Acknowledgment. We are grateful to the National Science Foundation for support of this work.

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(13) A difference in kinetic and product isotope effects is well recognized as unambiguous evidence for a reaction intermediate. This mechanistic test has been developed and nicely used by Stephenson and co-workers to establish the presence of a reaction intermediate in the reaction of singlet oxygen with olefins, a process which is also a formal ene reaction. L. M. Stephenson, D. E. McClure, and P. K. Sysak, *J. Am. Chem. Soc.*, **95**, 7888 (1973); D. J. Crieghton, J. Hajdu, and D. S. Sigman, *ibid.*, **98**, 4619 (1976); A. A. Frimer, P. D. Bartlett, A. F. Boschung, and J. G. Jewett, *ibid.*, **99**, 7977 (1977); S. B. Grinda, M. Orfanopoulos, and L. M. Stephenson, *ibid.*, **101**, 3111 (1979), and references cited therein.

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(17) Melting points were determined in open capillaries and are uncorrected. Boiling points, taken from distillations, are likewise uncorrected. Infrared (IR) spectra were calibrated with a polystyrene standard. Chemical shifts of magnetic resonance spectra are reported in δ (ppm) relative to an internal tetramethylsilane standard. Mass spectral (MS) data were obtained by C. Cook and associates using a Varian MAT CH-5, gas chromatography MAT 112 spectrometer (GC/MS), and high-resolution (HRMS) and field ionization mass spectral (FIMS) data were obtained with a Varian MAT 731 spectrometer.

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Mechanism of Anodic Cleavage of Benzyl Ethers

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Abstract: Kinetic isotope effects and substituent effects are utilized to elucidate the mechanism of the anodic oxidation of benzyl ethers at platinum in acetonitrile. All of the data, including some previously published results, are consistent with a mechanism involving phenylalkoxy carbonium ions. Much of the data is incompatible with a previous mechanistic proposal involving initial oxidative cleavage of the benzylic carbon-oxygen bond.

In 1972 Mayeda, Miller, and Wolf (MMW) published a study of the electrochemical oxidation of several benzyl ethers.[1] The reaction products were of primary interest, but a mechanism was also proposed, based upon several pertinent observations and literature analogies. In 1977 Lines and Utley (LU) studied the oxidation of dibenzyl ether, using similar conditions, and proposed an alternative mechanism.[2] It is the objective of the present work to resolve the mechanistic question raised by these papers.

Because the MMW and LU studies involved similar conditions, but produced some dissimilar results and quite different mechanistic conclusions, it is important to review these papers. Other studies of anodic benzyl ether oxidations have been reported, but these contain little mechanistic information and the results of interest are cited later. In the MMW study, preparative electrolyses employed a platinum foil anode, divided cell, acetonitrile solvent, Ag/0.1 M $AgNO_3$ reference electrode, and potentiostatic conditions. The electrolyte was 0.1 M lithium perchlorate and sodium carbonate was generally added to the anolyte. Oxidations were carried nearly to completion and the products were isolated and quantitated.[3] Two representative and apposite samples are

$$\underset{\mathbf{1}}{PhCH_2OR} \xrightarrow{-1.9\ \text{faradays mol}^{-1}} \underset{\mathbf{2}\ (50\%)}{PhCHO} + \underset{(60\%)}{ROH}$$

$$R = \text{2-octyl}$$

$$\underset{\mathbf{3}}{PhCH_2OCH_2Ph} \xrightarrow{-4.2\ \text{faradays mol}^{-1}} \underset{(46\%)}{\mathbf{2}} + \underset{(33\%)}{PhCO_2H}$$

This study also established that benzyl alcohol oxidized to benzaldehyde at the potential used for preparative oxidations of benzyl ethers, but that aliphatic alcohols were stable. Because this potential, 1.9 V, corresponded to the potential for oxidation of toluene it was proposed that the initial step in the

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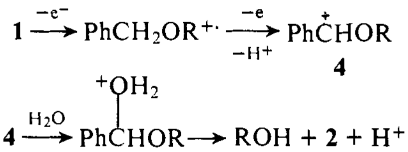
mechanism is loss of an electron from a π orbital of the benzyl group. MMW argued, using data from photoelectron spectroscopy and electrochemistry, that the nonbonding electrons on oxygen could only be lost at higher potentials.

Initial electron loss produces a cation radical and based on analogies with the oxidation of alkyl aromatics the next two steps were proposed to be loss of a proton to some base and loss of a second electron. The sequence of these two events and the identity of the base are unknown.



$$1 \xrightarrow{-e^-} PhCH_2OR^{+\cdot} \xrightarrow[-H^+]{-e} \underset{4}{Ph\overset{+}{C}HOR}$$

$$4 \xrightarrow{H_2O} Ph\overset{^+OH_2}{\overset{|}{C}}HOR \rightarrow ROH + 2 + H^+$$

The resulting phenylalkoxy carbonium ion (**4**) was proposed to hydrolyze as shown. The relevant results were that an oxidation of *l*-2-octyl benzyl ether gave octanol with retention of configuration and oxidation of diphenylmethyl dodecyl ether in acetonitrile containing 0.5% water, which was ^{18}O enriched, showed incorporation of the ^{18}O into the product, benzophenone, but not the dodecanol. These results were consistent with the literature[4] on the mechanism of hydrolysis of benzaldehyde acetals.

This MMW mechanism applied to **1** predicts consumption of 2 faradays (F) mol^{-1} and produces 2 mol of acid. It was shown that during the oxidation of **3** the benzyl alcohol was converted to **2**. Therefore, $n = 4$ was predicted for this case. These predictions approximately agreed with the experimental results. It may be noted that the water necessary for the hydrolysis steps is either added or adventitiously present in the solvent and especially the electrolyte, $LiClO_4$.[5] The water content of the anolyte was not reported, but can be estimated to be greater than 0.05 M. Of course, in these experiments the Na_2CO_3 will tend to buffer the anolyte and provide a further source of oxygen nucleophiles. In the absence of sodium carbonate, using dried acetonitrile, the major products from **3** were **2** and benzylacetamide (**5**).

LU studied only dibenzyl ether oxidation in acetonitrile, but used a variety of electrolytes. All reactions were again performed potentiostatically at a platinum anode. The products were generally not isolated, but were analyzed by direct injection of the anolyte into a gas-liquid chromatograph (GLC). The one experiment closest to the MMW conditions employed 0.5 M sodium perchlorate and added sodium carbonate. After passage of 1.0 F mol^{-1} at 2.0 V vs. $Ag/AgClO_4$ (0.1 M), 90% of the reactant **3** had disappeared, producing PhCHO (~30%), *N*-benzylacetamide (**5**, 10%), and a small amount of benzyl alcohol (**6**).[7] No benzoic acid was found.

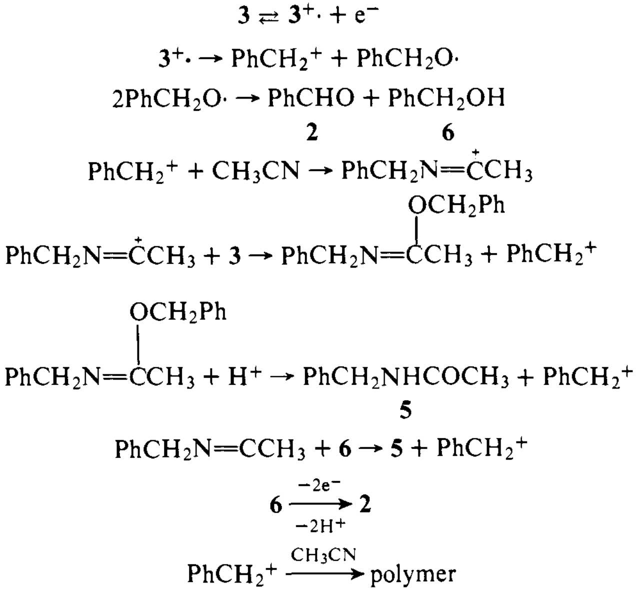
Most of the LU experiments utilized dried acetonitrile without added sodium carbonate. In these cases the major products after passage of 1 F mol^{-1} were **2** and **5**. The molar yields of each of these products were typically 50%. Since there are 2 mol of benzylic products possible from 1 mol of **3**, this indicates that ca. 50% of the product was uncharacterized.[7] If electrolysis was continued beyond 1 F mol^{-1}, the yields of **2** and **5** declined. The formation of **5** had been reported previously by MMW when dried acetonitrile without added sodium carbonate was used. LU emphasized one major discrepancy in the MMW and LU results for **3**. That is the coulometry as determined by exhaustive electrolysis. LU found 1 F mol^{-1}; MMW found 4 F mol^{-1}.

LU also performed cyclic voltammetric studies to probe the coulometry/mechanism problem. Using comparisons of the peak current (i_p) for **3** and ferrocene at a sweep rate, $\nu = 0.3$ V s^{-1}, an $n = 2.4$ was estimated. From a study of the dependence of the peak current, i_p, on the sweep rate, ν, it was concluded that the data were consistent with the ECE process (where E = electron transfer and C = chemical reaction). These results will be discussed in more detail (vide infra).

Product stability studies of both MMW and LU agree in the conclusion that amide **5** and alcohol **6** can be oxidized at the potential used to oxidize **3**. Furthermore, although **3** is stable in the anolyte, MMW[1] showed that in their acidic anolytes **6** was converted to **5** if no sodium carbonate was present.

The data collected by LU were interpreted by them in terms of a mechanistic scheme which is described here in Scheme I. They cite two salient features of this mechanism to be (1) the ether is anodically cleaved in a one-electron process; (2) benzaldehyde is a disproportionation product. Thus, it was proposed that an initially formed cation radical ($3^{+\cdot}$) decomposes by carbon-oxygen bond cleavage yielding a benzyl cation and a benzyloxy radical. Two benzyloxy radicals then disproportionate to give benzaldehyde and benzyl alcohol. The benzyl alcohol **6** is consumed by oxidation to benzaldehyde or by the further chemical reaction shown. The benzyl cations are proposed to react with acetonitrile in a conventional fashion forming $PhCH_2N{=}C^+CH_3$ which in turn leads to a "polymer" or reacts with **3** or **6** to eventually form benzylacetamide. The latter two reactions were unprecedented, but were useful to explain isotopic labeling results in which ^{18}O dibenzyl ether gave ^{18}O-labeled **2** and **5**.

Scheme I



$$3 \rightleftarrows 3^{+\cdot} + e^-$$

$$3^{+\cdot} \rightarrow PhCH_2^+ + PhCH_2O\cdot$$

$$2PhCH_2O\cdot \rightarrow \underset{2}{PhCHO} + \underset{6}{PhCH_2OH}$$

$$PhCH_2^+ + CH_3CN \rightarrow PhCH_2N{=}\overset{+}{C}CH_3$$

$$PhCH_2N{=}\overset{+}{C}CH_3 + 3 \rightarrow PhCH_2N{=}\overset{OCH_2Ph}{\overset{|}{C}}CH_3 + PhCH_2^+$$

$$PhCH_2N{=}\overset{OCH_2Ph}{\overset{|}{C}}CH_3 + H^+ \rightarrow \underset{5}{PhCH_2NHCOCH_3} + PhCH_2^+$$

$$PhCH_2N{=}CCH_3 + 6 \rightarrow 5 + PhCH_2^+$$

$$6 \xrightarrow[-2H^+]{-2e^-} 2$$

$$PhCH_2^+ \xrightarrow{CH_3CN} polymer$$

In retrospect it can be seen from Scheme I that the *nonelectrochemical* reaction of **3** with $PhCH_2N^+CCH_3$ tends to reduce the apparent *n* value for preparative runs. Indeed, since this reaction generates two new benzyl cations, it is catalytic, could give very low apparent *n* values, and could explain the discrepancy between CV and preparative *n* values. Although the coulometry did not require a new mechanism for cleaving $3^{+\cdot}$ and the ^{18}O results were not pertinent to this part of the reaction, LU also proposed a fundamentally different mechanism for the electrochemical reaction of **3** involving cleavage of the carbon-oxygen bond of $3^{+\cdot}$, rather than formation of **4** (R = $PhCH_2$), by carbon-hydrogen bond breaking. It must be emphasized that the intermediacy of **4** is not inconsistent with their results. Indeed, LU did not attempt to rule out **4** as an intermediate. We wished to provide a definitive differentiation between the LU and MMW proposals for the reaction of $3^{+\cdot}$ and since LU did not offer any rationale for the difference in their experimental results and those of MMW we were also compelled to resolve that discrepancy.

Results and Discussion

Resolution of Experimental Discrepancies. A careful perusal of the published work demonstrated a number of differences in the experimental conditions employed. MMW used a 2-in.^{2} electrode, 0.01-0.05 M solutions of **3**, and wet electrolyte and isolated products by column chromatography. LU employed a 2-cm^2 electrode, 0.2 M solutions of **3**, and dried acetonitrile and analyzed the products by GLC. We have performed oxidations under a variety of conditions. These studies demonstrate that the previous work of both groups is correct and reveal the cause of the differences. Three representative and illustrative experiments are described.

Under the MMW conditions (0.1 M $LiClO_4$, 0.01 M **3**, anolyte 0.1 M in H_2O) oxidation at 1.9 V vs. Ag/$AgNO_3$ was essentially complete after passage of 4 F mol^{-1}. Workup by extraction with water and ether followed by GLC analysis gave a 88% yield of benzaldehyde, i.e., 7.4 mmol of **2** from 4.2 mmol of **3**. At intermediate stages small amounts of **6** and benzyl benzoate were detected, but no **5** or benzoic acid was present. This result corresponds well, with the exception of the benzoic acid, with the MMW report. MMW isolated benzoic acid after column chromatography. We have now found that considerable conversion of benzaldehyde to benzoic acid occurs during this chromatographic separation.

In order to further check the coulometry problem, samples were withdrawn, as done by LU, and directly analyzed by GLC. After passage of 3 F mol^{-1} current was still passed, but >90% of **3** had apparently reacted. It was, however, observed that the yields of recovered **3** calculated by direct GLC injection or by workup and GLC analysis did not correspond well, direct injection giving smaller apparent yields. Therefore, we have also used a "modified direct injection" where pyridine was added to withdrawn samples before GLC analysis. This, indeed, makes a difference giving higher apparent amounts of **3**. Using this method *n* is calculated to be ca. 4.

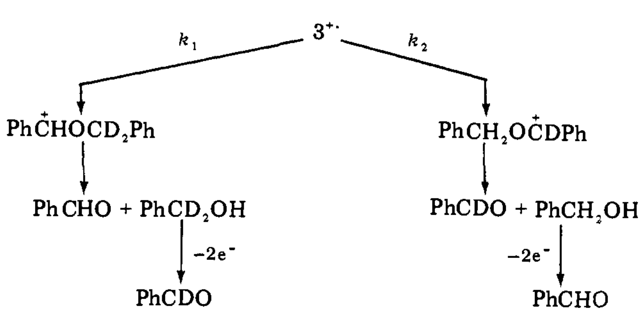
An oxidation was also performed using the same electrode and the same concentration of **3**, but with dried 0.1 M $NaClO_4$ and carefully dried acetonitrile (2 mM H_2O). The anolyte was assayed to be 9 mM in water. Essentially all **3** was consumed and the current had dropped to background after passage of 2 F mol^{-1}. Direct GLC analysis showed that 2.07 mmol of **3** produced 2.06 mmol of **2** and 1.87 mmol of benzylacetamide (**5**). Thus, as suggested by MMW, drier solvent gives **5** instead of alcohol. **5** is only slowly consumed and is found as a major product. Alcohol **6** is rapidly oxidized and its formation and further oxidation account for the doubled *n* value and doubled benzaldehyde yield under the wet MMW conditions.

Using the same electrode, 0.1 M $NaClO_4$, dry (2 mM H_2O) acetonitrile, but with 0.2 M **3** (defined here as "LU conditions") the LU results were reproduced. Thus, the yields of **2** and **5** dropped and $n = 1$ when all of **3** was consumed. This experiment demonstrates that the higher concentrations used by LU account for the low coulometry and low yields. It seems likely that a competing nonelectrochemical consumption of **3** lowers the apparent *n* value. The data clearly suggest that under all conditions the electrochemical conversion of **3** to **2** plus **5** is an $n = 2$ reaction, not $n = 1$.

Improbability of C-O Cleavage in $3^{+\cdot}$. LU propose that $3^{+\cdot}$ cleaves unimolecularly to form benzyl cation and benzyloxy radical. This type of reaction is known in the gas phase. By comparing the ionization potential of benzyl methyl ether (8.8 eV)[8] and the appearance potential of $C_7H_7^+$ from benzyl methyl ether (11.8 eV)[8] the activation energy for cleavage can be estimated as 3 eV. This should also represent a good estimate for the minimum activation energy for the C-O cleavage reaction of other benzyl alkyl ethers including dibenzyl ether. Because of solvation, 3 eV cannot be considered an accurate estimate for the activation energy of the solution-phase reaction. Note, however, that $3^{+\cdot}$ and $PhCH_2^+$ have the same charge and that this charge is delocalized over one benzene ring. This suggests that the cleavage rate will not be dramatically affected by solvation and that $3^{+\cdot}$ in solution at room temperature should cleave with a half-life of many hours or days. Since CV at high sweep rates shows no evidence of $3^{+\cdot}$, its lifetime is actually less than 10^{-2} s at room temperature. The discrepancy between the calculated and observed values is obvious.

It may be noted that no pertinent gas-phase data exist for evaluation of the MMW mechanism. The mechanism is, however, fully consistent with electrochemical mechanisms demonstrated for alkylbenzene and benzyl alcohol oxidations.[9]

Isotope Effects on Oxidation of 3. In order to gain definitive experimental evidence about the oxidative mechanism for **3** we have synthesized and oxidized α,α-dideuteriodibenzyl ether and measured the deuterium content of the products. Consider first the result expected from the MMW mechanism. As shown in the following scheme this mechanism will involve a competitive deprotonation (k_1) and dedeuteration (k_2), and there should be a kinetic isotope effect favoring the former. This can be experimentally observed by measuring the isotope composition of the product benzaldehyde, **2**, or the benzyl alcohol, **6**. It can also be seen from the scheme that the isotope effect on k_1, k_2 could be obscured by the further oxidation of **6** to **2**. Thus, at high conversion one might expect to see only **2** and the PhCHO/PhCDO ratio would be 1.0. By examining the product **6** this problem can be avoided. As a control experiment, we have prepared authentic $PhCD_2OH$ and have oxidized a 1:1 mixture of $PhCH_2OH$ and $PhCD_2OH$ under MMW conditions to an extent of 1 F mol^{-1}. The unoxidized alcohols were then recovered and mass spectrometry demonstrated, not unexpectedly, that $PhCH_2OH/PhCD_2OH = 1.0$. Thus, alcohol oxidation does not change the isotopic composition and the observed $PhCD_2OH/PhCH_2OH$ ratio should be a direct measure of k_1/k_2.



Turning now to the LU mechanism for reaction of $3^{+\cdot}$ and ignoring secondary isotope effects it is predicted that the cation radical will fragment randomly producing equal amounts of $PhCH_2\dot{O}$ and $PhCD_2\dot{O}$. Since OD alcohols become OH alcohols upon aqueous workup, the $PhCD_2OH/PhCH_2OH$ ratio will be determined by the rates of reactions designated by k_5–k_8.

$$3^{+\cdot} \xrightarrow{k_3} PhCH_2^+ + PhCD_2O\cdot$$

$$3^{+\cdot} \xrightarrow{k_4} PhCD_2^+ + PhCH_2O\cdot$$

$$2PhCH_2O\cdot \xrightarrow{k_5} PhCHO + PhCH_2OH$$

$$2PhCD_2O\cdot \xrightarrow{k_6} PhCDO + PhCD_2OD$$

$$PhCH_2O\cdot + PhCD_2O\cdot \xrightarrow{k_7} PhCHO + PhCD_2OH$$

$$PhCH_2O\cdot + PhCD_2O\cdot \xrightarrow{k_8} PhCDO + PhCH_2OD$$

$$\frac{PhCH_2OH}{PhCD_2OH} = \frac{k_5[PhCH_2O\cdot]^2 + k_8[PhCH_2O\cdot][PhCD_2O\cdot]}{k_6[PhCD_2O\cdot]^2 + k_7[PhCH_2O\cdot][PhCD_2O\cdot]} \qquad (I)$$

This rate equation can be reduced to one involving only rate constants k_5, k_6, k_7, and k_8. As can be seen from the four transition states shown in Figure 1, reactions 5 and 7 are protium transfers and in the absence of secondary isotope effects $k_5 = k_7$. Likewise $k_8 = k_6$. This model, therefore, predicts $PhCD_2OH/PhCH_2OH = 1.0$.

Using MMW-type conditions (0.1 M $LiClO_4$) the benzyl alcohol **6** was produced by oxidation of α,α-dideuteriodibenzyl ether and isolated. Analyzed by mass spectroscopy it proved to be 65% $PhCD_2OH$ and 35% $PhCH_2OH$. PhCHDOH was absent. This ratio gives $k_H/k_D = 1.9 \pm 0.2$. There is considerable error in the isotope effect because it is very sensitive to the exact proportions determined by MS. There is no question, however, that a primary kinetic isotope effect is observed in agreement with the MMW mechanism and in disagreement with the LU proposal.

This conclusion must, however, be considered further in terms of possible secondary isotope effects. For the MMW mechanism there should be a secondary isotope effect due to the second proton or deuteron attached to the carbon reaction center. This secondary isotope effect will increase k_H/k_D by a factor of perhaps 1.1. This has no effect on the conclusion. The LU mechanism presents a more complex situation which can be treated as follows. It is predicted from theory and analogous experimental results that k_3/k_4 will be increased by a factor α due to the fact that formation of $PhCH_2^+$ is more favorable than that of $PhCD_2^+$. This ratio k_3/k_4 will, however, be decreased by a factor β, due to the fact that formation of $PhCH_2\dot{O}$ is more favorable than formation of $PhCD_2\dot{O}$. Thus, instead of assuming that $[PhCH_2\dot{O}] = [PhCD_2\dot{O}]$, consideration of secondary isotope effects gives $\beta[PhCH_2\dot{O}] = \alpha[PhCD_2\dot{O}]$. Using the transition states in Figure 1 it can be concluded that $k_5 = \gamma k_7$ and $k_8 = \gamma k_6$, where γ is the secondary isotope effect on disproportionation. Beginning again from eq I and using these definitions of α, β, and γ it can be shown that $PhCH_2OH/PhCD_2OH = \alpha\gamma/\beta$.

The magnitude of α can be estimated by literature analogy to be less than 1.25.[10,11] Secondary isotope effects analogous to β or γ for alkoxy radicals have to our knowledge not been measured. Useful data do exist for carbon-based radicals, i.e., from $PhCH(CD_3)N_2CH(CD_3)Ph$ decomposition, and from this we estimate that $\beta = \gamma = 1.04$.[11a] In any case, β and γ will be smaller than α and tend to cancel. The predicted isotope effect for the LU scheme is then less than 1.25, in disagreement with experiment.

A similar analysis for reactions under the LU conditions utilizes the isotopic composition of the benzylacetamide (**5**) derived from α,α-dideuteriodibenzyl ether. According to the LU mechanism the electrochemically generated **5** should be formed without isotopic discrimination from a primary isotope effect; the secondary isotope effect should be small and as above, i.e., $PhCH_2NHCOCH_3/PhCD_2NHCOCH_3 = 1.0$–$1.25$. The nonelectrochemical routes (Scheme I) to **5** also do not involve breakage of the benzylic C–H bond and likewise should show no primary isotope effect.

A MMW-type mechanism, i.e., via **4**, could be applied to LU conditions if allowance is made for the absence of oxygen nucleophiles other than reactant **3**. We have not attempted to produce any ^{18}O results and assume that some process for oxygen transfer from **3** to $PhCH_2NCCH_3^+$ like that proposed by LU (Scheme I) is involved. Consider the isotope result expected for any mechanism involving initial formation of **4** by loss of two electrons and one proton. In one such process benzyl cation could be lost from **4** in an S_N1 reaction. In another, acetonitrile would displace benzaldehyde from **4** in an S_N2 reaction. In either case the resulting nitrilium ion eventually produces **5**.

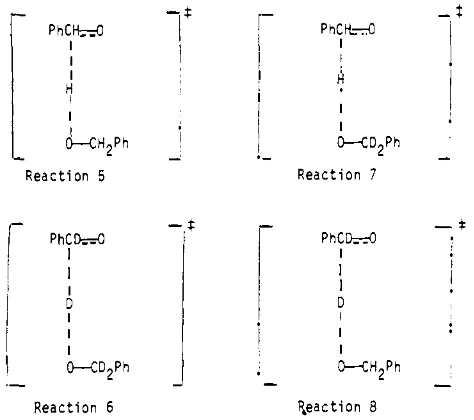


Figure 1.

$$3 \rightarrow 3^{+\cdot} \rightarrow 4$$

$$4 \rightarrow PhCH_2N{=}C^+CH_3 + PhCHO$$

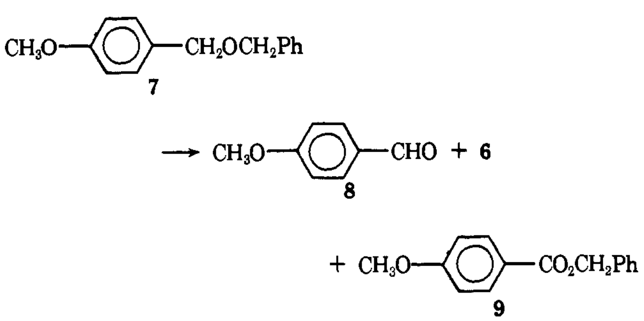
$$PhCH_2N{=}C^+CH_3 \rightarrow \rightarrow 5$$

It is predicted for these mechanisms involving **4** that formation of **5** from α,α-dideuteriodibenzyl ether will show a primary isotope effect. The magnitude of this effect should be similar to that found for formation of **6** under MMW conditions. A further prediction is that the same isotope effect should show up in the benzaldehyde, i.e., $PhCH_2NHCOCH_3/PhCD_2NHCOCH_3 = PhCDO/PhCHO$. All of this assumes that the nonelectrochemical reactions do not interfere.

The experimental results were obtained by oxidizing α,α-dideuteriodibenzyl ether under LU conditions to 1 F mol^{-1}. The benzaldehyde was isolated by collection from the GLC and **5** was isolated by column chromatography (see Experimental Section). MS analysis showed that $PhCD_2NHCOCH_3/PhCH_2NHCOCH_3 = 1.56$ and $PhCHO/PhCDO = 1.56$. These results are in agreement with the intermediacy of **4** under LU conditions. The small primary isotope effects deserve comment. Because the lifetime of $3^{+\cdot}$ is short, deprotonation must be fast. If it is also very exothermic, then a highly unsymmetrical transition state would be involved and a small isotope effect would be expected.

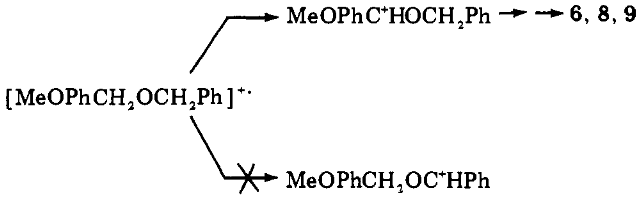
Oxidation of Unsymmetrical Benzyl Ethers. Consider the products from $PhCH_2OR$ oxidations where R is not benzyl. The products, 2-octanol, and **2**, from **1** isolated by MMW provide an example. These products were accommodated by the MMW mechanism. According to the LU scheme these products could arise by cleavage of an initial cation radical to produce a benzyloxy radical and a 2-octyl cation would then go on to 2-octanol and the benzyloxy radicals would produce **2** by disproportionation. This proposal cannot, however, account for the retention of configuration in the alcohol found by MMW, since 2-octyl cations should produce complete or extensive racemization. Alternatively, if the cation radical cleaves, it seems more likely that cleavage to a benzyl cation and an octyloxy radical would occur. If cleavage took place in this direction, however, the products are irrational. The octyloxy radicals should, for example, produce 2-octanone by disproportionation and this product is absent. A second MMW example is dodecyl diphenylmethyl ether, where cation radical cleavage would undoubtedly form diphenylmethyl cations and dodecyloxy radicals. The latter should, by the LU proposal, give dodecanal. This product is not formed.

It seems unreasonable to us to argue that dibenzyl ether has a mechanism different from other benzyl ethers, but to provide a more closely analogous example we have oxidized *p*-methoxydibenzyl ether (**7**). Triply distilled acetonitrile with



0.1 M $LiClO_4$ and a platinum anode were used. The anolyte, analyzed by GLC, was 0.15 M in water. After passage of 2 F mol^{-1} at 1.6 V the current had returned to the background level. The anolyte was then worked up and analyzed by GLC. The products (% yield) were: recovered **7** (5%), benzyl alcohol (65%), *p*-methoxybenzaldehyde (45%), and benzyl *p*-methoxybenzoate (26%). The current yields and material yields were identical, and the material balance was very good. No benzaldehyde or *p*-methoxybenzyl alcohol was formed.

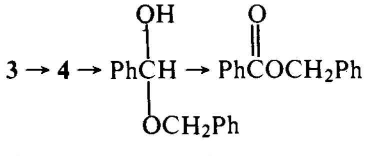
The cleanness of the experimental result is remarkable in this case. It comes in part from the fact that benzyl alcohol and *p*-methoxybenzaldehyde are electroinactive at this potential. All of the products from this reaction are fully consistent with the MMW mechanism since deprotonation to form the *p*-methoxybenzyl cation should be preferred.



The results are inconsistent with the LU mechanism since cleavage to produce the more stable *p*-methoxybenzyl cation and benzyloxy radical should be preferred in that mechanism. The benzyloxy radicals would give benzaldehyde, which was, however, absent.

Under the LU conditions all the *p*-methoxydibenzyl ether was consumed after passage of 0.25 F mol^{-1}. The electrode was then coated with a purple slime. Only traces of the expected products were present. Clearly the competing nonelectrochemical destruction of ether dominates this reaction.

It may be noted that both MMW and the present study found products like benzyl benzoate and benzyl *p*-methoxybenzoate (**8**). These products are quite consistent with the MMW mechanism, by oxidation of the intermediate hemiacetal. The LU mechanism does not easily lead to such byproducts.



$$3 \rightarrow 4 \rightarrow \underset{\displaystyle OCH_2Ph}{\overset{\displaystyle OH}{PhCH}} \rightarrow Ph\overset{\displaystyle O}{\overset{\|}{C}}OCH_2Ph$$

Consider further two specific experiments in which *p*-methoxybenzyl octyl ether was oxidized. The two reactions were run identically at 1.5 V to 2 F mol^{-1} using MMW conditions. In one experiment the anolyte was concentrated by evaporation, then taken up in water and ether, and the products were extracted. An 81% yield of octanol was determined and no octyl *p*-methoxybenzoate was present. Alternatively, the reaction was worked up by simply adding water to the anolyte and extracting with ether. In this case an 18% yield of ester and a 53% yield of octanol were formed. It seems clear that ester was formed, but that distilling the solvent from the acidic medium caused hydrolysis. This may, therefore, also be involved in the formation of high isolated alcohol yields by other workers.[2,12,13]

Evidence from Cyclic Voltammetry. As indicated in the introduction, LU presented CV data in support of their mechanism. From the dependence of the peak current (actually the current function, $i_pC^{-1}\nu^{-1/2}$, where C is [3] and ν is sweep rate) on ν it was concluded that the data were consistent with an ECE process. At $\nu = 0.8$ and 0.4 V s^{-1} the current function was the same. At lower ν (0.08–0.2 V s^{-1}) the current function increased. This behavior could, indeed, be consistent with an ECE process, but other data presented by LU are not consistent with this conclusion. The ECE interpretation of these data implies that one is observing the reversible one-electron E reaction at large ν and the two-electron ECE process during the longer times available at smaller ν.[14] LU report that there is no evidence for reversibility (as judged by the absence of a cathodic peak on the return half-cycle) even at 30 V s^{-1}. Thus, it cannot be a classical ECE case with only the E step observed at 0.4 V s^{-1}. In fact, LU determined $n = 2.4$ at 0.3 V s^{-1}. It seems likely that the current function data were collected over too narrow a range of ν to be interpretable, but certainly there is no useful mechanistic evidence here. Similarly, a qualitative observation of a shift in anodic peak potential with ν is interpreted by LU as being consistent with an ECE process. This observation is, in fact, consistent with virtually any mechanism since it only implies kinetic control of the voltammetric response.

Mechanistic Summary. The LU mechanism for cleavage of $3^{+\cdot}$ is shown to be improbable based on gas-phase data and inconsistent with the results of kinetic isotope effect studies. All the data for various compounds under either "wet, low-concentration" MMW conditions or "high-concentration, dry" LU conditions are internally consistent if one utilizes the key intermediate **4** under all conditions and has a competing nonelectrochemical destruction of reactant under LU conditions. The MMW mechanism is also consistent with a large body of evidence on alkylbenzene and benzyl alcohol oxidations.[9]

It must be emphasized that no evidence is available concerning the details for formation of **4**, like adsorbed intermediates, the timing of various electron-transfer and chemical steps, or whether these electron-transfer steps occur in solution or at the electrode surface. We have also ignored the possibilities arising from the high concentrations of electrogenerated acid near the electrode surface. These questions could in principle be answered by careful voltammetric studies, but these have so far proven impractical owing to the electrode filming encountered on the platinum anode.

Experimental Section

Materials. Lithium perchlorate was used without drying. Sodium perchlorate dihydrate and alumina were dried at 140 °C and 1 mmHg. Baker LC-grade acetonitrile was used. The analysis for water content was done by GLC employing a Poropak P column (1/8 in. × 6 ft), injection $T = 200$ °C, column T programmed from 80 to 130 °C at 8 °C/min. The water content was determined by comparing the areas of the water and the acetonitrile peaks using standard curves. Three drying procedures were used: (a) 200–300 mL (dry volume) of new 3 Å molecular sieve was added to 1 gal of LC-grade acetonitrile. After 5 days the water content was found to be 6 mM. (b) Acetonitrile (250 mL) was refluxed for 3 h under dry N_2 with 1 g of calcium hydride and then distilled. The water content was found to be 2.05 mM. However, there appeared an additional peak in the chromatogram that was unidentified and of approximately the same area as the water peak. (c) Acetonitrile which had been stored over 3 Å molecular sieves was allowed to percolate down through a column of dried alumina under N_2. For 250 mL of solvent, approximately 50–60 mL of alumina was employed. The water content found was 2.2 mM. This was the easiest and fastest method for obtaining very dry acetonitrile and was used for all experiments under LU conditions. (d) Acetonitrile was distilled from (1) NaH, (2) P_2O_5, and (3) CaH_2. This material was used for oxidations under MMW conditions.

Analyses. Products were analyzed using a Varian Model 3700 gas chromatograph with a 3-m glass column packed with 10% SE-30 on Chromosorb W. Peak areas were determined on a Perkin-Elmer M-2 calculating integrator using bibenzyl as an internal standard. Products were identified by coinjection of standard samples and by gas chromatography-mass spectroscopy (GC-MS) on a Hitachi RMU-6DX. Products that were isolated by column chromatography were identified by mass spectroscopy using an AEI MS-30. This instrument was also used for the isotope analyses. Typically, eight scans were computer averaged for each sample. All product spectra were compared with spectra of authentic samples taken on the same instrument. Product yields are based on the initial amount of substrate added.

α,α-Dideuteriobenzyl Alcohol.[15] To a cooled, stirred slurry of $LiAlD_4$ (1.0 g, 23.8 mmol) in ether was added an ether solution of freshly distilled ethyl benzoate (6.0 g, 40 mmol) over 20 min. The solution was refluxed gently for 2 h after addition was complete, then cooled and hydrolyzed with 10 mL of 5% aqueous NaOH. The organic layer was decanted from the solid inorganic residue. The residue was washed well with ether. The combined organic phases were dried over magnesium sulfate and concentrated. Unreacted starting material was removed by column chromatography on silica gel. The yield of alcohol was 2.0 g (18 mmol). When the NMR spectra was taken of a diluted sample the peak at δ 2.35 was shifted upfield: NMR δ 2.35 (s, 1 H), 7.34 (s, 5 H); IR (neat) 3325, 3040, 1500 cm^{-1}; MS *m/e* (rel intensity) 110 (100.00), 109 (50.04), 108 (14.67). The intensity ratio $(I_{109} + I_{108})/I_{110}$ was the same as I_{107}/I_{108} for benzyl alcohol. The spectroscopic evidence suggests the extent of dideuteration to be >95%. As a further check the MS of an equal molar mixture of dideuterated and undeuterated **3** was run. The *m/e* 110, 109, 108, and 107 peak intensities were in quantitative agreement with complete dideuteration.

α,α-Dideuteriodibenzyl Ether.[15] To a solution of α,α-dideuteriobenzyl alcohol (1.5 g, 13.6 mmol) in 1,2-dimethoxyethane (50 mL) was added benzyl bromide (2.3 g, 13.6 mmol). The mixture was cooled to 0 °C and sodium hydride (1.0 g, 20.9 mmol, 50% dispersion in oil) was added over 5 min. The NaH was first washed with ether to remove oil. The temperature was allowed to rise, more sodium hydride was added (0.5 g, 10.4 mmol), and stirring was continued. At the end of 2 h the solution was refluxed for 20 min. The solution was poured over ice and extracted with methylene chloride and the organic phase was washed with 10% NaOH and with H_2O. The solution was dried over magnesium sulfate and concentrated. Column chromatography of the crude product mixture yielded 1.4 g (51%) of dibenzyl-α,α-d_2 ether as a colorless liquid: NMR δ 4.45 (s, 2 H), 7.20 (s, 10 H); MS *m/e* (rel intensity) 94 (100.00), 93 (76.64), 92 (35.89), 91 (30.75).

4-Methoxydibenzyl Ether.[16] To a solution of 4-methoxybenzyl alcohol (7.0 g, 51 mmol), prepared from $NaBH_4$ reduction of anisaldehyde, in 1,2-dimethoxyethane (100 mL) was added benzyl bromide (17.4 g, 100 mmol). The solution was cooled to 0 °C and sodium hydride (3.0 g, 62 mmol, 50% dispersion in oil) was added over 10 min. The NaH was washed with ether to remove oil before using. The temperature was allowed to rise and more sodium hydride was added (1.0 g, 83 mmol). Stirring was continued for 2 h. Water was added (50 mL) and the solution was extracted with methylene chloride, dried over magnesium sulfate, and concentrated. Excess benzyl bromide was removed by vacuum distillation and column chromatography of the crude product yielded 10.0 g (86%) of 4-methoxydibenzyl ether: NMR δ 3.70 (s, 3 H), 4.41 (s, 2 H), 4.48 (s, 2 H), 7.05 (s, 5 H), 7.43 (m, 4 H).

4-Methoxybenzyl Octyl Ether. 1-Octanol (3.3 g, 25 mmol) was stirred with sodium hydride (1.8 g, 37.6 mmol) in anhydrous dimethylformamide (50 mL) until gas evolution had ceased. The solution was treated with an equimolar amount of 4-methoxybenzyl chloride (4.0 g, 25 mmol). After 1 h an additional portion of 4-methoxybenzyl chloride was added (0.8 g, 5 mmol) so that it was present in 20% excess. The solution was stirred overnight, then poured over ice. The resultant suspension was extracted with methylene chloride. The organic phase was washed with 10% aqueous NaOH and with H_2O, then dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography on silica gel to yield 6.2 g (97%) of 4-methoxybenzyl octyl ether as a colorless liquid: NMR δ 0.9-1.3 (m, 15 H), 3.43 (t, 2 H), 3.79 (s, 3 H), 4.42 (s, 2 H), 7.09 (m, 4 H); IR (neat) 2950, 2875, 1250, 1100 cm^{-1}.

Benzyl Anisoate. Benzyl alcohol (5.0 g, 46 mmol) in toluene was treated with *p*-anisoyl chloride (5.0 g, 30 mmol) and 2 equiv of pyridine. The mixture was stirred overnight, then filtered down a short column of activated alumina (activity I). Pyridine was removed by distillation of the pyridine-toluene azeotrope (110.2 °C) to yield 2.5 g (34%) of the colorless liquid: NMR δ 3.82 (s, 3 H), 5.34 (s, 2 H), 7.41 (m, 5 H), 7.53 (m, 4 H).

Octyl Anisoate. 1-Octanol (2.6 g, 20 mmol) in toluene was treated with *p*-anisoyl chloride (5.1 g, 30 mmol) and 2 equiv of pyridine. The mixture was stirred overnight, then filtered down a short column of activated alumina (activity I). Pyridine was removed by distillation of the pyridine-toluene azeotrope (110.2 °C) to yield 2.0 g (38%) of the colorless liquid: NMR δ 0.87-1.30 (m, 15 H), 3.82 (s, 3 H), 4.26 (t, 2 H), 7.43 (m, 4 H).

Oxidations under MMW Conditions. Oxidations were performed in a three-compartment cell at a platinum sheet anode. The three compartments were separated by glass frits. Potentials were measured against a Ag/0.1 M $AgNO_3$ reference electrode. The electrolyses were done at room temperature. The solvent used was acetonitrile with 0.1 M $LiClO_4$ as supporting electrolyte. The acetonitrile was purified by method d or used directly. The volume of solution was 130 mL. In some experiments the anodic potential was pulsed to 0.0 V for 0.5 s in every 10 s. This had little effect but allowed slightly higher currents and shorter electrolysis times. The number of coulombs passed during the cathodic pulse was negligible. During the electrolysis the anolyte was stirred with a magnetic stirring bar. In all cases the anolyte was blanketed with nitrogen to prevent autoxidation of aldehyde products. From 2 to 4 mmol of substrate was added to the anolyte. The coulometry was accomplished with an electronic counter and the reported *n* values are uncorrected for the background. Oxidations were discontinued when the current had returned to background. The reactions were worked up by addition of water to the anolyte and extraction with ether or methylene chloride. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed by rotary evaporation. The product mixtures were analyzed as indicated above.

Oxidation of 3. Dibenzyl ether (0.84 g, 4.2 mmol) was oxidized under MMW conditions at 1.9 V. The background current was 15 mA. After the substrate was added the current was 400 mA. At intervals of 0.25 F mol^{-1} 1-mL samples were removed from the anolyte, added to weighed amounts of internal standard, and analyzed directly by GLC. Following GLC analysis the samples were neutralized with pyridine and analyzed again by GLC. The coulometry was uncorrected for the amount of substrate removed by the samples. After the passage of 3.9 F mol^{-1} the current had returned to the background level and the electrolysis was discontinued. The amount of benzaldehyde in the final volume of anolyte was 6.65 mmol. This corresponds to a 88% yield. Although 15 mL of anolyte was removed during the electrolysis, the actual loss of volume was only about 8 mL owing to compensatory solvent flow from the catholyte compartment of the cell.

Dibenzyl ether was also oxidized using dried solvent (method c), dry electrolyte, and dilute solutions of **3**. The cell and electrodes were the same as above. **3** (2.07 mmol) was oxidized in 80 mmol of 0.1 M $NaClO_4$-CH_3CN solution at 1.9 V for 2.08 F mol^{-1}. Analysis by GLC before or after workup gave very similar results. The yields: **2** (2.06 mmol), **5** (1.87 mmol), **3** (0.1 mmol), **6** (nil). This corresponds to a material balance of 95%.

To reproduce the LU conditions a solution (7 mL) composed of 1.44 mmol of **3**, alumina-dried acetonitrile, and dry sodium perchlorate (0.1 M) was placed in the compartment of a small, three-compartment cell. A Ag/0.1 M $AgNO_3$ reference electrode was used and a platinum anode (0.98 cm^2) and a nitrogen bubbler were also placed in the anode compartment. The anolyte assayed at 9 mM in water. The catholyte was stirred with a magnetic stirrer. The initial current at 1.9 V was 78 mA. GLC analysis during the run indicated that the reaction proceeded according to the LU report. For example, at 0.6 F mol^{-1} the current was 46 mA and there were present **2** (0.36 mmol), **6** (0.07 mmol), **5** (0.31 mmol), and **3** (0.57 mmol). At 1 F mol^{-1} the current was 32 mA and the materials found were **2** (0.54 mmol), **6** (0.054 mmol), **5** (0.785 mmol), and **3** (0.18 mmol). The benzyl alcohol never exceeded 0.055 mmol and after 1.2 F mol^{-1} the concentrations of all these species dropped off sharply.

Oxidations of α,α-Dideuteriodibenzyl Ether. The deuterated ether was oxidized following the same procedure as for the undeuterated **3** and the *i,t* characteristics were identical. Using MMW conditions after passage of 1 F mol^{-1} and workup the isotopic compositions of

6, **2**, and **3** were estimated by GC-MS. These data were quantitatively unreliable, but suggested that PhCHO/PhCDO ≈ 1.5-2.0, $PhCH_2OH/PhCD_2OH$ ≈ 2.0, and the recovered **3** was isotopically unchanged. **6** and **3** were isolated by column chromatography on silica gel and analyzed by MS. The spectrum of reisolated **3** was identical with that of the original reactant.

The ratio of deuterated to protiated benzyl alcohol is calculated from the *m/e* 110/108 intensity ratio in the following manner. The peak intensity *m/e* 110 is corrected for the ^{13}C contribution of the fragment with *m/e* 109. The intensity of *m/e* 108 is corrected for the ^{13}C contribution from *m/e* 107 and for the contribution from M − 2 daughter ions from *m/e* 110. This latter contribution was determined by using the 110/108 intensity ratio in a spectrum of authentic dideuterio alcohol.

Using the LU conditions (see description for **3**) the reaction was terminated at 1 F mol^{-1}. The workup involved the addition of 3 mL of saturated NaCl and 25 mL of Et_2O to the electrolysis solution. The layers were separated and the organic layer was extracted again with 2 mL of saturated NaCl plus 1 mL of H_2O. The combined aqueous phases were extracted with 3 × 30 mL of diethyl ether, dried with anhydrous $MgSO_4$, and filtered, and the solvent was evaporated to give a light brown oil containing the amide and the aldehyde. This mixture was stored in a sealed flask in a freezer (or at −78 °C) to prevent decomposition of the aldehyde. The pure aldehyde was collected by GLC using the usual conditions. The amide **5** was separated by column chromatography on Al_2O_3 with a 30% Et_2O/70% Skelly F solvent system. Attempted isolation of the aldehyde from the column gave benzoic acid.

The isotopic composition of isolated **5** was determined for three different oxidations using the intensities of *m/e* 152-149. The data for one sample were *m/e* (rel intensity) 152 (10.76), 151 (90.68), 150 (13.12), 149 (63.52). The spectrum of undeuterated **5** showed *m/e* (rel intensity) 150 (9.01), 149 (78.88), 148 (4.50). Assuming no isotope effect for the fragmentation process and accounting for fragment ion and ^{13}C intensities, these data fit a ratio $PhCD_2NHCOCH_3/PhCH_2NHCOCH_3$ = 1.55. Without correction for fragment ions the ratio is 1.42. The average value for three experiments was 1.56.

Benzaldehyde plus benzaldehyde-d_1 was collected and similarly analyzed. Authentic benzaldehyde shows *m/e* (rel intensity) 106 (100), 105 (98). Authentic benzaldehyde-d_1 shows *m/e* (rel intensity) 107 (96), 106 (8), 105 (100). The oxidation product shows *m/e* (rel intensity) 107 (41.76), 106 (66.18), 105 (100). This calculates to PhCHO/PhCDO = 1.59. Analysis of the product from a different oxidation gave 1.54.

Competitive Oxidation of α,α-Dideuteriobenzyl Alcohol and Benzyl Alcohol. Equal molar amounts of α,α-deuterated (33.5 mg, 0.310 mmol) and protiated benzyl alcohol (34.3 mg, 0.311 mmol) were competitively oxidized using MMW conditions at 1.9 V. The background current was 2 mA. After the substrate was added the current was 50 mA. Electrolysis was carried out to 1 F mol^{-1}, at which time the current was 20 mA. After workup the benzyl alcohols were separated from benzaldehyde products by preparative GLC from which the alcohols were recovered. The ratio of protiated and deuterated benzyl alcohol was determined by low-energy MS (11 and 14 eV) using the *m/e* 110 and 108 to be 1.02 ± 0.05.

Preparative Oxidation of 4-Methoxydibenzyl Ether. 4-Methoxybenzyl benzyl ether was oxidized at 1.6 V under MMW conditions. The background current was 2 mA. The initial current after the addition of substrate was from 30 mA. After passage of 2 F mol^{-1} the electrolysis was discontinued. The final current was 4 mA. After workup the product mixture was analyzed by GLC and by GC-MS. The products were benzyl alcohol (69%), *p*-anisaldehyde (48%), and anisic acid benzyl ester (28%). A small amount of starting material (5%) was also recovered.

Preparative Oxidation of 4-Methoxybenzyl Octyl Ether. 4-Methoxybenzyl octyl ether was oxidized under MMW conditions at 1.6 V. The background current was 2 mA. The initial current was 40 mA. After the passage of 2 F mol^{-1} the electrolysis was discontinued. The final current was 2 mA. After workup the product mixture was analyzed by GLC. The products were 1-octanol (53%), *p*-anisaldehyde (29%), and anisic acid octyl ester (18%). A small amount of starting material was recovered.

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