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Carbon-Oxygen Bond-Cleavage Reactions by Electron Transfer. 4. Electrochemical and Alkali-Metal Reductions of Phenoxynaphthalenes

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Abstract: The reductions of 1- (**1**) and 2-phenoxynaphthalene (**2**) to their respective radical anions were observed at −2.42 and −2.48 V vs SCE. Cyclic voltammetric and chronoamperometric studies indicate that both radical anions have half-lives that are greater than 100 s in dry *N,N*-dimethylformamide. Controlled-potential electrolysis of the ethers resulted in relatively slow, regioselective carbon-oxygen bond cleavage to produce phenol and naphthalene. The intermediacy of the naphthyl radical or the naphthyl anion in the reductive pathway was tested by the use of an intramolecular radical trap in the form of a 2-(3′-butenyl) substituent, i.e., 2-(3′-butenyl)-1-phenoxynaphthalene (**3**). Formation of 1-methylbenz[*e*]indan (**4**) upon the electrochemical reduction of **3** in the absence and presence of D_2O confirmed the presence of the 2-(3′-butenyl)naphthyl radical in the radical-anion cleavage mechanism. Reduction of the phenoxynaphthalenes with Na/HMPA in tetrahydrofuran resulted in slow regioselective cleavage while reduction with Na-K alloy/tetraglyme quantitatively cleaved the ether bond more rapidly. The intermediacy of the naphthyl anion, which is produced via the ether dianion in the Na-K alloy reduction, was demonstrated by the reduction of **3** at −78 and 0 °C. Reduction of **3** at −78 °C produced only 2-(3′-butenyl)naphthalene (**5**) whereas reduction at 0 °C produced both **5** and **4**, the latter by anionic cyclization.

We have recently reported on the reaction pathways for carbon-oxygen bond cleavage of the diphenyl ether radical anion using both electrochemical and chemical techniques.[1,2] Formation of the radical anion was shown to occur at a very negative potential, −2.95 V vs SCE. The *o*-3′-butenyl substituent was utilized as an intramolecular radical probe to prove the intermediacy of the phenyl radical in the unimolecular fragmentation of the radical anion. Scheme I summarizes the reaction pathway for the diphenyl ether radical anion, which cleaves at a first-order rate constant (k) of 4×10^5 s^{-1}.

Scheme I

$$\mathrm{PhOPh} + e^- \rightleftarrows \mathrm{PhOPh}^{\bullet -} \tag{1}$$

$$\mathrm{PhOPh}^{\bullet -} \xrightarrow{k} \mathrm{Ph}^{\bullet} + {}^{-}\mathrm{OPh} \tag{2}$$

$$\mathrm{Ph}^{\bullet} \xrightarrow{\mathrm{SH}} \mathrm{PhH} \tag{3}$$

It is known that larger polycyclic aromatic ethers (e.g., naphthyl ethers) undergo reductive carbon-oxygen bond cleavage,[3] but whether this occurs by a pathway similar to that of diphenyl ether or a completely different scheme is not known. In view of the expected differences in reduction potentials, we have embarked on a study of the reductive cleavage of larger polycyclic aryl ethers. We report herein on the reductive carbon-oxygen bond cleavage of phenoxynaphthalene.

Except for our work[3] there have been no reports in the literature on the reductive cleavage of phenoxynaphthalenes by either electrochemical or chemical means. Related work in the area of naphthyl ethers includes a report by Eargle on dinaphthyl ethers in which a dianion intermediate was proposed to cleave to the naphthyl anion and naphthoxide ion (reactions 4-7).[4]

$$\mathrm{ArOAr} + e^- \rightarrow \mathrm{ArOAr}^{\bullet -} \qquad \mathrm{Ar} = \mathrm{C_{10}H_7} \tag{4}$$

$$\mathrm{ArOAr}^{\bullet -} + e^- \rightarrow \mathrm{ArOAr}^{2-} \tag{5}$$

$$\mathrm{ArOAr}^{2-} \rightarrow \mathrm{Ar}^- + {}^{-}\mathrm{OAr} \tag{6}$$

$$\mathrm{Ar}^- \xrightarrow{\mathrm{SH}} \mathrm{ArH} \tag{7}$$

Although the literature is sparse for diaryl ethers containing the naphthyl moiety, Itoh and co-workers have treated naphthyl decyl ethers with various alkali metals.[5] They observed regioselectivity in the cleavage of the carbon-oxygen bond (e.g., alkyl carbon-oxygen vs aryl carbon-oxygen) as a function of the alkali metal and solvent. They proposed that alkyl carbon-oxygen bond cleavage occurred via a radical-anion intermediate whereas aryl carbon-oxygen bond cleavage occurred by a dianion intermediate.

The objectives of the current study are to determine the reaction pathways and regioselectivity of reductive bond cleavage of phenoxynaphthalenes. Both electrochemical techniques and chemical reductants with an intramolecular radical or anion probe are used to elucidate the reaction pathways.

Results and Discussion

Cyclic Voltammetry. Cyclic voltammetric data in dry *N,N*-dimethylformamide (DMF) indicate that 1-phenoxynaphthalene (**1**) is reduced at −2.42 V vs SCE at 25 °C (Figure 1A). Figure 1B shows the cyclic voltammogram for naphthalene, which is reduced at $E_p = -2.52$ V vs SCE for comparison. Cyclic voltammograms of **1**, which were obtained over a large range of scan rates (0.01 to 10 V/s), result in a $\Delta E_p = 60$ mV and a peak current ratio (i_{pc}/i_{pa}) of unity. The current function for the cathodic wave, $i_{pc}/v^{1/2}C$, was constant over the same range of scan rates and comparable to that for the reduction of *m*-tolunitrile, a known one-electron reduction process. Furthermore, single-potential-step chronoamperometric data obtained at an applied potential of −2.6 V produce an $it^{1/2}/C$ value that is constant (0.1 s $< t <$ 100 s) and consistent with a one-electron, diffusion-controlled process. Thus, the electrochemical data show that ether **1** is reduced to a relatively stable radical anion in a dry, aprotic solvent such as DMF at a potential that is 100 mV positive of that for the reduction of naphthalene. The electrochemical reduction of 2-phenoxynaphthalene (**2**) occurs at a potential that is 60 mV more negative ($E_p = -2.48$ V vs SCE) than that for **1**. All of the cyclic voltammetric data indicate a similar degree of electrochemical and chemical reversibility for the radical anion of 2-phenoxynaphthalene relative to that for 1-phenoxynaphthalene.

Addition of proton donors to the solution of **1** caused the anodic current for the reoxidation of the radical anion in the cyclic

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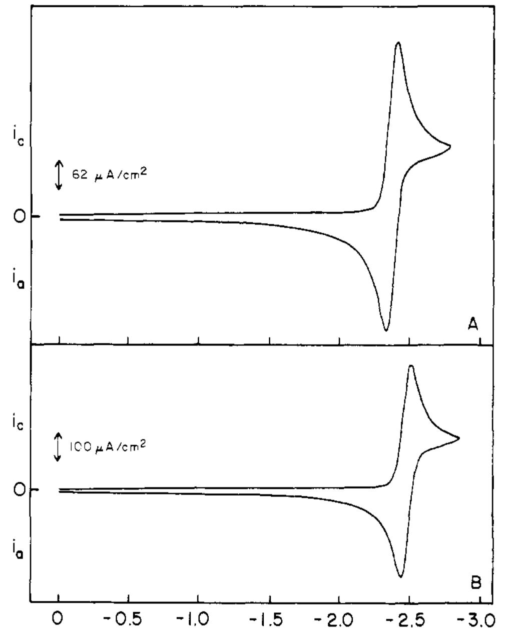

Figure 1. Cyclic voltammograms in 0.2 M TBAP/DMF at a scan rate of 0.1 V/s on a platinum electrode: (A) 8.8 × 10^{-3} M 1-phenoxynaphthalene, (B) 9.8 × 10^{-3} M naphthalene.

voltammogram to decrease. In addition, the magnitude of the cathodic peak current doubled, which indicated an overall two-electron reduction process. Both *p*-cresol ($pK_a = 19$) and 1,1,1,3,3,3-hexafluoroisopropyl alcohol ($pK_a = 17.6$) protonated the radical anion to the extent that the radical-anion reoxidation wave disappeared at a scan rate of 1.0 V/s if the proton donor was present in 10-fold excess. These data are consistent with a report by Saveant in which the naphthalene radical anion was reported to be protonated at a pseudo-first-order rate constant of 1400 s^{-1} in the presence of 10-fold excess of phenol.[6] Thus, hydrogenation of ether **1** occurred upon reduction in the presence of relatively strong proton donors. It should be noted that weaker proton donors such as water with a pK_a of approximately 32 in DMF had little effect on the cyclic voltammetric data.[7]

Finally, extensive experiments were conducted in an attempt to observe formation of the dianion of **1** by the further reduction of the radical anion at more negative potentials. The reductive background limit in aprotic solvents has been shown to be dependent on the nature of the tetraalkylammonium ion.[8,9] Therefore, tetra-*n*-heptylammonium perchlorate, as well as tetra-*n*-butylammonium perchlorate, was used in attempts to extend the background limit. In addition, lithium perchlorate and sodium tetraphenylborate were tested as electrolytes in tetrahydrofuran. Although a background limit of -3.10 V vs SCE was obtained using sodium tetraphenylborate in alumina-dried THF, further reduction of the radical anion to the dianion of the ether was not observed.

Cyclic voltammetric studies in 0.2 M sodium tetraphenylborate/DMF indicate that **1** is reduced at $E_p = -2.48$ V vs SCE, which is 60 mV more negative than the E_p for the reduction of **1** using tetrabutylammonium perchlorate as the supporting electrolyte. Inspection of cyclic voltammograms indicates a similar degree of electrochemical and chemical reversibility (i.e., $E_{p,a} - E_{p,c} = 65$ mV and $i_{p,a}/i_{p,c} = 1$) for the radical anion in the presence of either the tetrabutylammonium cation or the sodium cation. Thus, the E_p data indicate that sodium ion does not form a better contact ion pair with the radical anion of **1** than does the tetrabutylammonium ion in DMF as might be expected from the crystallographic ionic radius of these cations. The tetrabutylammonium ions are apparently less solvated than sodium ions in DMF with the result that the bulky, highly solvated sodium ions interact less strongly with the radical anion of **1** than does the tetrabutylammonium ion. In a related study on the electroreduction of aromatic compounds in the presence of various cations, Bewick and Avaca have concluded that a key factor is the ratio of contact ion pairs to solvent-separated ion pairs.[10] Thus, our E_p data support a slight increase in this ratio for the tetrabutylammonium ion case relative to that for the sodium ion. In another series of studies, Peaver has concluded that the degree of ion pairing for quinone radical anions, which are more polar than the radical anion of **1**, is essentially the same with sodium, potassium, and tetraalkylammonium ions in DMF.[11]

Table I. Controlled-Potential Electrolysis of 1-Phenoxynaphthalene[a] (**1**)

		products,[b] % yield			
entry no.	conditions	**1**	phenol	naphthalene	dihydronaphthalenes, tetralins
1	1.0 F/mol on Hg	80	9	10	
2	1.0 F/mol on Hg/0.1 M D_2O	98	1	trace	
3	2.5 F/mol on Hg/0.1 M cresol	20[c]	20	8	6
4	10.0 F/mol on Hg	1	84	37	13
5	9.9 F/mol on Pt/0.2 M D_2O	2	70	18	28
6	2.9 F/mol on Pt in 0.2 M $NaBPh_4$	3	87	70	NA[d]

[a] Electrolysis of the ether (10–20 mM) was carried out at -2.5 V vs SCE (radical-anion formation) in DMF (0.2 M TBAP at 25 °C except entry 6), which was in 0.2 M $NaBPh_4$. [b] Product yields are based upon the initial amount of the ether and were determined by GC and HPLC. [c] Significant amounts of the Birch reduced ethers (dihydrophenoxynaphthalenes) were identified by GC–MS analysis. [d] NA = not analyzed.

Both single- and double-potential-step chronoamperometry data (1 s < t < 100 s) indicate that the radical anion of **1** is stable up to times of 100 s in the presence of 0.2 M sodium tetraphenylborate. Thus, the electrochemical data indicate that disproportionation of the radical anion in the presence of sodium ion does not appear to be an important pathway in this time domain.

Controlled-Potential Electrolysis. A series of electrolyses at a potential that was consistent with radical-anion formation of **1** were conducted (Table I). Decomposition of the radical anion was found to be very slow with small amounts of naphthalene and phenol formed after the addition of 1 faraday/mol (see entries 1 and 2) over the time period of a 1-h electrolysis. Reoxidation of the resultant blue-green solution at -1.0 V indicated that a substantial amount (e.g., 50%) of the radical anion had disappeared; however, the amount of cleavage was small. Apparently a significant amount of charge was transferred from the radical anion to background processes including those involving impurities or the electrolyte/solvent system. Furthermore, addition of a strong proton donor (*p*-cresol) resulted in disappearance of the radical anion (entry 3). Protonation of the ether radical anion apparently occurred in this case because the yield of phenol was low and considerable amounts of Birch reduction products (e.g., dihydrophenoxynaphthalene) were identified by GC–MS analysis.

Larger amounts of C–O bond cleavage reflected by higher phenol yields were obtained if the electrolysis was carried out by addition of the charge in 2 faraday/mol increments (entries 4 and 5). After the addition of each 2 faraday/mol increment, the electrolysis was stopped and the rest potential monitored until a rest potential of -2.0 V was reached, and then a subsequent increment of charge was added at the applied potential of -2.5 V. The success of incremental addition of charge toward cleavage can be attributed to a "cleaning-up" effect of the electrolyte/solvent

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Tble II. Electrochemical Reduction of 2-(3′-Butenyl)-1-phenoxynaphthalene (3)[a]

entry no.	conditions	products,[b] % yield				
		1	phenol	1-methylbenz[*e*]indan (**4**)	2-(3′-butenyl)-naphthalene (**5**)	cyclized (**4**)/ uncyclized (**5**)
1	Pt cathode, 7 faraday/mol	21	57	47	5	9.4
2	Hg cathode, 5 faraday/mol	5	65	68	7	9.7
3[c]	Hg cathode, 5 faraday/mol	1	74	63	8	7.9
4[d]	Hg cathode, 5 faraday/mol	47	59	29	7	4.1

[a] The electrolysis of the ether (17–25 mM) was carried out in DMF/0.2 M TBAP. Controlled-potential electrolyses were carried out at −2.5 V vs SCE. [b] Product yields are based upon the initial amount of ether and were determined by GC and HPLC. [c] The electrolysis was carried out in the presence of 0.20 M D_2O. [d] The electrolysis was carried out in the presence of 0.14 M sodium isopropylate.

system in order to allow the relatively slow cleavage of the radical anion to occur.

Controlled-potential electrolyses of **1** were carried out using sodium tetraphenylborate as the electrolyte (e.g., entry 6). The charge was added in an incremental manner (i.e., 1 faraday/mol) as in the case with the tetrabutylammonium perchlorate electrolyte. However, the rest potential decayed to −2.0 V at a slower rate (30 vs 10 min) using sodium tetraphenylborate. In addition the current efficiency toward C–O bond cleavage was increased with 97% cleavage after the addition of 2.8 faraday/mol. The improved current efficiency and the slow decay in the rest potential in the presence of sodium ion indicate (1) transfer of charge from the relative stable radical anion of **1** to the sodium ion is more chemically reversible for the sodium ion than the tetrabutylammonium ion and (2) disproportionation of the radical ion is not significantly increased in the presence of sodium ion vs tetrabutylammonium ion.

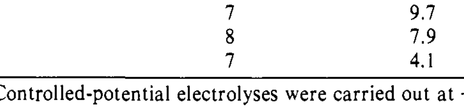
Chemical Reduction with Alkali Metals. Three different types of chemical reductant systems were used in the reductive cleavage of **1** and **2**: (1) Na/hexamethylphosphoric triamide (HMPA) in THF at 25 °C, (2) K/HMPA in dimethoxyethane (DME) at reflux, and (3) Na-K alloy/tetraglyme in THF. All three reductant systems resulted in virtual quantitative cleavage of both **1** and **2** if the conditions were optimized.

Reduction of ether **1** with the Na/HMPA/THF produced greater than 95% cleavage to phenol if a molar ratio of 1:8:2 of ether/Na/HMPA was used for a 24-h reaction time at 25 °C. When the reaction was monitored as a function of time under the same conditions, approximately 50% phenol formation was noted after 5 h. Reaction of **2** using the same ratios of 1:8:2 for the ether/Na/HMPA produced yields of greater than 98% phenol after 5 h. In addition, if the ratio of ether/Na was 1:1, only 14% of the ether **2** was cleaved to phenol even after 24 h. Thus, a molar ratio of ether/Na, which is smaller than 1:2, and reaction times greater than 1 h were required for quantitative cleavage of the ether using Na in HMPA as the reductant. The cleavage reaction was regioselective in that less than 3% naphthol was obtained compared to 95% phenol; therefore, cleavage at the naphthyl carbon–oxygen bond is preferred. These results suggest that the ether radical anion, which is probably produced under these conditions, reacts relatively slowly as noted in the electrochemical experiments.

Reduction of the ether **2** in DME using K/HMPA in a molar ratio of 1:8:2 of the ether/K/HMPA produced phenol in better than 98% yield after a 1-h reaction time at the reflux temperature of DME (bp 84 °C). The combination of a stronger reducing agent (i.e., K vs Na) and elevated temperature results in a more rapid disappearance of the ether concomitant with formation of phenol. Although the temperature alone could have caused this difference, a second possible explanation of this behavior is that the ether radical anion was further reduced to the dianion (vide ante). In addition, it should be noted that the cleavage was regioselective in that only a trace of 1-naphthol was obtained in the product mixture.

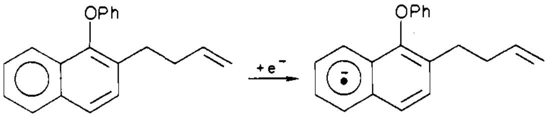
The most reactive of the chemical reductants that was employed in this study was the Na-K alloy using tetraglyme as the electron mediator in THF. Cleavage of the C–O bond of both **1** and **2** to form quantitative yields of phenol was found to occur using a reaction time of 5 min at a temperature of 0 °C. Furthermore, even at −78 °C, the time necessary for 93% phenol formation was only 10 min. Again, cleavage of the naphthyl carbon–oxygen bond dominated the reaction pathway because only trace amounts of naphthols were found in the product mixture. The reduced temperature would be expected to significantly decrease the rate of cleavage of the radical anion. The rapid disappearance of ether at these lower temperatures with concurrent phenol formation under these conditions clearly suggests that the species undergoing cleavage was not the radical anion but most probably the dianion (vide ante).

Intermediacy of the Naphthyl Radical. The intramolecular cyclization of the *o*-3′-butenylphenyl radical has been shown by Beckwith to undergo a regiospecific reaction to form 1-methylindan.[12] We have previously used this reaction to demonstrate the intermediacy of the phenyl radical in the electrochemical cleavage of an *o*-3′-butenyl-substituted diphenyl ether.[13,14] Recently, Beckwith has reported that the 2-(3′-butenyl)naphthyl radical undergoes an even more rapid intramolecular cyclization reaction than the corresponding phenyl system to form 1-methylbenz[*e*]indan (**4**) (eq 8).[15] The 2-(3′-butenyl) substituent was employed in the current study as a probe for the intermediacy of the naphthyl radical in both electrochemical and chemical reductive cleavage of 2-(3′-butenyl)-1-phenoxynaphthalene (**3**) and the products determined for the ratio of **4**/2-(3′-butenyl)-naphthalene (**5**).



(8)

Electrochemical Cleavage of 3. Cyclic voltammetric experiments on **3** produced an electrochemically reversible wave at −1.72 V vs Cd/Cd(II)/DMF (−2.47 V vs SCE) (Figure 2A). Controlled-potential electrolyses were carried out on **3** by addition of charge in an incremental manner as previously described for **1**. Table II is a summary of a series of electrolyses of **3** under different conditions. Controlled-potential electrolysis of **3** at −2.5 V vs SCE on either a Pt or Hg cathode (entries 1 and 2) produced significant cleavage of the naphthyl carbon–oxygen bond with concomitant phenoxide ion formation (eq 9 and 10). Cyclic



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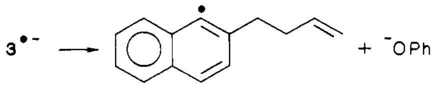

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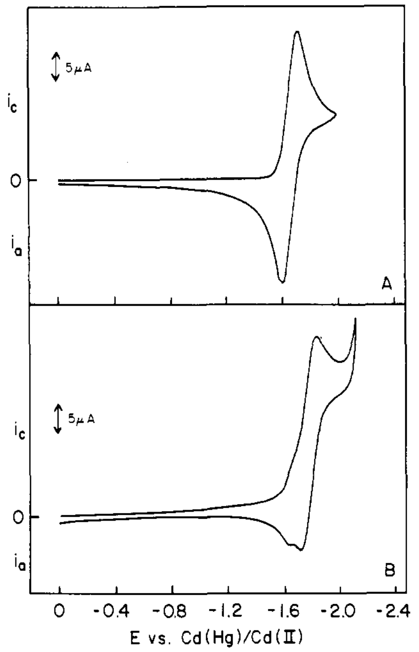


Figure 2. Cyclic voltammograms in 0.2 M TBAP/DMF at a scan rate of 0.1 V/s on a platinum electrode: (A) 1.7 × 10^{-2} M 2-(3′-butenyl)-1-phenoxynaphthalene, (B) solution A after the addition of 5 faraday/mol in a controlled-potential electrolysis experiment.

voltammetry after electrolysis indicated significant disappearance of **3** and formation of an electroactive species, which was reduced at −2.58 V vs SCE (Figure 2B). The reduction potential of this species is consistent with that of an alkyl-substituted naphthalene. Inspection of Table II shows that the predominant product of the naphthyl moiety was the indan **4**, which resulted from the cyclization of the 2-(3′-butenyl)naphthyl radical (eq 8). The ratios of the yields of indan **4**/naphthalene **5** were typically found to be between 9:1 and 10:1 on both platinum and mercury electrodes. The relatively high yields of cyclized product are consistent with the intermediacy of a naphthyl radical.

Formation of the cyclized indan **4** can also occur by cyclization of a 2-(3′-butenyl)naphthyl anion intermediate (vide post). We have previously reported on the analogous reaction of the electrochemically generated *o*-3′-butenylphenyl anion to form 1-methylindan.[13] The naphthyl anion intermediate can be formed by decomposition of the ether dianion, which could be produced by disproportionation of the radical anion. Alternately, the naphthyl radical could be further reduced to the anion either at the electrode surface or in solution by the radical anion of the ether. Therefore, reduction of **3** was carried out in the presence of a 10-fold excess of D_2O, which has been shown to substantially decrease the yield of 1-methylindan by deuteration of the *o*-3′-butenylphenyl anion to form 3′-butenylbenzene-d_1. The results for the reduction of **3** under these conditions (Table II, entry 3) clearly show that the presence of D_2O has little effect on the relative yields of indan **4**/naphthalene **5**. These data indicate that the naphthyl anion is not an important intermediate in the reaction pathway for electrochemical reduction of **3** at a potential of −2.5 V.

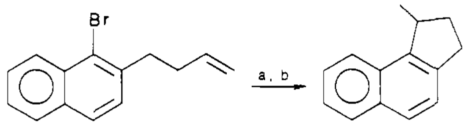
Saveant has shown that alcoholates are more effective hydrogen atom donors than the corresponding alcohols.[16] Controlled-potential electrolysis of **3** at −2.5 V using sodium isopropylate as a hydrogen atom donor in DMF/TBAP was carried out (entry 4). A significant decrease in the ratio of cyclized **4**/uncyclized **5** naphthalene products was obtained under these conditions. Thus, the above data indicate that the important precursor to products in the electrochemical reaction pathway is the naphthyl radical, which results from slow unimolecular fragmentation of the radical anion.

Table III. Cyclization of 1-Bromo-2-(3′-butenyl)naphthalene (**6**) via the Aryllithium Derivative or the Corresponding Radical[a]

entry no.	solvent	reaction time (temp), h (°C)	product yields[b] (d_1),[c] %	
			indan **4**	naphthalene **5**
1	THF	2 (−78)	0	100 (100)
2	THF	0.5 (23)	29 (4)	70 (1)
3	THF	1 (23)	30 (1)	70 (1)
4	Et_2O	1 (23)	15 (80)	85 (80)
5	Et_2O	28 (23)	90 (1)	9 (1)
6[d,e]	THF	0.5 (−78)	45	50
7[d,f]	THF	0.5 (−78)	75	20

[a] The aryllithium derivative was prepared by mixing 1 equiv (0.3 mol) of the bromide and 2 equiv of BuLi (0.6 mol) for 0.5 h at −78 °C in the solvent indicated (10 mL) under argon and then quenching with D_2O (99.8% d_1). [b] Product yields are mole percent based upon the initial amount of **6** and determined by GC and GC-MS. [c] Deuterium incorporation was determined by MS and was shown by fragmentation to be on the methyl group in the case of indan **4** and on the ring in the case of naphthalene **5**. [d] The radical intermediate was generated by action of solvated metal on ArBr (0.3–0.5 equiv) dissolved in THF (2 mL). [e] The ArBr was added to lithium naphthalene (10 equiv) in THF (10 mL). [f] The ArBr was added to Na-K alloy (0.2 mL, 1:5 molar ratio) and tetraglyme (1.0 mL) in THF (10 mL).

Scheme II



6 **4**

[a] Key: (a) *n*-BuLi, 23 °C, 28 h; (b) 10% sulfuric acid.

Chemical Cleavage of 3. As noted above, the 2-(3′-butenyl)naphthyl radical undergoes facile intramolecular cyclization to ultimately form the indan **4**. However, the 2-(3′-butenyl)naphthyl anion is also capable of undergoing slow cyclization to form the same regiospecific product. Table III summarizes the results obtained when 1-lithio-2-(3′-butenyl)naphthalene was formed by treating 1-bromo-2-(3′-butenyl)naphthalene (**6**) (see Scheme II) with *n*-butyllithium at −78 °C in THF or diethyl ether. Quenching of the reaction after 2 h with D_2O produced 100% of 2-(3′-butenyl)naphthalene (**5**) with 100% deuterium incorporation (entry 1). These data indicate that no cyclization or other reactions of the aryl lithium compound occurred at this temperature. However, if the solution was warmed to 23 °C and then quenched with D_2O, a significant amount of indan **4** was produced in THF (entries 2 and 3) with very little deuterium incorporation in either the indan **4** or the uncyclized naphthalenes. Furthermore, if the reaction was run in diethyl ether, the cyclized product was formed slowly in 90% yield over a 28-h period (entries 4 and 5) and this reaction was used for the preparation of indan **4** (see Scheme III). The above results indicate that an anionlike cyclization of the aryllithium reagent to the double bond can slowly occur at 23 °C.[16] The detailed kinetics for the cyclization of the 2-(3′-butenyl)naphthyl anion and the *o*-3′-butenylphenyl anion will be reported elsewhere.[17]

To ensure that radical cyclization would occur at −78 °C as was observed electrochemically at room temperature, 1-bromo-2-(3′-butenyl)naphthalene (**6**) was treated with a homogeneous alkali-metal solution at −78 °C (see entry 6 and 7, Table III). When lithium naphthalene or Na-K alloy/tetraglyme was used at −78 °C, indan **4** was formed in yields of 45% and 75%, respectively. The remainder of the material was uncyclized naphthalene **5**. The radical anion of bromonaphthalene decomposes very rapidly (k_d = 4 × 10^8 s) to give the naphthyl radical.[18] Homogeneous one-electron reduction here to the radical anion resulted in formation of the corresponding 2-(3′-butenyl)naphthyl

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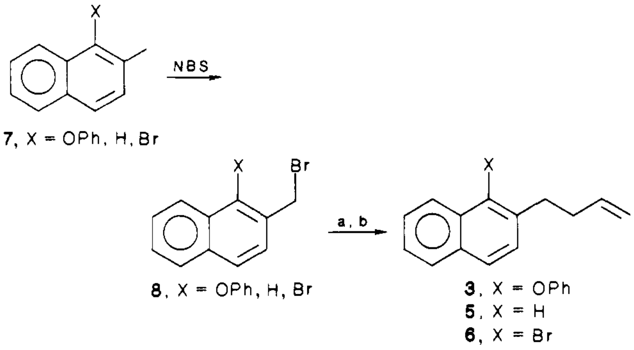
Table IV. Reductive Cleavage of 2-(3′-Butenyl)-1-phenoxynaphthalene[a] (3)

entry no.	time (temp),[c] min (°C)	products,[b] % yield					
		phenol	benz[*e*]indan (**4**)	reduced benz[*e*]indan[d]	naphthalene (**5**)	reduced naphthalene[e]	cyclized uncyclized
1	30 (−78)	30 (−7)	<1	6	48	36[f]	0.08
2	5 (0)	98	17	6	36	35	0.32
3	10 (0)	95	23	7	29	30	0.51
4	15 (0)	90	27	8	28	29	0.61
5	20 (0)	90	28	9	26	34	0.62
6	30 (0)	96	29	10	20	34	0.72

[a] The cleavage reaction was carried out by dissolving 0.6 mmol of the ether in dry THF (2 mL) and adding this solution to 10 mL of dry THF containing 0.1 mL of Na–K alloy (1:5 mole ratio) and 1.0 mL of tetraglyme. [b] Product yields (mol %) are based on the original amount of ether and determined by an internal standard GC technique. [c] At the end of the reaction time, the reaction was quenched with methanol. Less than 2% of the ether was found in the reaction mixture after quenching. [d] The reduced benz[*e*]indan was identified as 9b,5-dihydro-1-methylbenz[*e*]indan by GC–MS. [e] The reduced naphthalene was identified as 6-(3′-butenyl)-1,4-dihydronaphthalene by GC–MS. [f] The reduced naphthalene yields included 31% 6-(3′-butenyl)-1,4-dihydronaphthalene and 5% 6-(3′-butenyl)-1,2,3,4-tetrahydronaphthalene.

Scheme III[a]



[a] Key: (a) allylmagnesium chloride; (b) 10% sulfuric acid.

radical, which cyclized to the indanyl radical isolated as indan **4**. The large component of uncyclized product could have formed by (a) hydrogen abstraction before cyclization or (b) further reduction of the radical to the anion, which was stable at −78 °C. Both the rate of electron transfer from the electron source and the concentration of this source would affect the formation of the open-chain naphthalene **5** while the intramolecular cyclization would take place irrespective of these factors. The ratio of indan **4**/naphthalene **5** would vary depending on starting conditions and electron source. Thus, factor (a) would have little effect. Furthermore, submission of the naphthalene **5** to reductive cleavage conditions resulted in Birch reduction to form a product tentatively identified as 6-(3′-butenyl)-1,4-dihydronaphthalene in ca 80% yield. A maximum of only 5% of indan **4** was observed in this mixture, indicating indan formation did not occur from the product **5**. Thus, cyclization of the 2-(3′-butenyl)naphthyl radical takes place rapidly and selectively at −78 °C.

The conditions for a test of naphthyl radical vs anion intermediacy, which use the 2-(3′-butenyl) substituent, were applied to the chemical reductive cleavage of ether **3**. The reduction of **3** was carried out using the Na–K alloy/tetraglyme system, and the results are shown in Table IV. Reductive cleavage of **3** at low temperature (−78 °C) resulted in quantitative cleavage after 30 min with a 96% yield of phenol (entry 1). Cleavage occurred exclusively by the naphthyl carbon–oxygen bond with no detectable naphthol formation. In addition, indan **4** was not observed as a product of this reaction. However, a small amount (6%) of a Birch reduced form of indan **4**, 9b,5-dihydro-1-methylbenz[*e*]indan, was detected. More importantly, appreciable yields of indan **4** and reduced indan (entry 2) were obtained if the temperature was increased to 0 °C. The yield of indan **4** increased with increasing time for the reaction at this temperature until a yield of 29% was reached after 30 min (entries 2–6). Reduced forms of the indan were found in all of the reactions with yields of 6–10%. Interestingly, the degree of apparent cyclization to indan **4** (ca. 30%) in the reductive cleavage of **3** in THF was found to be approximately the same as that for the aryllithium compound (entry 2, Table III). The key conclusion that can be drawn from the above data is that the 2-(3′-butenyl)naphthyl radical is not an intermediate at low temperature (i.e., −78 °C) because only 6% cyclization was observed. Furthermore, the data indicate that the 2-(3′-butenyl)naphthyl anion is an important intermediate in the reaction pathway.

In order to more directly prove the intermediacy of the naphthyl anion, the above reaction was quenched with D_2O instead of methanol in order to trap the anion so as to produce 2-(3′-butenyl)naphthalene-d_1. In this experiment, the reductive cleavage of **3** was carried out in THF for 5 min at −78 °C, followed by warming of the solution to 0 °C for 1 min and then quenching with D_2O. The time frame for this experiment was limited to minimize protonation of anionic intermediates by the solvent. The resultant naphthalene **5** (60% yield) had 30% deuterium incorporation (as d_1) on the naphthyl ring. In addition, the indan **4** (8% yield) was found to have 87% monodeuteration in the methyl group.

The above data clearly indicate that the naphthyl anion and not the naphthyl radical is the important intermediate when ether **3** is cleaved with a relatively powerful reducing agent (i.e., Na–K alloy/tetraglyme). In contrast, the naphthyl radical was shown to be the key intermediate in the electrochemical reduction and cleavage of **3**, when the radical anion of **3** is selectively formed by the controlled-potential experiment.

Conclusions. The electrochemical reduction of 1- and 2-phenoxynaphthalene to their radical anions was observed at −2.42 and −2.48 V vs SCE, respectively. Electrochemical studies using both cyclic voltammetry and chronoamperometry indicate that the above radical anions were both stable in dry DMF with a half-life greater than 100 s. Further reduction of the radical anion to the dianion could not be electrochemically observed. However, long-time controlled-potential electrolysis experiments (greater than 1 h in duration) resulted in slow cleavage of the ether products. The intermediacy of the naphthyl radical was conclusively demonstrated by the use of an intramolecular radical trap in the form of the 2-(3′-butenyl) substituent on the ether, i.e., 2-(3′-butenyl)-1-phenoxynaphthalene (**3**). Formation of 1-methylbenz[*e*]indan (**4**) in the absence or in the presence of D_2O confirmed the presence of the 2-(3′-butenyl)naphthyl radical intermediate. Bond cleavage of the radical anion is regioselective in that the naphthyl carbon–oxygen bond was cleaved rather than the phenyl carbon–oxygen bond.

Reduction of the phenoxynaphthalenes with Na/HMPA in THF also resulted in regioselective cleavage of the naphthyl carbon–oxygen bond. Under these conditions, cleavage occurred slowly with 50% phenol formation after 5 h at 25 °C. However, reductive cleavage of the phenoxynaphthalenes occurred much more rapidly if a stronger reducing agent such as Na–K alloy/tetraglyme was used. The intermediacy of the naphthyl anion in the Na–K alloy reaction pathway was demonstrated by the utilization of the same 2-(3′-butenyl) substituent as was used to prove radical intermediacy in the electrochemical reduction. Low-temperature (−78 °C) cleavage resulted in a high yield of phenol, but only 6% cyclization to indan **4** was observed. Significant yields of indan **4** were produced in the reduction of **3** at

0 °C. These data suggest that the dianion of phenoxynaphthalene is produced with the Na–K alloy/tetraglyme system, while the relatively stable radical anion is produced when Na/HMPA is employed as the reductant.

The combination of electrochemical techniques and chemical reductants indicates that the radical anion is relatively stable but decomposes slowly to produce phenoxide ion and the naphthyl radical. Although the further reduction of the ether radical anion to the dianion could not be electrochemically observed, the dianion of the phenoxynaphthalenes can be produced with strong reductants. Rapid decomposition of the ether dianion results in the formation of the naphthyl anion and the phenoxide ion. Work in progress indicates that electrochemically generated dianions of phenoxyphenanthrene and phenoxyanthracene can be produced and their chemistry will be subsequently reported.

Experimental Section

Instrumentation. Cyclic voltammetric, chronoamperometric, and controlled-potential electrolysis experiments were performed with a PAR Model 173 potentiostat equipped with a Model 179 digital coulometer. Potential wave forms were generated by a digital-controlled, multifunctional generator[19] coupled to the PAR 173. All electrochemical data were recorded on a Houston 2000 X-Y recorder or a Tektronix 5103N storage oscilloscope. All electrochemical measurements were made with positive feedback electronic compensation of ohmic potential loss.

A Jeol FX-60 NMR spectrometer was used to obtain ^{13}C and ^{2}H spectra while a Varian EM-390 NMR was used to obtain ^{1}H spectra. All chemical shifts measured and reported herein are with respect to Me_4Si (δ 0). IR spectra were obtained on a Nicolet MX-S FT-IR. High-resolution mass spectrometry (HRMS) was performed by the Midwest Center for Mass Spectrometry, University of Nebraska. Mass spectra for routine work was obtained on a GC–MS, Hewlett-Packard Model 5790A GC equipped with a mass-selective detector Model 5970A. The GC was equipped with a 0.25 mm × 30 m poly(dimethylsiloxane) (Alltech RSL-150) capillary column.

Electrochemical Experiments. The solvent used was *N*,*N*-dimethylformamide (DMF, Burdick and Jackson, spectroscopic grade). The DMF containing the supporting electrolyte, tetrabutylammonium perchlorate (TBAP, Southwestern Analytical Chemicals, dried in vacuo, 100 °C, 24 h) was purified by passage through a column of freshly activated alumina (Woelm W2000 neutral-grade Super I, 550 °C, 24 h, in vacuo). All solvent preparation, including alumina treatment, took place in a Vacuum Atmospheres HE-43-2 Dri-Lab glovebox equipped with a HE-493 Dri-Train as previously described.[20] The DMF/TBAP solution was transferred to an all-glass vacuum line and subsequently degassed by several freeze–pump–thaw cycles. The dry, degassed solvent/electrolyte solutions were stored and introduced into airtight, all-glass electrochemical cells in the glovebox. The electrochemical cells for cyclic voltammetry and controlled-potential electrolysis have been previously described.[21]

The working electrode for cyclic voltammetric experiments was a Beckman platinum button (No. 39273), with an area of approximately 0.23 cm^2. Long-time chronoamperometric studies ($t > 5$ s) were performed on a planar platinum electrode (geometric area 0.95 cm^2), which was modified by the addition of a 6-mm glass mantle to minimize the effect of edge diffusion. The reference electrode used in most experiments was a cadmium amalgam, which was in contact with dry DMF, saturated with $CdCl_2$ and NaCl.[22] The potential of this electrode was –0.75 V vs the aqueous saturated calomel electrode. Controlled-potential electrolyses were performed in an all-glass vacuum-tight cell, which has been previously described, using either a platinum basket or mercury pool as the working electrode.[1]

Product analyses of the electrolysis mixtures were accomplished by a combination of gas chromatography (GC) and high-pressure liquid chromatography (HPLC). Deuterium incorporation and identification of unknown components were carried out by coupled GC–mass spectroscopy (GC–MS). GC analysis was done with a Shimadzu GP-6AM chromatograph equipped with dual-flame ionization detectors and dual 3% Dexsil 300 6-m column and a Hewlett-Packard 3390A integrator. Electrolyzed solutions were extracted as previously described prior to GC or GC–MS analysis.[19] Quantitation of the naphthol products was accomplished by isocratic HPLC with an Altex 110A pump and LDC 1203 UV detector (254 nm). The electrolysis solutions were acidified with perchloric acid and injected directly into a C18 reverse-phase column (Alltech, 4.6 mm × 25 cm, 5-μm particle size). Mobile-phase composition (acetonitrile/4% aqueous acetic acid) was varied to effect separation. Calibration curves were prepared daily and employed for all chromatographic analysis.

Chemicals. The tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. HMPA was distilled from Na metal, degassed, and then stored in a glovebox. Tetraethyleneglycol dimethyl ether (tetraglyme) (Aldrich) was dried by passing it through a column of freshly activated (300 °C, 24 h, in vacuo) alumina. The *n*-butyllithium (Aldrich) was 2.0 M, which was confirmed by titration.[23]

General Chemical Cleavage Conditions. The metal (Na, K, or Na–K alloy, 1–8 equiv) was stirred with THF (10 mL) under argon or nitrogen with the electron-transfer agent (tetraglyme, HMPA, or just solvent) until the solution was blue. The ether (0.6 mmol) and the GC standard (dodecane) in THF (2 mL) were then added, and the mixture was stirred for the times and at the temperatures indicated in Table IV. The reaction was quenched with H_2O, D_2O, methanol, or methanol-*O*-d_1. Excess Na from HMPA reactions was removed before quenching, and inverse quenching of Na–K alloy runs was employed. The mixture was acidified with dilute HCl solution, extracted with ether, washed with saturated brine, and dried over $MgSO_4$. The products were quantitated by gas chromatography using the internal standard previously added.

1- and 2-Phenoxynaphthalenes were prepared from 1- or 2-bromonaphthalene (10 g), potassium phenoxide (9.56 g), and copper dust (0.1 g) following a literature procedure.[24] The products were purified by column chromatography (silica gel, eluted with hexane) and recrystallized from ethanol.

1-Phenoxynaphthalene: mp 50.0–50.5 °C (lit.[24] mp 54 °C); ^{13}C NMR ($CDCl_3$) δ 157.7, 152.9, 134.8, 129.6, 127.6, 126.8, 126.4, 125.7, 123.2, 123.0, 122.0, 118.4, 113.3.

2-Phenoxynaphthalene: mp 43–44 °C (lit.[24] mp 45 °C); MS *m*/*e* (RA) 218 (100, M$^+$) 219 (15, M + 1), 220 (0.3, M + 2), 192 (14), 191 (16).

2-Methyl-1-phenoxynaphthalene (7) was prepared by a modified Ullman reaction procedure.[23] 1-Bromo-2-methylnaphthalene (31.0 g, 140 mmol, Aldrich) was heated with potassium phenoxide [29.0 g, 219 mmol; prepared by heating phenol (20.6 g, 219 mmol) with KOH pellets (14.4 g, 219 mmol) in MeOH in vacuo], and Cu dust (1.34 g, 21.1 mmol) at 220–240 °C under argon with stirring for 3 h. The cooled reaction mixture in diethyl ether (0.5 L) and water (0.8 L) was separated and filtered through glass wool. Distillation of the ether yielded a tan solid, which was chromatographed (pentane/activated alumina) to yield 2-methyl-1-phenoxynaphthalene (**7**) (26.6 g, 81%) as white crystals: mp 73–74 °C; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3 H, $-CH_3$), 6.65–7.85 (m, 11 H, Ar*H*). MW. Calcd for $C_{17}H_{14}O$: 234.1045. Found: 234.1042.

2-(Bromomethyl)-1-phenoxynaphthalene (8). The ether **7** (9.70 g, 41.4 mmol) was refluxed 7 days with *N*-bromosuccinimide (8.20 g, 46.1 mmol) and benzoyl peroxide (0.1 g) in CCl_4 (400 mL). The cooled solution (–5 °C) was filtered through glass wool to remove the succinimide. Distillation of the solvent yielded crude 2-(bromomethyl)-1-phenoxynaphthalene (**8**) (14.5 g): ^{1}H NMR (CCl_4) δ 4.50 (s, 2 H, $-CH_2Br$), 6.65–7.90 (m, 11 H, Ar*H*).

2-(3′-Butenyl)-1-phenoxynaphthalene (3). The crude bromide **7** (14.5 g) was dissolved in THF (50 mL) and added dropwise with stirring to a THF solution of allylmagnesium chloride (200 mL of 0.90 M, 180 mmol). The solution was refluxed 12 h. Note: quantitative displacement of the bromide was necessary, because **7** and **3** form an azeotrope. The excess Grignard reagent was quenched by addition of 10% H_2SO_4 (100 mL). The product was extracted into diethyl ether (80 mL) and dried over $MgSO_4$. Distillation of the solvent followed by vacuum distillation [bp 145 °C (0.20 mmHg)] yielded pure (GC analysis), clear liquid **3** (8.94 g, 64% yield from 1-bromo-2-methylnaphthalene): ^{1}H NMR ($CDCl_3$) δ 2.25 (q, J = 8 Hz, 2 H, $-CH_2-$), 2.70 (t, J = 8 Hz, 2 H, ArCH_2-), 4.75 (s, 1 H, *cis*-C*H*), 4.90 (d, J = 7 Hz, 1 H, *trans*-C*H*), 5.50–5.90 (m, 1 H, $-CH=$), 6.70–7.90 (m, 11 H, Ar*H*); MS (GC–MS) *m*/*e* (RA) 275 (M + 1, 5.5), 274 (M$^+$, 24), 234 (17), 233 (M – C_3H_5, 100), 231 (18), 215 (66), 205 (28), 204 (18), 203 (31), 202 (25), 190 (18), 189 (17), 178 (15), 165 (20), 139 (16), 128 (25), 115 (20), 78 (27), 51 (34); ^{13}C NMR ($CDCl_3$) δ 29.7 ($-CH_2-$), 34.1 (ArCH_2-), 115.0 ($=CH_2$), 121.4, 122.3, 125.5, 126.1, 127.7, 128.0, 128.2, 129.5, 130.9, 133.6 (aryl carbons), 137.9 ($-CH=$), 147.1, 159.1 (ethereal carbons).

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MW. Calcd for $C_{20}H_{18}O$: 274.1358. Found: 274.1360.

2-(Bromomethyl)naphthalene (9). 2-Methylnaphthalene (1.71 g, 12.0 mmol), *N*-bromosuccinimide (2.30 g, 12.9 mmol), and benzoyl peroxide (0.1 g) were refluxed 7 days in CCl_4 (50 mL). The solution was filtered and the solvent removed to yield the crude 2-(bromomethyl)naphthalene (**9**) (2.56 g): ^1H NMR (CCl_4) δ 4.58 (s, 2 H, ArCH_2Br), 7.05–7.70 (m, 7 H, ArH).

2-(3′-Butenyl)naphthalene (5). Freshly prepared, crude bromide **9** (2.56 g) in THF (15 mL) solution was added dropwise to a THF solution of allylmagnesium chloride (50 mL of 0.90 M, 45 mmol). The solution was refluxed 12 h, and then the excess Grignard reagent was quenched by the addition of 10% H_2SO_4 (40 mL). The butene **5** was extracted into ether (40 mL) and dried over $MgSO_4$. After solvent removal, the product was vacuum distilled [bp 85 °C (0.20 mm Hg)] to yield 1.59 g of clear liquid **5**, pure by GC analysis: MS (GC–MS) *m/e* (RA) 183 (M + 1, 3.3), 182 (M^+, 16), 142 (12), 141 (M – C_3H_7, 100); ^1H NMR ($CDCl_3$) δ 2.35 (q, J = 7 Hz, 2 H, –CH_2–), 2.80 (t, J = 7 Hz, ArCH_2–), 4.90 (s, 1 H, *cis*-CH), 5.05 (d, J = 8 Hz, 1 H, *trans*-CH), 5.60–6.10 (m, 1 H, –CH=), 7.10–7.80 (m, 7 H, ArH). MW. Calcd for $C_{14}H_{14}$: 182.1096. Found: 182.1090.

1-Bromo-2-(bromomethyl)naphthalene (10). 1-Bromo-2-methylnaphthalene (9.20 g, 41.6 mmol, Aldrich), *N*-bromosuccinimide (8.60 g, 48.3 mmol), and benzoyl peroxide (0.1 g) were refluxed in CCl_4 (400 mL) for 6 days. The chilled (–5 °C) solution was filtered through glass wool and the solvent distilled to yield the crude 1-bromo-2-(bromomethyl)naphthalene (**10**) (13.3 g): ^1H NMR (CCl_4) δ 4.80 (s, 2 H, –CH_2Br), 7.30–7.70 (m, 5 H, ArH), 8.25 (d, J = 10 Hz, 1 H, ArH-8).

1-Bromo-2-(3′-butenyl)naphthalene (6). The crude bromide **10** (13.3 g) in THF (30 mL) solution was added dropwise with stirring to a THF solution of allylmagnesium chloride (400 mL of 0.90 M) and the resulting mixture refluxed 2 h. The product **6** was worked up by addition of 10% H_2SO_4 (80 mL), extracted with diethyl ether, and dried over $MgSO_4$. Removal of solvent followed by vacuum distillation [bp 110 °C (6×10^{-2} mmHg)] yielded clear liquid **6**, pure by GC analysis (8.01 g, 30.7 mmol, 74% yield from 1-bromo-2-methylnaphthalene): ^1H NMR ($CDCl_3$) δ 2.50 (q, J = 8 Hz, 2 H, –CH_2–), 3.05 (t, J = 8 Hz, 2 H, ArCH_2), 4.90 (s, 1 H, *cis*-CH), 5.15 (d, J = 9 Hz, 1 H, *trans*-CH), 5.70–6.30 (m, 1 H, –CH=), 7.50–8.00 (m, 5 H, ArH), 8.30 (d, J = 10 Hz, 1 H, ArH-8); ^{13}C NMR ($CDCl_3$) 34.0 (–CH$_2$–), 36.9 (ArCH$_2$–), 115.2 (=CH$_2$), 123.6, 125.7, 127.1, 127.2, 127.3, 127.9, 128.0, 132.5, 133.1 (aryl carbons), 137.6 (–CH=), 139.1 (ArCCH$_2$–). MW. Calcd for $C_{14}H_{13}Br$: 260.0201 (M^+), 262.0181 (M + 2). Found: 260.0209 (M^+), 262.0186 (M + 2).

1-Methylbenz[*e*]indan (4). 1-Bromo-2-(3′-butenyl)naphthalene (**6**) (1.41 g, 5.40 mmol) was treated with *n*-BuLi (4.8 mL of 2.0 M solution, 2 equiv) while stirring in diethyl ether (150 mL) at –78 °C for 2 h. The solution was then warmed to 23 °C for 28 h. The reaction mixture was quenched with methanol (20 mL), washed twice with a 10% NaOH solution (30 mL), and dried over $MgSO_4$. Removal of solvent yielded the crude, 1-methylbenz[*e*]indan (**4**) (0.95 g), which contained ca. 10% 2-(3′-butenyl)naphthalene. Chromatography (pentane/5% $AgNO_3$ on silica) of the crude product yielded clear, liquid **4**, pure by GC analysis (0.760 g, 4.18 mmol, 77.4% yield): ^1H NMR ($CDCl_3$) δ 1.45 (d, J = 8 Hz, 3 H, –CH_3), 1.70–2.10 (m, 1 H, H_a), 2.20–2.60 (m, 1 H, H_b), 2.70–3.30 (m, 2 H, –CH$_2$–), 3.50–3.90 (m, 1 H, methine), 7.20–7.90 (m, 6 H, ArH); MS (GC–MS) *m/e* (RA) 183 (M + 1, 4.5), 182 (M^+, 22.5), 180 (M – 2, 2), 168 (13), 167 (M – CH_3, 100), 165 (23), 152 (19). MW. Calcd for $C_{14}H_{14}$: 182.1096. Found: 182.1084.

6-(3′-Butenyl)-1,4-dihydronaphthalene (11). Compound **11** was isolated (by preparative GC) from the reaction mixture that resulted from the treatment of **5** with the Na-K/tetraglyme/THF ether cleavage system: ^1H NMR ($CDCl_3$) δ 2.30 (q, J = 7 Hz, 2 H, ArCH$_2$CH_2–), 2.65 (t, J = 7 Hz, 2 H, ArCH_2–), 3.35 (d, J = 1.5 Hz, 4 H, ArCH_2CH=), 4.85 (s, 1 H, *cis*-CH), 5.05 (d, J = 10 Hz, 1 H, *trans*-CH), 5.55–6.05 (m, 1 H, –CH=CH$_2$), 5.90 (t, J = 1.5 Hz, 2 H, ArCH$_2$CH=), 7.05–7.85 (m, 3 H, ArH); MS (GC–MS) *m/e* (RA) 185 (M + 1, 2.0), 184 (M^+, 12.5), 144 (13), 143 (M – C_3H_5, 100), 129 (10), 128 (5).

9b,5-Dihydro-1-methylbenz[*e*]indan (12). Compound **12** was also obtained from the reaction mixture of the room-temperature cleavage of **3** by preparative GC and spectroscopically characterized: ^1H NMR ($CDCl_3$) δ 1.25 (d, J = 8 Hz, 3 H, CH_3), 1.50–2.30 (m, 2 H, –CH_2–), 2.40–2.80 (m, 2 H, –CH$_2$–), 2.90–3.30 (m, 1 H), 3.35 (d, J = 8 Hz, 2 H, ArCH_2–), 3.55 (d, J = 10 Hz, 1 H, ArCH–), 6.35 (t, J = 8 Hz, 1 H, ArCH$_2$CH=), 7.20–7.90 (m, 4 H, ArH); MS (GC–MS) *m/e* (RA) 185 (M + 1, 3.2), 184 (M^+, 18.5), 170 (14), 169 (M – CH_3, 100), 167 (10), 129 (20), 128 (11).

6-(3′-Butenyl)-1,4-dihydro-5-phenoxynaphthalene (13) and 6-(3′-Butenyl)-1,2,3,4-tetrahydronaphthalene (14). Compounds **13** and **14** were tentatively identified by their GC–MS. Quantitation was performed assuming similar compounds **13** and **14** had the same GC response factor as **3** and **5**, respectively. Compound **13**: MS (GC–MS) *m/e* (RA) 277 (M + 1, 4.5), 276 (M^+, 20.2), 236 (18), 235 (M – C_3H_5, 100), 233 (15), 115 (10), 78 (20). Compound **14**: MS (GC–MS) *m/e* (RA) 186 (M^+, 18.0), 146 (12.5), 145 (M – C_3H_5, 100), 144 (8), 143 (23), 130 (8), 129 (12), 115 (9).

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Cation Transport Using Anthraquinone-Derived Lariat Ethers and Podands: The First Example of Electrochemically Switched "On/Off" Activation/Deactivation

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Abstract: Anthraquinone undergoes one- and two-electron reduction to form either radical anions or dianions. When a crown-ether-type macrocycle or a polyethyleneoxy side chain is attached, the reduced aromatic and the oxygen donor groups cooperate to bind the cation. Binding of Li^+ or Na^+ is greater when anthraquinone is reduced because there is a charge–charge interaction between it and the cation. This property has been used to facilitate transport. Thus, reduction at the source phase enhances cation binding, and oxidation in the receiving phase induces cation release. Activation/deactivation was effected electrochemically. The ligands studied in a bulk CH_2Cl_2 phase were 1-((9,10-dioxo-1-oxanthracenyl)methyl)-15-crown-5, **1**; 1-((9,10-dioxo-1-oxanthracenyl)methyl)-18-crown-6, **2**; 1-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)anthracene-9,10-dione, **3**; 1-(2-(2-(2-(2-octadecyloxyethoxy)ethoxy)ethoxy)ethoxy)anthracene-9,10-dione, **4**. The first example of an electrochemically activated (reduction) and deactivated (oxidation) cation transport system based on anthraquinone ligands is demonstrated.

The ability of synthetic ionophores such as crown ethers and cryptands to bind and transport cations has fascinated the chemical community almost since the introduction of these molecules.[1,2] Most of these studies have utilized liquid membrane systems, and

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