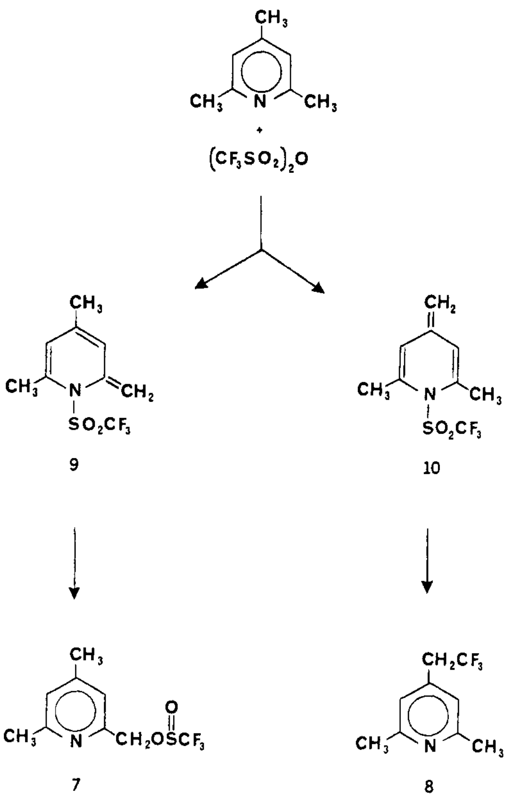
Scheme II



sulfinyl]oxy]methyl]-4,6-dimethylpyridine (7, 5%) and 4-(2,2,2-trifluoroethyl)-2,6-dimethylpyridine[9] (8, 62%) but no 4-[[(trifluoromethyl)sulfinyl]oxy]methyl-substituted derivative (Scheme II). This behavior argues in favor of a concerted reaction[10] for formation of compound 1 from the intermediate 4 (and 7 and 9). Also, if the reactions of 2,6-lutidine and *s*-collidine to produce 2,2,2-trifluoroethyl-substituted pyridines are mechanistically similar, the conversion of 4 into 2 should be a nonconcerted process since the comparable transformation (10 → 8) for *s*-collidine cannot be concerted. From among the simplest intermediates for this reaction (4 → 2), only **6a** can be excluded rigorously because $CF_3SO_2^-$ is stable under the reaction conditions and, thus, cannot be a source of the CF_3 group.

The reaction between *s*-collidine and triflic anhydride also was conducted with diphenylmethane as the solvent. It was anticipated that if the trifluoromethyl radical were involved in this reaction, 1,1,2,2-tetraphenylethane (11) would be formed; however, no 11 was produced. Although the negative CIDNP (repeated with *s*-collidine with the same result as described above for 2,6-lutidine) and diphenylmethane experiments are not conclusive, they argue against the intermediacy of a radical pair such as 5 in the formation of 2 (Scheme I). The combined effect of this information is to favor the intermediate **6b**.

Finally, the case for using a highly hindered base such as 2,6-di-*tert*-butyl-4-methylpyridine[11] (12) when preparing reactive triflates is strengthened by the present study. Compound 12 does not react with triflic anhydride. When salts such as 3 cannot be formed, reactions such as those described here do not take place.

Acknowledgment. We appreciate the helpful suggestions of Professor A. H. Andrist and the financial support of The Standard Oil Company of Ohio.

Registry No. 1, 85371-04-6; 2, 85371-05-7; 7, 85371-06-8; 8, 85371-07-9; 2,6-lutidine, 108-48-5; triflic anhydride, 358-23-6; *s*-collidine, 108-75-8.

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[9] Characterizing data for compound 7: ^{1}H NMR (CDCl$_3$) δ 6.92 (s, H-3, H-5), 5.26, 5.05 (CH$_2$, J = 12.7 Hz), 2.42 (s, CH$_3$), 2.22 (s, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 158.46 (C$_6$), 152.98 (C$_2$), 148.69 (C$_4$), 124.32 (C$_5$), 123.14 (q, CF$_3$, $^1J_{CF}$ = 338.32 Hz), 120.32 (C$_3$), 70.42 (CH$_2$), 24.09 (CH$_3$), 20.92 (CH$_3$) (off-resonance decoupling produced the expected multiplicity for each signal); mass spectrum (CI, methane), m/z (rel intensity) 254 (31), 136 (11), 121 (46), 120 (100). Compound 7 was homogeneous by TLC and VPC but, like compound 1, decomposed upon standing. Characterizing data for compound 8: bp 173–175 °C; ^{1}H NMR (CDCl$_3$) δ 6.81 (s, H-3, H-5), 3.21 (q, CH$_2$, $^3J_{HF}$ = 10.6 Hz), 2.46 (s, CH$_3$(2)); ^{13}C NMR (CDCl$_3$) δ 158.35 (C$_2$, C$_6$), 139.25 (C$_4$), 125.33 (q, CF$_3$, $^1J_{CF}$ = 276.81 Hz), 121.65 (C$_3$, C$_5$), 39.60 (q, CH$_2$, $^2J_{CF}$ = 30.11 Hz), 24.40 (CH$_3$(2)) (off-resonance decoupling produced the expected multiplicity for each signal); mass spectrum (CI, methane), m/z (rel intensity) 230 (3), 218 (15), 190 (100), 170 (42). Compound 8 was homogeneous by TLC and VPC. Anal. Calcd for $C_9H_{10}F_3N$: C, 57.14; H, 5.34; N, 7.40. Found: C, 56.99; H, 5.30; N, 7.49.

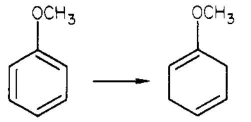
[10] This reaction appears to be an example of a [2,3] sigmatropic rearrangement: Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, West Germany, 1971; p 130.

[11] Anderson, A. G.; Stang, P. J. *J. Org. Chem.* **1976**, *41*, 3034; *Org. Synth.* **1981**, *60*, 34.

Birch Reductions of Methoxyaromatics in Aqueous Solution

Summary: A Birch-like electroreduction of methoxyaromatics in aqueous solutions was achieved, probably through the intermediacy of a tetrabutylammonium amalgam.

Sir: The Birch reduction[1] using an alkali metal in ammonia has often been applied to methoxyaromatics. As shown for anisole, the dihydroaromatic products are



1 4

formed regioselectively and many of these products have been found to be useful in the synthesis of complex molecules.[2] Reduction of simple aromatics has also been achieved by electrochemically generating lithium metal in an amine solvent[3] or in HMPA.[4] Benzene and toluene have also been cathodically reduced in diglyme.[5] In the present study we set out to develop an electrochemical alternative to the tedious, somewhat dangerous alkali metal, ammonia procedure. Ultimately, it should be possible to develop a procedure that is as effective and less expensive by using electricity in place of the alkali metal and an aqueous electrolyte in place of ammonia. In this communication we report that cathodic reduction using

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[1] Birch, A. J.; Rao, G. S. *Adv. Org. Chem.* **1972**, *8*, 1–65.

[2] Dryden, H. L., Jr. "Organic Reactions in Steroid Chemistry"; Fried, J., Edwards, J. A., Eds.; Van Norstrand Reinhold: New York, 1972; Vol. 1, pp 1–60.

[3] Benkeser, R. A.; Kaiser, E. M.; Lambert, R. F. *J. Am. Chem. Soc.* **1964**, *86*, 5272. Benkeser, R. A.; Kaiser, E. M. *Ibid.* **1963**, *85*, 2858.

[4] Sternberg, H. W.; Markby, R. E.; Wender, I.; Mohilner, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 4191; *J. Electrochem. Soc.* **1966**, *113*, 1060.

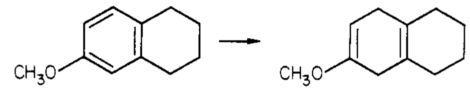
[5] Misono, A.; Osa, T.; Yamagishi, T.; Kodama, T. *J. Electrochem. Soc.* **1968**, *115*, 266.

Table I. Effect of the Electrolyte Concentration on the Current Yields (T = 60 °C)

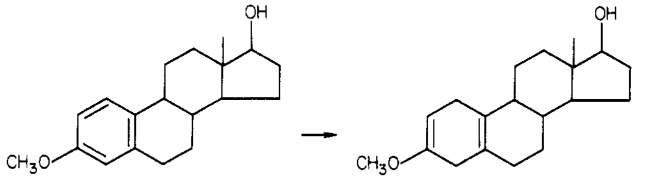
TBAOH, M	current yields, % 4	5	6
0.39	36		
0.77	50	24	2
1.54	55	40	18

a concentrated aqueous solution of tetrabutylammonium hydroxide (TBAOH) gives satisfactory yields of Birch products from methoxyaromatics, including a steroid. These conditions have previously been used only for reduction of benzene and more easily reduced aromatics.[6] We also report a mechanistic observation which suggests that tetraalkylammonium amalgams are involved in the reaction sequence.

We have investigated the electroreduction of the methoxyaromatics **1**, **2**, and **3**, which, in principle, are more difficult to reduce than benzene. Constant-current electrolysis was performed by using aqueous TBAOH, a mercury pool cathode (3.5–6 cm diameter), stainless steel anode, and an undivided cell. The amount of substrate used was 0.3–7 g; the volume was 15–100 mL. The reaction mixture consisted of two phases, one of the aqueous TBAOH and one of the aromatic substrate. **1** and **2** are liquids and **3**, even though a solid, becomes an oil when in contact with the aqueous layer. The reaction mixture was magnetically stirred, and the products obtained were identified as the dihydroderivatives **4**,[7] **5**,[8] and **6**.[9]



2 **5**



3 **6**

The buildup of product was followed by using NMR with 1,1,2,2-tetrachloroethane as an internal standard. It was possible to run electrolyses to completion, and the isolated product yield was typically 80% for **4** and **5** and 95% for **6**. These are similar to the yields reported[7-9] for the corresponding Birch reductions. The current yields depended strongly on the electrolyte concentration and the temperature. They increased with increasing electrolyte concentration, and results are shown in Table I. They also increased with increasing temperature, reaching a plateau at 60 °C, and representative results for **1** are shown in Table II. The amount of product formed when 0.77 M electrolyte was used at 25 °C from both **2** and **3** was negligible, and the maximum current yields were obtained with 1.54 M TBAOH at 60–70 °C. Varying the current density in the range of 29–86 mA cm^{-2} had no effect on the reaction.

Table II. Effect of Temperature on the Current Yield of 4 (0.77 M TBAOH)

T, °C	current yield, %
25	8
45	35
60	50
80	45
90	45

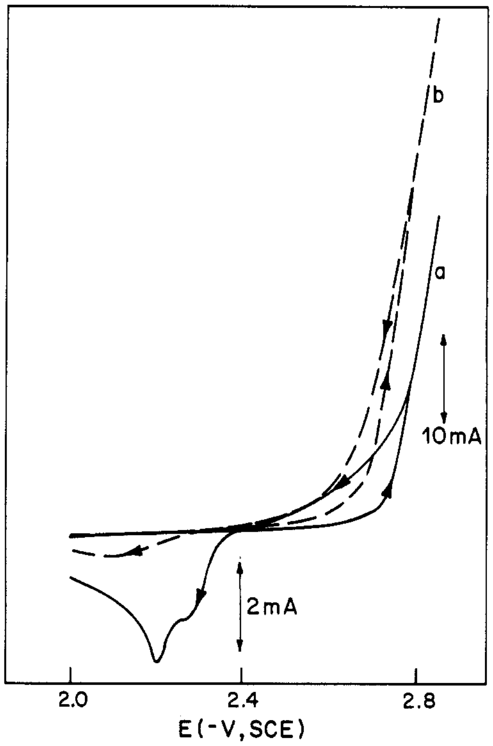


Figure 1. Cyclic voltammograms at 5 V s^{-1}. Data collected digitally and plotted with a scale change at the end of the first half-cycle (from 10 mA/division to 2mA/division): (a) 1 M TBAOH in H_2O; (b) 5 mL of (a) + 15 μL of benzene.

Current–potential measurements at conditions identical with the optimal conditions for preparative electrolyses are extremely difficult. However, reproducible and interpretable results were obtained by using an aqueous 1 M TBAOH solution at 25 °C. Benzene was used as the aromtic substrate since under these particular conditions it reduces with higher current yield than **1**, **2**, and **3**. Polarographic measurements and cyclic voltammetry on a HMDE were impossible due to the low surface tension of mercury under the experimental conditions, and measurements were performed by using a small mercury pool (0.4 cm^2). Steady-state voltammograms (2 mV s^{-1}) showed that benzene does not have a reduction wave up to −2.85 V (SCE),[10] thus indicating that it is not directly reduced in the potential region under investigation. Cyclic voltammograms using the electrolyte solution with and without benzene revealed more interesting information. At a scan rate of 5 V s^{-1} the electrolyte solution showed an oxidation peak, due to a product formed on the cathodic half-cycle (Figure 1a). Addition of benzene to the solution caused the anodic peak to disappear (Figure 1b). On the basis of reports on the reduction of the tetramethylammonium[11] and dimethylpyrrolidinium[12] cations in nonaqueous media, the cathodic product may be a tetrabutylammonium

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(6) Coleman, J. P.; Wagenknecht, J. H. *J. Electrochem. Soc.* **1981**, *128*, 322.

(7) Birch, A. J.; Chamberlain, K. B. *Org. Synth.* **1977**, *57*, 107.

(8) Wilds, A. L.; Nelson, N. A. *J. Am. Chem. Soc.* **1953**, *75*, 5360.

(9) Pelc, B. *Collect. Czech. Chem. Commun.* **1962**, *278* 2706.

(10) The choice of a reference electrode, which would be stable in the base and the high negative potentials, was tedious. A silver wire dipping in the background solution was found suitable, and its potential measured vs. SCE was found to be +3 mV.

(11) Littlehailes, J. D.; Woodhall, B. J. *Discuss Faraday Soc.* **1968**, *45*, 187.

(12) Miller, E. K.; Nanjundiah, C. *J. Electroanal. Chem. Interfacial Electrochem.*, in press.

amalgam. We propose that the electrolytic process forms an amalgam, which is consumed by reducing benzene.

$$\mathrm{TBA^+ + e + Hg \rightarrow TBA(Hg)_n}$$

$$\mathrm{Ar + TBA(Hg)_n \rightarrow Ar^{-\cdot} + TBA^+ + Hg}$$

$$\mathrm{Ar^{-\cdot} \dashrightarrow ArH_2}$$

Thus, the electrolyte plays a catalytic role. TBAOH seems to serve a further important purpose by providing an aqueous medium with a high hydrogen overvoltage. UV studies indicate that the electrolyte also increases the solubility of the organic substrates in the aqueous layer by acting as a phase-transfer agent for the aqueous and organic phases that constitute the reaction mixture.

To summarize, we have shown that electrochemical reduction of methoxyaromatics, including steroids, is possible. The products in high chemical yield are the corresponding 1,4-dihydro derivatives. We have presented evidence that the reaction is an indirect electron transfer, possibly involving a tetrabutylammonium amalgam as an intermediate.

Acknowledgement is made to the National Science Foundation and the Research Corporation for funding this work.

Registry No. 1, 100-66-3; 2, 1730-48-9; 3, 1035-77-4; 4, 2886-59-1; 5, 3469-31-6; 6, 1091-93-6.

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Catalytic Synthesis of Oxalate Esters

Summary: A new catalyst system, palladium(II) acetate, cobalt(II) acetate, triphenylphosphine, and 1,4-benzoquinone, produces oxalate esters in high selectivity from carbon monoxide, oxygen, and alcohol. Up to 140 mol of dimethyl oxalate is obtained per mole of palladium while only traces of dimethyl carbonate or methyl formate are formed.

Sir: The oxidative coupling of carbon monoxide in the presence of alcohol to yield oxalate esters has been known for several years (eq 1).[1] Palladium is the metal of choice

$$\mathrm{2CO + 2ROH + 0.5O_2 \rightarrow ROC(O)C(O)OR + H_2O} \quad (1)$$

for this conversion, and systems both stoichiometric[2] and catalytic[3,4] in palladium are known. While the stoichiometric reaction produces oxalates in good yield, most of the catalytic conversions suffer from the simultaneous formation of formate and carbonate esters. An exception is the related heterogeneous palladium-catalyzed conversion of nitrite esters to oxalate esters reported by workers at Ube Industries.[5] Although oxalic acid is now produced on a moderate scale, oxalate esters are primarily of industrial interest as intermediates in the syngas-based route to ethylene glycol (eq 2).[6] This communication describes

$$\mathrm{ROC(O)C(O)OR + 4H_2 \rightarrow HOCH_2CH_2OH + 2ROH} \quad (2)$$

a highly selective catalyst system for the formation of oxalate esters from carbon monoxide, alcohol, and oxygen.

The high-yield stoichiometric conversion of carbon monoxide, methanol, and palladium(II) to dimethyl oxalate has recently been reported.[2] Rivetti and Romano have reported that above 50 °C and under moderate carbon monoxide pressure (300–750 psi), bis(triphenylphosphine)palladium(II) acetate in methanol cleanly produces dimethyl oxalate and acetic acid while being reduced to a mixture of palladium(0) carbonylphosphines. Below 50 °C no reduction occurs, but an intermediate methoxycarbonyl addition product can be isolated (eq 3).

$$\mathrm{(Ph_3P)_2Pd(OAc)_2 + CO + MeOH \rightarrow (Ph_3P)_2Pd(OAc)[C(O)OMe] + HOAc} \quad (3)$$

The effect of other phosphines, carbon monoxide pressure, and base on the rate and selectivity has been reported for this conversion.[7]

For a system to be catalytic in palladium, some other stoichiometric oxidant must be present. Quinones are well-known oxidants capable of oxidizing palladium(0) to palladium(II). However, in conjunction with palladium(II) chloride as catalyst, Fenton and Steinwand have reported very low yields of diethyl oxalate when benzoquinone was used as the stoichiometric oxidant.[1] In contrast, in the present work it has been found that high yields of oxalate esters can be obtained with catalytic amounts of bis(triphenylphosphine)palladium(II) acetate. With 0.5–2 mol% of catalyst at 60–80 °C under 1000 psi of carbon monoxide, yields of 60–95% on the basis of 1,4-benzoquinone are obtained.[8] The reaction time and temperature can be reduced if 10–25 equiv (based on palladium) of acetic acid are included.

Although this reaction is clean and highly selective, it is not without problems. Little or no catalysis is seen in the absence of triphenylphosphine, which is removed from the reaction solution by the known Michael addition to benzoquinone.[9] Furthermore, the phosphine–quinone adduct also undergoes Michael addition to benzoquinone to yield an insoluble polymer. Thus, oxalate yields can be variable, depending on the extent of these unrelated side reactions, and this system is unlikely to find any commercial application.

The preferred stoichiometric oxidant for any large-scale application of the oxalate synthesis is oxygen. A number of systems have been described, primarily in the patent literature, that utilize oxygen for the catalytic synthesis of oxalate esters from carbon monoxide.[4] Generally, these systems employ a second metal cocatalyst that in its higher oxidation state will oxidize palladium(0) to palladium(II) and that will be returned to the higher oxidation state by

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(1) (a) Fenton, D. M.; Steinwand, P. J. U.S. Patent 3 393 136, 1968. (b) Fenton, D. M.; Steinwand, P. J. *J. Org. Chem.* **1974**, *39*, 701.

(2) Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1978**, *154*, 323.

(3) (a) Zehner, L. R.; Sauer, R. W.; Heffron, J. J. U.S. Patent 4 005 128, 1977. (b) Nishimura, K.; Uchiumi, S.; Fujii, K.; Nishihira, K.; Yamashita, M.; Itatani, H. *Ibid.* 4 229 589, 1981. (c) Nishimura, K.; Fujii, K.; Nishihira, K.; Matsuda, M.; Uchiumi, S. *Ibid.* 4 229 591, 1981.

(4) (a) Yamasaki, T.; Eguchi, M.; Uchiumi, S.; Iwayama, A.; Takahashi, M.; Kurahashi, M. U.S. Patent 3 994 960, 1976. (b) Zehner, L. R. *Ibid.* 4 005 129, 1977. (c) Yamasaki, T.; Egushi, M.; Uchiumi, S.; Nishihiro, K.; Yamashita, M.; Itatoni, H. *Ibid.* 4 138 587, 1979.

(5) Tahara, S.; Fujii, K.; Nishihira, K.; Matsuda, M.; Mizutare, K. European Patent Application 0 046 983, 1982.

(6) Sherwin, M. B. *Hydrocarbon Process.* 1981, *60*, 79.

(7) Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1979**, *174*, 221.

(8) A typical procedure is as follows: A stainless steel microreactor was charged with $Pd(OAc)_2$ (0.03 mmol), Ph_3P (0.09 mmol), 1,4-benzoquinone (3.0 mmol), diglyme (1.6 mmol), methanol (31 mmol), and carbon monoxide (1000 psi). After being heated at 65 °C with gentle shaking for 1 h, the reactor was cooled, pressure was released, and the contents were analyzed by gas chromatography using diglyme as an internal standard. Products formed were dimethyl oxalate (2.5 mmol, 83%), dimethyl carbonate (0.02 mmol, 0.7%), and hydroquinone.

(9) Ramirez, F.; Dershowitz, S. *J. Am. Chem. Soc.* **1956**, *78*, 5614.

0022-3263/83/1948-1779$01.50/0