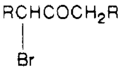
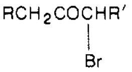
lectivity could be improved by operation at lower temperatures and in a different solvent.

The lack of diastereoselectivity notwithstanding, these reactions have a number of potentially very attractive advantages for effecting directed aldol condensations: (a) the electrolyses are carried out under neutral conditions, and furthermore, the lanthanum enolate intermediates are themselves not very basic;[6] (b) α-bromo ketones are more easily reduced electrochemically than almost any of the common functional groups of organic chemistry;[1,10] (c) enolate formation and hence aldol condensation occur at the point where the bromine atom is attached; (d) the electrolyses can be carried out at constant current with no decrease in yield, which means that they can be carried out more rapidly than at controlled potential, and a very simple power source could be used if desired;[11] (e) the reaction, as noted, is highly selective for aldehydes over ketones. Considerations a–c suggest the possibilities of effecting directed aldol reactions between components bearing a wide range of functional groups, including base-sensitive or other electron-accepting functionalities, and/or the possibility of regioselective aldol condensations, e.g., generation of **13** and **14** from regioisomeric bromo ketones **11** and **12**.



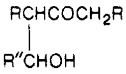
$\mathrm{R}\underset{\mathrm{Br}}{\underset{|}{\mathrm{C}}}\mathrm{HCOCH_2R'}$

11



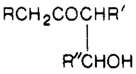
$\mathrm{RCH_2CO}\underset{\mathrm{Br}}{\underset{|}{\mathrm{C}}}\mathrm{HR'}$

12



$\mathrm{R}\underset{\mathrm{R''CHOH}}{\underset{|}{\mathrm{C}}}\mathrm{HCOCH_2R'}$

13



$\mathrm{RCH_2CO}\underset{\mathrm{R''CHOH}}{\underset{|}{\mathrm{C}}}\mathrm{HR'}$

14

We are exploring some of these synthetic implications, as well as carrying out more detailed mechanistic investigations. Finally, having successfully demonstrated that it is possible to facilitate the reaction between electrochemically generated enolates and aldehydes by added metal ions, we plan to proceed to examine the possibility of trapping more highly basic and therefore more challenging carbanions.

Experimental Section

Lanthanum and cerium chlorides and lithium perchlorate (Alfa Inorganics) were dried at 135 °C in vacuo overnight. THF was distilled from the sodium–benzophenone ketyl.

Lanthanum Bromide. Lanthanum oxide (Alfa) was dissolved in concentrated HBr containing excess ammonium bromide (to repress hydrolysis to insoluble LaOBr[8]) and heated on the steam bath to drive off most of the water; residual water and ammonium bromide were then removed in vacuo while (12–18 h) the temperature was slowly raised to 350 °C. Material prepared by this procedure is completely soluble in water, indicating the absence of LaOBr. Cerium bromide was prepared by a similar procedure, but its purity was variable from run to run.

Sample Electrolysis Procedure. Benzaldehyde (0.5 g, 4.7 mmol), bromo ketone **9a** (1.0 g, 4.7 mmol), 1.78 g of lanthanum bromide (4.7 mmol), and 100 mL of a 0.5 M solution of $LiClO_4$ in dry THF were added to a magnetically stirred divided cell; the anode compartment was a ceramic cup (Coors Porcelain Co. #60494) filled with the same $LiClO_4$/THF solution. The cathode was a carbon cloth electrode (Union Carbide Corp. No. X2014 WCA graphite cloth).[12] The cell was chilled in an ice bath and purged with N_2 for 3–5 min, and a constant current of 0.2 A was then passed for 110% of the calculated time for a two-electron reduction. Concentrated HCl (3 mL) in 10 mL of H_2O was added, and stirring was continued for 3 min. The THF was removed by rotary evaporation, 150 mL of CH_2Cl_2 was added, and the latter was separated, washed successively with 100-mL portions of H_2O and dilute aqueous Na_2SO_4, and dried over $MgSO_4$. The products were analyzed by quantitative HPLC (column, 5 × 250 mm, packed with a C_{18} reversed phase on 5-μm silica gel support; eluent, 60–70% methanol in water at 1.5 mL/min; detection at 240 nm). Pure samples of aldols for calibration of the HPLC procedure were isolated by chromatography over silica gel with elution by 85:15 hexane/ethyl acetate.

Acknowledgment. Financial support by the National Science Foundation (Grant #85-02078 to A.J.F.) is gratefully acknowledged, as is a grant from the same agency to Wesleyan University in partial support of the 400-MHz NMR spectrometer used in this work. Joseph Sokol and Jonathan Haber carried out a number of preliminary electrolyses.

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[10] Voltammetry at a glassy carbon microelectrode established the reduction potential of α-bromopropiophenone to be −1.5 V vs. Ag/0.1 M $AgNO_3$ in THF/0.5 M $LiClO_4$; this potential is unaffected by the addition of $LaBr_3$. Benzaldehyde is reduced at −1.9 V under these conditions, and $LaBr_3$ is reduced at an even more negative potential. We will report full details of the voltammetry later when a mechanistic study presently in progress is complete.

[11] Fry, A. J.; O'Dea, J. J. *J. Org. Chem.* **1975**, *40*, 3625. See, specifically pp 3627 and 3630 of this reference.

[12] Hand, R.; Carpenter, A. K.; O'Brien, C. J.; Nelson, R. F. *J. Electrochem. Soc.* **1972**, *119*, 74.

Electrochemical Reduction of (1-Bromo-2,2-dimethylpropyl)benzene in Dimethylformamide on Carbon Electrodes

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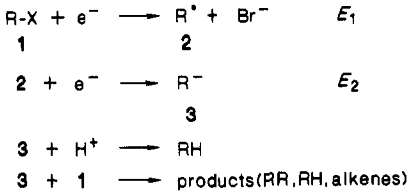
Received December 23, 1986

Products from the electrochemical reduction of (1-bromo-2,2-dimethylpropyl)benzene (**4a**) on carbon electrodes in dimethylformamide containing lithium perchlorate were found to depend upon the electrolysis potential. At relatively positive potentials the products are derived primarily from the coupling of two benzylic radicals, whereas at more negative potentials the products are derived from the corresponding carbanions. This establishes for the first time the mechanism of bibenzyl formation in the electrochemical reduction of benzyl bromides at nonmetallic electrodes. It has also been found that the *meso–dl* ratios of the 1,2-di-*tert*-butyl-1,2-diphenylethane products are dependent upon electrolysis potential and that head-to-head coupling of 1-phenyl-2,2-dimethylpropyl radicals is sterically restricted.

Many studies have been made into the mechanism of the electrochemical reduction of alkyl halides.[1,2] The general outlines of the electrode process are known (Scheme I). The initial, and potential-determining, step

Scheme I



$$\underset{1}{\text{R-X}} + e^- \longrightarrow \underset{2}{\text{R}^\bullet} + \text{Br}^- \qquad E_1$$

$$2 + e^- \longrightarrow \underset{3}{\text{R}^-} \qquad E_2$$

$$3 + \text{H}^+ \longrightarrow \text{RH}$$

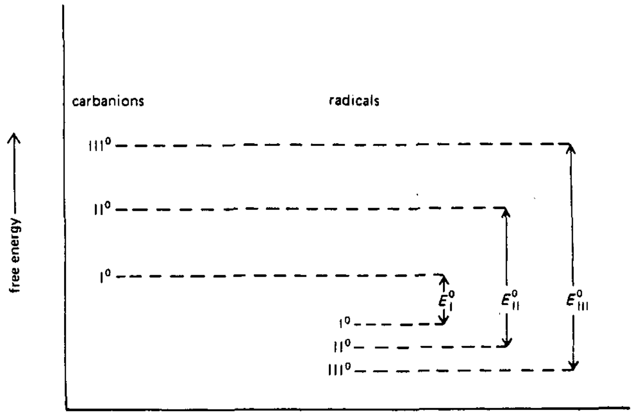
$$3 + 1 \longrightarrow \text{products(RR,RH,alkenes)}$$

involves transfer of one electron from the electrode to the substrate (1) at potential E_1 to generate a free radical (2). Often the reduction potential E_2 of 2 is positive of that of 1, and the radical therefore undergoes a second one-electron reduction to afford a carbanion (3), which finally reacts with either a proton in the medium or starting material to afford the final products.[1,2]

However, though Scheme I represents the broad features of the reaction pretty well, the actual situation is considerably more complex, and much still remains to be learned. For example, it is known that adsorption and adsorbed intermediates can play an important role.[3] The voltammograms of some alkyl halides are severely distorted by such effects.[4] At mercury and lead electrodes electrochemically generated intermediates such as 2 may even undergo chemical reaction with the electrode itself to afford organometallic intermediates and/or products.[2-5]

It is also increasingly clear that one of the central issues of alkyl halide electrochemistry concerns the relative values of E_1 and E_2 and, therefore, the lifetime of 2 after it is generated at the electrode surface. (Quite obviously, this point is closely related to the question whether the electrolysis products are derived from radical 2 or carbanion 3.) Early mechanistic discussions[2] assumed that E_2 is always positive of E_1 and that therefore radical 2 will generally be reduced to the carbanion 3 as rapidly as it is formed. Experience has shown that this is not always the case. Although it is probably true that for most substrates reduction of 2 is very fast and that products are derived only from 3,[6] the electrochemical behavior of several types of alkyl halide has been shown to be consistent with the postulate that for these substances E_2 is negative of E_1 and that radicals 2 are the precursors of the observed products.[1,3,7] At least one intermediate situation has been identified where radicals intervene as distinct intermediates, even though the final products are derived from carbanions, whence it may be concluded that for this system E_1 and E_2 are probably similar.[8]

Scheme II



One would expect that the electrochemical behavior of 1 should be sensitive to the nature of R. Some years ago one of us offered a unifying concept (Scheme II) to explain the apparent differences in reduction potentials of primary, secondary, and tertiary radicals.[9] The scheme simply summarizes the well-known facts that among primary, secondary, and tertiary species, (a) tertiary radicals are the most stable (b) tertiary anions are the least stable, and (c) the differences between primary, secondary, and tertiary are considerably greater for anions than for radicals. Since the reduction potential of a given radical should be related to the enthalpy difference between the radical and its corresponding carbanion, primary radicals should be easiest to reduce and tertiary hardest, and the differences in reduction potential as one proceeds through the series from primary to tertiary should be substantial. These considerations should manifest themselves in a variety of ways in the electrochemistry of alkyl halides. Radical-derived products are most likely in the electrolysis of tertiary halides and least likely during electrolysis of primary halides. Voltammetrically, a halide should exhibit a single two-electron wave when E_2 is positive of or close to E_1 and two one-electron waves when E_2 is well negative of E_1. It turns out that for alkyl bromides there is indeed a marked dependence of electrochemical behavior upon the degree of substitution in the R group. For example, primary and secondary bromides exhibit a single two-electron polarographic wave,[2-4] whereas tertiary bromides exhibit either two closely spaced waves or a single drawn-out wave, depending upon the solvent system employed.[10] These results imply that E_2 is positive of E_1 for primary and secondary bromides and that the two potentials are similar for tertiary bromides. The results of preparative-scale experiments on alkyl bromides support this hypothesis. Whereas the products are derived exclusively from carbanions when R is primary or secondary,[3] a study of the electrochemical reduction of *tert*-butyl bromide under conditions where it exhibits two waves showed that radical-derived products are formed at the first wave and carbanion-derived products at the second wave.[1] Further and in agreement with expectation, when one examines alkyl iodides, for which E_1 is positive of that for bromides, even secondary substrates show voltammetric and product behavior demonstrative of long-lived radical intermediates.[3,7]

It is not at all clear on the basis of these ideas what behavior one should expect for a benzylic bromide. Benzyl radicals and benzyl anions are *both* resonance stabilized, and therefore about all one can say is that the reduction potential of a benzyl radical ought at least to be less than that of a tertiary radical. Furthermore, benzyl bromides are also much easier to reduce than alkyl bromides,[2]

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[1] Vieira, K.; Peters, D. G. *J. Org. Chem.* **1986**, *51*, 1231 and references therein.

[2] Fry, A. J. *Synthetic Organic Electrochemistry*; Harper and Row: New York, 1972; Chapter 5.

[3] (a) Mbarak, M. S.; Peters, D. G. *J. Org. Chem.* **1982**, *47*, 3397. (b) Willett, B. C.; Peters, D. G. *J. Electroanal. Chem.* **1981**, *123*, 291.

[4] (a) McNamee, G. M.; Willett, B. C.; La Perriere, D. M.; Peters, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 1831. (b) La Perriere, D. M.; Carroll, W. F., Jr.; Willett, B. C.; Torp, E. C.; Peters, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 7561.

[5] Webb, J. L.; Mann, C. K.; Walborsky, H. M. *J. Am. Chem. Soc.* **1970**, *92*, 2042.

[6] This is true especially when R bears an attached electronegative atom. E.g. (a) Geminal dihalides: Fry, A. J.; Reed, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 8475. (b) α-Bromo ketones: Fry, A. J.; O'Dea, J. *J. Org. Chem.* **1975**, *40*, 3625.

[7] Cleary, J. A.; Mubarak, M. S.; Vieira, K. L.; Anderson, M. R.; Peters, D. G. *J. Electroanal. Chem.* **1986**, *198*, 107.

[8] Fry, A. J.; Mitnick, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 6207.

[9] Reference 2, p 175.

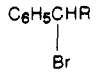
[10] (a) Glyme: Hoffmann, A. K.; Hodgson, W. G.; Maricle, D. L.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 631. (b) Dimethyl sulfoxide: Fry, A. J.; Krieger, R. L. *J. Org. Chem.* **1976**, *41*, 54. (c) Dimethylformamide: ref 1.

Table I. Products from the Electrochemical Reduction of (1-Bromo-2,2-dimethylpropyl)benzene as a Function of Potential

E^a	7, %		8 + 9, %	10, %	11, %	*meso–dl* ratio
	meso	*dl*				
−1.65	38	24	32	tr	6	1.58
−1.80	21	12	25	38	3	1.67
−1.90	13	6	13	62	6	2.21
−2.00	tr	tr	tr	85	15	$(2.1)^b$

[a] Electrolysis potential, vs. Ag/0.1 M $AgNO_3$. [b] Ratio difficult to measure accurately because of the small size of the two peaks.

making it even harder to estimate where E_2 ought to lie relative to E_1 and hence whether products from the electrochemical reduction of benzyl bromides will be derived from the corresponding radicals or anions. In this connection, an especially interesting mechanistic question is raised by reports that electrochemical reduction of benzyl bromides leads in part to the formation of bibenzyls.[11] These substances could arise by one of several pathways: (a) dimerization of intermediate free radicals, (b) S_N2 displacement upon the starting halide by the benzylic carbanion,[7] or (c) coupling of surface-bound organometallic species. Casanova proposed path c as the source of the dimeric products formed during the electrochemical reduction of (α-bromoethyl)benzene (**4b**) at a mercury cathode,[12] and Peters has argued that eicosane produced during the electrochemical reduction of 1-iodododecane at a carbon cathode is formed by path b.[7] However, as far as we are aware, the mechanism of bibenzyl formation at nonmetallic electrodes has not been established. The present study addresses this question. We have examined the electrochemical reduction of the hindered benzyl bromide (1-bromo-2,2-dimethylpropyl)benzene (**4a**) at a carbon cathode. We expected that if bibenzyl formation generally proceeds via the S_N2 route (path b), it should be severely inhibited with **4a** for steric reasons. We also examined the dependence of the product composition upon electrolysis potential, in order to obtain information relating to the relative values of E_1 and E_2 for benzyl systems. The only previous discussion of this point in the literature involves studies upon the electrochemical behavior of **5** and **6**, which are highly atypical and unrepresentative benzyl halides.[13]



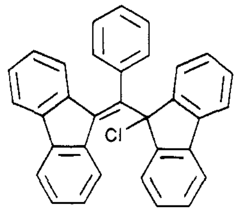
$$\underset{\displaystyle Br}{C_6H_5CHR}$$

4a, R = *t*-Bu
b, R = Me

Results

Bromide **4a** was prepared by the action of *N*-bromosuccinimide upon neopentylbenzene in carbon tetrachloride. Neopentylbenzene was prepared by the cuprene chloride promoted coupling of benzyl chloride and *tert*-butylmagnesium chloride, using a modification of the procedure used by Bullpitt and Kitching to synthesize neopentylnaphthalenes.[14]

(1-Bromo-2,2-dimethylpropyl)benzene (**4a**) exhibited a single broad, poorly defined irreversible voltammetric wave at ca. −1.8 V vs. Ag/0.1 M $AgNO_3$ at a glassy carbon electrode. Preparative electrolyses were carried out at controlled potential in dimethylformamide containing 0.1 M lithium perchlorate. The products were found to be highly dependent upon the electrolysis potential (Table I). At the most positive potential examined, −1.65 V, the major products are a mixture of *meso* and *dl* diastereomers of structure **7a**; there was also obtained from **4a** a mixture of substances incompletely resolved by gas chromatography but of slightly longer retention time then either diastereomer of **7**. The retention times and mass spectra of these substances indicate that they correspond to head-to-tail and tail-to-tail dimers (structures **8** and **9**). Very small amounts of such dimers were reported to be formed during the electrochemical reduction of (α-bromoethyl)benzene (**4b**).[12,15] At −2.00 V, the most negative potential employed for the electrolysis of **4a**, the major product was neopentylbenzene (**10**), together with a small amount of α-phenylneopentanol (**11**). Finally and strikingly, we observed a dependence of the *meso–dl* ratio upon electrolysis potential (see the last column of Table I) which is well outside experimental error.



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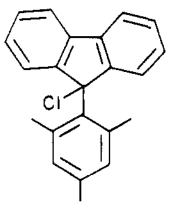

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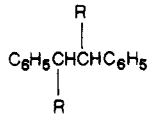
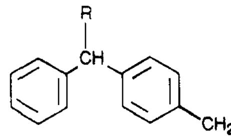


$$\overset{\displaystyle R}{\underset{\displaystyle R}{C_6H_5CHCHC_6H_5}}$$

7



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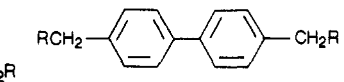
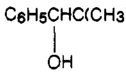


9

$C_6H_5CH_2C(CH_3)_3$

10



$$\underset{\displaystyle OH}{C_6H_5CHC(CH_3)_3}$$

11

$C_6H_5\dot{C}HR$

12

$C_6H_5\bar{C}HR$

13

Discussion

The fact that the reaction products are predominantly dimeric at an electrolysis potential of −1.65 V and that dimers are almost nonexistent after electrolysis at −2.00 V, a potential of only 0.35 V more negative permits several unambiguous mechanistic conclusions. First, the facts that (a) dimers are formed at all and (b) the products depend so sharply upon potential demonstrate that E_1 and E_2 have similar values. If E_2 were either considerably negative or considerably positive of E_1, dimers would be formed over the entire range of electrolysis potentials, by the radical coupling route or the S_N2 route, respectively. Second, the dimers must be formed by the coupling of two benzylic radicals. Since E_2 is close to E_1, the well-known exponential dependence of electron-transfer rate upon potential[16] results in a situation where radical **12** is relatively

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(11) Grimshaw, J.; Ramsey, J. S. *J. Chem. Soc. C* **1968**, 60.

(12) Yamasaki, R. B.; Tarle, M.; Casanova, J. *J. Org. Chem.* **1979**, *44*, 4519.

(13) Andrieux, C. P.; Merz, A.; Saveant, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 6097.

(14) Bullpitt, M. L.; Kitching, W. *Synthesis* **1977**, 316.

(15) We noted likewise that such dimers are formed in only very small amounts in the electrochemical reduction of (1-bromo-2-methylpropyl)benzene: T. A. Powers, unpublished work.

(16) Reference 2, Chapter 2.

long-lived (and hence able to undergo bimolecular dimerization) at −1.65 V but at −2.00 V is reduced almost as fast as it is formed. S_N2 displacement upon **4a** is indeed as slow as we had expected it would be. With this path precluded, the major reaction path open to carbanion **13a** is proton abstraction from the medium to form the corresponding alkane. Protonation of **13** by adventitious water in the solvent produces hydroxide ion: the latter presumably then attacks starting material **4** to afford **11**. Formation of alcohols by this mechanism has been observed previously.[4] It is not difficult to see why bromide should be displaced from **4a** by hydroxide but not by the much bulkier carbanion **13**.

Though **4a** affords substantial amounts of dimers resulting from head-to-tail or tail-to-tail coupling, this is known not to be significant with the α-methylbenzyl radical (**12b**, R = Me).[12,17] Apparently the steric congestion which is engendered by head-to-head coupling to produce dimers **7** slows this coupling mode sufficiently to permit the others, which produce less hindered products, to become competitive. (The formation of such dimers, incidentally, provides further evidence that bibenzyl formation proceeds by radical coupling, not by S_N2 displacement.)[18] The high degree of congestion in dimers **7a** is already known to result in a very anomalous conformational situation in these substances, especially the *dl* diastereomer.[18]

The other evidence for steric congestion in the head-to-head coupling mode is the nonunity *meso*–*dl* diastereomeric ratios observed in the coupling of **12a**. Radical **12b** affords a 50:50 *meso*–*dl* ratio even when generated under a wide variety of experimental conditions expressly designed to affect this ratio.[17] It has been argued that this is because dimerization of two radicals has no activation energy and hence cannot respond to steric effects.[17,18] Nonunity *meso*–*dl* ratios have however been observed in reactions leading to the *p,p′*-dichloro analogue of **7a**.[18] Though certain such dimerizations may have proceeded by ionic pathways, others clearly involved coupling of two radicals.[18] It has been pointed out by Ruchardt that nonunity *meso*–*dl* dimer ratios imply the existence of an activation energy for head-to-head coupling and that it is reasonable that steric hindrance created by the presence of two *tert*-butyl groups near the dimerization site should lead to an activation energy for dimerization.[18] It should be noted that it is the *meso* diastereomer which predominates in our electrochemical reactions, whereas the *dl* isomer was found to be the major product of dimerization of radical **12a** under Ruchardt's conditions.[18] Ruchardt and co-workers observed some reactions in which the *meso* diastereomer predominated but suggested that some or all of these might not involve radical coupling. Our results, which clearly do involve radical coupling, suggest that the stereochemical course of such couplings may be sensitive to the nature of the medium in which they occur. This hypothesis, which has some precedent,[17] is supported by the very unusual dependence of the *meso*–*dl* ratio upon electrolysis potential which we have observed. A variety of explanations involving generation of geometrically slightly different radical pairs of the electrode surface by kinetically selective processes might be adduced to explain this phenomenon, but we are not inclined to speculate further. This seems to be one of very few cases where the stereochemistry of an organic electrode reaction depends upon potential.[19]

It was concluded previously that E_2 is close to E_1 for benzyl bromides. Upon the basis of the results of Table I, one would estimate the reduction potential of α-alkylbenzyl radicals at ca. −1.9 V vs. Ag/0.1 M $AgNO_3$. While our work was in its final stages, we were pleased to read the report by Griller on the direct measurement of the reduction potentials of free radicals,[20] from which one may estimate a value of −1.91 V, in excellent agreement with our data. As expected (vide supra), this value is not as negative as that of the reduction potential of the *tert*-butyl radical (−2.56 V).[1]

Experimental Section

^1H NMR spectra were recorded in $CDCl_3$ on a Varian Associates XL-200 spectrometer. Analytical gas chromatography was carried out with a Gow-Mac Model 550P gas chromatograph equipped with a $^1/_8$ in. × 3 m SE-30 column, with the temperature programmed from 100 to 250 °C at a rate of 15 deg/min.

Dimethylformamide was distilled at reduced pressure from calcium hydride. Lithium perchlorate was dried overnight at 100 °C in an Abderhalden apparatus.

Neopentylbenzene (10). A solution of *tert*-butylmagnesium chloride was prepared by reaction between 37.0 g (0.4 mol) of *tert*-butyl chloride and 9.72 g (0.4 mol) of magnesium turnings in 500 mL of anhydrous ether. To this solution was added 9.9 g (0.1 mol) of cuprous chloride, followed by dropwise addition of 50.6 g (0.4 mol) of benzyl chloride at 0 °C. The reaction mixture was stirred overnight. After addition of 100 mL of dilute HCl, the ether layer was separated, washed with water, and dried over sodium sulfate. After removal of solvent by rotary evaporation, the residue was first fractionally distilled in vacuo (foaming) and then chromatographed over silica gel to remove bibenzyl and afford neopentylbenzene (**10**) in 30–50% yields: NMR δ 0.88 (s, 9 H), 2.49 (s, 2 H), 6.1–6.4 (m, 5 H).

(1-Bromo-2,2-dimethylpropyl)benzene (4a). A mixture of 10.4 g (70 mmol) of neopentylbenzene and 18.7 g (105 mmol) of *N*-bromosuccinimide in 75 mL of carbon tetrachloride was refluxed overnight. After removal of succinimide by filtration, and evaporation of solvent, the pale yellow solution was chromatographed over silica gel to afford first a small amount of unreacted neopentylbenzene and then 12.7 g (80%) of (1-bromo-2,2-dimethylpropyl)benzene (**4a**): NMR δ 1.06 (s, 9 H), 4.85 (s, 1 H), 6.2–6.45 (m, 5 H).

Electrochemical Reductions. Controlled-potential electrolyses were carried in DMF/0.1 M $LiClO_4$ by using a cell and reference electrode which have been described previously.[21] The cathode was a 10-cm^2 square of carbon cloth[22] (Union Carbide Corp. No. X2014 WCA graphite cloth). Reaction mixtures were analyzed by gas chromatography, both directly and after extraction with hexane (the latter treatment was preferred because the retention time of DMF is similar to that of neopentylbenzene, making quantitative analysis for the latter difficult; the ratio of *dl*- to *meso*-**7a** was shown, however, to be unaffected by this extraction process). Gas chromatographic analyses were calibrated by pure samples of individual components. The *meso* and *dl* diastereomers of **7a** were isolated by preparative gas chromatography; the major isomer was identified as *meso* both by NMR spectroscopy (the key difference between the two isomers is the location of the *tert*-butyl resonance at δ 0.53 for the *meso* diastereomer and δ 0.92 for *dl*) and by its longer gas chromatographic retention time.[18] An authentic sample of alcohol **11** for comparison of gas chromatographic retention time was prepared by reaction of **4a** (as an ether solution) with aqueous silver nitrate.

Acknowledgment. Financial support was provided by the National Science Foundation (CHE-85-02078).

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(17) Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867.

(18) (a) Hellmann, G.; Beckhaus, H. D.; Ruchardt, C. *Chem. Ber.* **1979**, *112*, 1808. (b) Eichin, K. H.; Beckhaus, H. D.; Hellmann, S.; Fritz, H.; Peters, E. M.; Peters, K.; von Schnering, H. G.; Ruchardt, C. *Chem. Ber.* **1983**, *116*, 1787.

(19) Fry, A. J. *Fortschr. Chem. Forch.* **1972**, *34*, 1.

(20) Wayner, D. D. M., Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 7764.

(21) Dostrovsky, I.; Samuel, D. *J. Chem. Soc.* **1954**, 658.

(22) (a) Reference 2, p 326. (b) Fry, A. J.; Touster, J. *J. Org. Chem.* **1986**, *51*, 3905.

(23) Hand, R.; Carpenter, A. K.; O'Brien, C. J.; Nelson, R. F. *J. Electrochem. Soc.* **1972**, *119*, 74.