+$, 34.2), 73 (65.4), 69 (HClO$_2$$^+$, 56.4), 55 (100); HRMS (CI) for C$_{17}$H$_{14}$O$_5$Cl (MH$^+$), calcd 333.0529, found 333.0512, error −5.0 ppm. Anal. Calcd for C$_{17}$H$_{13}$O$_5$Cl: C, 61.44; H, 3.95. Found: C, 60.63; H, 4.21.

Bromide 6: ^{1}H NMR δ 3.26 (q, 2H, J = 7 Hz), 3.57 (t, 2H, J = 7 Hz), 6.54 (t, 1H, J = 7 Hz), 7.45−7.56 (m, 2H), 7.59− 7.68 (m, 3H), 7.83 (d, 1H), 8.28 (q, 2H); ^{13}C NMR δ 31.9 (t), 33.95 (t), 126.9 (d), 127.4 (d), 127.5 (d), 127.7 (d), 128.2 (d), 133.0 (s), 130.4 (s), 131.8 (d), 132.2 (s), 132.24 (d), 132.5 (d), 132.9 (d), 136.6 (s), 140.7 (s), 184.6 (s); IR (cm^{-1}) 1662, 1598, 1474, 1383, 1315, 1287, 1098; EI-MS m/e (%) 314 (M + 2, 16.8), 312 (M$^+$, 16.5), 233 (40.8), 231 (25.8), 219 (45.6), 215 (100); HRMS (EI) for C$_{17}$H$_{13}$BrO, calcd 312.0150, found 312.0139, error −3.4 ppm.

Electrolysis of 9-Cyclopropylanthracene (1). 47.6 mg (0.218 mmol) of **1** in CH$_3$CN containing 2.5 M CH$_3$OH was electrolyzed at −30 mA for 35 min (3.0 equiv of electrons). Portions of the reaction mixture were subjected to aqueous and nonaqueous workup (vide supra) and quantitative ^{1}H NMR analysis. The results of this and other analogous runs are summarized in Table 2.

9-Cyclopropyl-10-methoxyanthracene (7). 1 (50.5 mg, 0.232 mmol) was electrolyzed at −30 mA for 25 min (2.0 equiv e$^-$'s). The progress of the electrolysis was monitored by GC and TLC (3:1 hexane:CH$_2$Cl$_2$) so as to stop the electrolysis when the yield of **7** was maximal. The anodic solution (30 mL) was extracted with ether and water several times, dried (MgSO$_4$), and concentrated. Yields (based upon ^{1}H NMR analysis) are summarized in Table 2. Flash column chromatography with a solvent gradient starting at 0% and finishing at 25% CH$_2$Cl$_2$/hexane yielded 18% (10.4 mg) of **7**: ^{1}H NMR δ 0.80 (m, 2H), 1.44 (m, 2H), 2.43 (m, 1H), 4.14 (s, 3H), 7.46− 7.55 (m, 4H), 8.34 (m, 2H), 8.77 (m, 2H); ^{13}C NMR δ 9.3 (t), 10.2 (d), 63.2 (q), 122.6 (d), 124.2 (s), 124.7 (d), 125.1 (d), 126.3 (d), 130.7 (s), 132.3 (s), 151.7 (s). IR (cm^{-1}) 1664, 1620, 1652, 1452, 1390, 1330, 1282, 1116, 1088, 1027; EI-MS m/e (%) 249 (M + 1, 8.5), 248 (M$^+$, 49), 247 (30), 233 (M − CH$_3$, 47), 217 (M − OCH$_3$, 100), 215 (89); HRMS (EI) for C$_{18}$H$_{16}$O, calcd 248.1201, found 248.1202, error 0.3 ppm.

Control Experiments. A 30 mL CH$_3$CN solution of **3** (27.7 mg) was divided into three portions: 1 mL of CH$_3$OH (2.5M) and 0.1 of g (0.1 M) of LiClO$_4$ were added to the first portion and the reaction was subsequently subjected to nonaqueous workup. TLC and GC of the resulting solution revealed only unreacted **3**. To the second portion were added 0.1 g of LiClO$_4$ and 1 drop of HBr (32%). The reaction mixture was subjected to nonaqueous workup. TLC and GC of resulting solution showed the complete conversion of **3** → **6**. The yield of **6** based on ^{1}H NMR analysis was 80%. To the third portion were added 0.1 g of LiClO$_4$ and 1 drop of HClO$_4$ (60−70%). Nonaqueous workup yielded 46% of **5** on the basis of ^{1}H NMR analysis.

Supporting Information Available: Discussion of electron stoichiometry and LSV, CV, and DCV plots for the oxidation of **1** and **2** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.