Electrooxidative Cleavage of Benzylic Ethers and Esters

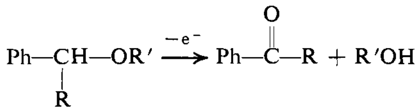
Sir:

We have been interested in developing new electrooxidative reactions[1] and in the course of investigating a more exotic process,[2] we have discovered that the potentiostatic oxidation of benzylic alcohols, ethers, and esters produces reasonable yields of carbonyl compounds (Table I). This is a simple yet unexpected reaction which requires revision of literature implications and suggests new synthetic procedures.

Table I. Oxidation Products[a]

	Substrate R	Substrate R′	mmol	V[b]	mfaraday	Products (%)[c]
1a	Ph	H	5.4	1.70	7.4	Benzophenone (64)
1b	Ph	CH_3	5.0	1.71	14	Benzophenone (77)
1c	Ph	$C_{12}H_{25}$	2.3	1.90	5.0	Benzophenone (70), dodecanol (70)
1d	H	H	6.5	1.87	16.5	Benzaldehyde (30), benzoic acid (40)
1e	H	CH_2Ph	3.1	1.90	13.0	Benzaldehyde (46), benzoic acid (33)[d]
1f	CH_3	H	4.1	1.90	8.5	Acetophenone (56)
1g	CH_3	$CH(CH_3)Ph$	2.0	1.90	14.5	Acetophenone (41)[d]
1h	H	$COCH_3$	3.3	1.90	10	Benzaldehyde (30)
1i	CH_3	COPh	1.0	1.95	6.2	Acetophenone (50), benzoic acid (50)
1j	H	CH_3	4.1	1.90	11.4	Benzaldehyde (46), benzoic acid (14)
1k	H	$c\text{-}C_6H_{11}$	2.6	1.80	9.0	Benzaldehyde (25), benzoic acid (31), cyclohexanol (53)

[a] Acetonitrile, lithium perchlorate, sodium carbonate anolyte; platinum anode. [b] Measured and reported *vs.* Ag|0.1 *N* $AgNO_3$ in acetonitrile. [c] Isolated products. Yield based on initial amount of **1**. [d] Based upon 2 mol of product/mol of reactant theoretical yield.



$$\mathrm{Ph{-}\underset{\displaystyle R}{\underset{|}{C}H}{-}OR'} \xrightarrow{-e^-} \mathrm{Ph{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R + R'OH}$$

1, R′ = alkyl, hydrogen, acyl;
R = hydrogen, alkyl, aryl

The oxidations were conducted in a three-compartment cell which separated the anode, cathode, and reference electrode solutions by glass frits. The anode was a platinum sheet (total area 2 in.^{2}) and the anolyte normally contained purified acetonitrile, lithium perchlorate, sodium carbonate, and, initially, about 500 mg of substrate. In those cases where aldehydes were formed the anolyte was blanketed with nitrogen to avoid autoxidation. Initial currents varied from 225 to 60 mA. Electrolysis was discontinued when the current dropped to 5 mA. The ether-soluble, water-insoluble products were identified spectroscopically and assayed by glc.

The cleavage of benzylic ethers is an especially interesting and novel reaction which could have utility in the production of benzaldehydes. More intriguing, however, is the fate of the nonbenzylic fragment, R′. Compounds **1c,k** demonstrate formation of R′OH in relatively high yield. Since reductive cleavage of benzylic ethers has considerable utility this oxidative process might also be useful for protecting alcohols. The conditions are very mild and a selective oxidative cleavage should be feasible if the benzylic electrophore has the lowest oxidation potential in the molecule. This could, for example, allow cleavage of the ether in preference to attack on an aliphatic alcohol, aldehyde, nitrile, or halide function. We will explore this possibility and optimize conditions for cleaving protected alcohols in the near future.

Similar reactions do not appear in the electrochemical literature and in fact the study of Lund implied that even benzylic alcohol to aldehyde conversions were not generally feasible.[3] He found that *p*-methoxybenzyl alcohol could be oxidized to the aldehyde if pyridine–acetonitrile was used as a solvent. Other benzyl alcohol oxidations were unsuccessful. We find that it is important in many of these processes to pulse the anode potential to more negative (~0 V) values for a second every minute. This does not reduce any appreciable amount of material (no apparent cathodic current) but does serve to clean the electrode and permit high currents. In the absence of pulsing the electrode becomes fouled and little product is formed. In addition to revising Lund's report, the above reaction is of interest because benzylic alcohols, ethers, and esters have been obtained as electrooxidation products of the corresponding hydrocarbons.[4] It is important to note that these side-chain substituted products[5-9] will not normally survive exhaustive electrolysis at potentials sufficient to directly oxidize the unsubstituted precursor.

$$\mathrm{ArCH_3} \xrightarrow{-2e^-} \mathrm{ArCH_2OR'} \xrightarrow{-2e^-} \mathrm{ArCHO}$$

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[1] L. L. Miller and E. A. Mayeda, *J. Amer. Chem. Soc.*, **92**, 5818 (1970); L. L. Miller and A. K. Hoffmann, *ibid.*, **89**, 593 (1967); L. L. Miller, E. Kujawa, and C. Campbell, *ibid.*, **92**, 2821 (1970).

[2] L. L. Miller, V. R. Koch, M. E. Larscheid, and J. F. Wolf, *Tetrahedron Lett.*, 1389 (1971).

[3] H. Lund, *Acta Chem. Scand.*, **11**, 491 (1957).

[4] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N.Y., 1970, Chapter 5.

[5] S. D. Ross, M. Finkelstein, and R. C. Peterson, *J. Amer. Chem. Soc.*, **86**, 4139 (1964).

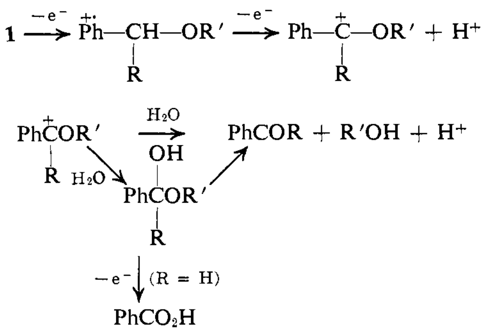
[6] L. Eberson, *ibid.*, **89**, 4669 (1967).

[7] L. Eberson and K. Nyberg, *Tetrahedron Lett.*, 2399 (1966).

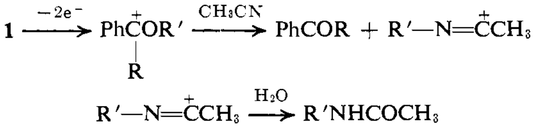
[8] L. Eberson and B. Olafsson, *Acta Chem. Scand.*, **23**, 2355 (1969).

[9] V. D. Parker and B. E. Burgert, *Tetrahedron Lett.*, 2411 (1968).

Mechanistically, we envisage a process similar to the following



Since oxygen nonbonded electrons are more difficult to ionize than toluene π electrons, the initial step of this reaction undoubtedly involves the phenyl group. This is rapidly followed by loss of a proton and a second electron transfer forming a carbonium ion. The work of Eberson and coworkers[6,7] provides strong analogy for the formation of benzylic cations and the attached oxygen function should make the present examples especially favorable. Several alternate reaction pathways exist for the benzylic cation, but due to the sodium carbonate these will all produce carbonyl products. The oxidation of dibenzyl ether in acetonitrile without added carbonate gives benzaldehyde and benzylacetamide. Since the starting ether is stable to the electrogenerated acid this implies that the carbonate is responsible for carbonyl products and the following reactions take place in its absence.



$$1 \xrightarrow{-2e^-} \underset{\displaystyle R}{Ph\overset{+}{C}OR'} \xrightarrow{CH_3CN} PhCOR + R'{-}N{=}\overset{+}{C}CH_3$$

$$R'{-}N{=}\overset{+}{C}CH_3 \xrightarrow{H_2O} R'NHCOCH_3$$

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Larry L. Miller,* J. Fredrick Wolf, Edward A. Mayeda
Department of Chemistry, Colorado State University
Fort Collins, Colorado 80521

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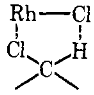
Molecular Oxygen as a Bridging Ligand in a Transition Metal Complex

Sir:

The catalytic hydrogenation activity[1] of chlorotris(triphenylphosphine)rhodium(I) is considered to be due to either (a) a vacant site in the five-coordinate species $RhH_2Cl[P(C_6H_5)_3]_2$, or (b) a six-coordinate species $RhH_2Cl[P(C_6H_5)_3]_2S$, where S is a weakly bound, and readily replaced, solvent molecule. Our attempts to produce suitable crystals of the methylene chloride adduct of this active hydrogenating species for an X-ray diffraction study have been unsuccessful. However, we decided to extend our investigation to other formally coordinatively unsaturated rhodium complexes where either chloroform or methylene chloride appears to be firmly retained in the solid state. The type of weak complex that was considered possible could be represented by



where a bond to a weakly coordinated chlorine atom could be reinforced by a hydrogen bond of a type that is well documented.[2,3] Our first choice was the apparently simple molecular oxygen complex[1,4] $RhClO_2[P(C_6H_5)_3]_2 \cdot CH_2Cl_2$. It is the surprising result of this investigation that we wish to report.

The complex was prepared by bubbling oxygen through a solution of the red form of chlorotris(triphenylphosphine)rhodium (0.25 g) in methylene chloride (15 ml) for 5 min. The first crop of brown diamagnetic crystals (~30% yield) was collected after a slow crystallization at 7° for 48 hr. All measurements were made on this material, which appears to be homogeneous.[5] Carbon and hydrogen analyses[6] (*Anal.* Calcd: C, 57.0; H, 4.1. Found: C, 57.7; H, 4.22) are in good agreement with the formulation, but chlorine analysis has proved difficult (calcd, 13.6; found, ~15) owing to the interference of rhodium and/or phosphorus. However, any serious objections to the formulation involve the identification of oxygen, and in addition to the evidence from the refinement (*vide infra*) some supporting data are available. The infrared spectrum (Nujol mull) shows a complex absorption at *ca.* 845 cm^{-1}, but this can be interpreted as being consistent with both a coordinated oxygen molecule and a perturbed methylene chloride molecule. The best supporting evidence for the assignment of oxygen comes from studies of the thermal decomposition products where molecular oxygen has been positively identified by gas chromatography.[7] Infrared spectra of solids remaining after heating to 200° *in vacuo* show the appearance of a band at ~1120 cm^{-1} which could be assigned to a triphenylphosphine oxide complex.[8]

The complex crystallizes in the triclinic crystal system with space group $P\bar{1}$; lattice parameters a = 13.889 (7), b = 13.678 (6), c = 11.433 (5) Å, α = 105.73 (4)°, β = 115.74 (3)°, γ = 100.97 (4)°; and two formula units per unit cell (ρ_{obsd} = 1.469 (by flotation), ρ_{calcd} = 1.470 g cm^{-3}). The structure has been solved from conventional Patterson and electron density maps, and has been refined using 1658 statistically reliable reflections measured on a manual Picker diffractometer with Cu Kα X-radiation with $2\theta \leq 80°$. The current model using a rigid-body description of phenyl groups has refined to a conventional reliability factor of 0.050

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[1] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

[2] J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 2243 (1967).

[3] M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *ibid.*, 7, 1570 (1968).

[4] M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 129 (1966).

[5] A second product has been identified in this system. These yellow orthorhombic crystals are the major product if the quantity of $RhCl(P(C_6H_5)_3)_3$ is significantly increased. We tentatively formulate this compound as $RhClO_2(P(C_6H_5)_3)_3 \cdot xCH_2Cl_2$, where x is in the range 2–3.

[6] Carried out in the microanalytical laboratory, Department of Chemistry, University of Alberta.

[7] We thank Dr. Alan Clement of this department for this measurement. No significant quantities of nitrogen were observed.

[8] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).