*J. Org. Chem.* **1996,** *61,* 3191−3194 **3191**

# Electrochemical Formation and Dimerization of α-Substituted Benzyl Radicals. Steric Effects on Dimerization

Albert J. Fry,*,† John M. Porter, and Peter F. Fry

*Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459*

*Received August 29, 1995*⊗

The mechanism of electrochemical cleavage of the carbon−halogen bond is well established.[1] Overall, the reduction consumes two electrons, which are transferred in two steps (Scheme 1). In the first (and potential-determining) step, one electron is transferred and the carbon−halogen bond is broken to produce a free radical. A second electron transfer then converts the radical to a carbanion. Generally, the carbanion abstracts a proton from the medium to produce the dehalogenated species RH, but in aprotic media the carbanion may be trapped by a variety of added electrophiles such as silyl halides,[2] activated alkenes,[3] and carbon dioxide and carbonyl compounds.[4] It is much more difficult to trap the corresponding radicals in these reductions. As a result of a great deal of experimentation in a number of laboratories, the reasons for this difficulty have gradually emerged. It turns out that for most alkyl halides, $E_1$, the potential necessary to produce the radical $R^•$, is *negative* of $E_2$, the reduction potential of the radical, so that $R^•$ is reduced very quickly as it is formed. Experimentally, this means that most alkyl halides exhibit a single two-electron voltammetric wave.[1a] By balancing the rate of electron transfer to the radical against an intramolecular isomerization process of known rate,[5,6] it can be estimated that the radical intermediates in most alkyl halide electrolyses have lifetimes less than 1 $\mu$s. In general, therefore, it will be especially difficult to trap such radicals intermolecularly. However, a few exceptions to this rule have emerged. The reduction potentials of alkyl radicals lie in the order I° < II° < III°, i.e., primary radicals are the easiest to reduce and tertiary are the hardest.[1,7] Alkyl iodides are easier to reduce than bromides, which in turn are easier to reduce than chlorides.[1] Considering this and the dependence of reduction potential on the degree of substitution in the radical, one can readily understand the fact that, for *tert*-butyl iodide $E_1$ is positive of $E_2$, resulting in two well-resolved voltammetric waves.[8] Secondary alkyl iodides give rise to long-lived radical intermediates,[9,10a] but primary iodides are reduced to carbanions.[10] Tertiary bromides represent a borderline situation: they exhibit two barely resolved one-electron waves in some solvents[11] and a single two-electron wave in others.[8] As long as the cathode does not consist of a material such as mercury which can react with radicals,[12] one may use the relative yield of radical coupling product RR as a good approximate measure of the lifetime (before reduction) of the radicals $R^•$ produced by electrochemical reduction of a given alkyl halide R-Hal. Such dimers are formed relatively rarely, and some apparent dimer-forming reactions actually correspond to $S_N2$ displacement on the alkyl halide by the carbanion intermediate.[9]

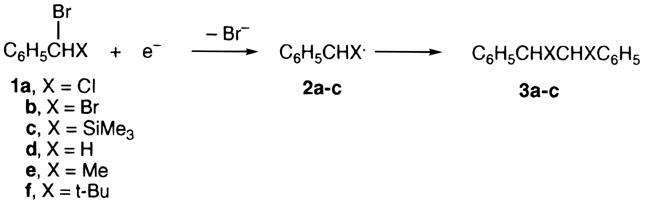
**Scheme 1**

$$\text{R-Hal} + e^- \xrightarrow{E_1} R^• + X^-$$

$$R^• + e^- \xrightarrow{E_2} R^-$$

$$R^- + H^+ \rightarrow RH$$

In this context, benzylic halides represent an interesting situation. Benzyl chlorides undergo the usual two-electron reduction to a benzylic carbanion,[13] but benzyl bromides **1d**−**f** exhibit two closely-spaced voltammetric waves in dimethylformamide (DMF), and the products change from radical type (RR) to carbanion type (RH) over electrolysis potentials of just a few tenths of a volt.[7,14] The α-chlorobenzyl radical (**2a**) is easier to reduce than benzal chloride ($C_6H_5CHCl_2$), so it cannot be produced by direct electrochemical reduction of benzal chloride.[15]



$$C_6H_5CH(Br)X + e^- \xrightarrow{-Br^-} C_6H_5CHX^• \longrightarrow C_6H_5CHXCHXC_6H_5$$

We recently showed, however, that **2a** can be prepared by indirect electrolysis, that is, by electrocatalytic reduction of benzal chloride by electrochemically generated cobalt(I) bis(salicylideneethylenediamine).[16] Under these conditions, radical **2a** undergoes efficient coupling to 1,2-

---

† Correspondence may be adressed to: Dr. Albert J. Fry, Department of Chemistry, Wesleyan University, Middletown, CT 06459. Phone: (203) 685-2622. Fax: (203) 685-2211. E-mail: afry@wesleyan.edu.

⊗ Abstract published in *Advance ACS Abstracts*, April 1, 1996.

[1] (a) Fry, A. J. *Synthetic Organic Electrochemistry*, 2nd ed.; Wiley: New York, 1989; Chapter 5. (b) Peters, D. In *Organic Electrochemistry*, 3rd ed.; Lund, H., Baizer, M. M., Eds.; Dekker: New York, 1991; pp 361−400.

[2] (a) Yoshida, J.-I.; Muraki, K.; Funahashi, H.; Kawabata, N. *J. Org. Chem.* **1986**, *51*, 3996. (b) Fry, A. J.; Touster, J. *J. Org. Chem.* **1989**, *54*, 4829.

[3] Baizer, M. M.; Chruma, J. L. *J. Org. Chem.* **1972**, *37*, 1951.

[4] (a) Silvestri, G.; Gambino, S.; Filardo, G.; Greco, G.; Gulotta, A. *Tetrahedron Lett.* **1984**, *25*, 4307. (b) Sibille, S.; d'Incan, E.; Leport, L.; Périchon, J. *Tetrahedron Lett.* **1986**, *27*, 3129. (c) d'Incan, E.; Sibille, S.; Périchon, J.; Moingeon, M. O.; Chaussard, J. *Tetrahedron Lett.* **1986**, *27*, 4175.

[5] (a) Fry, A. J.; Mitnick, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 6207. (b) Similar results are obtained in the electrochemical reduction of 6-bromo-1-hexene, where the product consists of roughly equal amounts of methylcyclohexane and 1-hexene.[6]

[6] Reed, R. G. Ph.D. thesis, Wesleyan University, 1971.

[7] (a) Fry, A. J.; Powers, T. A. *J. Org. Chem.* **1987**, *52*, 2498. (b) Yamasaki, R. B.; Tarle, M.; Casanova, J. *J. Org. Chem.* **1979**, *44*, 4519.

[8] Hoffmann, A. K.; Hodgson, W. G.; Maricle, D. L.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 631.

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

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

[11] (a) Vieira, K. L.; Peters, D. G. *J. Org. Chem.* **1986**, *51*, 1231. (b) Fry, A. J.; Krieger, R. L. *J. Org. Chem.* **1976**, *41*, 54.

[12] (a) Webb, J. L.; Mann, C. K.; Walborsky, H. M. *J. Am. Chem. Soc.* **1970**, *92*, 2042. (b) Casanova, J.; Rogers, H. R. *J. Am. Chem. Soc.* **1974**, *96*, 1942.

[13] Marple. L. W.; Hummelstedt, L. E. I.; Rogers, L. B. *J. Electrochem. Soc.* **1960**, *107*, 437.

[14] Yamasaki, R. B.; Tarle, M.; Casanova, J. *J. Org. Chem.* **1979**, *44*, 4519.

[15] Fry A. J.; Sirisoma, U. N. *J. Org. Chem.* **1993**, *58*, 4919; **1994**, *58*, 2914.

[16] (a) Fry, A. J.; Sirisoma, U. N.; Lee, A. S. *Tetrahedron Lett.* **1993**, *34*, 809. (b) Fry, A. J.; Singh, A. H. *J. Org. Chem.* **1994**, *59*, 8172.

S0022-3263(95)01577-5 CCC: $12.00

**Table 1. Reduction Potentials of α-Substituted Benzyl Bromides, $C_6H_5CH(X)Br$**[a]

| compd | X | $-E_p$[b] |
|---|---|---|
| **1a** | Cl | 1.53 |
| **1b** | Br | 1.52 |
| **1c** | $SiMe_3$ | 1.52 |
| **1d** | H | 1.48 |
| **1e** | Me | 1.55 |

[a] Voltammograms measured as 1.5 mM solutions in acetonitrile/0.1 $Bu_4NPF_6$ *vs* the Ag/0.1 M $AgNO_3$ reference electrode.

dichloro-1,2-diphenylethane (**3a**) (which then undergoes a second electrocatalytic conversion to a mixture of stereoisomeric stilbenes).[15,16] We were interested in preparing radicals such as **2a** by direct electrolysis, which would be experimentally more convenient. Our previous work on the electrochemical reduction of (α-bromoneopentyl)benzene[7a] suggested an approach which might be adaptable to the synthesis of substituted benzyl radicals. As mentioned above, $E_1$ and $E_2$ are very similar for benzyl bromide. It seemed that it ought to be possible to produce substituted benzyl radicals without their undergoing further reduction to carbanions by carrying out direct electrochemical reduction of the corresponding bromides at relatively positive potentials. A secondary advantage of this mode of radical synthesis over the electrocatalytic route should be the fact that at such potentials a wide variety of radical traps could be added to the electrolysis medium without the concern that they might themselves undergo electrochemical reduction.

## Results and Discussion

**Synthesis of Substituted Benzyl Bromides.** Bromination of benzyl chloride by N-bromosuccinimide in refluxing benzene afforded α-bromobenzyl chloride (benzal chlorobromide, **1a**). Similar bromination of benzyltrimethylsilane (**6a**) afforded (α-bromobenzyl)trimethylsilane (**1c**). Bromides **1b**, **1d**, and **1e** were commercial samples.

**Voltammetry.** The reduction potentials of the various α-substituted benzylic bromides **1** were measured by linear sweep voltammetry at a glassy carbon electrode in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP). Potentials were measured relative to a Ag/0.1 M $AgNO_3$ reference electrode (Table 1).[17] All of the benzylic bromides exhibited a sharp, highly symmetrical voltammetric peak at *ca.* −1.5 V (see supporting information). The shape of the peaks is highly suggestive of adsorption of the halides on the carbon surface. This conclusion is reinforced by the presence in the voltammograms of a small voltammetric prewave at *ca.* −1.2 V and the appearance of the waves at platinum- and mercury-coated platinum electrodes, where the substrates gave rise to broad, poorly-defined voltammograms and the prewave was considerably larger. (α-Chlorobenzyl)trimethylsilane (**6b**) exhibited a voltammetric peak potential at −2.10 V. The peak potential of benzal chloride appeared at −2.20 V.

**Electrochemical Reduction.** Each halide was subjected to controlled-potential electrochemical reduction in acetonitrile. Acetonitrile was used because it is a poorer hydrogen atom donor toward electrochemically generated benzyl radicals than is dimethylformamide, which has often been used in the past for electrochemical experiments in this laboratory.[18,19]

Electrochemical reduction of chloride **1a** at −1.2 V afforded a 52:48 mixture of the *meso* and *dl* diastereoisomers of 1,2-diphenyl-1,2-dichloroethane (**3a**) in 93% yield, together with a small amount of *trans*-stilbene (2−3%). Coulometry indicated the consumption of 1.25 electrons/molecule of **1a**. Controlled-potential electrolysis of either diastereomer of **3a** is reported to afford only *trans*-stilbene.[20]

Controlled potential electrochemical reduction of geminal dibromide **1b** in acetonitrile containing TBAHFP at −1.2 V consumed 1.25 faradays/mol of **1b** and resulted in the formation of a mixture of stereoisomeric stilbene dibromides (**3b**) and α-bromostilbenes (**8**) in 69% (*meso:dl* = 5:1) and 31% yield, respectively, together with a trace of *trans*-stilbene. Formation of **8** is probably due to the presence of adventitious water in the solvent and/or supporting electrolyte. We have repeatedly observed in this laboratory that electrolyses in wet solvents form hydroxide ion (electrolysis of water), which in this experiment would convert **3b** into **8.** Formation of **3b** requires 1 faraday/mol of **1b** and formation of **8** requires 2 faraday/mol of **1b** (the additional 1 faraday is required to produce 1 equiv of hydroxide). To produce the observed products, 1.31 faradays/mol should have been consumed, in good agreement with the observed current consumption. The methyne protons of the major and minor diastereomers of **3b** appear at $\delta$ 5.50 and 5.30, respectively, in the $^1H$ NMR spectrum. The fact that the major product from the radical dimerization is *meso*-**3b** was established by addition of $Br_2$ to *trans*-stilbene to afford the authentic *meso* diastereomer, which exhibited its methyne resonance at $\delta$ 5.50. It should be pointed out that electrochemical reduction of **1b** consistently resulted in decay of the electrolysis current to quite low levels (decay of the initial current from 100 to 5 mA) before all of the starting material had been consumed; in the experiment described above, about 35% of the starting dibromide remained unreacted. We attribute this to a partial passivation phenomenon, which we previously observed with this dibromide.[2b] An electrolysis carried out for a long time at very low current did result in total consumption of **1b** but resulted in a mixture consisting of 71% of a 5.4:1 mixture of *trans*- and *cis*-stilbenes, 15% of a mixture of stereoisomers of **8**, and 14% of a mixture of the stereoisomers of **3b**. Apparently, **3b** is slowly converted into stilbenes under these conditions (see Discussion). Regardless of the side reactions which consume **3b** in these experiments, it is notable that electrolysis of **1b** results in 100% conversion to dimeric products.

Electrochemical reduction of **1c** at −1.2 V at 0 °C in acetonitrile containing 0.1 M $LiClO_4$ consumed 0.98 electrons per mole of **1c**. The product consisted of a mixture of four isomeric compounds of molecular formula $C_{20}H_{30}Si_2$ in 94% crude yield in the ratio 39:33:19:9, together with a trace of a fifth substance of mass $C_{30}H_{44}Si_3$ identified only by gas chromatography−mass spectrometry (GC−MS). The first two of these substances proved to be *meso*- and *dl*-1,2-bis(trimethylsilyl)-1,2-diphenylethane (**3c**), respectively.[21−23] After multiple flash chromatographic separations, the purified yields of *meso*- and *dl*-**3c** were 21 and 18%, respectively. Although

---

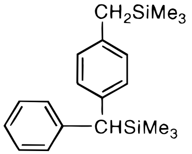
[17] Fry, A. J.; Touster, J. *J. Org. Chem.* **1986**, *51*, 3905.

[18] Savéant, J.-M. *Bull. Soc. Chim. Fr.* **1988**, 225.

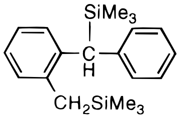
[19] The C−H bond heterolytic bond dissociation energy of $CH_3CN$ is 93−95 kcal/mol, only a few kcal/mol less than that of ethane (98 kcal/mol): Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311.

[20] Lund, H.; Hobolth, E. *Acta Chem. Scand.* **1976**, *30B*, 895.

not high, the 39% combined purified yield of the diastereomers of **3c** is substantially better than from the previous literature procedure for preparation of this substance.[23] The remaining products are a mixture of [*p*- and *o*-(trimethylsilyl)benzhydryl]trimethylsilanes, **4** and **5**, respectively. The two compounds are separable by capillary GC−MS, but not by flash chromatography. Their structures could be assigned by the $^1H$ NMR spectrum of the roughly 2:1 mixture and by their mass spectral cracking patterns. Two other experiments of mechanistic significance should be mentioned here. Benzyltrimethylsilane (**6a**) was produced in low yield in addition to *meso*- and *dl*-**3c**, **4**, and **5** when the electrolysis of **1c** was carried out at $-1.3$ V. Electrochemical reduction of (α-chlorobenzyl)trimethylsilane (**6b**) at $-1.7$ V produced only **6a**.



**4**



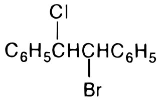
**5**

$C_6H_5CHXSiMe_3$

**6a**, X = H
**b**, X = Cl

The voltammetric wave in the vicinity of $-1.5$ V vs Ag/0.1 M $AgNO_3$ exhibited by each of the benzyl bromides **1a-c** corresponds to reductive cleavage of the carbon−bromine bond to afford the corresponding α-substituted benzyl radical (**2**).[1] As we showed previously with α-bromoneopentyl bromide,[7a] the dimeric products produced in the electrolysis must be produced by dimerization of the intermediate radicals. The waves for the substituted halides **1a**−**c** are not significantly different from that of benzyl bromide (**1d**), probably because of the modest stabilizing effect of halogen[24] and silicon[25] on carbon-centered radicals. It is critically important to produce these radicals at quite positive potentials in order to avoid reduction to the corresponding carbanions. This is evident from the reduction of **6b**, which produced only benzyltrimethylsilane (**6a**) even when electrolysis was carried out at $-1.7$ V (at the foot of its voltammetric wave). Thus, even at the most positive potential at which the electrochemical cleavage of the carbon−chlorine bond of **6b** can be effected, the intermediate radical **2c** is still quickly reduced (the reduction potentials of benzyl radicals are about $-1.6$ to $-1.8$ V).[7,26] Similarly, reduction of benzal chloride (reduction potential = $-2.2$ V) affords carbanion-derived products.[16b] Fortunately, it is possible to carry out the preparative scale electrochemical reduction of the benzyl halides **1a**−**c** at $-1.2$ V, well positive of the voltammetric peak potential and the reduction potential of the radical. The actual electroactive species is probably the adsorbed halide, whose reduction potential is presumably somewhat positive of that of the peak potential.

The three dimers **3a**−**c** are each different with respect to further cathodic electrochemistry. The stereoisomers of dimer **3c** are electroinactive and are stable to the electrolysis conditions. The reduction potential of dichloride **3a** is substantially negative ($\approx$1 V) of the potential ($-1.2$ V) at which the electrolysis was carried out.[20] For this reason, the few percent of stilbene produced in the electrolysis could not possibly be produced by direct electrochemical reduction of **3a** at $-1.2$ V. It is probably formed by $S_N2$ attack of electrochemically-generated bromide ion on **3a** to afford the vicinal bromochloride **7**, which is reducible to stilbene at the electrolysis potential.[27−29] The *meso* and *dl* diastereomers of dibromide **3b**, the initial products of reductive coupling of benzal bromide (**1b**), are readily reduced to stilbene at the electrolysis potential.[29]


$C_6H_5CH(Cl)CH(Br)C_6H_5$

**7**

$C_6H_5CH{=}CBrC_6H_5$

**8**

The formation of substantial amounts of head-to-tail coupling products in the electrochemical reduction of **1c** warrants comment. The electrochemical reduction of 1-bromo-1-phenylethane (**1e**) affords a mixture of dimers analogous to those produced from **1c**, but in different proportions. Head-to-tail dimers constitute less than 3% of the products.[7b] The proportion of head-to-tail coupling of radicals of the type $C_6H_5CHR^{\bullet}$ rises to 28% with R = $SiMe_3$ (present work) and 44% with R = *t*-Bu.[7a,30] There is a rough correlation between the conformational *A*-value[31] and the proportion of head-to-tail product as the R group increases in size through methyl ($A = 1.7$), trimethylsilyl ($A = 2.5$), and *tert*-butyl ($A \geq 4.7$).[31] There is also a second variable to consider: the *meso*:*dl* ratio of head-to-head dimers. Greene pointed out the fact that in principle this ratio should be unity because there is no activation energy for dimerization of radicals and therefore the transition states cannot respond to steric factors.[32] However, it is now known that this stricture can break down when R is very bulky, since head-to-head coupling brings the two groups into close proximity. There ought to be a greater than additive[33] steric effect on dimerization; for example, the steric energy of *cis*-1,3-diaxial dimethylcyclohexane is more than twice the *A*-value of methyl.[34] This effect is apparently sufficiently large for the coupling of sterically hindered radicals to result in an activation energy for radical dimerization.[35] Nonunity *meso*:*dl* ratios have been observed in cases

---

(21) Huang, H. H. *Austr. J. Chem.* **1976**, *29*, 2415.

(22) Hauser and Hance[23] reported the synthesis of **3c** in 1952 without discussion of its stereochemistry; their reported mp of 150-152 °C corresponds to the *meso* diastereomer.

(23) Hauser, C. R.; Hance, C. R. *J. Am. Chem. Soc.* **1952**, *74*, 5091.

(24) Cain, E. N.; Solly, R. K. *J. Am. Chem. Soc.* **1972**, *94*, 3830.

(25) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1*, **1976**, *72*, 2908.

(26) (a) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635; (b) Hapiot, P.; Konovalov, V. V.; Savéant *J. Am. Chem. Soc.* **1995**, *117*, 1428; (c) Wayner, D. D. M.; Sim, B. A.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 4853.

(27) There is ample precedent for $S_N2$ attack on starting material in electrolyses of alkyl halides; see, e.g., ref 10b and: Fry, A. J.; Fry, P. F. *J. Org. Chem.* **1993**, *58*, 3496.

(28) Fawell, P.; Avraamides, J.; Hefter, G. *Aust. J. Chem.* **1991**, *44*, 791.

(29) Dibromide **3b** is reduced at $-0.62$ V vs Ag/0.1 M $AgNO_3$: Inesi, A.; Rampazzo, L. *J. Electroanal. Chem.* **1974**, *54*, 289.

(30) Powers, T. A. B. A. Thesis, Wesleyan University, 1986.

(31) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; pp 695−697.

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

(33) Steric interaction energies rise sharply as the distance between the two interacting groups decreases, though there is no general agreement on how to represent the functional dependence of the repulsive van der Waals' interaction on distance. Some investigators model such interactions using an exponential function, while others prefer an $r^{-12}$ function: Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, D.C., 1982.

(34) (a) Reference 31, pp 701−702. (b) The experimental *cis*-1,3-diaxial dimethyl interaction energy of 3.7 kcal would undoubtedly be far greater ($\gg$100 kcal) except for the distortions which the cyclohexane ring undergoes to minimize the steric repulsion between the two methyl groups: Allinger, N. L.; Miller, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 2145.

where the head of the radical is highly sterically hindered.[36] The effect requires very large R groups; even the relatively bulky trimethylsilyl groups result in a very modest increase in the *meso*:*dl* ratio (1.18 in the present work) over the value of 1.00 observed for R = methyl.[32]

## Experimental Section

**Benzal Chlorobromide (1a).** Benzyl chloride (25.0 g, 0.2 mol) and *N*-bromosuccinimide (35.0 g, 0.2 mol) were heated in 200 mL of benzene for 2 h with 0.05 g of azobisisobutyronitrile. After filtration of the mixture, the resulting solution was distilled *in vacuo* (45 °C/0.5 mm) to afford **1a** (28.8 g, 70%) (lit.[37] bp 31.5 °C/0.15 mm); $^1$H NMR $\delta$ 7.6 (dd, 2 H), 7.35−7.45 (m, 3 H), 6.76 (s, 1 H).

**(α-Bromobenzyl)trimethylsilane (1c).** Benzyltrimethylsilane (**6a**) (20 g, 0.12 mol) and *N*-bromosuccinimide (21.7 g, 0.12 mol) were allowed to react in benzene at reflux as in the preceding synthesis of **1a**. After removal of the solvent, analysis by GC−MS demonstrated the residue to be a 11:46:43 mixture of **6a**, (α-bromobenzyl)trimethylsilane (**1c**), and (α,α-dibromobenzyl)trimethylsilane (**9**). Distillation *in vacuo* afforded **1c**[23] (8 g, 55%) [*m*/*e* 244, 242, 199, 201, 169, 171, 90, 73 (100)] and **9**[23] (9 g, 63%) [*m*/*e* 324, 322, 320, 251, 249, 247, 205, 203, 201, 170 (100), 168 (100), 89, 73]. After two distillations, dibromide **9**, which had previously been reported as a liquid, crystallized upon standing, mp 30−31 °C.

**Representative Electrochemical Reduction. Electrochemical Reduction of 1c.** (α-Bromobenzyl)trimethylsilane (**1c**) (5.185 g, 21.3 mmol) was dissolved in 50 mL of an 0.1 M solution of LiClO$_4$ in CH$_3$CN. The solution was placed in a divided cell[38] containing a graphite cloth[39] cathode, Ag/0.1 M AgNO$_3$ reference electrode, N$_2$ inlet and outlet, magnetic stirring bar, and an anode compartment consisting of a cylindrical tube terminating in a coarse fritted disk covered with a methylcellulose/BuN$_4$PF$_6$/DMF conducting gel[38] and a graphite cloth anode imbedded in the gel. The anolyte was 0.1 M LiClO$_4$ in CH$_3$CN containing a small amount of hydrazine as anodic depolarizer. Electrolysis was carried out at −1.2 V. Over a period of 36 h the electrolysis current decayed from 25 mA to background level (5 mA). The cathode had to be shaken at intervals to prevent passivation by a deposit of crystalline product. The electrolysis was terminated after a passage of 2026 C; the theoretical current consumption is 2060 C. The cell was rinsed with pentane, and the combined solvents were removed by rotary evaporation. The residue was extracted with pentane, washed twice with distilled water and saturated brine, and dried over MgSO$_4$, and the pentane was removed. Analysis by a combination of GC−MS and NMR spectroscopy (the combination of two spectroscopies is necessary because the *ortho* head-to-tail isomer **5** is not resolvable from *meso*-**3c** by GC−MS) showed the product to consist of a 39:33:19:9 mixture of *meso*:*dl*:para:ortho dimers *meso*-**3c**, *dl*-**3c**, **4**, and **5**. The crude product (3.269 g, 94%) was flash chromatographed over silica gel with pentane as eluent to afford 0.741 g (21%) of *meso*-1,2-bis(trimethylsilyl)-1,2-diphenylethane (**3c**) [mp 150−152 °C (lit.[23] 150−152 °C); $^1$H NMR $\delta$ 7.1−7.3 (m, 10 H), 2.70 (s, 2 H), −0.42 (18 H); *m*/*e* 326 (m$^+$) 309, 253, 223, 180, 179, 73 (100)], followed by 0.624 g (18%) of *dl*-**3c** [$^1$H NMR $\delta$ 6.87 (m, 4 H), 7.0−7.1 (m, 6 H), 2.60 (s, 2 H), −0.086 (s, 18 H); *m*/*e* 326 (m$^+$), 309, 253, 223, 179, 180, 135, 73 (100)], followed by a 2:1 inseparable mixture of [*p*-(trimethylsilyl)-benzhydryl]trimethylsilane (**4**) and its *ortho* isomer **5**, 0.513 g (15%). The mixture of **4** and **5** was submitted for microanalysis. Anal. Calcd for C$_{20}$H$_{30}$Si$_2$: C,73.54; H,9.26. Found: C,73.47; H, 9.34. The $^1$H NMR spectra of **4** and **5** could be assigned because of the unequal amounts of the two isomers in the mixture; injection of this mixture into the GC−MS spectrometer after chromatographic separation of the *meso* isomer permitted measurement of the mass spectrum of **5**. *Para*-isomer **4**: $^1$H NMR $\delta$ 7.0−7.3 (9 H), 3.46 (s, 1H) and 2.02 (s, 2H), .02 (s, 9 H), −0.03 (s, 9 H); *m*/*e* 326 (m$^+$), 311, 253, 238, 223, 180, 179, 178, 145, 73 (100). **5**: $^1$H NMR $\delta$ 7−7.3 (m, 9 H), 3.63 (s, 1 H), 2.17 and 1.89 (AB quartet, $J$ = 13.9 Hz, 2H), .08 (s, 9 H), −0.02 (s, 9 H); *m*/*e* 326 (m$^+$), 238, 223, 179, 178, 165, 73 (100).

**Electrochemical Reduction of 1a.** Electrolysis of **1a** (2.0 g) at −1.2 V afforded 1.14 g (93%) of a mixture shown by GC−MS and $^1$H NMR analysis to consist of a 51:47:2 mixture of *meso*-**3a**, *dl*-**3a**, and *trans*-stilbene, respectively.

**Electrochemical Reduction of 1b.** Electrochemical reduction of **1b** carried out in the usual manner consumed 1.25 faradays/mol of **1b** and afforded a mixture that consisted of 35% of **1b** and 65% of a 61:39 mixture of **3b** and **8** by GC−MS.

**Acknowledgment.** Financial support was supplied by the National Science Foundation under Grant No. CHE-9413128. Latorya Hicks purified **9** and obtained it in crystalline form for the first time in this laboratory. A summer fellowship for Ms. Hicks (Lane College) was provided by a National Science Foundation Research Experience for Undergraduates (NSF-REU) grant to the Wesleyan University Chemistry Department.

**Supporting Information Available:** Voltammograms of compounds **1a**−**e** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO951577F

---

(35) Eichin, K.-H.; McCullough, K. J.; Beckhaus, H.-D.; Ruchardt, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 934.

(36) Peyman, A.; Beckhaus, H.-D.; Kramer, D.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1991**, *124*, 1989.

(37) Mark, V. U. S. Patent 3 420 900; *Chem. Abstr.* **1969**, *70*, 67765s.

(38) Reference 1, Chapter 10. Electrolysis cells were obtained from The Electrochemicals Co., 116 Maple Shade Rd., Middletown, CT 06459.

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