Radical Ion Probes. 6. Origin of the High Intrinsic Barrier to Nucleophile-Induced Ring Opening of Arylcyclopropane Radical Cations

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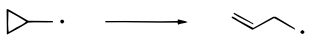
Abstract: Radical cations generated from 1-cyclopropylnaphthalene (**1**), 1-bromo-4-cyclopropylnaphthalene (**2**), and 2-cyclopropylnaphthalene (**3**) were studied electrochemically. Oxidation of all these substrates in CH_3CN in the presence of CH_3OH leads to cyclopropane ring-opened products, i.e., the corresponding (1,3-dimethoxypropyl)-naphthalenes. However, the rate constant for methanol-induced ring opening (Ar-c-$C_3H_5^{\bullet+}$ + CH_3OH → ArCH-($^{\bullet}$)$CH_2CH_2O(H^+)CH_3$) is extremely small (<20 M^{-1} s^{-1} for the α-cyclopropylnaphthalenes) despite the fact that ring opening is exothermic by nearly 30 kcal/mol. These results are explained on the basis of a product-like transition state for ring opening wherein the positive charge is localized on the cyclopropyl group, and thus unable to benefit from potential stabilization offered by the aromatic ring.

Introduction

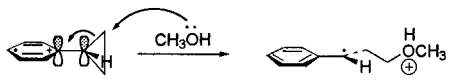
The fate of a cyclopropyl group incorporated into a substrate participating in a chemical process often provides useful mechanistic information about the importance of radicals and/or radical ions as intermediates along the reaction pathway. In earlier work, we examined the chemistry of radical anions which undergo ring opening in analogy to the cyclopropylcarbinyl → homoallyl neutral free radical rearrangement (eq 1), and the suitability of these reactions as "probes" for single electron transfer (SET).[1−4]



(1)

Cyclopropane derivatives are also frequently employed as probes for radical *cation* intermediates in a number of important chemical and biochemical oxidations.[5−8] However, information regarding the rate of ring opening of cyclopropane-containing radical cations (and the effect of substituents on that rate) is somewhat scarce. To address this issue, we initiated a study of the chemistry of radical cations generated from cyclopropylarenes.

Dinnocenzo et al. have shown that ring opening of phenylcyclopropane radical cation occurs via a nucleophile-assisted (i.e., S_N2) pathway (eq 2).[9] This process has been well-

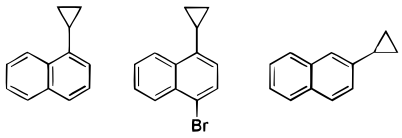


(2)

characterized in terms of its stereochemistry (inversion of configuration at carbon),[10,11] kinetics (first-order each in radical cation and nucleophile),[10,11] regiochemistry,[12,13] and kinetic isotope effects.[13] The rate of ring opening has been found to be highly sensitive to substituents on the aromatic ring: For a series of substituted phenylcyclopropane radical cations, a correlation to σ^+ was observed ($\rho \approx +2.2$).[13]

Results

Radical cations generated from **1**, **2**, and **3** in the presence of methanol were studied electrochemically. Preparative-scale electrolyses were performed in order to ascertain the nature of the products formed from oxidation of these substrates.[14] Voltammetric techniques such as cyclic and derivative cyclic



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voltammetry (CV, DCV) or linear sweep voltammetry (LSV) were employed to determine the rate law for the decay of $\mathbf{1}^{\bullet+}$,

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(3) Tanko, J. M.; Drumright, R. E.; Suleman, N. K.; Brammer, L. E., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 1785.
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(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.
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(12) Dinnocenzo, J. P.; Lieberman, D. R.; Simpson, T. R. *J. Am. Chem. Soc.* **1993**, *115*, 366.
(13) Dinnocenzo, J. P.; Zuilhof, H.; Lieberman, D. R.; Simpson, T. R.; McKechney, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 994.
(14) Anodic oxidation of cyclopropylarenes in the presence of CH_3OH generally leads to ring-opened products, i.e., the corresponding 1,3-dimethoxypropylarenes. See: Shono, T.; Matsumura, Y. *J. Org. Chem.* **1970**, *35*, 4157.

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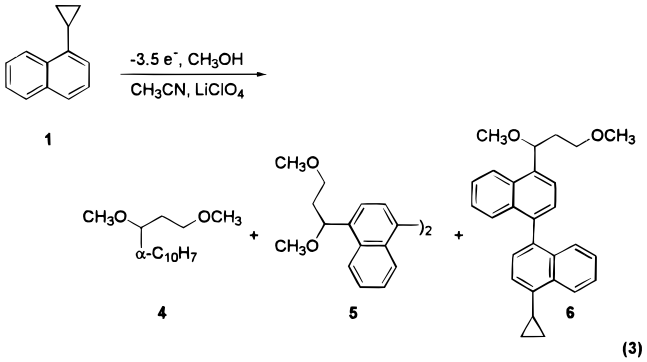
$2^{\bullet+}$, and $3^{\bullet+}$. The theory underlying these techniques has been fully described in the literature.[15,16] The results are summarized below.

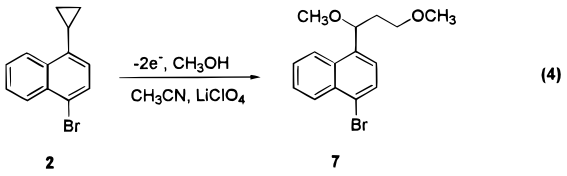
Product Studies. The anodic oxidation of **1** in CH_3CN/CH_3OH mainly produces cyclopropane ring-opened products: 1-(1,3-dimethoxypropyl)naphthalene (**4**) and dimer 4,4′-bis(1,3-dimethoxypropyl)-1,1′-binaphthalene (**5**, eq 3). In a typical run,



(3)

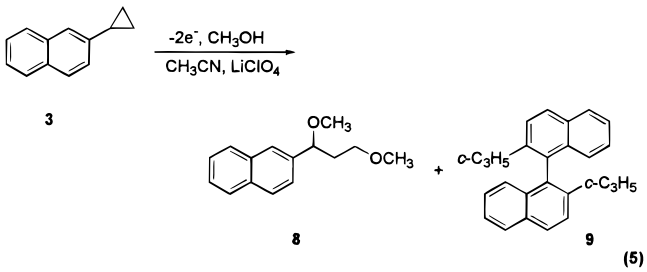
17.4% of **4**, 26.3% of **5**, and 7.5% of **1** were recovered after the transfer of 3.5 equiv of electrons. Minor product **6** was detected by GC/MS, but not isolated.

Oxidation of **2** yields exclusively cyclopropane ring-opened 1-bromo-4-(1,3-dimethoxypropyl)naphthalene (**7**), in 80% yield after the transfer of 2 equiv of electrons (eq 4). A 13.2% yield of **2** was also recovered.



(4)

The anodic oxidation of **3** in CH_3CN/CH_3OH yields, after the transfer of 2 equiv of electrons, 2-(1,3-dimethoxypropyl)-naphthalene (**8**) and dimer 2,2′-dicyclopropyl-1,1′-binaphthalene (**9**) as major products. The isolated yields of **8** and **9** were 16.2% and 17.5%, respectively (eq 5). In addition, a large amount of starting material (34.1%) was recovered.



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Voltammetry Studies. The cyclic voltammograms of **1** and **3** in CH_3CN are characterized by an initial oxidation wave (E_p = ~1130 mV for **1** and ~1160 mV for **3** at 400 mV/s) and continuous indistinguishable oxidation waves located at more positive potentials (Figures 1 and 2). Addition of methanol does not shift the position (i.e., peak potential) of the initial oxidation wave.

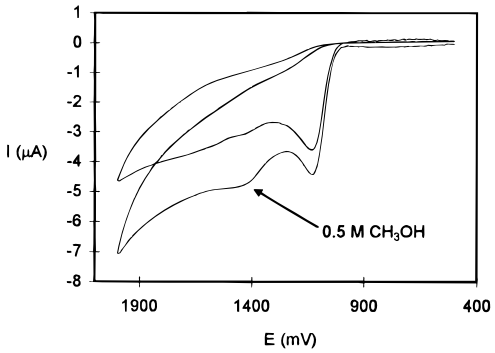

Figure 1. Cyclic voltammogram of 1-cyclopropylnaphthalene (**1**) in CH_3CN (0.5 M $LiBF_4$, 1.19×10^{-3} M **1**, $\nu = 400$ mV/s).

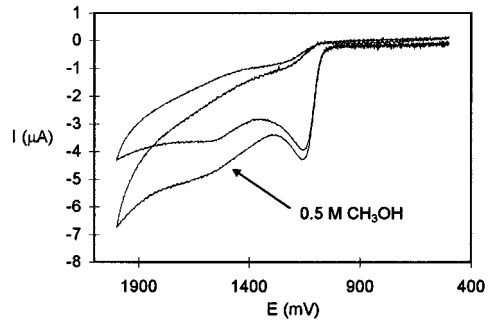

Figure 2. Cyclic voltammogram of 2-cyclopropylnaphthalene (**3**) in CH_3CN (0.5 M $LiClO_4$, 1.19×10^{-3} M **1**, $\nu = 400$ mV/s).

Because the initial waves are irreversible, LSV was employed to study the decay of $1^{\bullet+}$ and $3^{\bullet+}$. The peak potential (E_{pa}) of the initial oxidation wave of both substrates was found to vary as a function of both sweep rate (ν) and substrate concentration (C_A), but was independent of methanol concentration (Tables 1 and 2). These observations are in excellent agreement with a second-order rate law for radical cation decay, for which the theoretical response is $\partial E_p/\partial \log(\nu) = 19.7$, $\partial E_p/\partial \log([\mathbf{A}]) = -19.7$, and $\partial E_p/\partial \log([\mathbf{X}]) = 0$ (all in units of mV/decade, where **A** = substrate and **X** = CH_3OH).[15,16]

The cyclic voltammogram of **2** in CH_3CN is characterized by an initial oxidation wave (E_p = ~1245 mV, at 400 mV/s) and other subsequent oxidation waves located at much more positive potentials (Figure 3).

In the presence of methanol, the waves at more positive potentials appear to shift in the negative direction, but the initial oxidation wave is not affected. As was observed for **1** and **3**, the initial oxidation wave of **2** is irreversible, and thus, LSV is applicable. E_{pa} was found to vary as a function of both sweep rate and substrate concentration, but was independent of methanol concentration. The LSV results for the electrochemical oxidation of **2** (Table 3) are also consistent with a mechanism which is second-order in radical cation and zero order in methanol: $-d[\mathbf{2}^{\bullet+}]/dt = k[\mathbf{2}^{\bullet+}]^2$. Different supporting electrolytes and solvents do not alter the observed rate law.

When CH_2Cl_2 is used as solvent, the cyclic voltammogram of **2** changes significantly: The initial oxidation wave shifts to a more positive potential (ΔE_p = ~130 mV) and begins to merge with the subsequent oxidation waves (Figure 4, curve a). Unlike in CH_3CN, at higher sweep rates in CH_2Cl_2, the initial wave of **2** becomes reversible (Figure 4, curve b), indicating that $\mathbf{2}^{\bullet+}$ is longer-lived in CH_2Cl_2 than in CH_3CN. The DCV "reaction order approach" was employed to study

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Table 1. Observed LSV Response for the Oxidation of **1** in CH_3CN

electrolyte	$\partial E_p/\partial \log(\nu)^a$	$\partial E_p/\partial \log([\mathbf{1}])^b$	$\partial E_p/\partial \log([CH_3OH])^c$
0.5 M $LiBF_4$	19.5 ± 0.3 (1.19)	−18.2 ± 2.9 (1.19−9.52)	−0.34 ± 0.57 (1.19)
	18.8 ± 1.0 (2.26)	−23.1 ± 1.3 (0.476−9.52)	
	22.2 ± 0.9 (9.52)		
0.5 M $LiClO_4$	18.7 ± 0.3 (0.595)	−20.9 ± 2.8 (0.595−9.52)	1.50 ± 1.07 (6.85)
	20.0 ± 0.9 (9.52)	−19.3 ± 1.0 (1.67−12.9)	−0.20 ± 1.11 (1.25)

[a] 0.5 M CH_3OH, ν = 100−3000 mV/s; [**1**] (mM) appears in parentheses. [b] 0.5 M CH_3OH, ν = 400 mV/s; substrate concentration range (mM) appears in parentheses. [c] 0.025−0.5 M CH_3OH, ν = 400 mV/s; [**1**] (mM) appears in parentheses.

Table 2. Observed LSV Response for the Oxidation of **3** in CH_3CN (0.5 M $LiClO_4$)

electrolyte	$\partial E_p/\partial \log(\nu)^a$	$\partial E_p/\partial \log([\mathbf{3}])^b$	$\partial E_p/\partial \log([CH_3OH])^c$
0.5 M $LiBF_4$	16.8 ± 1.1 (1.2)	−20.5 ± 3.0 (1.19−7.14)	−0.54 ± 0.33 (1.2)
	18.4 ± 0.6 (7.1)		
0.5 M $LiClO_4$	18.6 ± 0.4 (1.2)	−22.0 ± 0.6 (1.19−7.14)	1.19 ± 0.37 (10)
	20.9 ± 0.4 (7.1)		

[a] 0.5 M CH_3OH, ν = 100−3000 mV/s; [**3**] (mM) appears in parentheses. [b] 0.5 M CH_3OH, ν = 400 mV/s; substrate concentration range (mM) appears in parentheses. [c] 0.025−0.5 M CH_3OH, ν = 400 mV/s; [**3**] (mM) appears in parentheses.

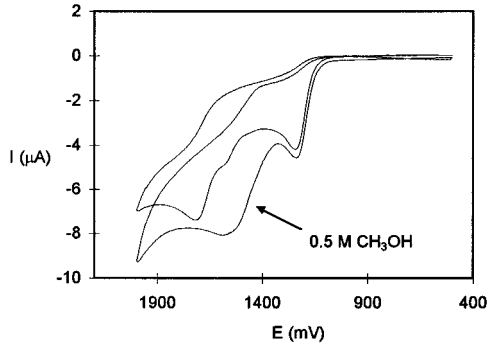

Figure 3. Cyclic voltammogram of 1-bromo-4-cyclopropylnaphthalene (**2**) in CH_3CN (0.5 M $LiBF_4$, 2.36 × 10^{-3} M **2**, ν = 400 mV/s).

decay of $\mathbf{2}^{\bullet+}$ (Table 4).[16] The results obtained from this analysis are also consistent with a bimolecular decay of $\mathbf{2}^{\bullet+}$ in CH_2Cl_2.[17]

Addition of CH_3CN or CH_3OH (CH_2Cl_2 solvent) slightly affects the cathodic to anodic derivative current ratio (I_{pc}'/I_{pa}'), resulting in an apparent reaction order of ca. 0.3. However, this small change in the derivative current ratio, coupled with the LSV results which show no change in E_p with CH_3OH concentration (in CH_3CN or 1:1 CH_3CN/CH_2Cl_2 solvents) suggest these observations are more the result of a solvent effect on the rate constant for disappearance of $\mathbf{2}^{\bullet+}$, rather than any significant participation of either CH_3OH or CH_3CN in the decay mechanism.

Because the rate law for the decay of $\mathbf{2}^{\bullet+}$ is now known, it becomes possible to calculate the second-order rate constant for disappearance of $\mathbf{2}^{\bullet+}$ in CH_2Cl_2. DCV was employed to obtain the experimental derivative peak current ratio (I'_{pc}/I'_{pa}) at various sweeprates for a given concentration of substrate. The data in the region of I'_{pc}/I'_{pa} = 0.4−0.8 were used in this analysis. Theoretical working curves were generated via digital simulation.[18] The rate constant for decay of $\mathbf{2}^{\bullet+}$ is found to be (3.9 ± 0.2) × 10^3 M^{-1} s^{-1} in CH_2Cl_2. Similarly, rate constants for decay of $\mathbf{2}^{\bullet+}$ in CH_2Cl_2 at various concentrations of CH_3CN or CH_3OH were obtained (Table 5). With an increase of CH_3CN or CH_3OH concentration, the rate constants for decay of $\mathbf{2}^{\bullet+}$ increase.

(17) $\partial \log(\nu_C)/\partial \log([\mathbf{2}]) \approx 1$ is consistent with two rate laws: $k[\mathbf{2}^{\bullet+}]^2$ or $k[\mathbf{2}][\mathbf{2}^{\bullet+}]$. However, only the former is consistent with the LSV results.

(18) Simulations were performed using *DigiSim 2.1 (R) - A General Simulation Program for Cyclic Voltammetry*, Rudolph M.; Feldberg, S. W., distributed by Bioanalytical Systems Inc., 2701 Kent Ave. West Lafayette, IN 47906.

Discussion

Oxidation of 1-Cyclopropylnaphthalene (1). LSV analyses for **1** reveal that decay of $\mathbf{1}^{\bullet+}$ in CH_3CN is second-order in radical cation and zero-order in methanol. Preparative electrolysis of **1** produces the cyclopropane ring-opened (1,3-dimethoxypropyl) products. These results suggest that attack of methanol at the cyclopropane ring must occur after the rate-determining step. The second-order rate law and appearance of **4, 5,** and **6** as products are consistent with a radical cation disproportionation and/or dimerization mechanism (Scheme 1).

Intermediate **10** may be formulated as a π-complex, or as a σ-bonded dication which may undergo ring opening as illustrated in Scheme 2. (Dication dimers are proposed intermediates leading to dehydrodimers (biaryls) frequently observed in the oxidations of aromatic hydrocharbons).[19]

Oxidation of 1-Bromo-4-cyclopropylnaphthalene (2). Both the LSV and DCV results for **2** are consistent with a rate law for decay of $\mathbf{2}^{\bullet+}$ which is second-order in radical cation and zero-order in methanol. Preparative electrolysis of **2** yields exclusively cyclopropane ring-opened product. These results suggest that the attack of methanol occurs after the rate-limiting step. A mechanism analogous to that proposed for decay of $\mathbf{1}^{\bullet+}$ is consistent with these results (Scheme 1). Because it is not possible to lose "Br^+" under these conditions, the dimerization pathway (**10** → **11**) is effectively "turned off", and only the monomeric, cyclopropane ring-opened product is produced.

As noted earlier, $\mathbf{2}^{\bullet+}$ is longer-lived in CH_2Cl_2 compared to that in CH_3CN. This observation is reasonable because CH_3CN is more polar than CH_2Cl_2. In general, oxidation potentials become more positive as the dielectric constant of the solvent decreases, attributable to variations in the solvation energy of the radical cations.[20] In a low-polarity solvent, disproportionation to a dication is less likely.

The rate constant for decay of $\mathbf{2}^{\bullet+}$, determined by fitting the DCV results to theoretical working curves generated via digital simulation is (3.9 ± 0.2) × 10^3 M^{-1} s^{-1} in CH_2Cl_2. Because the plot of log(k) vs log([CH_3CN]) is linear, these data can be used to extrapolate the rate constant in CH_3CN solvent. On this basis, we estimate the rate constant for decay of $\mathbf{2}^{\bullet+}$ to be 3.1 × 10^4 M^{-1} s^{-1} in CH_3CN.

(19) For a recent discussion of the dehydrodimerization of naphthalene radical cations to form binaphthyls, see: Eberson, L.; Hartshorn, M. P.; Persson, O. *J. Chem. Soc., Perkin Trans. 2* **1995**, 409. See also: Butts, C. P.; Eberson, L.; Hartshorn, M. P.; Persson, O.; Robinson, W. T. *Acta Chem. Scand.* **1995**, *49*, 253.

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Table 3. Observed LSV Response for the Oxidation of **2** in Several Solvent/Electrolyte Combinations

electrolyte/solvent	$\partial E_p/\partial \log(\nu)^a$	$\partial E_p/\partial \log([\mathbf{2}])^b$	$\partial E_p/\partial \log([CH_3OH])^c$
0.5 M $LiBF_4/CH_3CN$	19.5 ± 0.9 (6.79) 19.4 ± 0.7 (2.36)	−20.9 ± 2.8 (2.36−9.07) −21.5 ± 2.8 (1.59−13.8)	−1.2 ± 0.7 (6.79)
0.5 M $LiClO_4/CH_3CN$	20.3 ± 0.4 (2.36) 20.7 ± 0.6 (9.44)	−19.5 ± 1.0 (0.59−9.44)	−0.27 ± 0.6 (5.67)
0.25 M *n*-Bu_4NPF_8/CH_3CN	20.7 ± 0.5 (1.18) 20.8 ± 0.4 (9.44)	−18.1 ± 1.1 (1.18−9.44)	−5.9 ± 1.0 (1.18)
0.25 M *n*-Bu_4NPF_8/1:1 CH_3CN/CH_2Cl_2 (v/v)	19.3 ± 0.4 (2.36) 21.1 ± 0.4 (9.44)	−17.4 ± 2.0 (1.18−9.44)	−0.64 ± 0.5 (2.36)

[a] 0.5 M CH_3OH, ν = 100−6000 mV/s; [**2**] (mM) appears in parentheses. [b] 0.5 M CH_3OH, ν = 400 mV/s; substrate concentration range (mM) appears in parentheses. [c] 0.025−0.5 M CH_3OH, ν = 400 mV/s; [**2**] (mM) appears in parentheses.

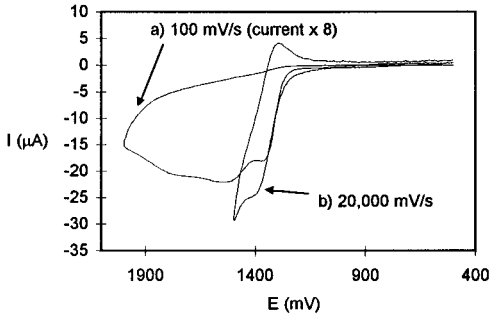


Figure 4. Cyclic voltammogram of 1-bromo-4-cyclopropylnaphthalene (**2**) in CH_2Cl_2 (0.5 M *n*-Bu_4NPF_6, 2.36 × 10^{-3} M **2**).

Table 4. Observed DCV Response for the Oxidation of **2** in CH_2Cl_2 and in the Presence of CH_3CN or CH_3OH

$\partial \log(\nu_c)/\partial \log([\mathbf{2}])$	$\partial \log(\nu_c)/\partial \log([\mathbf{X}])$
1.04 ± 0.04[a]	0.30 ± 0.01 ($\mathbf{X} = CH_3OH$)[b] 0.27 ± 0.01 ($\mathbf{X} = CH_3CN$)[c]

[a] 0.25 M *n*-Bu_4NPF_6, 0.00059−0.0059 M **2**. [b] 0.5 M *n*-Bu_4NPF_6, 0.00236 M **2**, 0.125−1.25 M CH_3OH. [c] 0.25 M *n*-Bu_4NPF_6, 0.00177 M **2**, 0.0958−3.83 M CH_3CN.

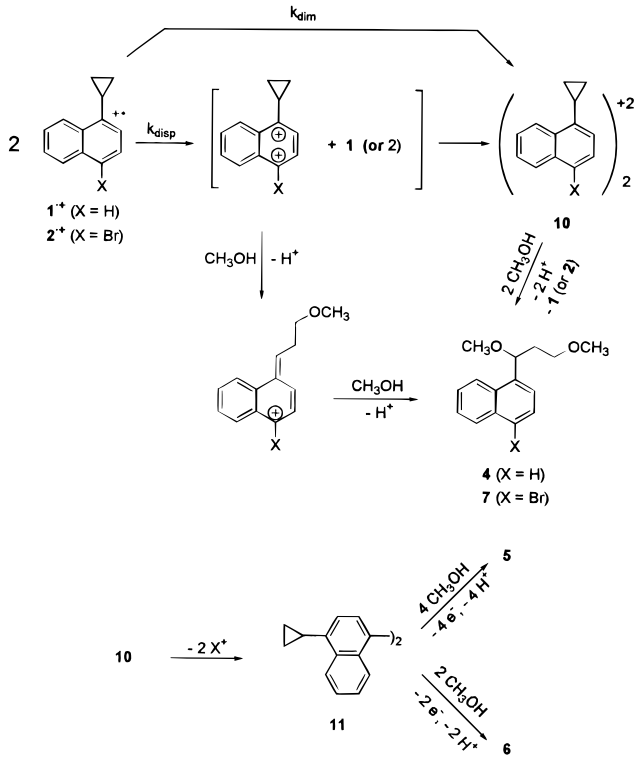
Table 5. Rate Constant for Decay of $\mathbf{2}^{\bullet+}$ (CH_2Cl Solvent Mixed with Varying Amounts of CH_3OH or CH_3CN)

[CH_3CN] (M)	k (M^{-1} s^{-1})	[CH_3OH] (M)	k (M^{-1} s^{-1})
0	3.9×10^3	0	3.9×10^3
0.0958	6.4×10^3	0.125	2.3×10^4
0.192	7.7×10^3	0.75	4.0×10^4
0.383	8.9×10^3	1.38	4.7×10^4
0.766	1.1×10^4		
1.92	1.4×10^4		
3.83	1.8×10^4		

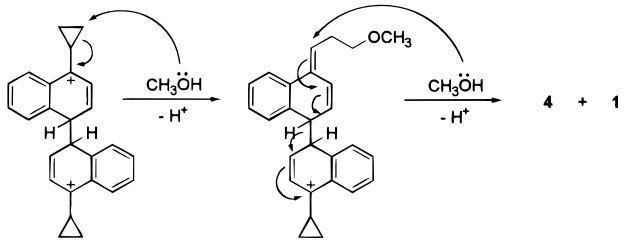
Oxidation of 2-Cyclopropylnaphthalene (3). The decay of $\mathbf{3}^{\bullet+}$ is found to be second-order in radical cation and zero-order in methanol. A mechanism analogous to that depicted in Scheme 1 is likely operative.

Estimated Rate Constant for Ring Opening of α-Cyclopropylnaphthalene Radical Cations. In the presence of methanol, oxidation of cyclopropylnaphthalenes **1**, **2**, and **3** leads mostly to cyclopropane ring-opened products, i.e., the corresponding 1,3-dimethoxypropyl derivatives. However, the radical cation of each of these substrates was found to decay via a rate law second-order in radical cation and zero-order in methanol, which means that methanol attack on the cyclopropane ring must occur after the rate-limiting step. Consistent with the observed rate law and nature of the products formed, we suggest that this second-order decay involves disproportionation and/or dimerization ($k = k_{disp} + k_{dim}$, Scheme 1). The important point is that regardless of its exact nature, this second-order process must be occurring at a rate significantly faster than methanol-induced cyclopropane ring opening (k[Ar-c-$C_3H_5^{\bullet+}$] ≫ k_{MeOH} [CH_3OH], Scheme 3).

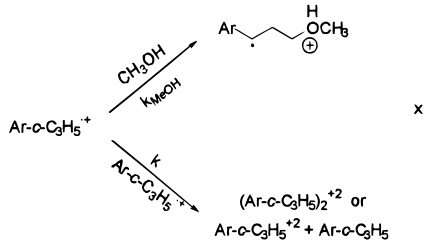
Scheme 1



Scheme 2

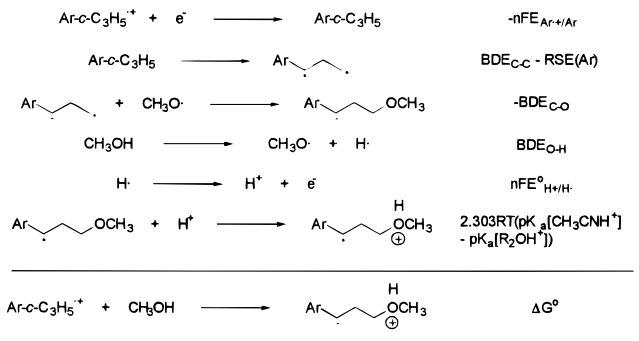


Scheme 3



Utilizing these results, it is possible to use this second-order process as a "clock" to estimate an upper limit for the rate constant for methanol-induced ring opening of α-cyclopropylnaphthalene radical cations (k_{MeOH}). In CH_3CN solvent, the rate law k[Ar-c-$C_3H_5^{\bullet+}$]^2 was observed over a range of CH_3OH

Scheme 4



concentrations from 0 to 1.4 M, with $k = 3.1 \times 10^4$ M^{-1} s^{-1}. The concentration of Ar-c-$C_3H_5^{\bullet+}$ never exceeds 0.01 M (the maximum concentration of substrate used in any of these experiments). Assuming that the rate of radical cation decay is at least 10 times faster than CH_3OH-induced ring opening (k[Ar-c-$C_3H_5^{\bullet+}$] $\geq 10k_{MeOH}$[CH_3OH]), one obtains $k_{MeOH} \leq 20$ M^{-1} s^{-1}.[21]

Dinnocenzo reports that the absolute rate constant for the methanol-induced ring opening of C_6H_5-c-$C_3H_5^{\bullet+}$ is 9.5×10^7 M^{-1} s^{-1} in CH_3CN.[12] Thus, *the change from phenyl to α-naphthyl results in (at least) a 6 order of magnitude diminution in the rate of cyclopropane ring opening.*

Thermodynamic Considerations. A possible explanation for the extremely low rate of ring opening of cyclopropylnaphthalene radical cations may be related to the relative stability of naphthalene vs benzene radical cations; i.e., because of the intrinsic stability of the naphthalenes, 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.[2]

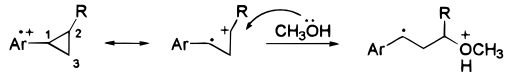
Using the thermodynamic cycle outlined in Scheme 4, it is possible to obtain an estimate of $\Delta G°$ for CH_3OH-induced ring opening of a cyclopropylarene radical cation in CH_3CN solvent. The pertinent $\Delta G°$ values for reactions i → vi were obtained as follows: (i) the oxidation potential of Ar-c-C_3H_5 (see the Supporting Information for details), (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,[22] (iii) the bond dissociation energy of a primary R−OCH_3 bond (BDE_{C-O} = 82 kcal/mol),[23] (iv) the H−O bond strength of methanol (BDE_{O-H} = 104 kcal/mol), (v) the standard potential of the $H^+/H^\bullet$ couple in CH_3CN (reported by Parker to be −1.88 V vs NHE),[24] and (vi) the difference in pK_a between CH_3CN and the ether oxygen (pK_a(CH_3CN) = −10.12;[25] pK_a($CH_3CH_2OCH_2CH_3$) = −3.59).[26] The results of this analysis are summarized in Table 6. The surprising fact that emerges is that regardless of the identity of Ar, all these ring openings are *substantially* exothermic.

Table 6. $\Delta G°$ for the Methanol-Induced Ring Opening of Cyclopropylarene Radical Cations in CH_3CN

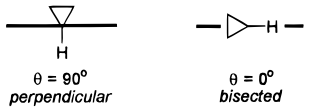
aryl group	$E°_{Ar^{\bullet+}/Ar}$ (V vs NHE)	RSE (kcal/mol)	$\Delta G°$ [a] (kcal/mol)
phenyl	2.58	10.2	−39.1
α-naphthyl	1.99	13.1	−28.4
β-naphthyl	2.02	12.5	−28.5

[a] $\Delta G° = 30.7 - 23.1E°_{Ar^{\bullet+}/Ar}$ − RSE (Ar) kcal/mol; see the text and Scheme 4.

Scheme 5



Stereoelectronic Considerations. 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.[27]

The conformational preference(s) of α-cyclopropylnaphthalene radical cation was explored using SCF-MO theory (AM1, CI = 1). Earlier studies have found that the neutral molecule adopts a conformation midway between bisected and perpendicular (θ = 54°) because the normally preferred bisected conformation is destabilized by steric interactions between the cyclopropyl group and the peri-hydrogens.[28] In contrast α-cyclopropylnaphthalene radical cation exhibits no overwhelming conformational preference, presumably because removal of an electron increases the magnitude of the interaction between the cyclopropyl HOMO and the π-system. Structures with $\theta = 0°$ and 54° are degenerate (within 0.1 kcal/mol) and separated by a barrier of approximately 0.5 kcal/mol. For β-cyclopropylnaphthalene radical cation, AM1 calculations predict the bisected confromation to be favored by 1.2−1.6 kcal/mol.

Thus, for α- or β-cyclopropylnaphthalene radical cations, the bisected conformation is readily accessible, suggesting that stereoelectronic factors are *not* responsible for the extraordinarily sluggish rate of ring opening.

Ring Opening of Cyclopropylarene Radical Cations. Dinnocenzo reported the effect of alkyl substituents on the rate and regiochemistry of the methanol-induced (S_N2) ring opening of phenylcyclopropane radical cations.[12,13] Generally, alkyl substituents on the cyclopropane ring increase the rate of ring opening, with nucleophilic attack occurring at the most hindered position (C-2, Scheme 5).[29] These observations were explained on the basis that the alkyl group could stabilize the partial positive charge on the carbon undergoing substitution. It was further argued on the basis of the Hammond postulate that these reactions have an early (reactant-like) transition state and that

(21) This kinetic analysis is based upon k for $\mathbf{2}^{\bullet+}$. It is expected that k_{MeOH} for $\mathbf{1}^{\bullet+}$ is even slower. Dinnocenzo (ref 13) has shown that, for substituted phenylcyclopropane radical cations, the rate of nucleophile-induced ring opening correlates to σ^+ (and is facilitated by electron-withdrawing groups). For Br, $\sigma^+ = 0.15$, vs 0.0 for H.

(22) RSEs for $ArCH_2^\bullet$ were taken as the difference in the bond strength of $ArCH_2$−H (88.0, 85.1, and 85.7 kcal/mol for Ar = C_6H_5 and α- and β-$C_{10}H_7$, respectively) and CH_3CH_2−H (98.2 kcal/mol). Bond strengths were taken from McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. The BDE of β-$C_{10}H_7CH_2$−H was not available and was estimated using $\Delta H_f°$ values obtained using SCF-MO theory (AM1).

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

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

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

(27) 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.

(28) Drumright, R. E.; Mas, R. H.; Merola, J. S.; Tanko, J. M. *J. Org. Chem.* **1990**, *55*, 4098.

(29) For a related discussion pertaining to reactions of nucleophiles with vinylcyclopropane radical cations, see: Herbertz, T.; Roth, H. D. *J. Am. Chem. Soc.* **1996**, *118*, 10954.

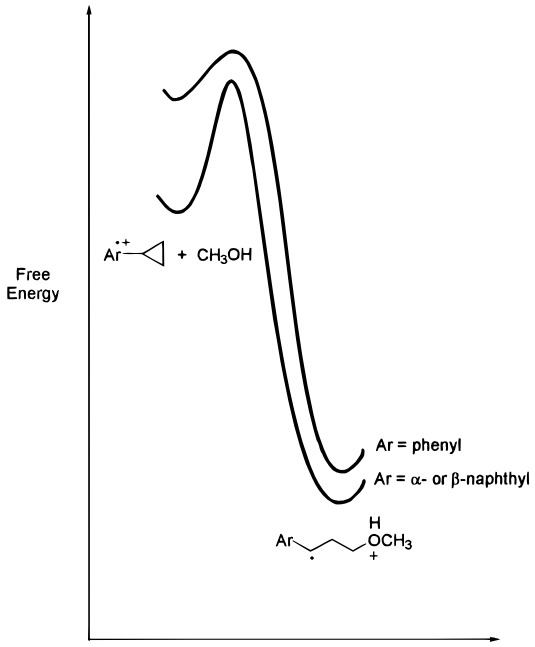


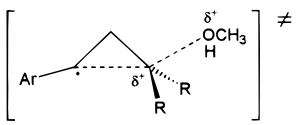
Figure 5. Proposed effect of different aryl groups on the stabilities of reactants, transition states, and products for CH_3OH-induced ring opening of Ar-c-$C_3H_5^{\bullet+}$.

the charge distribution in the transition state was similar to the radical cations themselves.[12]

An early (reactant-like) transition state would imply that the rate of the reaction would be only modestly affected by changes in $\Delta G°$ for the reaction (i.e., $\partial\Delta G^{‡}/\partial\Delta G° < 0.5$). Our results show that, for decay of Ar-c-$C_3H_5^{\bullet+}$, the change from Ar = phenyl to Ar = α-naphthyl results in at least a 6 order of magnitude decrease in rate, corresponding roughly to a difference in free energies of activation ($\Delta\Delta G^{‡}$) for these two processes of at least 8.2 kcal/mol. The difference in $\Delta G°$ for these two processes ($\Delta\Delta G°$) is 10.7 kcal/mol. Thus, $\Delta\Delta G^{‡}/\Delta\Delta G° \geq 0.77$, suggestive of a transition state which is more product-like than reactant-like.

As the data in Table 6 reveal, two important factors contribute to $\Delta G°$ for these ring opening reactions: The ability of the aryl group to stabilize the ring-closed radical cation (manifested by the difference in redox potentials, $\Delta E°_{Ar^{\bullet+}/Ar}$) and the ability of the aryl group to stabilize the benzylic radical formed after ring opening (ΔRSE). Of these two, the effect of the aryl group on radical cation stability is far more profound.

These observations are consistent with a transition state for ring opening in which spin density is delocalized over C-1 (the benzylic carbon) and the aromatic ring, but charge is highly localized at C-2 and oxygen (e.g., **12**). As such, in the transition



12

state, the aryl group can stabilize the radical portion of the developing distonic radical ion (presumably to a lesser degree than for the fully developed radical), but will have little effect on the positive charge (Figure 5). (This proposal is consistent with recent transition state calculations for ring opening of C_6H_5-c-$C_3H_5^{\bullet+}$ by CH_3OH which reveal that, in the progression from reactant to transition state, there is an increase in positive charge at C-2 (from 0.19 to 0.4) at the expense of the phenyl group (from 0.68 to 0.28)).[13]

Thus, nucleophile-induced ring opening of cyclopropylarene radical cations provides an intriguing exception to the Hammond postulate in that they are overwhelmingly exothermic yet, in terms of the distribution of charge and spin, have transition states which are more product-like than reactant-like. Moreover, the effect of the aromatic ring on the rate is primarily due to changes in the free energy of the reactant, with only a modest effect on the free energy of the transition state for ring opening.

Implications for the Use of Cyclopropane-Substituted Compounds as SET Probes. Cyclopropane-containing substrates are frequently employed as probes for single electron transfer. The implicit assumption in such a study is that if a paramagnetic intermediate (neutral free radical or radical ion) is produced, it will undergo ring opening. Earlier work dealing with neutral free radicals and ketyl radical anions has shown that the rate constant for ring opening is quite large when the ring opening is thermodynamically favored. For example, $\Delta G°$ for the cyclopropylcarbinyl → homoallyl radical rearrangement (eq 1) is −3.1 kcal/mol, and the rate constant is 1.2×10^8 s^{-1}.[30] Similarly, ring opening of radical anion **13** (eq 6) is estimated to be exothermic by about 2 kcal/mol (R = phenyl or vinyl), and the rate constant is $>10^5$ s^{-1}.[3,31]

13 **14** **(6)**

In the case of Ar-c-$C_3H_5^{\bullet+}$, despite the fact that ring opening enjoys an enormous thermodynamic driving force, the process occurs at a dramatically slower rate. Clearly, the intrinsic barrier to ring opening is greater for ring opening of these radical cations.

The unique activation/driving force relationship for radical cation ring opening is likely attributable to the fact that the process is bimolecular (nucleophile-assisted). The rate of ring opening is governed by the amount of positive charge transmitted to the cyclopropane ring via resonance (Scheme 5), and the fact that this charge becomes localized in the transition state (e.g., **12**).

For neutral radicals or ketyl anions, it is *spin* rather than charge which is transmitted to the cyclopropyl group upon ring opening. Because ring opening is unimolecular, spin (and charge for the radical anions) is not localized in the transition state and the intrinsic barrier to ring opening is considerably lower.

For arylcyclopropane radical cations, and presumably other systems which would undergo nucleophile-assisted ring opening, the fact that the ring opening reaction may enjoy a potent thermodynamic driving force is no guarantee that the ring opening will occur at an appreciable rate. Indeed, it is likely that many of the substrates discussed herein would fail to detect a bona fide SET process. Thus, these results reveal a new (and unexpected) complication in the design and utilization of SET probes.

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(31) Tanner, D. D.; Chen, J. J.; Luelo, C.; Peters, P. M. *J. Am. Chem. Soc.* **1992**, *114*, 713.

Experimental Section

General Procedures. Nuclear magnetic resonance spectra (^{1}H, ^{13}C, 2D NMR) were obtained on either a 270 MHz Bruker or a 400 MHz Varian FT NMR spectrometer. All chemical shifts are reported in δ units relative to TMS (δ 0.00 ppm) in $CDCl_3$. Infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. Low-resolution mass spectra were obtained from a Fisons VG Quattro triple quadrupole mass spectrometer. GC/MS was performed on a Fisons GC 8060 GC with a VG Quattro MS. Gas chromatographic analysis was performed on a Hewlett-Packard HP 5890A instrument equipped with an FID detector and an HP 3393A reporting integrator. Analyses were accomplished on an Alltech Econo-CAP SE-54 capillary column (30 × 0.25 mm). High-pressure liquid chromatography (preparative and analytical scale) was performed using a Beckman System Gold Model 128 solvent pump system. Detection was accomplished using a Beckman System Gold Model 166 UV/vis detector. Integration was accomplished with an IBM 486/SI running Beckman System Gold Software. Samples were analyzed and separated using Beckman C-19 reversed phase columns (analytical, 4.6 mm × 250 mm; preparative, 21.2 mm × 150 mm) with acetonitrile/water solvent mixtures. Flash chromatography (Merck, grade 9385 silica gel, 230−400 mesh, 60A) and preparative thin layer chromatography (PTLC, Whatman, silica gel plates, 250 μm layer, UV_{254}) were performed using the indicated solvent systems.

Materials. Lithium perchlorate, lithium tetrafluoroborate, and tetrabutylammonium hexafluorophosphate were purchased from Aldrich and 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. Methylene chloride was refluxed with P_2O_5 and distilled before use. Methanol (Baker HPLC grade) was dried by stirring over calcium hydride, followed by distillation. 1-Cyclopropylnaphthalene,[32] 1-bromo-4-cyclopropylnaphthalene,[33] and 2-cyclopropylnaphthalene[32] were prepared according to published procedures.

Electrochemistry. 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.[2] Voltammetric measurements were performed on solutions which contained 0.5 M supporting electrolyte. The solutions were prepared by weighing the electrolyte into an oven-dried 10 mL volumetric flask and then placing the volumetric flask together with all voltammetry cell pieces into a Baxter DP-22 vacuum drying oven under vacuum (30−40 mmHg) at 40 °C for at least 8 h. CH_3CN and the desired amount of CH_3OH were added into the septum-sealed volumetric flask via syringe. The resulting solution was transferred to the 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 in diameter) was prepared for use by polishing with alumina slurry. A Ag/Ag^+ (0.10 M in CH_3CN) electrode was used as the reference electrode. A Pt wire (2 cm in length, 2 mm in diameter) was used as the auxiliary electrode. The voltammetry cell was set in a Fisher FS-14 ultrasonic tank 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 the oscillation value). All experiments were performed at ambient temperature (23 °C).

Preparative electrolyses (general) were performed on solutions which contained 0.1 M $LiClO_4$ in CH_3CN containing CH_3OH and the substrate. The solutions were prepared as described for the voltammetric experiments. A conventional H-cell, with two compartments separated by a medium glass frit (22 mm in diameter), was utilized. A 60 mL portion of the electrolyte solution 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 a Pt gauze (45 mesh, 30 mm × 20 mm). For the cathodic compartment, a coiled copper wire (2 mm in diameter, 50 cm 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 between −30 and −40 mA. Both the anodic and cathodic compartments were purged with argon, and agitated via ultrasound during electrolysis. GC and TLC were employed to monitor the progress of the electrolysis. After aqueous workup, the products were separated by flash column chromatography (or preparative TLC) and characterized by NMR, IR, MS, and other methods.

Electrolysis of 1-Cyclopropylnaphthalene (1). Run 1. 1 (44 mg, 0.2619 mmol) in the presence of 2.5 M CH_3OH was electrolyzed at −30 mA for 42 min, passing 3.0 equiv of electrons. The solution was worked up with H_2O/diethyl ether. The PTLC of the workup solution with 3:1 hexane/ethyl acetate yielded the following compounds.

1-(1,3-Dimethoxypropyl)naphthalene: TLC (hexane:ethyl acetate = 3:1) R_f = 0.40; ^{1}H NMR ($CDCl_3$) δ 2.13 (m, 2H), 3.21 (s, 3H), 3.35 (s, 3H), 3.38 (m, 1H), 3.60 (m, 1H), 5.07 (t, 1H), 7.50 (m, 3H), 7.55 (d, 1H), 7.78 (d, 1H), 7.87 (m, 1H), 8.22 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 37.82 (t), 56.96 (q), 58.71 (q), 69.42 (t), 78.41 (d), 123.44 (d), 123.82 (d), 125.45 (d), 125.48 (d),125.89 (d), 127.89 (d), 128.80 (d), 131.15 (s), 133.90 (s), 137.70 (s); IR ν (cm^{-1}) 3157, 3062, 2985, 2899, 2827, 1600, 1518, 1475, 1394, 1116 (s), 809 (s), 785 (s); MS (EI) *m*/*e* 231 (1.52, M + 1), 230 (7.92, $M^{\bullet+}$), 172 (13.2), 171 (100), 165 (15.2), 128 (19.2); HRMS (EI) $C_{15}H_{18}O_2$, obsd 230.130 066, calcd 230.130 680 0, error −2.7 ppm.

4,4′-Bis(1,3-dimethoxypropyl)-1,1′-binaphthalene: TLC (hexane:ethyl acetate = 3:1) R_f = 0.21; ^{1}H NMR ($CDCl_3$) δ 2.23 (m, 2H), 3.40 (s, 3H), 3.41 (s, 3H), 3.46 (m, 1H), 3.70 (m, 1H), 5.18 (m, 1H), 7.29 (t, 1H), 7.44 (d, 1H), 7.50 (t, 2H), 7.67 (d, 1H), 8.31 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 37.91 (t), 57.15 (q), 58.76 (q), 69.49 (t), 78.43 (d), 123.27 (d), 123.52 (d), 125.50 (d), 125.75 (d), 127.46 (d), 127.55 (d), 131.15 (s), 133.28 (s), 137.50 (s), 138.25 (s); IR ν (cm^{-1}) 3081, 3047, 2988, 2939, 2904, 2831,1733, 1670, 1601, 1523, 1474, 1454, 1391, 1303, 1258, 1214, 1175, 1121 (s), 857, 778 (s); MS (EI) *m*/*e* 460 (2, M + 2), 459 (10, M + 1), 458 (44, $M^{\bullet+}$), 427 (3), 401 (3.6), 400 (23.2), 399 (100), 427 (5), 325 (22.4), 252 (17.6), 170 (8.6); HRMS (EI) $C_{30}H_{34}O_4$, obsd 458.244 507, calcd 458.245 709 9, error −2.6 ppm.

Run 2. 1 (41.1 mg, 0.2446 mmol) in the presence of 2.5 M CH_3OH was electrolyzed at −40 mA for 35 min, passing 3.5 equiv of electrons. The solution was worked up with H_2O/diethyl ether. The ether layer was analyzed by HPLC and contained 2.94 mg (7.45%) of starting material, 9.42 mg (17.4%) of 1-(1,3-dimethoxypropyl)naphthalene, and 14.1 mg (26.3%) of 4,4′-bis(1,3-dimethoxypropyl)-1,1′-binaphthalene (HPLC conditions: 9:1 CH_3CN/H_2O, flow rate 1 mL/min; λ = 224 nm; C_{18} column).

Electrolysis of 1-Bromo-4-cyclopropylnaphthalene (2). Run 1. 2 (64.6 mg, 0.2627 mmol) in the presence of 2.5 M CH_3OH was electrolyzed at −40 mA for 33 min, passing 3.0 equiv of electrons. The solution was worked up with H_2O/diethyl ether. PTLC of the workup solution with CH_2Cl_2 yielded the following compound.

1-Bromo-4-(1,3-dimethoxypropyl)naphthalene: 40.8 mg (50.4%); TLC (CH_2Cl_2), R_f = 0.44; ^{1}H NMR ($CDCl_3$) δ 2.09 (q, 2H), 3.29 (s, 3H), 3.34 (m, 1H), 3.35 (s, 3H), 3.61 (m, 1H), 5.05 (t, 1H), 7.42 (d, 1H), 7.58 (m, 2H), 7.79 (d, 1H), 8.22 (d, 1H), 8.31 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 37.89 (t), 57.06 (q), 58.74 (q), 69.20 (t), 78.02 (d), 122.46 (s), 123.75 (d), 124.28 (d), 126.72 (d), 126.94 (d), 127.98 (d), 129.64 (d), 132.06 (s), 132.38 (s), 138.01 (s); IR ν (cm^{-1}) 3076, 3045, 2990, 2929, 2892, 2831, 1595, 1571, 1510, 1473, 1448, 1387, 1314, 1257, 1203, 1161, 1118 (s), 1014, 842, 769; MS (EI) *m*/*e* 310 (6.8, M + 2), 308 (8, $M^{\bullet+}$), 252 (10), 251 (100), 249 (97.6), 165 (14.8), 153 (20,8), 152 (38.4), 127 (21.2), 126 (26), 45 (78.4); HRMS (EI) $C_{15}H_{17}O_2Br$, obsd 308.0410, calcd 308.041 191 1, error −0.6 ppm.

Run 2. 2 (56.6 mg, 0.2301 mmol) in the presence of 2.5 M CH_3OH was electrolyzed at −40 mA for 17.2 min, passing 2.0 equiv of electrons. The solution was worked up with H_2O/diethyl ether. ^{1}H NMR analysis of the ether layer showed that it contained 56.7 mg (80%) of 1-bromo-4-(1,3-dimethoxypropyl)naphthalene, and GC analysis showed 7.5 mg (13.2%) of unreacted starting material.

(32) Hahn, R. C.; Howard, P. H.; Kong, S.-M.; Lorenzo, G. A.; Miller, N. L. *J. Am. Chem. Soc.* **1969**, *91*, 3558.

(33) Prepared by the bromination of 1-cyclopropylnaphthalene using Br_2/CCl_4/Fe(dust).

Electrolysis of 2-Cyclopropylnaphthalene (3). 3 (82.21 mg, 0.49 mmol) in the presence of 5.0 M CH_3OH was electrolyzed at −60 mA for 27 min, passing 2.0 equiv of electrons. The solution was worked up with H_2O/diethyl ether. PTLC of the workup solution with 3:1 hexane/ethyl acetate yielded 18.2 mg (16.2%) of 2-(1,3-dimethoxypropyl)naphthalene, and a mixture of 2,2′-dicyclopropyl-1,1′-binaphthalene and starting material. A second PTLC with hexane as solvent gave 14.3 mg (17.5%) of 2,2′-dicyclopropyl-1,1′-binaphthalene. The amount of unreacted starting material was estimated from GC analysis to be 28 mg (34.1%).

2-(1,3-Dimethoxypropyl)naphthalene: TLC (hexane:ethyl acetate = 3:1) $R_f = 0.41$; ^{1}H NMR ($CDCl_3$) δ 1.95 (hextet, 1H), 2.17 (hextet, 1H), 3.25 (s, 3H), 3.33 (m, 1H), 3.34 (s, 3H), 3.51 (m, 1H), 4.46 (t, 1H), 7.47 (m, 3H), 7.74 (s, 1H), 7.85 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 38.01 (t), 56.75 (q), 58.65 (q), 69.15 (t), 80.81 (d), 124.36 (d), 125.79 (d), 125.86 (d), 125.86 (d), 126.08 (d), 127.70 (d), 127.83 (d), 128.36 (d), 133.10 (s), 133.23 (s), 139.38 (s); IR ν (cm^{-1}) 3156, 3064, 2984, 2935, 2897, 2825, 1473, 1387, 1112 (s), 824, 760; MS (EI) *m*/*e* 231 (3, M + 1), 230 (15), 215 (1.5), 171 (100), 155 (20), 141 (15); HRMS (EI) $C_{15}H_{18}O_2$, obsd 230.1300, calcd 230.130 680 0, error −2.8 ppm.

2,2′-Dicyclopropyl-1,1′-binaphthalene: TLC (hexane) $R_f = 0.36$; ^{1}H NMR ($CDCl_3$) δ 0.60 (m, 1H), 0.74 (m, 3H), 1.53 (m, 1H), ∼7.10 (m, 2H), ∼7.21 (m, 1H), ∼7.38 (m, 1H), ∼7.87 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 8.46 (t), 9.07 (t), 13.38 (d), 121.43 (d), 124.76 (d), 126.04 (d), 126.06 (d), 127.71 (d), 127.85 (d), 131.81 (s), 133.02 (s), 135.01 (s), 139.85 (s); IR ν (cm^{-1}) 3156, 3082, 3058, 3008, 2954, 2923, 2856, 1626, 1595, 1510, 1467, 1381, 1332, 1100, 1045, 818, 750; MS (EI) *m*/*e* 335 (30, M − 1), 334 (100, M), 319 (20), 305 (40), 289 (30), 278 (40), 277 (40), 276 (50), 265 (30), 263 (25); HRMS (EI) $C_{26}H_{22}$, obsd 334.171 936, calcd 334.172 150 9, error −0.6 ppm.

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Supporting Information Available: LSV and DCV plots for data summarized in Tables 1−4, dimensionless working curves for the EC_{dim} mechanism used to obtain the rate constants in Table 5, details regarding the estimate of k for $2^{\bullet+}$ in CH_3CN, and details pertaining to the estimates of $E°$ values in Table 6 (27 pages). See any current masthead page for ordering information and Internet access instructions.

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