Electrooxidation of Benzylic Ethers, Esters, Alcohols, and Phenyl Epoxides

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Abstract: Compounds with the structure $ArCH_2X$ (X = OH, OR, and OCOR) were oxidized at a platinum electrode in acetonitrile. The major products of controlled potential electrolysis were ArCHO and XH. The mechanism of benzyl ether cleavage was studied. A scheme involving initial electron loss from the aromatic moiety, formation of an alkoxyphenyl carbonium ion, and cleavage of RO *via* a hemiacetal is indicated.

This study arose from a desire to reconcile demonstrations that certain materials were electrooxidatively cleaved with reports that these same materials were major products in similar electrolyses. Recent studies have demonstrated the feasibility of anodic side chain substitution reactions. These reactions convert hydrocarbons to benzylic alcohols, acetamides, ethers, or esters. The one mechanistic facet that has been established in most of these reactions is that the oxidation is initiated by removal of electron(s) from the aromatic π system.

$$ArCH_3 \longrightarrow ArCH_2X + H^+ + 2e^-$$

$$X = OH, OR, OCOR, NHCOCH_3$$

When this is the case, it is not clear why the product should survive. The oxidation potential of $ArCH_2X$ is quite similar to that of the hydrocarbon and exhaustive electrolysis even at controlled potentials should often consume $ArCH_2X$. Both Parker and Burgert[1] and Eberson and Olofsson[2] have investigated the products of toluene oxidation in wet acetonitrile at platinum. They each found benzylacetamide, benzyl alcohol, benzaldehyde, and benzoic acid and theorized that benzaldehyde and benzoic acid could indeed arise from further oxidation of benzyl alcohol. They did not indicate the exact pathway for this conversion.

Lund[3] reported the first modern study of an $ArCH_2X$ oxidation. He found that *p*-methoxybenzyl alcohol could be converted to *p*-methoxybenzaldehyde in pyridine–acetonitrile at a platinum electrode. The conversion of benzyl alcohol to benzaldehyde was, however, not successful.

The oxidation of substituted arylmethyl ethers in methanol has been reported.[4] For *o*-, *m*-, and *p*-methyl and *p*-methoxy, the yield of aryl aldehydes ranged from 61 to 72%. It was proposed that a hemiacetal acetate or acetal was formed by the reaction of solvent or electrolyte with a phenylmethoxy carbonium ion. The acetal or hemiacetal acetate was then hydrolyzed under acidic work-up to yield the aldehyde. However, when methanol is used as the solvent for these oxidations, the exact reaction pathway is not easily discerned for the competing oxidation of methanol may lead to the involvement of the methanol cation radical or radicals. Parker and Burgert[5] indicated that the methoxylation of tetralin in methanol arises from the reaction of a methanol radical and tetralin. The possibility of the methanol cation radical acting as an oxidizing agent has not yet been explored.

The conversion of *tert*-benzylic alcohols $PhCR_2OH$ to ketones has been studied by Maruyama and Marakami.[6] They used an undivided cell and a mixture of the alcohol, dioxane, water, and sodium hydroxide. Again, the conversions were fairly high in yield, but mechanistic considerations are precluded by the concomitant oxidation of hydroxide ion.

Since we are interested in new electrosynthetic reactions, we have investigated the oxidation products from $ArCH_2X$, X = OH, OR, and OCOR, in acetonitrile and have found an interesting and useful reaction. Some mechanistic details of this reaction have also been elucidated and these explain certain aspects of the above reports.

Results

The oxidations were conducted potentiostatically in a three compartment cell which separated the anode, cathode, and reference electrode solutions by glass frits. Sodium carbonate was generally added, 0.1 *N* $LiClO_4$ was used as the electrolyte and approximately 0.5 g of substrate was oxidized. In those cases where aldehydes were obtained, the anolyte was blanketed by nitrogen to avoid autoxidation. Initial currents varied from 220 to 60 mA and the electrolysis was discontinued when the current dropped to 5 mA. In order to maintain high currents, it was often necessary to pulse the anodic potential to more negative values (~ 0 V) for 1 sec every minute. This technique did not reduce any appreciable amount of substrate and served to keep the electrode from becoming fouled. In the absence of pulsing, the current fell to very low values. At the present time, there appears to be no molecular criteria by which pulsing may be determined to be necessary. Table I lists the compounds oxidized and the products that were identified spectroscopically and assayed by glc.

Benzylic alcohols, ethers, and esters are all converted to carbonyl compounds under these reaction conditions. It can be seen from Table I that exhaustive oxidation will eventually convert any benzyl alcohol, ether, epoxide, or ester to the corresponding benzaldehyde plus benzoic acid or to the corresponding aryl ketone. For the ethers, the yield varied from 60 to 70% for the

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(3) H. Lund, *ibid.*, **11**, 1323 (1957).

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Table I. Oxidation Products and Reactants

Reactants	Amount, mmol	Anode potential,[a] V	mFaraday	Products (yield %)[b]
Benzyl methyl ether	4.1	1.90	11.4	Benzaldehyde (46) Benzoic acid (14)
Benzyl *tert*-butyl ether	3.04	1.95	6.4	Benzaldehyde (46.5)
Benzyl ether	3.1	1.90	13.0	Benzaldehyde (46)[c] Benzoic acid (33)[c]
Benzhydryl methyl ether	5.0	1.70	14.0	Benzophenone (77)
Benzhydryl dodecyl ether	2.3	1.90	5.0	Benzophenone (70) Dodecanol (70)
Benzyl cyclohexyl ether	2.6	1.80	9.0	Benzaldehyde (25) Cyclohexanol (53) Benzoic acid (31)
p-Methoxybenzyl methyl ether	3.3	1.30	4.9	*p*-Methoxybenzaldehyde (65)
1-Phenylethyl ether	2.0	1.90	14.5	Acetophenone (41)
Benzyl acetate	3.3	1.90	10.0	Benzaldehyde (30)
1-Phenylethyl benzoate	1.0	1.95	6.2	Acetophenone (50) Benzoic acid (50)
trans-Stilbene oxide	2.55	1.70	3.4	Benzophenone (27) Diphenylacetic acid (17)
Tetraphenylethylene oxide	2.86	1.70	9.0	Benzophenone (96.5)[c]
2-Octyl benzyl ether	4.5	1.90	8.7	Benzaldehyde (50) 2-Octanol (60)

[a] Potential of working electrode *vs.* Ag|0.01 *M* $AgNO_3$. [b] Based on added reactant. [c] Based on 2 equiv of products/1 equiv of reactant theoretical yield.

carbonyl product and from 10 to 30% for the acid. The yield of aliphatic alcohol varied greatly because those with low boiling points were evaporated during work-up. Alcohols with higher boiling points were isolated in 50–70% yield. For the esters, the yield for the carbonyl product and acid was 30–50%. The yield for carbonyl products from the epoxides was 30–95%. For the alcohols, the yield of carbonyl products was 50–70% and 30% for the acid. Thus, side-chain-substituted toluenes, $ArCH_2X$, will generally be oxidized at similar potentials, but the corresponding carbonyl compounds, ArCOR, will not oxidize. Controlled potential electrolysis will also allow aliphatic products, *e.g.*, ROH from $PhCH_2OR$, to survive. If the original substrate is composed of two benzylic fragments, each of these will be eventually converted to carbonyl products. The most striking example of this is the clean conversion of tetraphenylethylene oxide to 2 equiv of benzophenone.

Variation of product yields with changing reaction conditions was investigated. The yield of benzaldehyde from benzyl methyl ether was found to be the same when tetramethylammonium tetrafluoroborate or $LiClO_4$ was employed as the electrolyte. It was also possible to use either Na_2CO_3 or aqueous acetonitrile as the solvent system without affecting the yield of benzaldehyde. If, however, dry acetonitrile (distilled twice from P_2O_5) with no added Na_2CO_3 was employed, the yield of benzaldehyde was reduced from 60 to 15%. It was also found for *p*-methoxybenzyl methyl ether that pyridine gave a higher yield of aldehyde than did Na_2CO_3. Pyridine could not be used for unsubstituted benzyl ethers since it oxidizes at 1.6 V and the ethers oxidize at 1.8 V.

Discussion

Mechanism. It is known that perchlorate ion oxidizes in acetonitrile at about 2.3 V.[1,2,7–9] Although radicals[7–11] from this oxidation could conceivably be involved in cleavage, the use of potentiostatic oxidation abrogates this possibility and limits the possible mechanistic pathways.

Assuming, therefore, that oxidation is initiated by electron transfer from the substrate molecule, the next question concerns the nature of the highest occupied molecular orbital since this is the orbital that will lose an electron most easily. Photoelectron spectroscopy has revealed that the nonbonded electrons on oxygen are more difficult to ionize than the π electrons in toluene. Therefore, the oxidation potential of the π electrons should be lower than that for the oxygen electrons.[12–14] This is experimentally observed. Toluene oxidizes at 1.96 V while methanol oxidizes beyond 2.5 V. In benzyl alcohol, the two functionalities should approximately retain their identity and electrochemical properties since there is no direct conjugation between them. Each may influence the other slightly through inductive forces, but the observed potential of 1.7–1.9 V is well below that of methanol and is in the range needed for toluene oxidation. Also, it can be seen from Table II that the oxidation potentials are sensitive to substitution on the phenyl ring. The half-wave potential for benzyl alcohol (2.0 V), *p*-methylbenzyl alcohol (1.59 V), and *p*-methoxybenzyl alcohol (1.25 V) have been reported.[15] Oxidation of the nonbonded electrons should again be only slightly affected by the substituents on the phenyl ring.

The key intermediate in the overall reaction, a phenylalkoxy carbonium ion, is formed rapidly by loss of a proton and an electron from the initial cation radical.

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(9) J. P. Billon, *Bull. Soc. Chim. Fr.*, 863 (1962).

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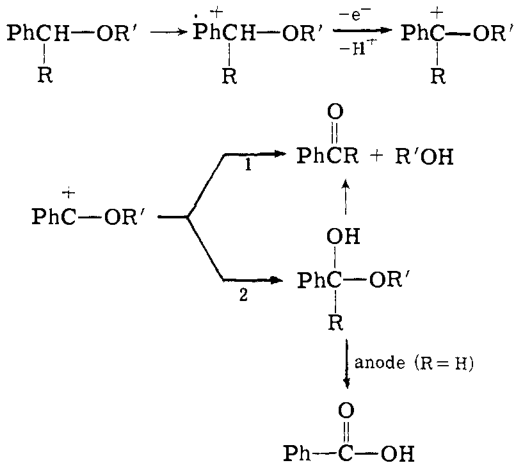
Table II. Oxidation Products and Reactants

Reactants	Anode potential,[a] V	Products (yield %)[b]
Benzyl alcohol	1.90	Benzaldehyde (30) Benzoic acid (40)
p-Methoxybenzyl alcohol	1.30	*p*-Methoxybenzaldehyde (60)
o-Methoxybenzyl alcohol	1.30	*o*-Methoxybenzaldehyde (60)
m-Methoxybenzyl alcohol	1.40	*m*-Methoxybenzaldehyde (~1)
1-Phenylethanol	1.70	Acetophenone (56)
o-Benzylvanillyl alcohol	1.10	*o*-Benzylvanillin (90)
Cumyl alcohol	1.90	Acetophenone (62)

[a] Potential *vs.* Ag|0.1 *M* $AgNO_3$. [b] Based on added reactant.



The sequence of these steps is not determined from the available data. This process is well documented for alkylbenzene oxidations and should be especially favorable for these alkoxy-substituted cations. It should be noted that pathway 1 alone cannot explain the appearance of benzoic acid. Further oxidation of the aldehyde is not possible since it oxidizes at a much higher potential, *e.g.*, *p*-methoxybenzyl alcohol ($E_{1/2}$ = 1.2 V) and *p*-methoxybenzaldehyde ($E_{1/2}$ = 1.6 V).[15] The appearance of acid even under an atmosphere of nitrogen rules out oxidation by air. Therefore, the possible mechanisms are a combination of pathways 1 and 2 or only 2.

The behavior of phenylalkoxy carbonium ions has received previous attention, and it has been concluded that the primary mode of reaction involves path 2. Westheimer[16] found when di-*tert*-butylbenzaldehyde acetal was hydrolyzed in 1 *M* solution of sodium acetate in 86% acetic acid (0.3% excess ^{18}O), the recovered *tert*-butyl alcohol (60–85%) showed only the normal abundance of ^{18}O. Bourns[17] found for the hydrolysis of di-*n*-butyl and diallyl benzaldehyde acetals in 0.5 mol of water containing 0.4% excess ^{18}O and 2 drops of HCl that the alcohols contained the normal abundance of ^{18}O while the benzaldehyde was found to be enriched. If acetals were originally enriched with ^{18}O, the alcohols were found to be enriched by the same amount as the acetal after hydrolysis. Lucas[18] studied the acid hydrolysis of di-*d*-2-octyl benzaldehyde acetal in 5% phosphoric acid. The isolated 2-octanol had a specific rotation of +7.91° while the starting alcohol had a specific rotation of +7.93°. Our data are in complete agreement with all of the preceding results, as is expected if the phenylalkoxy carbonium ion is formed. Benzhydryl dodecyl ether was oxidized in acetonitrile containing 0.5 ml of 9.3% enriched $H_2{}^{18}O$. The mass spectra of the isolated products indicated that the dodecyl alcohol incorporated no ^{18}O while the benzophenone was enriched in ^{18}O by 9.06%. Stereochemical data were obtained from the oxidation of optically active *l*-2-octyl benzyl ether. The products were separated by chromatography on a silica gel column. The isolated 2-octanol was found to have a specific rotation of −9.0° while the original *l*-2-octanol had a specific rotation of −9.15°.

A trapping experiment using benzhydryl methyl ether and methanol in acetonitrile reinforces this argument. The nmr spectrum of the oxidation mixture revealed the presence of starting material, benzaldehyde, and dimethyl benzaldehyde acetal in the ratio 2:3:2. The latter results from scavenging of intermediate phenylmethoxy cations by methanol.

It should be emphasized that the use of methanol as a trap is quite different from using methanol as a solvent. In the latter, addition of the alcohol, ether, or ester does not change the amount of current being passed so direct oxidation of the compound is undeterminable. With methanol as a trap, addition of compound does increase the amount of current being passed indicating that the compound is oxidized directly. The difference in the discharge potential for methanol as a solvent and as a trap is due to the great difference in concentration.

Products. The overall yield and nature of products are determined by several factors, including the stability of a product toward further oxidation. Aryl aldehydes and aliphatic alcohols are inert toward further oxidation because of their high ionization potentials. Controlled-potential electrolysis therefore allows selective oxidation of benzyl alcohols and ethers. In both aliphatic alcohol and aryl aldehyde, the ionization potential is determined by the oxygen atom. The carbonyl group has a great effect on the π electrons in the aryl aldehyde since it is in conjugation with the π system. Because of the greater nuclear charge, the net effect of the oxygen atom is to lower the π and nonbonding molecular orbital energies and increase the oxidation potential. A second factor is the competition between proton loss from the cation radical or dication and other reaction pathways. One such pathway could be attack on the phenly ring. Although no effort was made to isolate or identify products from such a reaction, similar reactions of this type have been reported for alkylbenzenes.[19] The yields of aldehydes from *p*- and *m*-methoxybenzyl alcohols are, however, of interest in this regard. The *p*-methoxy group evidently lowers the energy of activation for proton loss due to its resonance effect while the *m*-methoxy would lower the energy of activation for attack on the ring. For *p*-methoxy, the yield of aldehyde was 70% while for *m*-methoxy, there were no aldehydes observed. In vanillyl alcohol to vanillin conversion, the resonance effect favors both attack on the ring and proton loss, but the ring attack is hindered by the ortho substituents.

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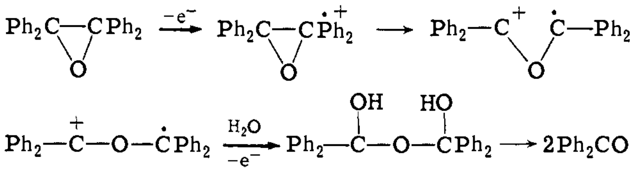
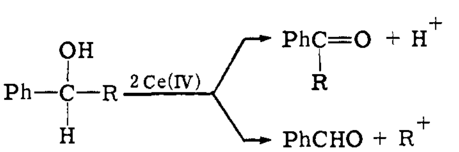
Another alternative pathway to carbonyl compound formation exists for reactants like 1-phenylethyl benzoate and 1-phenylethyl ether. Loss of a proton from the intermediate carbonium ion to form an alkene is expected to be important. This product should be further oxidized and subsequently cut down yields of acetophenone.

If no benzylic hydrogens are present, cleavage of carbon–carbon bonds can result. Although tetraphenylethylene oxide is chemically stable in the anolyte, it gives a very clean cleavage reaction. The following mechanism accounts for benzophenone formation.

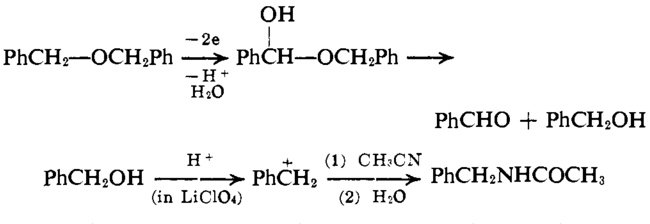


This is an intriguing reaction because it involves cleavage of a carbon–carbon single bond. It may have some analogy in chemical oxidative cleavages of alkylphenylcarbinols[20] by cerium(IV).



When R was methyl, acetophenone was formed exclusively, and if R was isopropyl or *tert*-butyl, benzaldehyde was formed exclusively. Therefore, cleavage of the carbon–carbon bond in the epoxide seems reasonable since the diphenylalkoxy carbonium ion and radical should be even more stable than *tert*-butyl or isopropyl cations. Interestingly, cleavage of a methyl group is observed in both the chemical[21] and anodic oxidation of cumyl alcohol (Table II). The yield of acetophenone is 60% in the anodic oxidation.

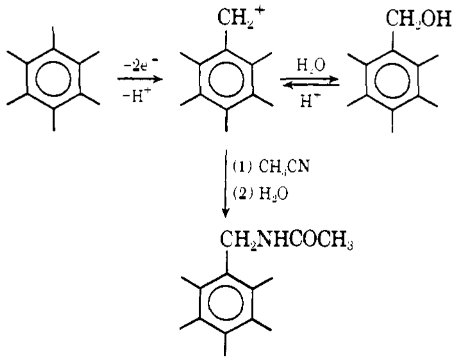
Although it was shown that benzyl ethers are stable to the acid formed in these oxidations, it is quite clear that benzyl alcohols are not stable. When dibenzyl ether was oxidized with $LiClO_4$ and no Na_2CO_3, *N*-benzylacetamide was one of the products. With $NaBF_4$ and no Na_2CO_3, no *N*-benzylacetamide was found. The following scheme is proposed.



$$PhCH_2—OCH_2Ph \xrightarrow[-H^+,\ H_2O]{-2e} PhCH(OH)—OCH_2Ph \longrightarrow PhCHO + PhCH_2OH$$

$$PhCH_2OH \xrightarrow[\text{(in LiClO}_4)]{H^+} Ph\overset{+}{C}H_2 \xrightarrow[(2)\ H_2O]{(1)\ CH_3CN} PhCH_2NHCOCH_3$$

This scheme was tested by observing the aldehyde to amide ratio. The anolyte was split into two parts with the first part being immediately worked up. An aldehyde:amide ratio of 1.6:1.0 was determined. Benzyl alcohol was added to the second part and the solution was allowed to stand for 1 hr. After work-up, the aldehyde:amide ratio was 1.05:1.0. Therefore, the formation of the amide was concluded to be derived, at least in part, from the acid amidolysis of benzyl alcohol. With $NaBF_4$, this acid amidolysis is apparently lacking. This result may have greater ramifications if one recalls the study by Nyberg[21] on the oxidation and subsequent acetamidization of hexamethylbenzene. If $NaClO_4$ was used, the ratio of *N*-pentamethylbenzylacetamide to pentamethylbenzyl alcohol was 95:5. If tetra-*n*-butylammonium tetrafluoroborate was used, the ratio of amide to alcohol was 5:95. Although water is known to be a much better nucleophile, the predominance of amide has perplexed many investigators. The current hypothesis is that the tetrafluoroborate anion preferentially solvates water at or near the electrode surface. An alternate scheme would be the following.



This would account for the differences in nucleophilicities. More detailed mechanistic studies are being done in order to completely ascertain the exact effect of the electrolyte and will be reported.

The synthetic scope of oxidative cleavages is currently being explored. It is a common synthetic procedure to use benzyl groups to protect reactive alcohols. At present, there are two means of debenzylation: catalytic hydrogenolysis and alkali metal reduction. Oxidative cleavages would give an added dimension since both of the preceding are reductive processes. A review of Table I indicates that reasonable yields of the alcohol and retention of configuration can be obtained and the conditions are chemically mild. Chemical debenzylation by trityl fluoroborate has recently been reported for methylbenzyl, *p*-methoxybenzyl, and other substituted ethers.[22] The yield of carbonyl compound was 75 and 25%, respectively, for the methyl- and *p*-methoxybenzyl ethers. The most significant point was that a high yield of alcohols was realized. Major advantages indicated for trityl fluoroborate debenzylation were the mild, neutral conditions. It was also implied that cleavage of other types of protecting groups such as bismethylenedioxy, tetrahydropyranyl, and benzyloxycarbonyl were possible. It seems clear that anodic and trityl cation debenzylations are mechanistically related in that both involve the intermediate phenylalkoxy carbonium ion.

Experimental Section

A modified "H" cell was employed as a three-compartment electrochemical cell. The anode compartment held approximately 100 ml of anolyte, the cathode held 50 ml of catholyte, and the reference held 10 ml of 0.1 *N* $AgNO_3$ in acetonitrile. The anode compartment was separated from the cathode by a 1.5-in. diameter glass frit

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(20) W. S. Trahanovsky and J. Cramer, *J. Org. Chem.*, **36**, 1890 (1971).

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and from the reference by a 0.25-in. diameter glass frit. The porosity of the frits was fine. The anode compartment was also fitted with a ground glass lid. The lid had an inlet and outlet for the passage of nitrogen gas. A 2-in.^{2} platinum sheet was employed as the anode and was suspended from the lid. A stainless steel sheet was used as the cathode, and a silver wire for the reference. A Model 61RS or 70HV 1/90 Wenking potentiostat was employed for controlled-potential electrolysis. For pulsing, a square wave from a Model 126 VCF Exact sweep generator was employed. Cyclic voltammograms were recorded on a Varian X–Y recorder.

The acetonitrile (Baker Analyzed reagent) was distilled once or twice from P_2O_5 and stored over molecular sieves (Fisher, type 5A). The $LiClO_4$ (anhydrous reagent, G. F. Smith Chemical Co.) was dried at 110°. Anhydrous Na_2CO_3 was added to all oxidations except where noted. Silica gel powder (Baker Analyzed reagent, 60–200 mesh) was used for liquid chromatography. Eluents were purified by distillation.

Products and starting materials were analyzed by ir on a Perkin-Elmer 457 grating spectrometer. Nmr spectra were taken on a Varian A-60A spectrometer and chemical shifts are reported in δ. Mass spectra were measured with an A.E.I. Model MS-12 spectrometer. Glc analysis was performed with an F & M research chromatograph Model 5750 equipped with a programmed temperature unit and both thermal conductivity and hydrogen flame detectors, or with a Varian Aerograph Model 90-P gas chromatograph equipped with a thermal conductivity detector. An 8 ft × 0.25 in. 5% S.E. 30 Chromosorb W column was used. Melting points were measured by a Fisher-Johns melting point apparatus in °C and are uncorrected. Optical rotations were measured by a Perkin-Elmer 141 polarimeter.

Synthesis of Compounds. Benzhydryl Methyl Ether. This compound was prepared according to the method of Kostanecki and Lampe.[23] Benzhydrol (5 g) was dissolved in 125 ml of methanol and 7 drops of concentrated H_2SO_4 was added. The solution was stirred overnight. The solution was worked up by adding water and ether. The ether layer was extracted with a Na_2CO_3 solution, washed with water, and dried with $MgSO_4$. The solvent was evaporated and the resulting liquid was vacuum distilled. 3.8 g (70.5%) of product was collected: ir (neat) 3050, 1200, 970, 760, and 700 cm^{-1}; nmr ($CDCl_3$) δ 3.3 (s, 3), 5.2 (s, 1), and 7.2 (m, 10).

Benzyl *tert*-Butyl Ether. Benzyl chloride (10 g) was added to 75 ml of glyme. Potassium *tert*-butoxide (9 g) was then added, and the solution was refluxed overnight. The solution was worked up with water and ether. The ether layer was dried with $MgSO_4$ and then the solvent was evaporated. The residue was then distilled and 8.0 g (60%) of the ether was collected: bp 201° (lit.[24] 201–203°); ir (neat) 3050, 1700, 1200, 920, 750, and 700 cm^{-1}; nmr ($CDCl_3$) δ 7.2 (s, 5), 4.3 (s, 2), and 1.2 (s, 9).

Benzhydryl Dodecyl Ether. Benzhydrol (3 g) was added to 75 ml of dodecyl alcohol. Concentrated HCl (1.0 ml) was added and the solution was refluxed for 4 hr. The solution was extracted with water and ether. The ether layer was worked up in the usual manner. The resulting solution was vacuum distilled and 3 g (52%) of the ether was collected: bp 210° (1.5 mm); ir (neat) 3050, 1200, 920, 750, and 700 cm^{-1}; nmr ($CDCl_3$) δ 0.9 (d, 3), 1.2 (s, 20), 3.4 (t, 2), 5.3 (s, 1), and 7.3 (s, 10).

Anal. Calcd for $C_{25}H_{36}O$: C, 85.3; H, 10.2. Found: C, 85.02; H, 10.45.

Benzyl Cyclohexyl Ether. Cyclohexanol (10 g) was added to 100 ml of glyme. Sodium hydride (4.5 g of 57% oil dispersion) was added and the solution was stirred for 30 min. Benzyl chloride (12 g) was then added and the solution refluxed for 6 hr. Work-up with water and ether and then vacuum distillation yielded 7 g (37%) of the ether: bp 94° (0.5 mm) (lit.[25] bp 166° (37 mm)); ir (neat) 3050, 1200, 750, and 700 cm^{-1}; nmr ($CDCl_3$) δ 1.0–2.0 (m, 10), 3.2 (s, 1), 4.5 (s, 2), and 7.3 (s, 5).

***l*-2-Octyl Benzyl Ether.** *l*-2-Octanol (4 g) was added to 100 ml of glyme. Sodium hydride (1.2 g of 57% oil dispersion) was then added and the solution was stirred for 30 min. Benzyl chloride (4 g) was added and the solution refluxed for 4 hr. Work-up with water and ether and then vacuum distillation yielded 2.0 g (65%) of the ether: bp 100° (0.1 mm) (lit.[26] 154° (18.0 mm)); ir (neat) 3050, 1200, 750, and 700 cm^{-1}; nmr ($CDCl_3$) δ 0.8–1.6 (m, 16), 3.5 (m, 1), 4.5 (s, 2), and 7.3 (s, 5).

Tetraphenylethylene Oxide. *m*-Chloroperbenzoic acid (85%, 5.1 g) in 70 ml of chloroform was added to tetraphenylethylene (8.2 g) in 60 ml of chloroform at room temperature. A few crystals of trichloroacetic acid were added, and the solution was allowed to stand overnight. The mixture was worked up by adding ether, extracting with Na_2CO_3 solution, and washing with water. The chloroform–ether layer was dried with $MgSO_4$ and the solvent evaporated. The resulting solid was recrystallized from ethyl acetate yielding 4.0 g (47%) of the product: mp 208–210° (lit.[27] mp 209–210.2°).

Oxidation of Compounds. Benzhydryl Dodecyl Ether in the Presence of Labeled Water. Benzhydryl dodecyl ether (1.0 g) was added to the anolyte which was 0.1 *N* $LiClO_4$ in acetonitrile. The acetonitrile was distilled twice from P_2O_5 just prior to oxidation. $H_2{}^{18}O$ (0.5 ml of 9.13% enriched) was added and no Na_2CO_3 was added. The potential was 1.90 V and the initial current was 230 mA. The oxidation was terminated after 5 hr. Water was then added to the anolyte and then extracted with chloroform. The chloroform layer was dried with $MgSO_4$ and then the solvent was evaporated. The residue was placed on a silica gel column and eluted with 15% chloroform in Skelly Solve. The products, benzophenone and dodecanol, were identified by nmr and glc. The label was analyzed by a mass spectrometer. Benzophenone had 9.06% enrichment while the alcohol had none.

***l*-2-Octyl Benzyl Ether.** *l*-2-Octyl benzyl ether (1.0 g) was added to the anolyte which was 0.1 *N* $LiClO_4$ in acetonitrile. The acetonitrile was distilled once from P_2O_5. The potential was 1.90 V and the initial current was 300 mA. The oxidation was terminated after 3 hr. The anolyte was worked up in the usual manner, and the residue placed on a silica gel column. Products were identified by nmr and glc. The eluent was 40% chloroform in Skelly Solve. The specific rotation of the isolated *l*-2-octanol was taken in methanol and was found to be −9.0°. The original *l*-2-octanol had a specific rotation of −9.15° in methanol.

Benzyl Methyl Ether in the Presence of Methanol. Methanol (15 ml) was added to 60 ml of acetonitrile which was 0.1 *N* in $LiClO_4$. The acetonitrile was distilled once from P_2O_5. The background current at 1.8 V was 40 mA. No Na_2CO_3 was added. Benzyl methyl ether (0.5 g) was added and the current rose to 100 mA at 1.8 V. The oxidation was terminated after 5 hr. A basic extraction with ether and $NaHCO_3$ left a residue and nmr indicated that starting material, benzaldehyde, and dimethyl benzaldehyde acetal were present. The latter was confirmed by comparison with an nmr of an authentic sample. The ratio of products was 2:3:2. The residue was added to 50 ml of 30% aqueous acetonitrile. Concentrated HCl (1.0 ml) was added and the solution was refluxed for 15 min. Basic extraction again left a residue and nmr indicated that only starting material and benzaldehyde were present. The ratio of products was 2:5, respectively.

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