(t, 3 H, $J = 7.0$ Hz). Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 85.10; H, 5.18.

5-(Hydroxymethyl)benzo[*a*]pyrene (6c). As described for the synthesis of **6a**, 0.19 g (0.59 mmol) of **5c** was allowed to react with an ethereal suspension of LAH. Workup provided 0.17 g (100% yield) of light yellow solid, mp 196–199 °C. An analytical sample, mp 203–204.5 °C, was obtained by recrystallization from benzene: TLC R_f 0.21 (10% ethyl acetate in toluene); IR (KBr) 3400–3050 cm^{-1} (COH); ^{13}C NMR (Me$_2$SO-d_6) 137.34, 130.87, 129.35, 128.46, 127.86, 127.73, 127.62, 127.28, 126.60, 125.59, 125.31, 124.93, 123.32, 123.19, 122.56, 121.23, 61.68. ^{1}H NMR (Me$_2$SO-d_6) δ 9.09–7.23 (m, 11 H), 5.52 (s, 1 H), 5.14 (s, 2 H). Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.09; H, 5.19.

5-(Chloromethyl)benzo[*a*]pyrene (7c). As described for the synthesis of **7a**, 47 mg (.17 mmol) of **6c**, in 5 mL of dry benzene, was allowed to react with 47 mg (0.39 mmol) of $SOCl_2$. Workup afforded 48 mg (100% yield) of bright yellow solid, mp 182–184 °C dec. An analytical sample, mp 184–185 °C dec, was obtained by recrystallization from benzene: TLC R_f 0.45 (30% cyclohexane in benzene), 0.77 (10% ethyl acetate in toluene). Anal. Calcd for $C_{21}H_{13}Cl$: C, 83.83; H, 4.36. Found: C, 83.68; H, 4.61. MS, *m/e* (relative intensity) 302 (M$^+$ + 2, 19.83), 301 (M$^+$ + 1, 13.17), 300 (M$^+$, 57.08), 265 (100).

Ethyl Benz[*a*]anthracen-12-ylacetate (3d). As described for the synthesis of **3c** 0.520 g (1.95 mmol) of 12-cyanomethylbenz[*a*]anthracene[24] was allowed to react with a solution of KOH (0.88g) in ethylene glycol (70 mL) and water (11 mL). After workup and subsequent hydrolysis of the collected amide, 0.36 g of carboxylic acid was obtained. Esterification of the crude acid was accomplished as described for the synthesis of **3c**. After workup, a brown oil was obtained. Purification was possible by passing the sample through an MPLC system, using an analytical column (0.9 × 100 cm) and using 10% hexanes in toluene as elutant. After the proper fractions were collected and the solvent evaporated, 0.30 g (58% yield over two steps) of light yellow oil was obtained: TLC R_f 0.57 (10% ethyl acetate in toluene); IR (neat) 1725 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.63–7.35 (m, 11 H), 4.84 (s, 2 H), 4.35 (q, 2 H, $J = 7.1$ Hz), 1.42 (t, 3 H, $J = 7.1$ Hz); ^{13}C NMR (CDCl$_3$) δ 172.29, 133.62, 132.43, 131.34, 131.00, 130.00, 128.28, 128.17, 127.99, 127.59, 127.00, 126.69, 126.44, 126.21, 125.23, 125.10, 124.11, 60.92, 38.94, 14.02. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.16, H, 5.83.

Ethyl Benzo[*a*]pyrene-11-carboxylate (5d). A solution of 0.14 g (0.44 mmol) of **4d** in 3 mL of dry benzene was added dropwise to a mixture of 81 mg (3.37 mmol) of NaH, 0.21 g (2.83 mmol) of ethyl formate, and one drop of dry ethanol in 3 mL of dry benzene. The resulting suspension was allowed to stir at room temperature until the bubbling ceased (18 h). The residual starting material detected by TLC was allowed to react by warming the mixture to ~40 °C and stirring at that temperature for 6 h. Workup as described for previous formylations provided 0.16 g of brown oil that was cyclized by allowing it to react with 15 mL of 5% MSA in CH_2Cl_2 as described for the synthesis of **7a**. Workup gave a brown oil that was purified by means of a silica gel column (2 × 8 in) using 10% hexanes in toluene as the eluant, providing 70 mg (59% yield over two steps) of yellow solid, mp 122–125 °C. An analytical sample, mp 128–130 °C, was obtained by recrystallization from 95% ethanol: TLC R_f 0.51 (toluene); IR (Nujol) 1703 cm^{-1} (C=O); ^{1}H NMR δ 8.71–7.85 (m, 11 H), 4.57 (q, 2 H, $J = 7.1$ Hz), 1.38 (t, 3 H, $J = 7.1$ Hz). Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 84.93; H, 5.23.

11-(Hydroxymethyl)benzo[*a*]pyrene (6d). As described for the synthesis of **6a**, 40 mg (0.12 mmol) of **5d** was allowed to react with an ethereal suspension of LAH. Workup provided 35 mg (100% yield) of bright yellow crystals, mp 191–194 °C. An analytical sample, mp 193–195 °C, was obtained by recrystallization from benzene: TLC R_f 0.48 (25% ethyl acetate in toluene); ^{1}H NMR (Me$_2$SO-d_6) δ 9.47–8.03 (m, 11 H), 5.85 (t, 1 H, $J = 5.5$ Hz), 5.34 (d, 2 H, $J = 5.5$ Hz); ^{13}C NMR (Me$_2$SO-d_6) δ 137.91, 131.73, 131.01, 130.32, 129.69, 129.44, 129.44, 128.85, 128.38, 127.91, 127.28, 126.50, 126.01, 125.82, 125.66, 125.27, 124.81, 65.27. Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.10; H, 5.13.

11-(Chloromethyl)benzo[*a*]pyrene (7d). As described for the synthesis of **7a**, 25 mg (0.09 mmol) of **6d** in 2.5 mL of dry benzene was allowed to react with 25 mg (0.21 mmol) of $SOCl_2$. Workup afforded 20 mg (75% yield) of bright yellow solid, mp 180–182 °C dec. An analytical sample, mp 183–185 °C dec, was obtained by recrystallization from benzene: TLC R_f 0.47 (30% cyclohexane in benzene), 0.74 (10% ethyl acetate in toluene). Anal. Calcd for $C_{21}H_{13}Cl$: C, 83.86; H, 4.36. Found: C, 83.60; H, 4.36. MS, *m/e* (relative intensity) 302 (M$^+$ + 2, 29.04), 301 (M$^+$ + 1, 19.04), 300 (M$^+$, 84.66), 265 (95.30).

Registry No. **3a**, 67194-44-9; **3b**, 67194-43-8; **3c**, 94500-47-7; **3d**, 94500-50-2; **4a**, 94500-41-1; **4b**, 94500-45-5; **4c**, 94500-48-8; **4d**, 94500-52-4; **5a**, 94500-42-2; **5b**, 94500-55-7; **5c**, 94500-49-9; **5d**, 94500-51-3; **6a**, 94500-43-3; **6b**, 86073-01-0; **6c**, 29852-45-7; **6d**, 94500-53-5; **7a**, 94500-44-4; **7b**, 94500-46-6; **7c**, 29852-26-4; **7d**, 94500-54-6; i, 68723-48-8; ii, 67411-86-3; 5-(cyanomethyl)chrysene, 85083-62-1; 12-(cyanomethyl)benz[*a*]anthracene, 78533-31-0; ethyl formate, 109-94-4.

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Selective Cathodic Birch Reductions

Essie Kariv-Miller,* Karl E. Swenson, Gaye K. Lehman, and Romano Andruzzi

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received May 29, 1984

The electroreduction of some difficult to reduce substrates was investigated by using aqueous tetrahydrofuran, tetrabutylammonium (TBA$^+$) electrolyte, and mercury cathodes. The reduction products formed in high yields and the current efficiencies were good. Benzene, anisole, 1,2,3,4-tetrahydro-6-methoxynaphthalene and β-estradiol 3-methyl ether reactions were carried out with constant current at room temperature and were found to be more selective than the corresponding alkali metal–ammonia reductions. Selective reduction of the carbonyl function of estrone methyl ether was achieved while the aromatic ring remained intact. The aqueous THF medium did not affect base-sensitive molecules and a reduction product from 17-α-ethynylestradiol 3-methyl ether could be obtained without loss of the ethynyl group. Most of the compounds studied did not exhibit polarographic waves. A reduction product of TBA$^+$ was observed by cyclic voltammetry and it is proposed that TBA "amalgam" may participate as a mediator in the reduction of the organic substrates.

In spite of of the recognized utility of Birch reductions,[1-3] the techniques have remained basically unchanged since the early investigations. Alkali-metal reductants, liquid ammonia or simple amine solvents, and some proton source

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Table I. Electroreduction of Benzene (0.25 M) Using TBA Electrolytes in Various Solvents (16 mA cm^{-2}, 22–25 °C)

composition of the medium	current efficiency for 1,4-dihydrobenzene (%)
1.5 M (TBA)OH in H_2O (60 °C)	70
(TBA)Br (0.2–1.5 M) in H_2O	0[b]
0.5 M (TBA)BF_4 in DMF	0
0.5 M (TBA)BF_4 in DMF + H_2O (4.4 M)	25
0.5 M (TBA)BF_4 in diglyme	0
0.5 M (TBA)BF_4 in diglyme + H_2O (4.4 M)	93[a]
0.5 M (TBA)BF_4 in THF	0
0.5 M (TBA)BF_4 in THF in H_2O (4.4 M)	97[a]

[a] Material balance for complete conversion was 70% (see Experimental Section). [b] Gas evolution visible.

are still generally used as the materials. Recently, however, it has been shown that reactions similar to those of the alkali metal/NH_3 type can be performed electrochemically in strongly basic, aqueous media containing tetraalkylammonium electrolytes. Specifically, aromatic compounds including benzene[4,5] and steroids[5] like β-estradiol 3-methyl ether were reduced to dihydro aromatic products under these conditions. Although some of the reactions were rather inefficient in terms of the quantity of electricity required, the chemical yields were quite high and were equal to or greater than the yields obtained by using alkali-metal–ammonia systems.

The new method involves the cathodic generation of intermediate reductants, which have been proposed to be tetraalkylammonium amalgams. These materials are unique[6] and provide powerful reducing agents that are more reactive than alkali-metal amalgams. They may allow reduction of otherwise inert functional groups.

In the present study, the goals were (1) to develop a solvent–electrolyte system which would not involve strongly alkaline solutions or require elevated temperatures[4,5] and which would increase the current efficiency of the aromatic reductions; (2) to widen the scope of functional groups that can be electrochemically reduced and (3) to look for functional group selectivity in the reduction of molecules containing more than one reducible group.

Results and Discussion

Improved Reduction of Aromatic Compounds. A previous result[5] suggested that mixed aqueous, organic solvents would be as good as the originally used aqueous tetrabutylammonium hydroxide (TBA)OH at 60–90 °C and that such mixed solvents might be useful at lower temperatures. In the present study benzene was reduced by using water, DMF, THF, or diglyme as solvents. In each case a tetrabutylammonium salt was the electrolyte, mercury was the cathode material, and some results are presented in Table I. Electrolysis in water with tetrabutylammonium bromide caused gas evolution and no organic product was formed. It is likely that hydrogen evolution which did not compete with the organic reduction in the basic (TBA)OH predominates in this neutral medium. Electrolysis in the dry solvents was also unsuccessful. Using mixed aqueous, organic solvents, reduction did occur. For example, the use of THF or diglyme each containing 4.4 M water gave high product yields and current efficiencies at room temperature. The ratio [product/charge-transferred] was constant throughout, and the reactions could be taken to completion. Similarly, high yields were obtained with solvents containing 3.9–16.7 M water. Higher or lower water concentrations resulted in lower current efficiencies. This is all quite reasonable since some proton source is required, but above 16.7 M water, the benzene starts to become insoluble and, instead water is reduced to hydrogen.

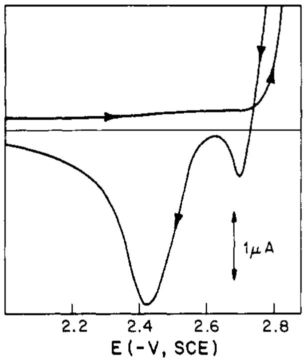

Figure 1. Cyclic voltammogram, $\nu = 0.2$ V s^{-1}, reversal $E = -3.2$ V, 0.5 M (TBA)BF_4 in THF with or without benzene (0.25 M).

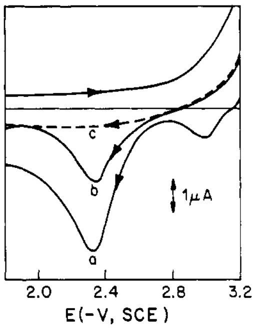

Figure 2. Cyclic voltammograms, $\nu = 10$ V s^{-1}, reversal $E = -3.2$ V: (a) 0.5 M (TBA)BF_4 in THF; (b) a + H_2O (1.1 M); (c) b + benzene (0.25 M).

In a typical experiment, the anolyte consisted of 5 mL of 0.5 M (TBA)BF_4 in the mixed solvent. The catholyte was 15 mL of the same solution containing 0.317 g (4.06 mmol) of benzene. GC analysis of samples during electrolysis was made with toluene as an internal standard. The relative molar amounts of benzene and dihydrobenzene showed current efficiency of 93% for diglyme and 97% for THF. The final material yield of 1,4-dihydrobenzene was 70%. Since no other product could be detected, it is likely that both benzene and dihydrobenzene were lost from the cell during the experiment.

The preparative results were well correlated with voltammetric measurements. As shown in Figure 1 the intermediate which forms on the mercury surface at very negative potentials can be detected by using cyclic voltammetry. Thus, using (TBA)BF_4 in THF there is, on the reverse half-cycle, an anodic peak due to the oxidation of the cathodically formed intermediate. Addition of benzene to this electrolyte solution causes no change in the voltammogram. In the presence of water no oxidation peak can be detected at 0.2 V s^{-1}. It can be observed at faster

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[4] Coleman, J. P.; Wagenknecht, J. H. *J. Electrochem. Soc.* **1981**, *128*, 322.

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Table II. Electroreduction of Methoxy Aromatics (16 mA cm^{-2})

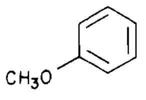
reactant	aqueous (TBA)OH[a] current efficiency (%)	(TBA)BF_4·THF[b] current efficiency (%)
1	55	78
2	40	65
3	18	55
4	0	55

[a] 1.5 M (TBA)OH, 60 °C. [b] 4.4 M H_2O in THF; 0.25 M (TBA)BF_4, 22–25 °C.

scan rates and a cyclic voltammogram at 10 V s^{-1} is shown in Figure 2. Addition of both benzene and water causes the oxidation peak to disappear even when a sweep rate of 10 V s^{-1} is used. All this can be explained if benzene accepts an electron from the "amalgam", and water drives the reaction by protonating the benzene anion radical.

It is important to point out that all the aromatic compounds studied here gave no cathodic voltammetric peak. All were reduced by electrolyzing in the "background" potential region where the presumed intermediate "amalgam" is formed and could mediate the reduction.

Aqueous THF, the solvent of choice for benzene reduction, is also suitable for reduction of methoxy aromatics. The corresponding 1,4-dihydro products are formed and the results for the test compounds **1**–**4** are presented in Table II. The yields of the isolated products were 70% for the 1,4-dihydro products of **1** and **2** and 85% for the products of **3** and **4**. It can be seen that the THF–H_2O solvent gives superior yields without elevated temperatures. The effect is especially drastic with the steroids **3** and **4**. Comparing these results with alkali metal–ammonia reduction, β-estradiol 3-methyl ether (**3**), for example, gives similar high yields using Li, K, and Na.[7] So the technical trade-off is electrochemistry in a more convenient, cheaper solvent or the use of a traditional chemical method.



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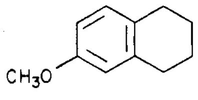

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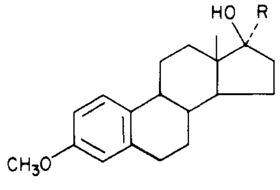


3, R = H
4, R = C_2H_5

Competitive Reductions of Aromatics, Ketones, Alkynes, and Alkenes. To date, little information exists about the reduction of functional groups using these conditions. In addition there is no information about functional group selectivity. In the present study it is demonstrated for the first time that an alkyne or an alkene can be reduced by using this method. The kinetic competition between a ketone and an aromatic, between an ether cleavage and hydrogenation, and between an alkyne and an alkene were also probed.

It is first noted that with one exception all the reactions (performed using controlled current) take place at the same potential. This can be rationalized by assuming that the formation of the intermediate "amalgam" is the rate-limiting process which determines the electrode potential. Only in the case of ketones, which appear somewhat easier to reduce, this is not true. Ketones give a voltammetric peak on the edge of background and the potential during preparative electrolysis is somewhat less negative.

Table III. Reduction of Estrone 3-Methyl Ether (5): 0.5 M (TBA)BF_4 in THF–H_2O (4.4 M), 22–25 °C

Q (% of 2 F mol^{-1})	current density, mA cm^{-2}	composition[a] of reaction mixture, % 3	6	5
100	16	76	8	16
300	16	14	86	0
100	8	>95	trace	0
300	8	8	92	0

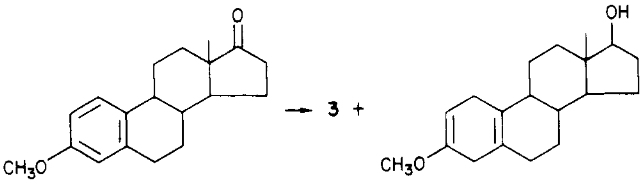
[a] Determined by NMR; the yield of the isolated crude product was >90%.

Table IV. Reduction of Benzyl Methyl Ether (7): 0.25 M (TBA)BF_4 in THF–H_2O (4.4 M), 16 mA cm^{-2}

Q (% of 2 F mol^{-1})	ratio of products in reaction mixture,[a] % 8	9	7
40	36	0	64
70	69	0	31
100	92	3	5
120	83	17	0
150	30	70	0
205	7	93	0

[a] GC relative ratios. The yield of the crude product was 70% (see Experimental Section).

Estrone 3-methyl ether (**5**) presents an interesting substrate for the new method, since, due to its low solubility, it cannot be satisfactorily reduced by the Birch method.[8] The formation of **6** from **5** was observed during electroreduction of **5** by using methylamine and a lithium electrolyte.[9] The current efficient reported was 44%; however, the reaction was not carried to completion. Estrone 3-methyl ether (**5**) presents ketone and methoxy aromatic structures for an intramolecular competition, and it might be expected that the reactions would, indeed, be competitive. An initial run demonstrated that ketone reduction was faster, so a series of experiments was performed in which the number of coulombs passed was varied. A minimum of 2 F mol^{-1} are required for each process. As shown in Table III, with a current of 16 mA cm^{-2}, passage of 2 F mol^{-1} gave mainly reduction to the aromatic alcohol **3**. Further reduction (6 F mol^{-1}) gave the doubly reduced dihydro aromatic alcohol **6**. Complete selectivity could be obtained by using lower current density (Table III). At 8 mA cm^{-2}, only the aromatic alcohol **3** was produced after passage of 2 F mol^{-1}. Further passage of current then hydrogenated the aromatic ring.



5 **6**

Both electron and proton transfer are important in determining these relative rates, and so the interpretation of the increased selectivity with lower current density is difficult. On or near the electrode surface are a variety of reactive species including the "amalgam", water, OH$^-$, radical anions, radicals, and anions. All of these may be intimately involved in determining concentration gradients of interest to the interpretation of relative rates. A useful,

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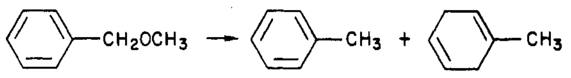
Table V. Reduction of 1-Hexyne: 0.5 M $(TBA)BF_4$ in $THF-H_2O$ (4.4 M), 16 mA cm^{-2}

	composition of reaction mixture,[a] %		
Q (% of 2 F mol^{-1})	1-hexene	hexane	1-hexyne
50	36	0	64
100	79	2	19
140	93	7	0
200	85	15	0

[a] GC relative ratios. The yield of the crude product was 70% (see Experimental Section).

if simplistic, view, however, is that it is kinetically easier to produce a ketyl radical than a cyclohexadienyl radical—each by transfer of one electron and one proton.

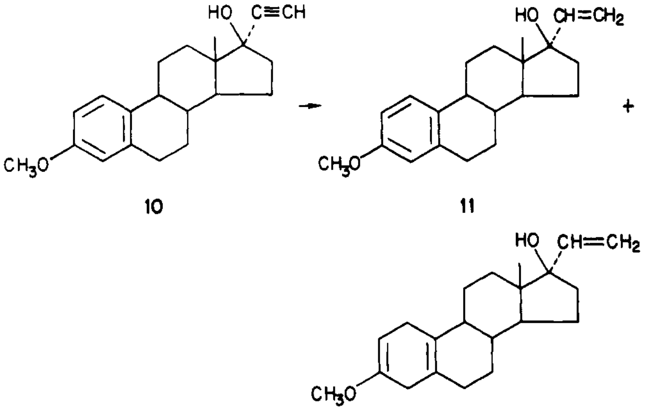
A similar situation, in which the extent of reduction could be controlled by controlling the number of coulombs passed, was encountered with benzyl methyl ether (Table IV). In this example, the cleavage reaction giving toluene and methanol occurs first and toluene can be obtained. Passage of further charge eventually leads to dihydrotoluene.



7 8 9

The reduction of alkynes using these conditions has not been previously reported, but based upon the $Na-NH_3$ standard[1-3] it should be possible. The reduction of 1-hexyne was investigated by using $THF-H_2O$ and $(TBA)BF_4$. Voltammetrically, there was no cathodic peak indicating reduction of 1-hexyne, but the preparative experiment was successful. Data in Table V show that 1-hexene can be cleanly produced if the coulometry is controlled. If more coulombs are passed, then the 1-hexene is slowly converted to hexane. The formation of hexane is to our knowledge the first indication that simple alkenes can be reduced electrochemically.

The reduction of alkynes is of interest in itself and it is important to note that the $THF-H_2O$ conditions are preferred to aqueous (TBA)OH where alkynes may undergo unfavorable rearrangements. An indication of this is in the reduction of steroid **10**. This compound yields only small amounts of **12** when treated with Na or Li/NH_3[8] or electrolysis using (TBA)OH.[5] Instead, it loses the ethynyl group due to the basic conditions and forms **5** which is consequently reduced to **6**. Electrolysis of **10** using the $THF-H_2O$ conditions yields after transfer of 4.4 F mol^{-1} a mixture of 90% **12** and 10% **11**. Our hope was to control the exclusive formation of **11**, but thus far conditions have not been found under which the triple bond/aromatic ring selectivity was high.



10 11 12

In summary, the present study shows that alkynes, alkenes, ketones, and aromatics can be cleanly reduced by using $THF-H_2O$ as the solvent and $(TBA)BF_4$ as the electrolyte. There are also indications of functional group selectivity, i.e., ketones before methoxy aromatics, alkynes before alkenes, benzyl ether cleavage before aromatic hydrogenation.

Experimental Section

General Considerations. Benzene was purchased from Malinckrodt (analytical reagent), methoxybenzene (**1**) from (Baker grade), and *n*-hexane, 1-hexyne, and 1-hexene from Aldrich; the steroids **3**, **5**, **10** (Sigma), and **4** (Steraloids) were used as purchased. 1,2,3,4-Tetrahydro-6-methoxynaphthalene (**2**) (Aldrich, technical) was distilled before use. Tetrabutylammonium tetrafluoroborate ($(TBA)BF_4$)[10] and benzyl methoxy ether[11] were prepared by known procedures. The solvents for preparative electrolyses were THF (Malinckrodt, analytical reagent, or MCB), Omnisolv, DMF (Fisher Centrified ACS grade), and diglyme (Aldrich). THF and diglyme were distilled from sodium benzophenone[12] and used immediately. DMF was dried over alumina (MCB, chromatographic grade) distilled in vacuo and stored over 4-Å molecular sieves (MCB).

NMR spectra were recorded on a Varian FT-80 or a Hitachi-Perkin-Elmer R-24B using $CDCl_3$ and tetramethylsilane as an internal standard. IR spectra were determined with a Perkin-Elmer 297 infrared spectrophotometer. Gas chromatography was performed on stainless steel columns (0.125 in.) on a Varian Model 3700 gas chromatograph (flame ionization detector and helium carrier gas) with a Hewlett Packard 3390A recording integrator.

Preparative Electrolyses. Instruments, Cells, and Electrodes. Preparative electrolyses were performed at constant current by using a Hewlett Packard 6266B or a Princeton Applied Research PAR-373 galvanostat and an Acromag Model 212-LX-1 coulometer.

A cylindrical cell, 12-cm high, with a mercury pool cathode (diameter 3.5 cm) at the bottom was used. An Alundum cup (Fisher AN 889) dipping into the cell served as the anode compartment and a 2-cm^2 Pt foil was the anode. We found this set-up satisfactory in spite of the high porosity of the cup which required replenishing the anolyte during long experiments. While trying other arrangements with less porous cups or glass frits, we encountered extensive clogging of the porous materials and high resistance. The reference electrode was a silver wire. It was placed in a fritted tube full with electrolyte solution dipping in the cell 1 mm from the cathode surface. The cell was fitted with a reflux condenser, and a slow flow of nitrogen was passed through the cell during the experiment.

Preparative Electrolyses and Identification of Products. Experiments were carried out at constant current (4–16 mA/cm^2) under nitrogen. Electrolyte solutions of the appropriate composition and substrate were added to the cathode compartment. Usually 1–4 mmol of substrate was dissolved in 15 mL, but amounts up to 18 mmol in 50 mL were used. The anolyte was electrolyte solution only (5–10 mL). The cell was allowed to reach constant temperature (10 min) before electrolysis was started. The potential of the working electrode vs. the silver wire was measured several times during electrolysis. It varied from one experiment to another in the range of −2.5 to −3.3 V but remained rather constant throughout each experiment (within 0.3 V). When the current was disconnected, the potential did not immediatedly decay to its open circuit value. Residual potentials could be measured and persisted for 6–12 h. A black-grey precipitate (TBA amalgam?) was usually visible during the electrolysis and for sometime after disconnecting the current. Upon "decomposition" it liberated metallic mercury. It may be of interest to note that during the electrolysis of **5**, grey precipitate appeared much later than in other cases. Samples (1 mL) were taken out at various

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reaction times and their composition was determined.

The samples of benzene and benzyl methyl ether were directly analyzed by GC using a 13-ft column of 6% OV-17 on 80/100-mesh Chromosorb W-AW and a 6-ft column of 10% Carbowax 20M on 80/100-mesh Chromosorb W-HP, respectively. The samples obtained from 1-hexyne were analyzed similarly with a 20-ft 20% β,β'-oxybis(propionitrile) on 80/100-mesh Chromosorb W-AW-DMCS. The mass balance was determined by calibration with GC standards: toluene for reduction mixtures of benzene; cyclopentanone for reduction mixtures of benzyl methyl ether **7**; and cyclohexane for reduction mixtures of hexyne. It was found to be only 70%. However, no byproducts were detected and the disappearance of substrates and formation of products were proportional to the amount of charge transferred throughout each electrolysis. This indicates that both substrate and product are lost from the catholyte either by evaporation with the nitrogen stream or by migration to the anolyte. No attempt was made to improve the mass balance since the above reactions were examples to prove a principle. The material balances for the reduction of the substrates with higher molecular weight were quantitative. To verify the nature of the products, they were isolated and compared with authentic samples (GC, NMR, IR).

The samples and reaction mixtures of all steroid substrates were worked up by pouring into water and then repeated extractions with ether. The organic fraction was washed with water and dried, and the solvent was removed. The residue was weighed and analyzed to determine composition and yield. The mass balance for these substrates was >90% and the composition of the mixtures was determined by NMR.

A detailed description of the analysis of the resaction mixtures of **1**–**4** has been reported.[5] The reaction mixtures from **5** were analyzed similarly. In this case the disappearance of the carbonyl function was also qualitatively followed by IR.

The final product of the reduction of **10** was **12**; which was identified by comparing its NMR spectrum with the one reported in the literature.[8] Analysis of the reaction mixtures at different reaction times seemed to indicate that the ethynyl function reacts faster than the aromatic ring. After transfer of charge equivalent to 2 F mol^{-1}, 47% of the ethynyls and 16% of the aromatic rings were reduced but 37% of the reactant were still present in the mixture. However, since we were not able to develop selective reduction of the ethynyl or the methoxy benzene functions of **10** only, we did not attempt resolution of the mixtures.

Electrochemical Measurements. Polarography and cyclic voltammetry were performed by using a Princeton Applied Research PAR-173 potentiostat, PAR-175 universal programmer, and a Houston Omnigraphic 2000 x–y recorder. CV's at fast potential scan rates were recorded on a Tektronix 5111 storage oscilloscope. Polarography was performed on a polarographic capillary from which the drops were knocked off every 0.2 s. A hanging mercury drop electrode was prepared[13] and used for cyclic voltammetry. The counterelectrode was a Pt wire and the reference was a SCE.

Acknowledgment. We are grateful to the National Science Foundation and the University of Minnesota Graduate School for support of this work.

Registry No. **1**, 100-66-3; **2**, 1730-48-9; **3**, 1035-77-4; **4**, 17550-03-7; **5**, 1624-62-0; **6**, 1091-93-6; **7**, 538-86-3; **8**, 108-88-3; **9**, 4313-57-9; **10**, 72-33-3; **11**, 6885-48-9; **12**, 4350-64-5; benzene, 71-43-2; 1,4-dihydrobenzene, 628-41-1; 1-hexyne, 693-02-7; 1-hexene, 592-41-6; hexane, 110-54-3.

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A Simple and Mild Esterification Method for Carboxylic Acids Using Mixed Carboxylic–Carbonic Anhydrides

Sunggak Kim,* Jae In Lee, and Youn Chul Kim

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea

Received June 18, 1984

A simple and mild esterification method using mixed carboxylic–carbonic anhydrides has been developed. Simple aliphatic carboxylic esters are prepared in high yields by the reaction of acids with equimolar amounts of chloroformates (2,2,2-trichloroethyl chloroformate is an exception) and triethylamine in the presence of a catalytic amount of 4-(dimethylamino)pyridine. Although aromatic acids give a mixture of the ester, the acid anhydride, and the carbonate under normal conditions utilized in this study, it is found that increasing the amount of 4-(dimethylamino)pyridine drastically decreases the formation of the acid anhydride and the carbonate, affording a satisfactory yield of the ester. This method reaches a limit with sterically hindered acids and the formation of the acid anhydride and the carbonate is favored.

The mixed carboxylic–carbonic anhydrides, reasonably stable and readily available compounds, have been of considerable interest for a long time. Their synthetic usefulness has been demonstrated in peptide synthesis[1] and in the reduction of carboxylic acids into the corresponding alcohols.[2]

The preparation of carboxylic esters by the decomposition of mixed carboxylic–carbonic anhydrides has been extensively studied by Tarbell[3] but the outcome of the mixed anhydride reaction was disappointing as a means for the preparation of esters in several instances.[4] In general, the decomposition of mixed carboxylic–carbonic anhydrides proceeds by two different pathways, yielding two types of products: the ester and the symmetrical acid anhydride and the carbonate (eq 1), although the course

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