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Regioselective Carbon–Oxygen Bond Cleavage Reactions of Aromatic Ethers and Esters with Potassium Metal/18-Crown-6/THF as the Electron-Transfer Reagent

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The facile carbon–oxygen bond cleavage reactions of a variety of aromatic ethers and esters were studied with an electron-transfer reagent that consisted of potassium metal and 18-crown-6 in tetrahydrofuran (THF). The relative rates of carbon–oxygen bond cleavage, with these aromatic ethers and esters under electron-transfer conditions, was studied in competition with the standard, diphenyl ether. The order of relative reactivities was as follows: phenyl 2-hydroxybenzoate (**10**) (>2.0); phenyl 2-methoxybenzoate (**11**) (>2.0); phenyl 4-methoxybenzoate (**12**) (>2.0); 2-methoxyphenyl benzoate (**13**) (>2.0); 4-methoxyphenyl benzoate (**14**) (>2.0); 4-hydroxyphenyl benzoate (**15**) (1.6); benzyl benzoate (**9**) (1.3); 4-methoxyphenyl phenyl ether (**5**) (1.15); phenyl benzoate (**8**) (1.04); diphenyl ether (**1**) (1.0); dibenzyl ether (**2**) (0.98); 2-methoxyphenyl phenyl ether (**6**) (0.97); benzyl phenyl ether (**3**) (0.96); phenethyl phenyl ether (**7**) (0.77); and 4-hydroxyphenyl phenyl ether (**4**) (<0.1). From these relative rates, it is clear that electron-donating groups increase the relative rates of C–O bond cleavage in aromatic esters. Conversely, a methoxyl group has no apparent effect on the relative rates of aromatic ether C–O bond cleavage, while a hydroxyl group dramatically decreases the rate. Proton donors, *tert*-butyl alcohol and hydroquinone, decreased the rate of diphenyl ether cleavage. The regioselectivity for C–O bond cleavage of esters **8**–**15**, i.e., carbonyl–oxygen versus carboxyl–carbon cleavage, showed selective carbonyl–oxygen bond cleavage. The regiochemistry for C–O bond cleavage reactions for the ethers **3**–**6** showed a preference for the benzyl–oxygen bond, whereas substitution of either a hydroxyl or methoxyl group in the 4 position of diphenyl ether provided data that showed selective cleavage in the substituted aryl groups. Substitution of a 2-methoxyl group in diphenyl ether changed the regiochemistry to cleavage in the unsubstituted aryl group. The overall results also imply that the theory of regioconservation of spin density may be operative in the cleavage of carbon–oxygen bonds in aromatic ethers and esters under electron-transfer conditions.

Introduction

The structure of coal is highly complicated, but present knowledge indicates that two linkages, among others, that are important to cleave to depolymerize coal are those associated with aromatic ethers and aromatic esters.[1-3] The facile depolymerization of coal at mild temperatures would potentially allow the structure to be ascertained without thermal alterations and as well conceivably provide a mechanism to liquefy coal. One method, which has been evaluated for the facile depolymerization of such complex matrices as coal, is the use of electron-transfer reagents. This includes sodium, lithium, and potassium metal in liquid ammonia or ethers[1] and potassium metal with 18-crown-6 in THF.[3] The problem associated with solving the structure of a polymeric material, such as coal, is to determine the exact nature of the smaller fragments for a total picture of the polymeric structure. Thus, model compound linkage studies are highly important to conduct in order to determine a structure–reactivity relationship and to provide vital information that can be related to the more complex structural situation.

In determining which of the above-mentioned chemical electron-transfer systems would provide new fundamental knowledge about the structure–reactivity relationships in the facile cleavage of C–O bonds in aromatic ethers and esters, we chose to examine these model compound coal linkages with the electron-transfer reagent potassium metal/18-crown-6/THF.[4] There have been relatively few studies on the use of K metal/18-crown-6/THF as a reducing agent for organic compounds[5] and none that included aromatic esters and aromatic ethers. Moreover, few studies, using the above-mentioned model linkages and chemical or electrochemical electron-transfer systems, have been directed toward structure–reactivity relationships and other detailed mechanistic aspects, such as regioselectivities in the C–O bond-cleavage reaction, substituent effects, the role of proton donors on the rate of C–O bond-cleavage reactions, and deuterium incorporation as a test to differentiate between one- and two-electron-transfer mechanisms.[6-20]

More recent mechanistic studies on aromatic ethers, using chemical and electrochemical methods to generate intermediates, clearly showed one-electron transfer, i.e., radical anion formation, as being the important reactive

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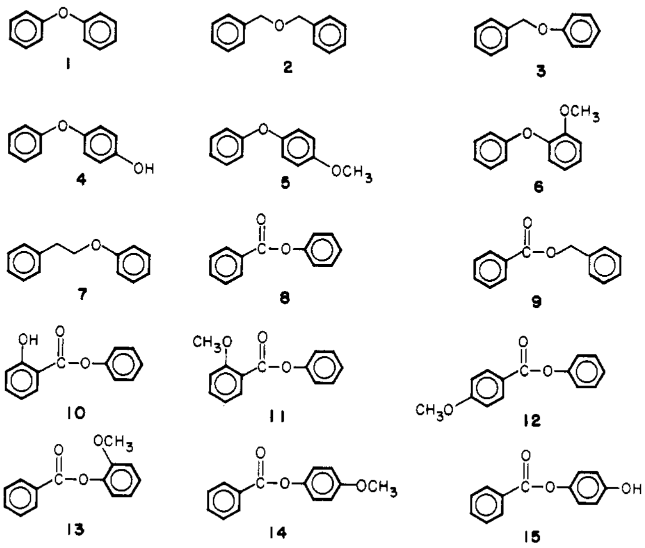
Chart I. Model Coal Compounds of Aromatic Ethers 1–7 and Aromatic Esters 8–15 Reacted under Electron-Transfer Conditions



species in these C–O bond-cleavage reactions.[6-9] Also, chemical and electrochemical electron-transfer studies were performed on a number of esters to generate radical anions and to show the mode of cleavage and products formed.[17-20] However, many factors appear to enter into the use of chemical reagents in the reductive C–O bond-cleavage reactions and include the metal reduction potential, solvent, temperature, metal ion chelating agent, and the metal/substrate ratio.[1,6]

Thus, in this paper, we present our results on studies involving the chemical reductive C–O bond-cleavage reactions, using aromatic ethers and esters as the model coal linkages with K metal/18-crown-6/THF as the electron-transfer reagent, in determining relative rates, regioselectivity, effects of proton donors on the relative rates, and deuterium incorporation to differentiate between one- and two-electron-transfer processes. As well, we will show that hydroxyl and methoxyl groups have a profoundly different effect on the C–O bond-cleavage reaction of aromatic esters in comparison to aromatic ethers.

Results

Relative Rates of C–O Bond Cleavage for Compounds 1–15 with K Metal/18-Crown-6/THF as the Electron-Transfer Reagent. The compounds **1**–**15** studied under electron-transfer reaction conditions, as model coal linkages with aromatic ether and ester functionalities, are shown in Chart I. The relative rates of C–O bond cleavage for compunds **1**–**15** with diphenyl ether (**1**) (k_{rel} = 1.0) as the competitive internal standard (the ratio that optimized product formation, K metal/18-crown-6/substrate/diphenyl ether, was 10/10/1/1 at 0 °C in 10 mL of THF) are shown in Table I.

Table I. Relative Rates of Carbon–Oxygen Bond Cleavage of Compounds 1–15 under Electron-Transfer Conditions Using K Metal/18-Crown-6[a]

substr	relative rate[b]	substr	relative rate[b]
10	>2.0[c]	8	1.04
11	>2.0	1	1.0
12	>2.0	2	0.98
13	>2.0	6	0.97
14	>2.0	3	0.96
15	1.6	7	0.77
9	1.3	4	<0.1
5	1.15		

[a] Reactions run in THF at 0 °C. [b] Competition experiments with compound **1** as standard were run with 0.18 mmol of each reactant and 1.79 mmol of potassium metal and 1.79 mmol of 18-crown-6 with undecane as GC internal standard. Plots of percent conversion vs time were linear up to 20 min. Least-squares regression analysis gave the slope (%/min), and each substrate rate was divided by compound **1** rate. (See Experimental Section for details of this competitive procedure). [c] A relative rate of >2.0 was based on the substrates **10**–**14** being totally reacted on mixing.

The relative rate sequence in Table I dramatically shows that aromatic esters substituted with methoxyl or hydroxyl groups, **10**–**15**, have reacted upon mixing and were assigned a relative rate of >2.0. The esters in general reacted faster than the ethers, although the unsubstituted ester, **8**, and diphenyl ether (**1**) had similar relative rates within the error limits of the techniques used. The only benzyl ester studied, **9**, was slower than any of the methoxyl or hydroxyl substituted esters, **10**–**15**, with the implication that the benzyl–oxygen bond may not be the site of C–O bond cleavage. It is also interesting to note that substitution of a methoxyl or a hydroxyl group in either the benzoic acid or phenol portion of esters **10**–**15** increases the rate of C–O bond cleavage, which suggests the importance of polar effects in the formation of intermediate radical anions and their subsequent C–O bond cleavage reactions.

The aromatic ethers **5** and **6**, with 2- and 4-methoxyl substituents, clearly showed no increase in the relative rates of C–O bond cleavage in competition with **1** as was observed for the substituted esters. As well, aromatic ethers **2** and **3** also provided relative rates that showed no special reactivity. However, aromatic ether **4** showed a dramatically reduced relative rate, and ether **7** also showed a moderate decrease in relative rate. We also wanted to establish whether aromatic amines and sulfides, which also constitute examples of model coal linkages,[1] reacted at faster or slower relative rates compared to **1**–**15**. We found that benzyl phenyl sulfide (**16**) had a relative rate of 1.02 and that diphenylamine only formed the nitrogen anion but did not undergo C–N bond cleavage.

Effect of Proton Donors on the Initial and Relative Rates of Carbon–Oxygen Bond Cleavage in 1 and 3. Many of the reported reductive cleavage reactions include the use of added proton donors to trap intermediates;[1,6,8] however, the effect on the cleavage rate has not been thoroughly addressed. We reacted compound **1** with K metal/18-crown-6/THF at 0 °C in the absence and presence of *tert*-butyl alcohol (*t*-BuOH) and found that the ratio of the initial rate of reductive cleavage of **1** was k(without *t*-BuOH)/k(with *t*-BuOH) = 5. Thus, the presence of *t*-BuOH significantly slows the rate of reductive cleavage of **1**. We also did not observe (GC analysis) any reduced aromatic ring products with **1** in the presence of *t*-BuOH. We also found that the relative rate of C–O bond cleavage of aromatic ether **3** in competition with **1** and in the presence of *t*-BuOH was retarded by a factor of 3.8. Similarly, addition of hydroquinone in the competitive reductive cleavage reaction of **3** led to a slight reduction of rate by a factor of 1.1. The lack of reduced aromatic ring products in the presence of *t*-BuOH suggests a possible protonation–reduction–elimination sequence for $[\mathbf{1}]^{\bullet-}$ that would still provide benzene and phenol.[6]

Regioselectivity and Product Identification in the Reductive Cleavage Reactions of Compounds 1–15. Table II summarizes the products that were formed in the reductive cleavage reactions of compounds **1**–**15**. We briefly studied the effect of the ratio of K metal/18-crown-6/substrate in order to maximize (10:10:1) the yields of these products, which were quantified when possible by using gas chromatography with undecane as the internal

Table II. Product Distributions in the Reactions of Compounds 1–15 with K Metal/18-Crown-6/THF[a]

	products (%)			
substr	benzene	ArH	ArOH	phenol
1	+[b]			100
2		47[c]	53[d,e]	
3		57[c]		43
4	+		+[f]	
5	+		77[g]	23
6	+	7[h]		93
7		100[i]		+
8	+			100
9	+		100[e]	
10	+			+
11	+			100
12	+			100
13	+		100[j]	
14	+		100[g]	
15	+		+[f]	

[a] Analysis by capillary gas chromatograph with undecane as an internal standard. Reactions run individually for up to 30 min at 0 °C in THF. Starting mmol ratios K/18-crown-6/substrate were 10:10:1. Yields are normalized to 100%. [b] "+" means present but not quantified. [c] Toluene. [d] Small amount of benzaldehyde was also found. [e] Benzyl alchol. [f] *p*-Hydroquinone. [g] 4-Methoxyphenol. [h] Methoxybenzene. [i] Ethylbenzene. [j] 2-Methoxyphenol.

standard. In addition, we made no attempt to quantify benzene, since it was present in the solvent, THF. Several interesting results were observed and include the fact that with the aromatic esters, no carboxylic acids (treatment of the reaction mixture with diazomethane provided no evidence for methyl esters) or aldehydes (GC-MS) were detected in these reductive cleavage reactions. There are two possible reasons that carboxylic acids were not found—either initial cleavage occurred at the carbonyl–oxygen bond or decarboxylation occurred after carboxyl–carbon bond cleavage. This latter postulate was verified in a control experiment with benzoic acid, which clearly showed that it was decarboxylated under our standard reductive cleavage conditions to produce benzene. Thus, decarboxylation or decarbonylation can conceivably occur under our reaction conditions with these aromatic esters. We also found that if methoxybenzene was formed in the reductive cleavage of methoxyl-substituted aromatic esters or ethers, it reacted further ($k_{rel} = 0.88$) to produce phenol.[1,6,13]

The products of the aromatic ester cleavage reactions of **8** and **10–15**, were phenol, substituted phenols, and benzene, while ester **9** provided benzyl alcohol and benzene. The aromatic ethers **2** and **3** clearly show benzyl–oxygen bond cleavage, while substituted ethers **4–6** showed different regioselectivities depending on whether the groups were ortho or para to the ether functionality. Both **4** and **5** underwent C–O bond cleavage to give hydroquinone and *p*-methoxyphenol, respectively. However, **5** also produced the C–O bond-cleavage product phenol, presumably from methoxybenzene. The ratio of 4-methoxyphenol/phenol was ~3.4:1 and shows a preference for the substituted phenol. Alternatively, **6** provided phenol from methoxybenzene and no guaiacol, 2-methoxyphenol, was detected, which is a dramatically different regioselective C–O bond-cleavage result for 2-methoxyl versus 4-methoxyl substituents.

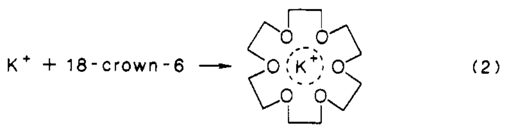
The aromatic esters **10–12** all gave phenol and benzene as products, which does not allow an unequivocal assignment of the regiochemistry. Moreover, as stated above, benzoic acid was decarboxylated and methoxybenzene demethylated, under our reductive cleavage conditions. However, by analogy to ester **8**, which showed only carbonyl–oxygen bond cleavage, we speculate that esters **10–12** predominantly undergo carbonyl–oxygen bond cleavage to give the aracyl radical and the phenoxide ion. The regiochemistry results for esters **13–15** are unequivocal and clearly show only carbonyl–oxygen bond cleavage. The only benzyl ester studied, **9**, provided a similar regiochemistry, i.e., carbonyl–oxygen bond cleavage, while no benzyl–oxygen bond cleavage was observed.

Deuterium Incorporation Studies To Differentiate One- and Two-Electron-Transfer Mechanisms Using Aromatic Ester 13. In some recent studies on the chemical and electrochemical generation of radical anions of aromatic ethers, Woolsey and Bartak and their coworkers[8,9] demonstrated the use of deuterium incorporation as a method to differentiate between one-electron (radical anion) and two-electron (dianion) mechanisms. We thought a similar study could be beneficial in determining whether benzene radicals or anions were present in our reductive cleavage of aromatic esters. We used compound **13** as our model, since it would provide the 2-methoxyphenoxide ion and the phenacyl radical. The phenacyl radical could lose carbon monoxide to give the phenyl radical, which can abstract hydrogen from THF or undergo further electron transfer to give the phenyl anion. The phenyl anion, if present, is long lived compared to the radical and would abstract deuterium upon workup with acetic acid-d_4. The results (GC-MS) clearly showed that no deuterium was incorporated into the benzene formed and strongly suggest that radical anions, not the dianions, are predominantly formed with aromatic esters, as was shown for aromatic ethers[6–9] under electron-transfer reaction conditions.

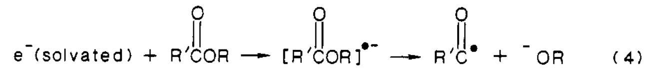
Discussion

Mechanistic Aspects Involved in the Carbon–Oxygen Bond Cleavage of Aromatic Ethers and Esters. The mechanism that is involved in the reductive cleavage of C–O bonds of aromatic esters and ethers using K metal/18-crown-6/THF is as follows (eq 1–5). Previous studies by Woolsey and Bartak[6–9] showed the intermediacy of the radical anion rather than the dianion for the reductive cleavage of aromatic ethers using chemical and electrochemical techniques. The present results also appear to indicate that a similar intermediate, the radical anion, is operative for both aromatic ester and ether C–O bond-cleavage reactions with K metal/18-crown-6/THF at 0 °C.

$$2K^0 \rightleftharpoons K^- + K^+ \tag{1}$$



$$K^- \longrightarrow K^0 + e^-(\text{solvated}) \tag{3}$$



$$e^-(\text{solvated}) + R'\overset{O}{\overset{\|}{C}}OR \rightarrow [R'\overset{O}{\overset{\|}{C}}OR]^{\bullet-} \rightarrow R'\overset{O}{\overset{\|}{C}}{}^{\bullet} + {}^-OR \tag{4}$$

$$e^-(\text{solvated}) + R'OR \rightarrow [R'OR]^{\bullet-} \rightarrow R'O^- + R^\bullet \text{ or } R'^\bullet + RO^- \tag{5}$$

The important implication of substituent effects on the product distribution in the reductive cleavage reactions of aromatic ethers was shown about 50 years ago by Sowa and his co-workers.[11] They studied the reactions of compounds **5** and **6**, among other aromatic ethers, with Na/liquid NH_3 and determined the regioselectivity for the cleavage of unsymmetrical aromatic ethers. They determined 4-methoxy; 2-, 3-, and 4-methyl; and 2-, 3-, and 4-amino substituted phenols as the major C–O bond-cleavage product, while 2-methoxyphenyl phenyl ether provided a slight preference for phenol by a factor of 1.2 (4-methoxy factor for 4-methoxyphenol to phenol was 4). The present results with ethers **5** and **6** (K/18-crown-6/THF, 0 °C) showed a 100% regioselectivity for **6** with C–O bond cleavage providing phenol and methoxybenzene, while no 2-methoxyphenol was detected. Compound **5** showed a high regioselectivity for C–O bond cleavage at the oxygen–phenyl bond to give 4-methoxyphenol as well as phenol (cleavage of the oxygen-4-methoxyphenyl bond) in a ratio of ~3.4:1. Apparently, the regioselectivity for C–O bond cleavage for the substituted aromatic esters studied **10–15** was not affected by substituents in either the benzoic acid or phenol portion, since they all showed carbonyl–oxygen bond cleavage.

The regioselectivity for the benzyl ethers **2** and **3** was different than the only benzyl ester studied, **9**. Both **2** and **3** provided C–O cleavage at the benzyl–oxygen bond, while **9** gave carbonyl–oxygen bond cleavage as did all the aromatic esters.

The substituent effects on the relative rates of C–O bond cleavage for both the aromatic ester and ether series were also quite different. The substituted aromatic esters **10–15** were faster than the standard **1**, while the substituted ether **5** was slightly faster than **1** by a factor of 1.2, and compound **6** had approximately the same relative rate compared to **1**. Compound **4**, or more probable the oxyanion of **4**, was extremely slow compared to **1** by a factor of >10.

The substituent effect results strongly suggested that polar effects in the transition state for C–O bond cleavage were important in both the aromatic ester and ether series. This was also verified by the studies of Maslak and Guthrie[15,16] on the C–O bond cleavage of radical anions from 4-nitrobenzyl phenyl ether and 4-nitrophenyl benzyl ether. The added electron will affect the polarization of the C–O σ bond to be cleaved to provide the oxyanion and a carbon radical. Thus, the theory of regioconservation of spin density espoused by Maslak and Guthrie[15,16] may be important in the cleavage of substituted aromatic ester radical anions, which appear to give an oxyanion and an aracyl radical. The substituents such as methoxy and hydroxyl in the benzoic acid portion of the aromatic esters **10–12** stabilize the polarization of the aracyl–oxygen bond of the radical anion. $^{-\bullet}\mathrm{ArC}(=\mathrm{O})(+)(-)\mathrm{OAr}$, in the transition state by an electronic effect, providing a kinetic acceleration in the C–O bond-cleavage reaction. Interestingly, while electron transfer to preserve spin density appears to occur in the benzoic acid portion of esters **13–15**, the relative rates of cleavage of **13** and **14** are still very fast, while the relative rate for **15** is somewhat slower. This above-mentioned similar argument also pertains to the benzyl ester **9**, which shows carbonyl–oxygen bond cleavage rather than the benzyl–oxygen bond under our reductive cleavage conditions.[17]

Another important thermodynamic factor pertains to a lowering of the reduction potential of the aromatic esters by these groups via a lowering of the energy of the lowest unoccupied molecular orbital (LUMO) to provide a more stable transition state on the energy profile. The aromatic ethers **5** and **6** clearly show a dramatic difference between 2- and 4-methoxyl substituents for regiochemistry but only show a difference in the relative rate factor of 1.2. The reduction potentials for aromatic ethers are slightly higher than those for the aromatic esters,[6,17] but electron-donating substituents will further raise the reduction potentials of aromatic ethers, making electron transfer more difficult thermodynamically.[6] Hence, the overall kinetic effect is to dramatically slow the C–O bond-cleavage reaction of the oxyanion of **4** under electron-transfer conditions. This substituent (O^-) possibly raises the energy of the LUMO and has a profound effect on the polarization of the C–O σ bond in the transition state, i.e., $^{-\bullet}\mathrm{Ar}(+)(-)\mathrm{OArO}-$, that would retard C–O bond cleavage. Thus, we can only speculate on the reasons for the differences in regiochemistry for **5** and **6**, and these reasons are concerned with the electron transfer to the aromatic ring that places high electron density on the carbon σ orbital ($\pi_1 \rightarrow \sigma^*$). In compound **5**, the electron is transferred to the unsubstituted aromatic ring possibly due to the 4-methoxy substituent raising the energy of the LUMO of the 4-methoxybenzene ring. In accordance with the theory of regioconservation of spin density, C–O bond cleavage in **5** provides the phenyl radical and 4-methoxyphenoxide anion. Alternatively, electron transfer to the benzene ring containing the 2-methoxyl substituent is favorable due to an ortho effect of oxygen that lowers the energy of the LUMO and provides an energetically more important transition state where the 2-methoxy group can stabilize the polarization of charge, i.e., $\mathrm{ArO}(-)(+)\mathrm{ArOCH_3}^{\bullet-}$. This then leads to C–O bond cleavage to provide the 2-methoxybenzene radical and the phenoxide ion.

Conclusions

Two important model coal linkages, those of aromatic esters and ethers, were studied under electron-transfer reaction conditions with K metal/18-crown-6/THF at 0 °C. The relative rate studies showed the following order: **10–14 >>>> 15 > 9 > 5, 8, 1, 6, 3 > 7 >>> 4**. The aromatic esters with electron-donating groups were extremely reactive and clearly showed that polar effects made important contributions to the transition state in these radical anion carbonyl–oxygen bond-cleavage reactions. The aromatic ethers studied did not show any pronounced rate enhancement, except compound **4**, which showed a marked decrease in its relative rate due to the formation of an oxyanion (*p*-hydroxy substituent).

The regioselectivity for C–O bond cleavage for the aromatic esters series was at the carbonyl–oxygen bond, while the aromatic ether series showed benzyl–oxygen bond cleavage and a dramatic difference between ortho and para methoxyl substituents that could be tentatively explained by the position of the LUMO and polar effects in the transition state. These radical anion reactions also appear to follow the theorem of regioconservation of spin density.

Finally, we feel that coal model compound studies are extremely important to pursue and can provide fundamental information that can be applied to the more complex situation of determining which coal linkages will be cleaved in the depolymerization of coal under electron-transfer conditions.

Experimental Section

Materials and Instrumentation. The solvent, tetrahydrofuran (THF), was distilled from sodium benzophenone ketal under nitrogen just prior to use. Potassium metal was purchased from Alfa Chemical Co. Compounds **1**, **2**, **4**, **8**, **9**, **10**, and 18-crown-6 were purchased from Aldrich Chemical Co. and their purity was checked by capillary GC analysis. The following compounds were synthesized by using procedures described in the literature: **3**,[21] **5**,[22] **6**,[22] **7**,[21] **11**,[23] **12**,[23] **13**,[23] **14**,[23] and **15**[24] and their composition was verified by GC-MS analysis. The capillary GC analyses were performed on an HP 5880A GC with a 15 m × 0.35 mm DB-5 (J&W) capillary column and a flame ionization detector (con-

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ditions: 35–260 °C at 3°/min). The GC-MS experiments were performed on a Finnigan 4023 quadrupole instrument with a 30 m by 0.3 mm DB-5 (J&W) capillary column. Reconstructed ion chromatograms were accomplished with the INCOS data system.

Relative Rate Procedure for Compounds 1–17 with K/18-Crown-6/THF as the Electron-Transfer Reagent. The relative rates for compounds **2–17** were obtained in competitive reactions with compound 1, diphenyl ether, which was assigned a relative rate of 1.0. The following procedure was used for all the relative rates shown in Table I: to a 50-mL Schlenk flask were added 0.07 g (1.79 mmol) of potassium metal, 0.43 g (1.79 mmol) 18-crown-6, and 10 mL of dry, degassed THF along with a stirring bar and a septum for substrate addition. These transformations were carried out in a single-stage Vacuum Atmospheres glovebox under argon and provided a deep blue solution of solvated electrons. In another Schlenk flask were added 28 μL (0.18 mmol) of diphenyl ether (**1**) and an equimolar amount of compounds **2–17** in 10 mL of THF along with 40 μL of undecane as an internal standard for GC analysis [experiments with added *tert*-butyl alcohol (0.36 mmol) or hydroquinone (0.36 mmol) were done with compounds **1** and **3**]. After this mixture was degassed, it was cannulated under argon into the blue THF solution of K/18-crown-6 at 0 °C. This caused the blue color to dissipate to provide, depending upon the substrate, a yellow-red clear solution. At intervals of ~1–5 min, 0.5-mL aliquots were removed via a syringe and quenched with a drop of glacial acetic acid (neutral to pH paper) prior to GC analysis. A control experiment with esters **8–15** showed no hydrolysis products during the glacial acetic acid workup. The products were identified by comparison to known standards and confirmed by GC-MS analysis. The quantitation was obtained with standard solutions, response factors, and concentration/area plots using the HP data station for digital integration of peaks. We also ran individual reductive cleavage reactions for **2–17** under similar conditions to insure product identification by standards, response factors, and GC-MS analysis.

The relative rates ($k_{\rm rel} = k_{\rm unk}/k_{\rm compd1}$) were calculated by using percent conversion of substrate vs time plots and a similar plot for 1 and obtaining the slope of these linear plots by a least-squares regression analysis. The slopes of substrates **2–17** were simply divided by that of **1** to obtain the relative rate. Aromatic esters **10–14** were too fast to measure accurately by our GC method, since they totally reacted upon mixing at 0 °C, and we defined these relative rates as being >2.0. The esters **8** and **9** and the ethers **1–3** and **5–7** had conversions in the range of 70–100% after 20 min, while ether **4** was ~5% converted after 20 min.

Deuterium Incorporation Experiments with Compound 13. In a similar reaction procedure to what was mentioned above, we reacted **13** with K metal/18-crown-6 in THF at 0 °C. The reaction mixture was quenched with glacial acetic acid-d_4 and was analyzed by GC-MS to clearly show no significant deuterium incorporation in the benzene present ($C_6H_6/C_6H_5D = 17$). The ratio of acetic acid-d_4/acetic acid-d_3 was found to be >2. The only other product, 2-methoxyphenol, was also verified by GC-MS. This signifies that benzene radicals are formed rather than phenyl anions and that radical anions are the important intermediates.

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Registry No. 1, 101-84-8; 2, 103-50-4; 3, 946-80-5; 4, 831-82-3; 5, 1655-69-2; 6, 1695-04-1; 7, 40515-89-7; 8, 93-99-2; 9, 120-51-4; 10, 118-55-8; 11, 65853-67-0; 12, 4181-97-9; 13, 531-37-3; 14, 1523-19-9; 15, 2444-19-1.

Electrochemical Reduction of Vicinal Dinitro Compounds[1]

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Six vicinal dinitro compounds and 1,1-dinitrocyclohexane have been studied by cyclic voltammetry, chronoamperometry, and controlled potential coulometry. For dinitro compounds **1–3**, the electrochemical reduction at mercury electrodes in DMF was shown to proceed by an ECE scheme comprising initial reduction to a radical anion, which expels nitrite, forming a β-nitroalkyl radical that is more easily reduced than the original dinitro compound. The rate constants for expulsion of nitrite from the anion radical were determined at 0 °C. Compounds **4** and **5** behaved similarly to **1–3** though additional reactions occur. The radical anion of *trans*-1,2-dinitrocyclopropane, **6**, reacts quickly and could not be detected. 1,1-Dinitrocyclohexane is reduced in an initial two-electron step forming nitrite and the anion of nitrocyclohexane. The latter reacts rapidly with starting material to form 1,1′-dinitrobicyclohexyl, **2**, which was detected by voltammetry.

The importance of electron transfer in a variety of organic reactions is now widely recognized. Of particular interest is the $S_{RN}1$ mechanism[2-17] depicted in eq 1–4, where group L is replaced by nucleophile Nu^-. A number of substitutions at both aromatic and aliphatic centers have been shown to occur via the $S_{RN}1$ mechanism. These reactions normally proceed under mild conditions, good

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