Use of Electrochemical Methods as an Alternative to Tin Reagents for the Reduction of Vinyl Halides in Inositol Synthons

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Several vinyl halides previously used in inositol syntheses were subjected to electrochemical reduction. The unreactivity of allylic alcohols or allylic ethers at the applied potentials allowed the selective reduction of vinyl halides to olefins. Electrochemical methods provide for selective reduction of vinyl iodides over vinyl bromides, with better yields than analogous tin methodology. Cinnamyl ethers were reductively cleaved at −3.2 V (vs $Ag/AgNO_3$) in the presence of alkyl allyl ethers to provide selective deprotection. The electrochemical reduction of vinyl halides in the presence of a vinyloxirane or vinylaziridine is accompanied by the solvolysis of the strained rings. Yields and conditions are reported and compared to those from standard tin-induced dehalogenation.

Introduction

The synthesis of conduritols, inositols, and conduramines from cyclohexdiene-*cis*-diols (**2**), obtained by enzymatic oxidation of halobenzenes with *Escherichia coli* JM109 (pDTG601), has been demonstrated in our laboratories.[1] Of particular importance to the second generation synthesis of these compounds is its overall efficiency and the "green" or environmentally benign nature of the transformations that follow the enzymatic step.[1e]

Electrochemical methods[2] of oxidation and reduction offer a versatile and nonstoichiometric alternative to widely used metal-based reagents. In particular, electrochemical reduction of aryl and vinyl halides has been documented in both mechanistic and synthetic studies.[3] We have already investigated the electrochemical oxidation of the C4−C5 double bond of **2** as an alternative to oxidation by *m*CPBA.[4] For example, in an earlier synthesis of conduritol F, oxidative functionalization at C4−C5 (*m*CPBA; H_3O^+)[4] was followed by reduction of the vinyl halide (nBu_3SnH/AIBN) to the protected conduritol F (**4**),[5] as shown in Scheme 1. This manuscript describes the electrochemical reduction of vinyl halides in various inositol synthons as an alternative to the use of tin reagents.

Results and Discussion

Five inositol intermediates (used in previous studies and that we require in large quantities for our current research on inositol oligomers)[6] were investigated (Table 1, entries 1−5). For each compound, we compared the yields from electrochemical reduction (mercury pool cathode) to those obtained with trialkyltin hydrides.

The starting materials for the halide reductions were produced by means of synthetic techniques optimized in our laboratories during previous ventures into inositol synthesis.[7] The anti epoxide **14** and related compounds

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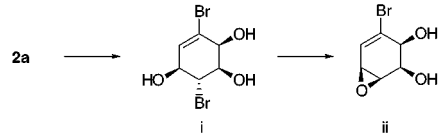
(1) For comprehensive reviews of arene *cis*-diol chemistry see: (a) Brown, S. M.; Hudlicky, T. In *Organic Synthesis: Theory and Applications*; Hudlicky, T., Ed.; JAI Press: Greenwich, CT, 1993; Vol. 2, pp 113−176. (b) Widdowson, D. A.; Ribbons, D. W.; Thomas, S. D. *Janssen Chim. Acta* **1990**, *8*, 3. (c) Carless, H. A. J. *Tetrahedron: Asymmetry* **1992**, *3*, 795. (d) Hudlicky, T.; Reed, J. W. In *Advances in Asymmetric Synthesis*; Hassner, A., Ed.; JAI Press: Greenwich, CT, 1995; p 271. (e) Hudlicky, T. In *Green Chemistry: Designing Chemistry for the Environment*; Anastas, P. T., Williamson, T., Eds.; ACS Symposium Series 626, American Chemical Society: Washington, DC., 1996; Chapter 14. (f) Hudlicky, T.; Thorpe, A. J. *J. Chem. Soc., Chem. Commun.* **1996**, 1993. (g) Hudlicky, T. *Chem. Rev.* **1996**, *96*, 3. (h) Hudlicky, T.; Entwistle, D. A.; Pitzer, K. K.; Thorpe, A. J. *Chem. Rev.* **1996**, *96*, 1195. (i) Grund, A. D. *SIM News* **1995**, *45*, 59. (j) Boyd, D. R. *Nat. Prod. Rep.* **1998**, 309. (j) Hudlicky, T.; Gonzalez, D.; Gibson, D. T. *Aldrichimica Acta* **1999**, in press.

(2) For reviews on electrochemical methods of synthesis, see: (a) Lund, H.; Baizer, M. M. *Organic Electrochemistry: An Introduction and a Guide*; Marcel Dekker: New York, 1991. (b) Volke, J.; Liska, F. In *Electrochemistry in Organic Synthesis*; Springer-Verlag: New York, 1994; pp 1−44, 90. (c) Utley, J. *J. Chem. Soc. Rev.* **1997**, *26*, 157. (d) Saiganesh, R.; Balasubramanian, K. K.; Venkatachalam, C. S. *J. Electroanal. Chem.* **1989**, *262*, 221. For recent applications, see: (e) Rossen, K.; Volante, R. P.; Reider, P. J. *Tetrahedron Lett.* **1997**, *38*, 777. (f) Frey, D. A.; Wu, N.; Moeller, K. D. *Tetrahedron Lett.* **1996**, *37*, 8317. (g) Moeller, K. D. *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1997; Vol. 185, p 50.

(3) (a) Fry, A.; Mitnick, M. A.; Reed, R. G. *J. Org. Chem.* **1970**, *4*, 1232. (b) Bhuvaneswari, N.; Venkatachalam, C. S.; Balasubramanian, K. K. *Tetrahedron Lett.* **1992**, *33*, 1499. (c) Urove, G. A.; Peters, D. G.; Mubarak, M. S. *J. Org. Chem.* **1992**, *57*, 786. (d) Miller, L. L.; Rienkena, E. *J. Org. Chem.* **1969**, *34*, 3359. (e) Fry, A. J.; Mitnick, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 6207.

(4) In preliminary experiments, syn epoxide **ii** was made by the electrochemical generation of bromohydrin **i**; the procedure for the electrochemical generation of **i** was adapted from unpublished results of G. Butora and L. Koroniak. This procedure provides a nice alternative to the synthesis of **ii**, whose protected version has been reported: Carless, H. A. J. *J. Chem. Soc., Chem. Commun.* **1992**, 234.



(5) Hudlicky, T.; Luna, H.; Olivo, H.; Andersen, C.; Nugent, T.; Price, J. D. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2907.

(6) Hudlicky, T.; Abboud, K. A.; Entwistle, D. A.; Fan, R.; Maurya, R.; Thorpe, A. J.; Bolonick, J.; Myers, B. *Synthesis* **1996**, 897.

(7) (a) Hudlicky, T.; Price, J. D.; Olivo, H. F. *Synlett* **1991**, 645. (b) Hudlicky, T.; Price, J. D.; Fan, R.; Tsunoda, T. *J. Am. Chem. Soc.* **1990**, *112*, 9439. (c) Hudlicky, T.; Fan, R.; Tsunoda, T.; Luna, H.; Andersen, C.; Price, J. D. *Isr. J. Chem.* **1991**, *31*, 229. (d) Desjardins, M.; Brammer, L. E., Jr.; Hudlicky, T. *Carbohydr. Res.* **1997**, *304*, 39. (e) Brammer, L. E., Jr.; Hudlicky, T. *Tetrahedron: Asymmetry* **1998**, *9*, 2011.

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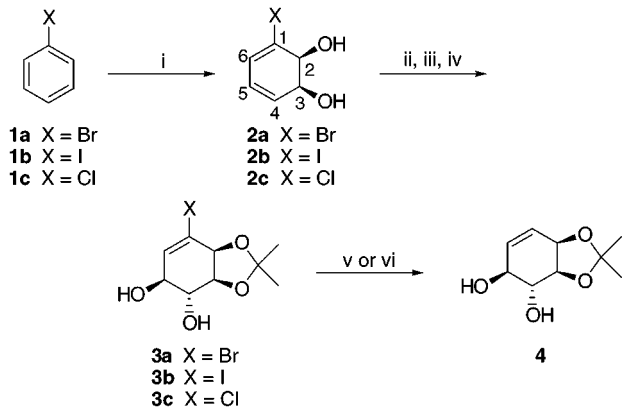
Scheme 1



were produced by means of *m*-CPBA in dichloromethane at 0 °C (Scheme 1, iii). Compound **14** was subjected to treatment with KOH in DME−H_2O to afford protected tetrol **3**, whose absolute stereochemistry corresponds to that of conduritol F. The conduritol C precursors (**5a** and **5b**) were generated by treating cyclohexadiene-*cis*-diol **2**, protected as the acetonide, with 1,3-dibromo-5,5-dimethylhydantoin (DBH) to produce a bromohydrin, whose closure (10% NaOH, DME) afforded the syn epoxide.[4] The epoxide was opened with KOH in DME−H_2O, as previously reported.[7d,e] Osmylation of protected *cis*-diols **2** (OsO_4, NMO, 3:1 acetone−H_2O) afforded conduritol E precursors **7a** and **7b**. The reduction of these compounds (Table 1, entries 1−5) forms the basis of our study.

Cyclic and Linear Sweep Voltammetry. Cyclic and linear sweep measurements were performed with a gold working electrode and a platinum auxiliary electrode, with a Ag/Ag^+ reference electrode (0.5785 V vs normal hydrogen electrode) consisting of a silver wire immersed in a 0.1 M solution of silver nitrate in acetonitrile. The voltammetry of all compounds was hampered by adsorption of material on the working electrode. In general for these compounds, the reduction waves were broad (with $E_p - E_{p/2} > 100$ mV) and exhibited a cathodic shift with increasing sweep rate. Reproducible voltammograms were obtained by polishing the electrode surface between successive sweeps, and by continuous stirring and degassing of the solution. (Specific voltammetric data is provided in the Supporting Information.)

Preparative Electrochemistry. We envisioned electrochemical reduction (controlled potential) as a competitive alternative to more typical methods of halide reduction (e.g., n-Bu_3SnH, $LiAlH_4$, silanes, or Al-amalgam) in these and related systems. Our goal was to optimize the yield of the reduction while keeping the complexity of the electrochemical apparatus to a minimum. (See the Experimental Section for details.) Our investigation began with the protected conduritol precursors in their halogenated form (Table 1, entries 1−5). Optimized electroreduction of the brominated conduritol F precursor (**3a**) at −3.2 V resulted in a 62% yield of the protected product **4**. The yield obtained from n-Bu_3SnH−AIBN for the same precursor was 80%. Similar results were obtained for the other conduritol precursors (entries 2−5): 59% yield with electrochemical reduction of **5a** at −3.0 V compared to 78% reduction with n-Bu_3SnH, 57% electroreduction of **7a** at −3.0 V vs 85% tin reduction, and 50% electroreduction of the iodo conduritol precursor **7b** at −3.0 V compared to a 67% tin reduction. There was no reaction of chloro derivative **5b** under the conditions; however, its reduction by n-Bu_3SnH−AIBN afforded **6** in 36% yield.[7c]

After the completion of our preliminary results (Table 1, entries 1−5), we wished to determine whether the electrochemical method is comparable in efficiency to the larger-scale n-Bu_3SnH experiments we have previously used.[5,7e] A larger electrochemical cell was constructed to accommodate a scale of 1−5 g of starting material. Compound **7a** was chosen for scale-up because of its ease of preparation and its general relationship to the other conduritol precursors. Unfortunately, the scale-up process did not result in an appreciable increase in the overall yield of the reduced product **8** over that from reduction with n-Bu_3SnH. Perhaps the most problematic step in the process was the separation of the product from the supporting electrolyte. Although the greatest yield (59%) was obtained with n-Bu_4NBF_4 as the charge carrier, it was the most difficult to separate from the product. On the other hand, the easiest charge carrier to remove from the reaction mixture ($Et_4N^+pTsO^-$, by recrystallization from ethyl acetate) gave the poorest yield (6%).

Selectivity Studies. Iodobromodiol **9** (prepared by fermentation of iodobromobenzene with *Pseudomonas putida*)[1j] was examined in an effort to effect a selective electrochemical reduction of the vinyl iodide over the vinyl bromide. Constant potential electrolysis of **9** at −2.3 V resulted in the desired *cis*-bromodienediol **10** in 73% yield, a yield superior to that from the reduction with n-Bu_3SnH. The electrolyses were completed in less than 15 min at this potential.

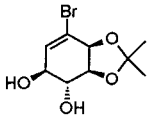
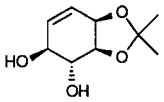
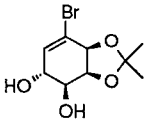
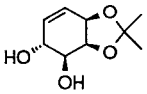
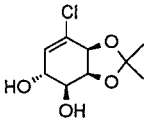
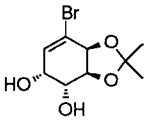
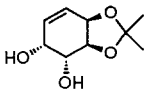
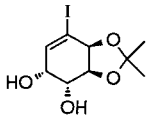
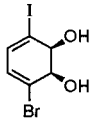
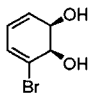
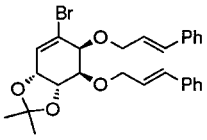
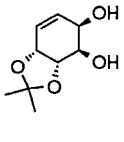
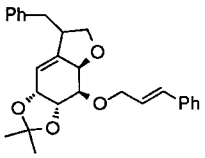
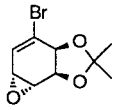
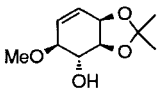
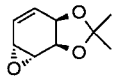
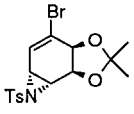
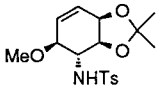
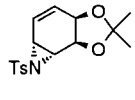
A compound that could, at least theoretically, undergo a radical cyclization in tandem with the halide reduction was cinnamyl ether **11**, Scheme 2. The cinnamoyl protected diol **11** was subjected to conditions of tin-mediated radical cyclization in order to produce a standard against which the results of electrochemical reduction could be measured. As expected, Bu_3SnH treatment provided the cyclized material as a 4:1 mixture of diastereomers. (The structure assignment can be found in the Supporting Information.) The linear sweep voltammogram of **11** showed a broad reduction peak at −3.2 V.

Preliminary bulk electrolyses were conducted at a constant −2.4 V on a gold foil rather than a mercury pool. Electrolysis resulted in the cleavage of the cinnamyl groups to afford an allylic alcohol and the acetonide-protected diol **12**. It was necessary to revert to the mercury pool working electrode because an extensive amount of adsorption was observed as the amount of starting material for successive electrolyses was increased. Other experiments using the Hg-pool cathode led to the same product (**12**). Although no radical cyclization was observed (in agreement with the studies of Fry,[3e] who has shown the initially formed radical undergoes rapid reduction to an anion), the result is interesting because of its potential as a method for mild deprotection of alcohols or diols.

Structural Analysis. Detailed information about the structures of compounds **11**, **13a**, and **13b** was obtained by NMR analysis (TOCSY, HSQC, and NOE); it is included in the Supporting Information.

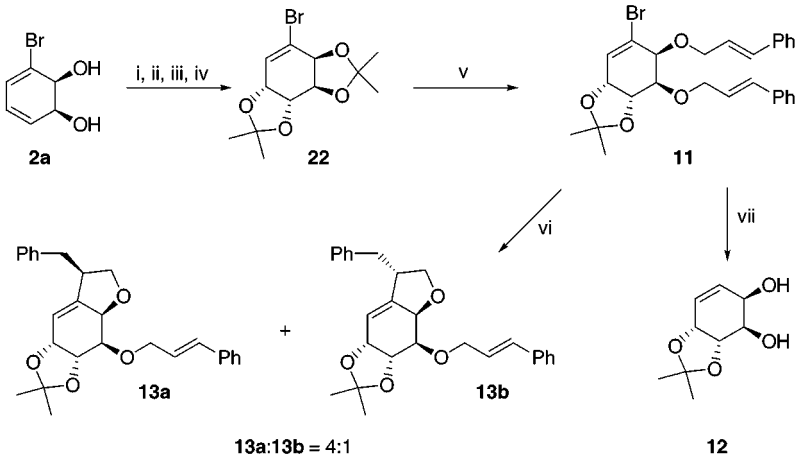
Reduction of Bromovinyl Oxiranes, and Aziridines. Epoxide **14** and aziridine **17** (Table 1, entries 8 and 9) were also investigated. The n-Bu_3SnH reduction of these materials resulted in dehalogenation products,

Table 1. Reduction of Vinyl Halides

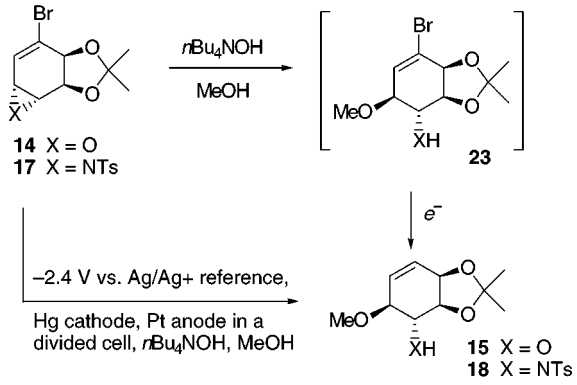
entry	starting material	applied potential	product of electrolytic reduction (% yield)	product of nBu$_3$SnH reduction (% yield)
1	 **3a**[a]	–3.2 V	 **4**[a] (62)	**4a** (80)
2	 **5a**[b,c]	–3.0 V	 **6**[b] (59)	**6** (78)
3	 **5b**	–3.0 V	no reaction	**6**[d] (36)
4	 **7a**[a]	–3.0 V	 **8**[e] (57)	**8**[e] (85)
5	 **7b**	–3.0 V	**8**[e] (50)	**8** (67)
6	 **9**	–2.2 V	 **10** (73)	**10**[f] (52)
7	 **11**	–3.2 V	 **12** (54)	 **13** (66)
8	 **14**[a]	–2.4 V	 **15**[g,h] (54)	 **16** (50)
9	 **17**[i]	–2.4 V	 **18**	 **19** (83)

[a] Reference 5. [b] Nguyen, B. V.; York, C.; Hudlicky, T. *Tetrahedron Lett.* **1997**, *53*, 8807. [c] Nugent, T.; Hudlicky, T. *J. Org. Chem.* **1998**, *63*, 510. [d] Reference 7c. [e] Reference 7. [f] Akgün, H.; Gonzales, D.; Martinot, T.; Hudlicky, T. Unpublished results. [g] Charge carrier: nBu$_4$NOH. [h] Reference 7b. [i] Tian, X.; Maurya, R.; Königsberger, K.; Hudlicky, T. *Synlett* **1995**, 1125.

Scheme 2



Scheme 3



16 in 50% yield and **19** in 83% yield, respectively. As one goal of our research is the development of a cost-effective tandem enzymatic-electrochemical synthesis of inositols, a major step toward that end would be debromination of the bromo epoxides and aziridines accompanied by ring-opening by nucleophiles. With that in mind, we subjected **14** and **17** to electrolysis in the presence of nBu$_4$NOH in methanol, anticipating that the electrolyte would serve as a source of hydroxide.

The constant potential electrolysis of **14** resulted in a 50% yield of **15**, the methylated derivative of protected conduritol F, and also a precursor to (−)-pinitol[7b] (Scheme 3). We concluded that the methoxide ion was opened of the epoxide (**23**) whereas the electrolysis effected the debromination in an overall CE-type process. The electrochemical reduction of the aziridine **17** under the same conditions produced methoxy-substituted dehalogenated tosylamide **18** (potential amino inositol synthon)[8] in 98% yield.

Experimental Section

All reactions in nonaqueous media were performed in flame-dried glassware under argon.

General Electrochemical Reduction. The electrolysis cell consisted of a 200-mL beaker containing a 0.5 cm layer of Hg as the working electrode, a simple Ag/Ag$^+$ reference electrode, and a platinum foil in a divided cell as the auxiliary electrode. An EG & G Princeton Applied Research Potentiostat-Galvanostat Model 263A maintained the desired voltage. A 0.1 M solution of the charge carrier (Et$_4$NBr or nBu$_4$NBF$_4$) in acetonitrile was added to the cell (50 mL per 100 mg starting material) and allowed to equilibrate with the divided cell (a fritted chamber). Excess oxygen was expelled from the electrochemical cell by passing an argon stream through the reaction mixture for 10−20 min. The starting material was dissolved in acetonitrile and added to the main compartment. The reduction was performed at a constant potential (see Table 1) until TLC analysis indicated disappearance of the starting material.

After the reaction was complete, the reaction mixture was decanted from the Hg pool and the solvent evaporated to yield a solid constisting of the product and the charge carrier. The product was extracted with warm EtOAc (when was used) or with water (for nBu$_4$NBF$_4$) The fractions in the former case were dried over MgSO$_4$ and filtered through Celite. Solvent (ethyl acetate or water) was then evaporated at reduced pressure to afford a product that typically required purification by column chromatography (10% H$_2$O deactivated flash silica gel) followed by recrystallization.

Electrochemical Reduction of 14 and 17. To 100 mL of 1 M Bu$_4$NOH in methanol in an electrolysis cell was added 250 mg of either **14** or **17**. The mixture was electrolyzed for 1 h at −2.4 V. Upon completion of the reaction, the solvent was evaporated, and the resulting solid was extracted with ethyl acetate (3 × 100 mL). The extract was concentrated in vacuo to yield crude product **15** or **18**. The product was purified by column chromatography (1:1 EtOAc−hexane).

[3a*S*-(3aα,4α,5β,7aα)]-4-[(*p*-Toluenesulfonyl)amino]-5-methoxy-3a,4,5,7a-tetrahydro-2,2-dimethyl-1,3-benzodioxole (20): R_f = 0.45 (1:1 EtOAc−hexane); $[\alpha]^{23.5}_D$ = 6.5° (c = 0.11, CHCl$_3$); mp = 113−114 °C; IR (KBr, 3%) 3201, 1317, 1100, 1065 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.82 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 5.87 (dd, J = 7.5, 10.5 Hz, 2H), 5.72 (d, J = 7.5 Hz), 4.59 (bs), 4.10 (dd, J = 3.3, 6.0 Hz, 1H), 3.62 (d, J = 9.0 Hz, 1H), 3.47 (q, J = 7.8 Hz, 1H), 3.04 (s, 3H), 2.4 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.4, 139.0, 131.7, 128.9, 127.2, 123.9, 110.4, 77.9, 76.0, 72.0, 56.8, 56.0, 27.7, 25.9, 21.3; HRMS FAB$^+$ (M + H) exact mass calculated for C$_{17}$H$_{24}$NO$_5$S 354.1375, found 354.1349. Anal. Calcd for C$_{17}$H$_{24}$NO$_5$S: C, 57.77; H, 6.56; N, 3.96. Found C, 57.63; H, 6.46; N, 3.87.

Halide Reductions with nBu$_3$SnH. To a mixture of substrate in dry THF was added 1.5 equiv of nBu$_3$SnH (97%), followed by a catalytic amount of AIBN. The reaction mixture was heated at reflux until TLC analysis showed the disappearance of starting material, after which time the solvent was removed under reduced pressure. The crude product was suspended in hexane and extracted with H$_2$O (**3a**, **5a**, **7a**, and **7b**) or acetonitrile (**11**, **14**, and **17**). For compounds **3a**, **5a**, **7a**, and **7b**, the water was evaporated under reduced pressure; the product was dissolved in ethyl acetate and then dried over MgSO$_4$ and filtered through Celite. The solvent was evaporated and the product recrystallized from ethyl acetate and hexane.

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Compounds **11**, **14**, and **17** required evaporation of the acetonitrile and subsequent column chromatography (flash silica gel).

[3a*R*-(3aα,4α,5α,7aα)]-6-Bromo-2,2-dimethyl-4,5-bis(3-phenyl-(*E*)-2-propenyloxy)-3a,4,5,7a-tetrahydro-2,2-dimethyl-1,3-benzodioxole (11). To a suspension of sodium hydride (720 mg, 30 mmol) in 10 mL of dry THF at 0 °C was added compound **22** (6.52 g, 24.6 mmol), and the resulting mixture was stirred for 30 min and then warmed to room temperature. Cinnamyl bromide (13.1 g, 66.5 mmol) dissolved in 20 mL of dry THF was added. After 24 h, the reaction was quenched with water. The organic components were extracted with Et_2O (3 × 100 mL). The combined organic layers were dried over $MgSO_4$ and filtered over Celite, and the ether was then removed under reduced pressure. Purification of product was achieved on flash silica gel with a 1:9 ethyl acetate:hexane as an eluent to yield 4.98 g of the dicinnamyl product as a yellow solid (40.6%). HPLC of the product displayed a single peak eluting at 11.3 min in a 80:20 MeCN: H_2O (5 mmol Et_3N/AcOH buffer system). $R_f = 0.24$ (EtOAC−hexane, 1:9); $[\alpha]^{23.5}_D = -105.5°$ ($c = 0.11$, $CHCl_3$); mp = 66−69 °C; IR (KBr): 3462, 2983, 1636, 1449, 1369, 1226, 1118, 1050, 964, 856, 691 cm^{-1}; HRMS FAB+ (M + H) exact mass calculated for $C_{27}H_{30}BrO_4$ 498.1986, found 497.1328. Anal. Calcd for $C_{27}H_{29}BrO_4$: C, 65.19; H, 5.88. Found C, 65.20; H, 5.91. (See Supporting Information for NMR data.)

2,2-Dimethyl-7-(phenylmethyl)-(3a*R*,4*R*,4a*R*, 8a*R*)-4*H*,6*H*,7*H*-furo[2′,3′:4,5]benzo[*d*][1,3]dioxol-4-yl-3-phenyl-(*E*)-2-propenyl Ether (13). A two-necked flask with condenser and three-way stopcock was charged with the starting material (**11**; 425 mg, 0.85 mmol) dissolved in 15 mL of dry THF, and the reaction mixture was brought to reflux, whereupon 1.5 equiv of nBu_3SnH (128 mg) and AIBN (cat.) were added. Following heating at reflux overnight, completion of the reaction was verified by TLC, and the reaction mixture was concentrated under reduced pressure. Flash chromatography (1:9 EtOAc−hexane) yielded a colorless oil (216 mg, 66.1%). HPLC analysis (80:20 acetonitrile−water, 5 mmol AcOH−Et_3N buffer) system revealed a pair of diastereomers in a 4:1 ratio.

13a: $R_f = 0.22$ (EtOAc−hexane, 1:9); $[\alpha]^{25}_D = -38.8°$ ($c = 0.27$, $CHCl_3$); IR (NaCl): 3007, 2933, 1718, 1601, 1495, 1453, 1361, 1236, 1114, 1056, 968, 885 cm^{-1}; HRMS CI; exact mass calculated for $C_{27}H_{30}O_4$: 418.5328, found 418.2144. Anal. Calcd for $C_{27}H_{30}O_4$: C, 77.48; H, 7.22. Found: C, 76.53; H, 7.30. (See Supporting Information for NMR data.)

13b: $R_f = 0.22$ (EtOAc−hexane, 1:9); IR (NaCl): 3008, 2934, 1719, 1602, 1496, 1454, 1382, 1326, 1162, 1115, 1058, 969, 886 cm^{-1}. Anal. Calcd for $C_{27}H_{30}O_4$: C, 77.48; H, 7.22. Found C, 77.14; H, 7.70. (See Supporting Information for NMR data.)

Conclusions

We have demonstrated that electrochemical techniques are reasonable alternatives to more traditonal chemical techniques for the dehalogenation of vinyl halides. Electrochemical methods minimize the use of toxic reagents and solvents, and they reduce or even eliminate the amount of toxic byproducts produced in traditional chemical methodology based on tin reagents. The yields obtained from electrolytic techniques are comparable to those obtained with tin reagents. We have also shown that electrochemical techniques are much better than tin reagents for selective dehalogenation of the dihalogenated cyclohexadiene diols **4**. Moreover, we have demonstrated the utility of the cinnamyl group as a potential protecting group for cyclohexadiene diols, as this functionality is easily removed selectively by means of potentiostatic techniques.

We have also demonstrated the potential for the incorporation of electrochemical techniques into the synthesis of conduritols and conduramines. This is of enormous value to our ongoing research into the development of tandem enzymatic−electrochemical syntheses of inositols, conduritols, conduramines, and amino inositols, the results of which will be reported in due course. Future research in this area will focus on replacing mercury in the electrochemical reactions with materials such as vitreous carbon in conjunction with current reversal techniques to reduce adsorbance on the electrode. Our ultimate goal is to develop "green" syntheses of inositols and amino inositols employing only electrochemical and enzymatic procedures in order to reduce the amount of byproducts and increase the effective mass yield of the target compounds.[9]

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Supporting Information Available: Supporting Information includes linear sweep voltammetric analyses (compounds **3a**, **5a**, **5b**, **7a**, **7b**, **9**, **11**, **14**, and **17**) and NMR data for structure and stereochemical proof of compounds **13a** and **13b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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