0.8 e Å$^{-3}$ were found in the final difference Fourier map very near the methyl carbons of the diethylaluminum moiety. All other peaks were less than 0.6 e Å$^{-3}$. All calculations were carried out on a VAX 11/750 computer with the CRYRM system of programs.

**$[Cp_2Zr(C,O\text{-}\eta^2\text{-}OCCHCH_2CMe_3)]_2(\mu\text{-}H)(\mu\text{-}AlEt_2)$ (X).** A toluene solution of Ia (1.057 g, 1.58 mmol) was treated with several equivalents (0.400 mL, 3.77 mmol) of neat $Et_2AlH$. A deep yellow solution formed and was stirred for 24 h at 80 °C. Removal of solvent in vacuo afforded a dark brown waxy residue that was washed with four 15-mL portions of cold (-30 °C) hexane to yield X as a white powder (0.444 g, 0.589 mmol). The dark brown washings were evacuated to dryness, redissolved in toluene, and stirred at 80 °C for an additional 6 h. Workup in a similar manner provided an additional 0.094 g (0.125 mmol) of X. Recrystallization of 0.100 g of X from 5 mL of $Et_2O$-hexane (3/2) at -20 °C afforded crystals suitable for X-ray diffraction: IR (Nujol) 2800 (vs), 2750 (vs), 1630 (m) ($\nu_{C=C}$), 1630 (s), 1310 (m), 1290 (m), 1255 (w), 1195 (w), 1180 (w), 1155 (w), 1020 (m), 1110 (m), 975 (m), 940 (m), 900 (m), 875 (m), 820 (s), 780 (s) cm$^{-1}$.

**X-ray Structure Determination of $[Cp_2Zr(C,O\text{-}\eta^2\text{-}OCCHCH_2CMe_3)]_2(\mu\text{-}H)(\mu\text{-}AlEt_2)$ (X).** A crystalline block (0.35 × 0.30 × 0.25 mm) of X was mounted approximately along *a* in a glass capillary under $N_2$. A series of oscillation and Weissenberg photographs indicated monoclinic symmetry and the space group *C*2/*c* (*hkl* absent for $h + k$ odd, *h*0*l* absent for *l* odd); data were collected on a Enraf-Nonius CAD-4 diffractometer with a graphite monochromator and Mo Kα radiation (λ = 0.7107 Å). The unit cell parameters (Table II) were calculated from the setting angles of 25 reflections in the range $20 < 2\theta < 35°$. A total of 9443 reflections, comprising four symmetry-equivalent data sets, were averaged to give a total of 2845 reflections. The three check reflections, collected every 10000 s of exposure time, showed no significant deviations in their intensities. The correction for absorption was negligible ($\mu$ = 0.544 mm$^{-1}$). The form factors were taken from Table 2.2B, Vol. IV, "International Tables for X-Ray Crystallography" (1974) for all atoms.

The position of the Zr atoms was derived from the Patterson map, and the Fourier map phased on this atom revealed the remainder of the structure. All H atoms were introduced into the model with fixed coordinates at idealized positions and individual isotropic *U*'s equal in magnitude to that of the adjacent heavy atom, plus 10-20%. Least-squares refinement of all non-hydrogen atoms with anisotropic $U_{ij}$'s, the scale factor, and the two parameters of the hydride H atom (*y* coordinate and *U*), minimizing $\sum_w[F_o^2 - (F_c/k)^2]^2$, with all the data (2845 reflections) led to $S = 1.76$, $R_F = 0.049$, and $R_{F'} = 0.033$;[56] final shift/errors <0.10. The maximum deviation found in the $\Delta\rho$ map is less than 0.8 e Å$^{-3}$. All calculations were carried out on a Vax 11/750 computer with the CRYRM system of programs.

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**Supplementary Material Available:** Atom labeling schemes (Figures 1-4), bond lengths and angles (Tables X1, X4, X8, X12), anisotropic Gaussian amplitudes (Tables X2, X6, X10), hydrogen atom coordinates (Tables X3, X7, X11), and structure factor amplitudes (Tables X5, X9, X13) (71 pages). Ordering information is given on any current masthead page.

# Cyclization Reactions of Electrochemically Generated *o*-(3-Butenyl)phenyl Anions and Radicals to 1-Methylindan

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**Abstract:** Phenyl anions are electrochemically generated upon direct reduction of bromobenzene at mercury and platinum electrodes. Phenyl radicals are the result of the homogeneous reduction of bromobenzene using an electron-transfer mediator, the *m*-tolunitrile radical anion, which is electrochemically generated. Homogeneous reduction of *o*-(3-butenyl)bromobenzene (**3**) by the above mediator results in appreciable intramolecular cyclization of an intermediate to yield a product ratio of 8:1 for 1-methylindan (**1**)/3-butenylbenzene (**2**). Direct electrochemical reductions of **3** result in product ratios of 2:1 and 1:1 for **1**/**2** on platinum and mercury, respectively. In contrast, direct electrochemical reduction of **3** in the presence of $D_2O$ or 2-propanol-*d* significantly decreases these product ratios to 0.2:1 and 0.05:1 on platinum and mercury, respectively. Furthermore, the deuterium incorporation results are consistent with trapping of the *o*-(3-butenyl)phenyl anion prior to reaction to form **1**. Product ratios for **1**/**2** are unaffected by the presence of $D_2O$ or 2-propanol-*d* when **3** is reduced by homogeneous electron transfer from the *m*-tolunitrile radical anion. Cyclization of the *o*-(3-butenyl)phenyl radical can be affected by the addition of the H atom donating species, sodium isopropylate. This allowed a minimum rate constant of $1 \times 10^7$ s$^{-1}$ to be estimated for cyclization of the *o*-(3-butenyl)phenyl radical. These data are consistent with intramolecular cyclization of both the *o*-(3-butenyl)phenyl radical and the *o*-(3-butenyl)phenyl anion to produce **1**.

Elucidation of an organic reaction mechanism often requires the deployment of various trapping schemes in order to detect reactive intermediates. Detection of aryl radicals as intermediates in reductive aryl halide reactions[1,2] has been accomplished by trapping the radicals with various anionic nucleophiles.[3,4] The resultant radical anions can propagate the aryl halide reduction via homogeneous electron transfer in a catalytic process by the $S_{RN}1$ mechanism.[3-5]

Unimolecular trapping processes involving intramolecular cyclizations between a free radical and double bond have been demonstrated for 5-hexenyl radicals,[6,7] in particular for 1-

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methyl-5-hexenyl radicals.[7,8] Analogous cyclizations have been shown for o-(allyloxy)phenyl[9-12] and o-(3-butenyl)phenyl radicals.[9b,10b,12] The intramolecular reactions exhibit regiospecificity in forming cyclopentylmethyl, dihydrobenzofuran, and methylindan derivatives, respectively, and proceed in a facile manner.[10b,13-15] The 5-hexenyl systems have been employed as radical probes[16] for the reactions of alkyl halides with (trimethyltin)sodium,[17] lithium dialkylcuprates,[18] $LiAlH_4$,[19] and *tert*-butyllithium.[20] Likewise, the analogous o-bromo(allyloxy)benzene has been utilized in studies of the reduction of aryl halides by $LiAlH_4$, which was proposed to occur via electron transfer with concomitant formation of an aryl radical.[21] Proposed free radical intermediates in these processes were partially based on evidence for cyclized products.

Lee and Filippo have challenged conclusions formulated from studies that deployed 5-hexenyl systems as radical probes.[22] They concluded that formation of cyclopentylmethyl derivatives could not be regarded as prima facie evidence for radical intermediates. These conclusions are especially noteworthy when examined with respect to the extensive literature dealing with organometallic derivatives of 5-hexenyl systems cyclizing to cyclopentylmethyl organometallics.[23-28] Anionic cyclization, although recognized as an alternative pathway in studies using 5-hexenyl radical probes, has been reported to be a slow[16,23b] and negligible[29] pathway relative to radical cyclization.

Garst and Hines have recently investigated the cyclization of (1-methyl-5-hexenyl)sodium[30] and observed that dimethylcyclopentane is produced in greater quantities than from previous studies.[29] In addition, a trans preference was noted for the dimethylcyclopentane isomers, which was in contrast to preferential cis cyclization of the analogous 1-methyl-5-hexenyl radical.[31] They concluded that although anionic cyclization can occur in significant amounts, cyclization from the 1-methyl-5-hexenyl radical and anion can be distinguished by careful examination of the cis/trans ratios for the dimethylcyclopentane isomers.[30]

Bailey and co-workers have prepared 5-hexenyllithium and monitored its transformation to (cyclopentylmethyl)lithium between −10 and +20 °C by $^1H$ NMR.[32] Although anionic cyclization was much slower than cyclization of the 5-hexenyl radical (by a factor of $10^8$–$10^{10}$), they noted that the half-life of the 5-hexenyl anion (5.5 min at 23 °C) was short when compared to the time scales of experiments employing 5-hexenyl systems as radical probes. In addition, no evidence for a competitive intramolecular 1,4-proton transfer was observed, which had been reported for 5-hexenylsodium[33] and (1-methyl-5-hexenyl)sodium.[30,34] Thus, formation of cyclized products cannot necessarily be used as diagnostic criteria for radical intermediates when employing 5-hexenyl systems as radical probes but must be accompanied with an awareness of the relative rates for radical and anionic cyclizations.

We became interested in trapping aryl radicals during our ongoing investigations of reductive carbon–oxygen bond cleavage of diaryl ethers.[35] Bunnett and co-workers have demonstrated the intermediacy of phenyl radicals in the cleavage of diphenyl ether in $K/NH_3$ by nucleophilic traps.[36] We have considered both nucleophilic and intramolecular cyclizations for aryl radical trapping in our ether studies. However, in view of the previously described literature dealing with the cyclization of alkyl anions, it was deemed necessary to determine whether an aryl anion, such as o-(3-butenyl)phenyl anion, will undergo similar intramolecular cyclization before deploying the butenyl substituent as an aryl radical probe. We report herein the selective generation of the o-(3-butenyl)phenyl anion and the o-(3-butenyl)phenyl radical from the electrochemical reduction of o-(3-butenyl)bromobenzene in *N,N*-dimethylformamide. Evidence will be presented that supports cyclization from both the phenyl anion and radical to yield 1-methylindan.

## Results and Discussion

In order to determine the extent of cyclization for o-(3-butenyl)phenyl anion, techniques that would allow for selective generation of phenyl anions vs. phenyl radicals were desired. Electrochemical reduction of a phenyl halide, o-(3-butenyl)bromobenzene, was selected for this purpose.

Previous studies on the electrochemical reduction of phenyl halides, based on coulometric measurements and product analysis, proposed an overall two-electron reduction with accompanying

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(13) 5-Hexenyl radical rearranges to the cyclopentylmethyl radical with a first order rate constant of $1 \times 10^5$ $s^{-1}$.[14] A rate constant of similar magnitude has been reported for the cyclization of the 1-methyl-5-hexenyl radical.[15] Minimum values of rate constants for the cyclization of o-(allyloxy)phenyl and o-(3-butenyl)phenyl radicals have been reported to be in the range $1.5 \times 10^5$–$6 \times 10^7$ $s^{-1}$, based on competitive rates of hydrogen atom transfer from tributylstannane.[10b]
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(34) Anionic cyclization can be distinguished from radical cyclization in 1-methyl-5-hexenyl systems by careful analysis of the cis/trans ratio for dimethylcyclopentane (vide ante). Garst et al.[30,33] have also suggested that anionic intermediates of 5-hexenyl systems can be detected by the presence of accompanying prototropic rearrangements, which can be detected by analysis of the uncyclized products. The absence of prototropic rearrangement in the investigation by Bailey et al.[32] may be due, in part, to the differences in cations (sodium vs. lithium) and serves to emphasize the care that must be taken when using the 5-hexenyl system as a radical probe.
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**Table I.** Electrochemical Reduction of Bromobenzene in DMF/TBAP[a]

| entry no. | type of reduction[b] | F mol$^{-1}$ | $D_2O$, mM | initial bromobenzene, mM | % bromobenzene remaining[c] | % benzene[c] | % monodeuterated benzene |
|---|---|---|---|---|---|---|---|
| 1 | direct on Pt | 2.1 | 170 | 26.2 | trace | 90% | 80% |
| 2 | direct on Pt | 2.2 | 240 | 49.2 | 2% | 92% | 85% |
| 3 | direct on Pt[d] | 2.6 | 330 | 26.1 | 19% | 67% | 88% |
| 4 | direct on Hg | 1.9 | 340 | 29.9 | trace | 102% | 95% |
| 5 | mediated on Pt | 2.0 | 310 | 25.3 | 7% | 81% | 7% |
| 6 | mediated on Pt[d] | 2.0 | 320 | 30.5 | trace | 85% | 9% |

[a] The concentration of TBAP was 0.1 M. [b] The applied potential was −2.65 V vs. SCE for the direct reductions and −2.25 V vs. SCE for the mediated reductions. [c] Product analysis by HPLC. Product yields are based on the initial concentration of bromobenzene. [d] The concentration of TBAP was 0.2 M.

protonation.[1] Reduction of phenyl halides at an electrode or by a 2:1 lithium–biphenyl adduct (a two-electron reductant) in the presence of $CO_2$ yielded substantial quantities of benzoic acid, suggesting phenyl anion intermediacy.[37] However, aryl radical intermediacy has been unequivocally demonstrated in the $S_{RN}1$ reactions of aryl halides, including phenyl halides.[3-5] Aryl radicals are produced by halide expulsion from aryl halide radical anions. Stabilized radical anions have been directly observed and lifetimes measured by classical electrochemical techniques for species such as 9.-chloroanthracene[38] and fluoro-substituted benzonitriles.[39] Lifetimes of a variety of aryl halide radical anions, which cannot be obtained by classical electrochemical techniques, have been determined by Saveant and co-workers through the application of indirect methods such as homogeneous redox catalysis.[40] Although lifetimes for bromo- or iodobenzene radical anions have not been reported to our knowledge, a minimum value of $1 \times 10^{10}$ $s^{-1}$ can be assigned for the decomposition rate constant (first order) by consideration of similar rate constants for 1-bromonaphthalene and 4-bromobenzonitrile.[41] Thus, an overall electrode reductive mechanism, consistent with diffusion rates of aromatic species in aprotic solvents, can be written for phenyl halides

$$PhX + e^-_{electrode} \rightleftarrows [PhX]^{-\cdot} \quad (1)$$

$$[PhX]^{-\cdot} \xrightarrow{fast} Ph^{\cdot} + X^- \quad (2)$$

$$Ph^{\cdot} + e^-_{electrode} \rightarrow Ph^- \quad (3)$$

$$Ph^- + SH \rightarrow PhH + S^- \quad (4)$$

Halide expulsion occurs in a facile manner such that the phenyl radical is produced near the electrode surface and can be further reduced[42] to a phenyl anion in a classical ECE mechanism. Competing pathways (eq 5 and 6) would occur if the radical anion can diffuse away from the surface before bond fragmentation.

$$Ph^{\cdot} + SH \rightarrow PhH + S^{\cdot} \quad (5)$$

$$Ph^{\cdot} + [PhX]^{-\cdot} \rightarrow Ph^- + PhX \quad (6)$$

de la Torre and Sease demonstrated that phenyl anions, produced from the electrochemical reduction of iodobenzene in DMF, were deuterated by $D_2O$.[43] In addition, Saveant showed that increasing the stability of an aryl halide radical anion (proceeding from 4-halobenzonitrile to 1-halonaphthalene and 9-haloanthracene) results in aryl radical formation further away from the electrode surface with concomitant competition between H atom abstraction and further reduction[38] (see eq 1–6).

A major termination step in the electrode-initiated $S_{RN}1$ reaction of aryl halides, further electrode reduction of intermediate aryl radicals, has been successfully minimized by deployment of an electron-transfer mediator.[44] The mediator is reduced to a radical anion at an electrode, poised at a potential so as not to cause concurrent reduction of the aryl halide. The resultant stable radical anion migrates away from the electrode and undergoes homogeneous electron transfer with the aryl halide substrate. The electron transfer proceeds readily due to a fast follow-up chemical reaction (halide expulsion) of the aryl halide radical anion. Nucleophilic trapping of the resultant aryl radical can then efficiently compete with further reduction from another mediator and propagation of the cycle can occur. In particular, Swartz produced and trapped phenyl radicals from the electrochemical reduction of bromobenzene by utilizing benzonitrile as a mediator.[44a]

**Selective Phenyl Anion and Radical Generation.** On the basis of the described literature (vide supra), phenyl anions should be generated by the direct electrode reduction of a phenyl halide. In contrast, phenyl radicals should be generated from phenyl halide reduction by use of an electron-transfer mediator. In order to clearly demonstrate this, a series of controlled-potential electrolyses were carried out by direct-electrode reduction vs. mediated reduction of bromobenzene (Table I) in *N,N*-dimethylformamide (DMF) with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte.

Direct reduction of bromobenzene ($E_{pc}$ = −2.80 V vs. SCE on platinum by cyclic voltammetry) was conducted on a platinum basket at a potential of −2.65 V in the presence of increasing concentrations of $D_2O$ (entries 1–3, Table I). The percentage of monodeuterium incorporation in the product, benzene, increases with increasing $D_2O$ concentration. These results, which are consistent with those of Sease,[43] indicate phenyl anion formation. However, as the concentration of $D_2O$ is increased, current efficiency decreases. Proton or water reduction is known to have a low overpotential on platinum with resultant formation of adsorbed H atoms on the metal surface. The occurrence of deuterium atom adsorption with subsequent D atom transfer to phenyl radicals needs to be considered for these reactions on platinum. As a result of these considerations, mercury, an electrode material that exhibits an extremely large overpotential for water reduction, was also selected for the investigation. Reduction of bromobenzene on mercury ($E_{pc}$ = −2.68 V) at a potential of −2.65 V in the presence of $D_2O$ is an overall two-electron process with >90% of the product, benzene, monodeuterated (entry 4, Table I). Therefore, electrode reduction of bromobenzene yields a phenyl anion that preferentially abstracts a deuterium ion from $D_2O$ in TBAP/DMF solution.

Controlled-potential electrolyses were conducted on bromobenzene by use of an electron mediator, *m*-tolunitrile[45] ($E_{pc}$ =

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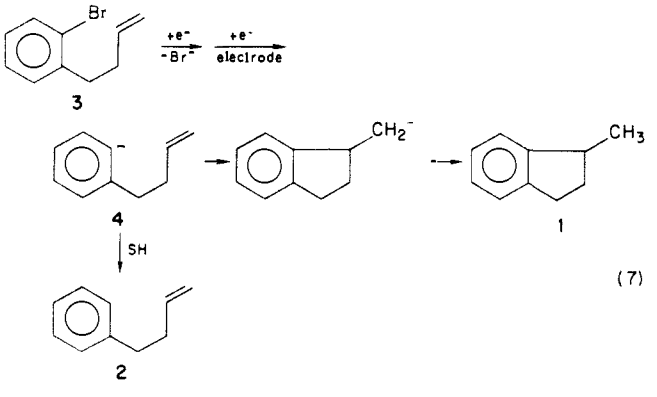
Table II. Electrochemical Reduction of *o*-(3-Butenyl)bromobenzene in DMF/TBAP[a]

| entry no. | type of reduction[b] | $[D_2O]$, mM | products[c] *o*-(3-butenyl) bromobenzene | 1-methyl-indan | 3-butenyl-benzene | ratio of cyclized/uncyclized |
|---|---|---|---|---|---|---|
| 1 | direct on Pt | none | 43% | 35% | 16% | 2:1 |
| 2 | direct on Pt | 400 | 55% | 8% (46%)[d] | 35% (100%)[d] | 0.2:1 |
| 3 | direct on Hg | none | 43% | 20% | 23% | 1:1 |
| 4 | direct on Hg | 400 | 48% | 2% (57%)[d] | 53% (100%)[d] | 0.05:1 |
| 5 | mediated on Pt | none | 49% | 41% | 5% | 8:1 |
| 6 | mediated on Pt | 400 | 67% | 31% (71%)[d] | 4% (42%)[d] | 8:1 |
| 7 | mediated on Hg | none | 43% | 39% | 5% | 8:1 |
| 8 | mediated on Hg | 400 | 45% | 45% (61%)[d] | 5% (25%)[d] | 8:1 |

[a] Concentration of *o*-(3-butenyl)bromobenzene was 25 mM in all runs that were duplicated. All electrolyses were terminated at 1.0 F $mol^{-1}$ except direct reduction on Pt in the presence of $D_2O$, which was terminated at 2.2 F $mol^{-1}$. All mediated electrolyses employed a 1:2 ratio of mediator/substrate. [b] The applied potential was −2.65 V vs. SCE in the direct reductions and −2.25 V vs. SCE in the mediated reductions. [c] Product analysis by gas chromatography, which was periodically checked by HPLC, and based on the initial concentration of *o*-(3-butenyl)bromobenzene. [d] Values in the parentheses represent the extent of monodeuterium incorporation as measured from mass spectral data.

−2.35 V on platinum), at a potential of −2.25 V (entries 5 and 6, Table I). Less than 10% of the benzene was deuterated when the electrolyses were conducted in the presence of a 10-fold excess of $D_2O$. Reduction of bromobenzene in this manner results in formation of the phenyl radical away from the electrode surface where H atom abstraction from solvent and/or electrolyte[47] can effectively compete with further reduction. These data suggest that less than 10% of the phenyl radicals are subsequently reduced to phenyl anions. In summary, direct electrode reduction of bromobenzene on Hg or Pt generates phenyl anions whereas homogeneous reduction by an electron mediator generates phenyl radicals.

***o*-(3-Butenyl)bromobenzene.** The electrochemical reduction of *o*-(3-butenyl)bromobenzene (**3**) was carried out under conditions similar to those employed for bromobenzene. As expected, the cyclic voltammetric behavior of **3** is virtually the same as noted for bromobenzene with $E_{pc} = -2.6$ V on Hg and $E_{pc} = -2.80$ V on Pt. Controlled-potential electrolyses were conducted on **3** in TBAP/DMF solutions in the absence or presence of $D_2O$ (entries 1–4, Table II). Interestingly, the direct reduction of **3** in anhydrous DMF yielded significant quantities of cyclized product, 1-methylindan. Direct electrode reduction of **3** resulted in a product ratio for 1-methylindan (**1**)/3-butenylbenzene (**2**) (cyclized/uncyclized) of approximately 2:1 on platinum and 1:1 on mercury (entries 1 and 3). These results indicate that cyclization of the *o*-(3-butenyl)phenyl anion (**4**), produced from direct reduction of **3**, can effectively compete with proton abstraction from electrolyte, proton-donating impurities, and/or solvent in TBAP/DMF solution (eq 7).




(7)

In order to further test this mechanism, the reduction of **3** was conducted in the presence of a 15-fold excess of $D_2O$. This results in substantial decrease in the yield of **1** with a concomitant increase in the yield of **2** (entries 2 and 4, Table II). The ratio of **1**/**2** decreases to a value of 0.2:1 on Pt and 0.05:1 on Hg when $D_2O$ is present. Furthermore, there is virtually 100% monodeuteration of **2**, which is the predominant product in the direct reduction of **3** with $D_2O$ present.

Since the intermediacy of phenyl radicals in phenyl halide reductions is well established (vide ante), it is conceivable that facile cyclization[10b,13] of the *o*-(3-butenyl)phenyl radical may occur before further electrode reduction. In addition, low current efficiencies due to concurrent $D_2O$ reductions on platinum (entry 2, Table II) with subsequent adsorbed D atoms can be envisioned to cause the observed increase in yield of **2** accompanied with 100% monodeuteration. However, experiments conducted on Hg under similar conditions, in which concurrent $D_2O$ reduction does not occur (vide ante), yield similar results as compared to those obtained on Pt. Therefore, these data are consistent with the mechanism illustrated in eq 7 in which cyclization of the *o*-(3-butenyl)phenyl anion to **1** can successfully compete with protonation in anhydrous TBAP/DMF solution.

Mass spectral data indicate significant (46–57%) but less than 100% deuterium incorporation on the methyl group of 1-methylindan, which is produced in minor amounts (2–8%) (entries 2 and 4). This decreased level in deuterium incorporation may represent small amounts of the *o*-(3-butenyl)phenyl radical being produced away from the electrode surface and undergoing cyclization before reduction. Swartz also noted that small quantities of phenyl radical were trapped by phenylthiolate in the direct reduction of bromobenzene.[44a]

The reduction of **3** was also carried out with an electron mediator, *m*-tolunitrile. With a 1:2 ratio of mediator/substrate, electrolyses were conducted at −2.25 V in the presence or absence of $D_2O$ (entries 5–8, Table II). Reduction of **3** under anhydrous conditions (entries 5 and 7) results in an increase for the product ratio of **1**/**2** from 2:1 for direct reduction to approximately 8:1 for mediated homogeneous reduction.[49] In contrast to the direct reduction, homogeneous reduction of **3** in the presence of a 15-fold excess of $D_2O$ does not significantly alter the cyclized/uncyclized product ratio. These data are consistent with the mechanism represented in eq 8 and 9 in which the principle reductive product of **3** for homogeneous reduction is the *o*-3-butenylphenyl radical (**5**), which readily cyclizes to **1**. Finally, it should be noted that the major product, 1-methylindan, exhibits 61–71% deuterium incorporation on the methyl group when homogeneous reduction of **3** is conducted in the presence of $D_2O$. This point will be discussed in greater detail (vide post).

**H Atom Donor Experiments.** A series of controlled-potential electrolysis experiments was conducted on **3** in the presence of

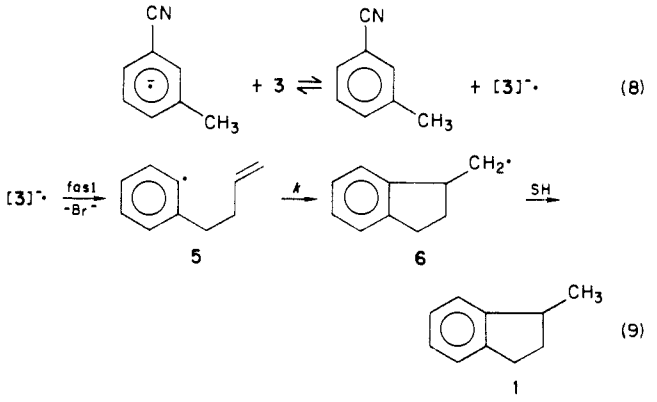
(45) Although Swartz et al. employed[44a] benzonitrile as an electron mediator, the benzonitrile radical anion has been shown[46] to decompose to eventually yield benzene in DMF when small amounts of water are present. Therefore, *m*-tolunitrile, which would form toluene in an analogous manner, was selected as the electron mediator.

(46) Romanin, A. M.; Gennaro, A.; Vianello, E. *J. Electroanal. Chem.* **1978**, *88*, 175–185.

(47) The principle source of H atoms for phenyl radicals is anticipated to be the solvent, DMF.[48] Abstraction of H atom from the tetrabutylammonium cation by phenyl radical in dimethyl sulfoxide ($Me_2SO$) has been shown.[44a]

(48) Russell, G. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 7.

(49) A product ratio of 7.7:1 for **1**/**2** was reported for the chemical reduction of *o*-(3-butenyl)iodobenzene.[50]



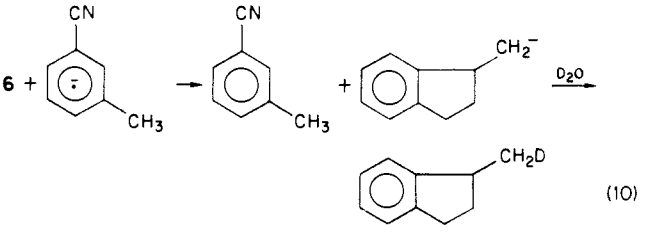

various H atom donors (Table III). A mediated reduction of **3** was conducted in the presence of diisopropyl ether (entry 1), a reactive H atom donor toward phenyl radicals but a poor proton source.[48] The ratio of **1**/**2** is not significantly altered even with the addition of a 25-fold excess of ether. Likewise, a 10-fold excess of dicyclohexylphosphine (DCPH) had no effect on the ratio of cyclized/uncyclized product.[51] These data indicate that hydrogen atom abstraction from either diisopropyl ether or DCPH cannot effectively compete with cyclization of **5**.

Bunnett and Boyle demonstrated that alcoholates are much more reactive H atom donors than the corresponding alcohol.[52] In particular, methoxide ion was observed to be 45 times more reactive than methanol toward the *p*-nitrophenyl radical. Saveant obtained the rate constant ($k = 2.2 \times 10^8$ $M^{-1}$ $s^{-1}$) for the H atom transfer reaction between isopropylate and 2-quinolyl radical in liquid ammonia.[53] It is anticipated that such a rate constant would represent a minimum value for a reaction between isopropylate and a phenyl radical at 25 °C in DMF. Sodium isopropylate was prepared and added to a TBAP/DMF solution. A mediated reduction of **3** was conducted in the presence of isopropylate. Due to limited solubility in DMF, the concentration of isopropylate in entry 2, Table III, represents a concentration estimate. Interestingly, the ratio of **1**/**2** decreases from 8:1 in the absence of alcoholate to a ratio of 5:1 in the presence of alcoholate. Applying the reported[53] isopropylate rate constant for H atom transfer, an estimate of a pseudo-first-order rate constant for reaction between isopropylate and *o*-(3-butenyl)phenyl radical can be obtained. A pseudo-first-order rate constant for H atom transfer under these conditions (0.15 M isopropylate) can be estimated to be at least $3 \times 10^7$ $s^{-1}$. Since H atom transfer can apparently compete with cyclization under the aforementioned conditions, a minimum rate constant of $1 \times 10^7$ $s^{-1}$ can be estimated for *o*-(3-butenyl)phenyl radical cyclization in DMF at 25 °C. Such a value is in agreement with the range of minimum rate constant values reported by Beckwith and Gara.[10b]

Controlled-potential electrolyses were conducted on **3** in the presence of a H atom and proton-donating additive, 2-propanol. In order to correctly assess the role of the additive, 2-propanol-*d* was selected. Direct reduction of **3** in the presence of 2-propanol-*d* results in a decrease of cyclized/uncyclized products to 0.2:1 on platinum and 0.04:1 on mercury (entries 3 and 4, Table III). In addition, 75–85% of the uncyclized product, **2**, is monodeuterated on the aromatic ring. These results, similar to those obtained with $D_2O$ as an additive, are consistent with deuterium ion abstraction from the labeled alcohol by the *o*-(3-butenyl)phenyl anion (eq 7). Furthermore, the presence of 2-propanol-*d* does not influence the ratio of cyclized/uncyclized products for the mediated reduction of **3** (entry 5). The addition of 2-propanol, a less reactive H atom donor than the corresponding alcoholate (vide ante), is not expected to affect the radical cyclization under these additive concentrations. These data are consistent with the radical cyclization mechanism for the mediated reduction of **3** illustrated in eq 8 and 9.

The direct reduction of **3** on a platinum electrode was examined in anhydrous DMF as a function of electrolyte concentration (entries 7–9, Table III). A decrease in the ratio of **1**/**2** from 3:1 to 1.2:1 was observed for an increase in the concentration of TBAP from 0.1 to 0.2 M, respectively. Although the overall product yields were low, the observed decrease in cyclized products with increasing TBAP concentration is nonetheless consistent with anionic cyclization. The principle source of H atoms in TBAP/DMF solution toward a phenyl radical is expected to be the DMF solvent,[47] and therefore radical cyclization should be unaffected by a change in TBAP concentration. However, TBAP is anticipated to be the principle source of protons (Hoffman elimination) in anhydrous TBAP/DMF solutions in a manner analogous to the reaction of phenyl anions with TEAP (tetraethylammonium perchlorate) in DMF.[43]

Further discussion on the deuterium incorporation of the methyl group in methylindan for mediated reductions of **3** is warranted. Significant deuterium incorporation was observed for the mediated reductions with $D_2O$ as an additive (60–70%, entries 6 and 8, Table II) and also 2-propanol-*d* (37%, entry 5, Table III) as an additive. This level of deuterium content may represent further reduction of the cyclized radical to an anion followed by $D^+$ abstraction (eq 10). Decreasing deuterium incorporation as a function of H atom




donating ability of the additive (2-propanol-*d* can donate H atoms whereas $D_2O$ cannot) and the relative stability of the radical **6** suggest that the reaction illustrated in eq 10 may effectively compete with H atom abstraction.[54] Reduction of **6** should be decreased by lowering the concentration of mediator, thereby decreasing the concentration of reductant. The ratio of *m*-tolunitrile/**3** was varied from 1:2 to 1:13 by decreasing the concentration of mediator in the presence of 2-propanol-*d*. As anticipated, the change in mediator/substrate ratio had a negligible effect on the product distribution (entries 5 and 6, Table III). Surprisingly, the level of deuterium incorporation in methylindan decreased only slightly. This is in contrast to the reaction shown in eq 10. Although there are other possible explanations for the level of deuterium incorporation, a firm argument cannot be presented at this time.[55]

## Summary

We have presented evidence for selective generation of the phenyl anion or phenyl radical from bromobenzene by either direct-electrode reduction or electron transfer from an electro-

(50) Bunnett, J. F. In "Extended Abstracts", 163rd Electrochemical Society Meeting, San Francisco, CA, May, 1983; Vol. 83-1, pp 968–969; Abstract No. 646.

(51) DCPH has been shown to be a H atom donating additive that could effectively compete with cyclization of the 1-methyl-5-hexenyl radical.[17,19] Attempts to use similar concentrations of DCPH failed due to the limited solubility of DCPH in DMF.

(52) Boyle, M. J., Jr.; Bunnett, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 1418–1422.

(53) Amatore, C.; Bodoz-Lambling, J.; Bonnel-Huyghes, C.; Pinson, J.; Saveant, J. M.; Thiebault, A. *J. Am. Chem. Soc.* **1982**, *104*, 1979–1986.

(54) Although the ESR spectrum for **6** has not been reported, the spectrum of the similar radical from 1,5-cyclization of the *o*-(allyloxy)phenyl radical has been recorded[10b] in aqueous solution.

(55) An alternative explanation is the participation of the mediator in deuterium-exchange reactions. Examination of the mass spectrum of *m*-tolunitrile, obtained by GC–MS analysis of an electrolysis solution of **3**, indicated substantial deuterium exchange on the aromatic ring (monodeuterated). No evidence for the dihydro derivative of *m*-tolunitrile was observed. Attack of $D^+$ from $D_2O$ at the para or ipso position of *m*-tolunitrile radical anion with respect to the cyano substituent followed by further reduction should yield an anionic intermediate that can readily transfer H or D atom so as to reform the *m*-tolunitrile radical anion. Thus, deuterium exchange on the mediator would result as well as the mediator acting as a D atom donor for a reaction between **6** and $D_2O$.

Table III. Electrochemical Reduction of o-(3-Butenyl)bromobenzene in DMF/TBAP.[a] Influences of Proton and H Atom Donor Additives

| entry no. | type of[b] reduction | additive (concn in M) | products[c] o-(3-butenyl)-bromobenzene | products[c] 1-methyl-indan | products[c] 3-butenyl-benzene | ratio of cyclized/uncyclized |
|---|---|---|---|---|---|---|
| 1 | mediated on Hg | diisopropyl ether (0.65) | 44% | 40% | 4% | 10:1 |
| 2 | mediated on Hg | sodium isopropylate (~0.15) | 53% | 32% | 6% | 5:1 |
| 3 | direct on Hg | 2-propanol-*d* (0.30) | 50% | 2% (36%)[d] | 50% (83%)[d] | 0.04:1 |
| 4 | direct on Pt | 2-propanol-*d* (0.30) | 50% | 8% (25%)[d] | 36% (75%)[d] | 0.22:1 |
| 5 | mediated on Hg | 2-propanol-*d* (0.32) | 56% | 33% (37%)[d] | 4% (32%)[d] | 8:1 |
| 6 | mediated on Hg[e] | 2-propanol-*d* (0.38) | 56% | 27% (33%)[d] | 3% (40%)[d] | 9:1 |
| 7 | direct on Pt[f] | | 9% | 54% | 18% | 3:1 |
| 8 | direct on Pt[f,g] | | 2% | 44% | 36% | 1.2:1 |
| 9 | direct on Pt[f,g] | | 3% | 44% | 34% | 1.3:1 |

[a] Concentration of o-(3-butenyl)bromobenzene was 25 mM in all runs. All electrolyses were terminated at 1.0 F mol$^{-1}$ unless otherwise indicated. All mediated electrolyses employed a 1:2 ratio of mediator/substrate unless otherwise stated. The concentration of TBAP was 0.1 M. [b] The applied potential was −2.65 V vs. SCE for the direct reductions and −2.25 V vs. SCE for the mediated reductions. [c] Product analysis by gas chromatography, which was periodically checked by HPLC. Yields are based on the initial concentration of o-(3-butenyl)bromobenzene. [d] Values in parentheses represent the extent of monodeuterium incorporation as measured from mass spectral data. [e] The ratio of mediator/substrate was 1:13. [f] Electrolyses were terminated at 2.0 mol$^{-1}$. [g] The concentration of TBAP was 0.2 M.

chemically generated mediator, respectively. This methodology has been applied to o-(3-butenyl)bromobenzene in order to selectively generate the o-(3-butenyl)phenyl anion and radical. Regiospecific cyclization[56] of the o-(3-butenyl)phenyl anion to form indanyl methide can effectively compete with proton abstraction in anhydrous TBAP/DMF solutions. Oxidation of the anion by oxygen[11b] to a radical with subsequent cyclization is unlikely due to extensive deoxygenation preparations (see experimental) and the absence of oxygenated products. In addition, evidence for prototropic rearrangement of the o-(3-butenyl)phenyl anion was not observed. Increasing the proton-donating ability of the solvent system with various additives effectively prevented anionic cyclization. The o-(3-butenyl)phenyl radical undergoes a similar regiospecific cyclization to yield the indanylmethyl radical. In contrast to anionic cyclization, addition of proton donors did not influence the radical cyclization reaction. Addition of a reactive H atom donor, isopropylate, demonstrated that H atom abstraction of the o-(3-butenyl)phenyl radical could effectively compete with the facile intramolecular cyclization. This enabled a rate constant of $1 \times 10^7$ s$^{-1}$ to be estimated as a lower limit for the radical cyclization, which is consistent with previously published data.[10b]

These results demonstrate that like the alkyl analogues, intramolecular cyclization of a 3-butenylaryl intermediate cannot be regarded as prima facie evidence of aryl radical intermediacy. Aryl anion intermediacy must also be considered. We have recently presented evidence for the preparation and subsequent cyclization of o-(3-butenyl)phenyllithium to indanyllithium derivative in anhydrous ethereal solvents at 23 °C.[57] In contrast to the o-(3-butenyl)phenyl radical, cyclization of the lithio derivative did not occur at −78 °C. In addition, cyclization of the lithio derivative has been observed to be approximately 10 orders of magnitude slower than for the o-(3-butenyl)phenyl radical, consistent with the kinetic observations for the alkyl analogues.[32] Although anionic cyclization can occur in significant quantities in aprotic organic solvents, conditions can be selected (temperature, etc.) such that the 3-butenyl substituent can be successfully deployed as a radical probe. Work on the effect of the cation in the cyclization reaction of the o-(3-butenyl)phenyl anion is in progress.

## Experimental Section

**Instrumentation, Cells, and Electrodes.** Cyclic voltammetric and controlled-potential electrolysis experiments were carried out with a PAR Model 173 potentiostat equipped with a Model 179 digital coulometer. Cyclic voltammetric waveforms were generated by using a digital-controlled, multifunction generator[58] coupled with the PAR 173. All electrochemical experiments were conducted at 25 ± 1 °C. $^1$H and $^{13}$C NMR spectra were recorded with a Varian EM-390 and a JEOL FX-60, respectively. NMR values are in ppm downfield from internal $Me_4Si$ ($\delta$ = 0 ppm).

Electrochemical solvent–electrolyte, electroactive chemicals, and additives were introduced into airtight, all-glass electrochemical cells in a Vacuum Atmospheres HE-43-2 Dri-Lab glovebox equipped with a HE-493 Dri-Train. The cells for controlled-potential electrolysis were conventional three-electrode electrolysis cells that have been previously described.[59]

The working electrode for the electrolysis experiments was either a large cylindrical piece of platinum gauze or a mercury pool. The auxiliary electrode for an electrolysis experiment was a large coil of platinum wire, which was isolated from the bulk solution by means of a glass frit and a bridge containing saturated TBAP/DMF solution. A spherical platinum-bead electrode was used as a probe electrode for CV when an electrolysis was conducted on the platinum gauze. A planar mercury electrode was prepared via amalgamation of a planar gold electrode (Bioanalytical Systems, Inc.) with mercury and used in conjunction with the mercury pool. The reference was a saturated calomel electrode (SCE) isolated from the bulk solution by means of a glass frit and a bridge containing 0.1 M TBAP/DMF solution.

**Chemicals.** Electrochemical-grade tetra-*n*-butylammonium perchlorate (TBAP) (Southwestern Analytical Chemicals) was used as the supporting electrolyte. *N*,*N*-Dimethylformamide (DMF) (Burdick and Jackson, spectroscopic grade) solutions of 0.1 M TBAP were dried by passage through a column containing freshly activated, anhydrous alumina (Woelm W200 neutral grade Super 1) in the glovebox. The DMF/TBAP solutions were transferred to an all-glass vacuum line and subsequently degassed by several freeze–pump–thaw cycles. Dry, deoxygenated DMF/TBAP solutions were then stored in the glovebox prior to use.[60] All subsequent solutions for electrolysis experiments were prepared in the glovebox, whose atmosphere was periodically checked for oxygen and water content with an exposed 25-W tungsten filament light bulb (typical lifetimes of >3 days indicated sub-ppm levels of contaminants in the argon atmosphere).

3-Butenylbenzene (**2**) was prepared by coupling benzylmagnesium chloride with allyl bromide.[61] Distillation afforded pure **2** by GC analysis. The $^1$H NMR of **2** was in agreement with reported NMR data.[62] 1-Methylindan (**1**) was prepared by methylation of 1-indanone (Aldrich) with methyllithium (Aldrich) followed by reduction with Li/$NH_3$/$NH_4Cl$.[63] Purification by distillation yielded pure **1** (GC analysis), whose $^1$H NMR was in agreement with reported spectral data.[64]

o-(3-Butenyl)bromobenzene (**3**) was prepared by coupling o-bromobenzyl bromide with allylmagnesium chloride. A solution of o-bromobenzyl bromide (Aldrich) (6.34 g, 25.37 mmol) in THF (30 mL) was added dropwise with stirring to a THF solution of excess allylmagnesium

(56) Cyclization of the o-(3-butenyl)phenyl anion and radical to yield eventually tetralin was observed in only trace amounts (<2%).
(57) Ross, G. A.; Koppang, M. D.; Bartak, D. E.; Woolsey, N. F. *J. Am. Chem. Soc.* **1985**, *107*, 6742–6743.
(58) Bartak, D. E.; Hundley, H. K.; Van Swaay, M.; Hawley, M. D. *Chem. Instrum. (N.Y.)* **1972**, *4*, 1–13.
(59) Gores, G. J.; Koeppe, C. E.; Bartak, D. E. *J. Org. Chem.* **1979**, *44*, 380–385.
(60) For further experimental details on solvent–electrolyte purification procedures, see: Koppang, M. D.; Woolsey, N. F.; Bartak, D. E. *J. Am. Chem. Soc.* **1984**, *106*, 2799–2805.
(61) Hurd, C. D.; Bollman, H. T. *J. Am. Chem. Soc.* **1933**, *55*, 699–702.
(62) Reich, H. J.; Shah, S. K.; Chow, F. *J. Am. Chem. Soc.* **1979**, *101*, 6648–6656.
(63) Lipsky, S. D.; Hall, S. S. *Org. Syn.* **1976**, *55*, 7–11.
(64) Franz, J. A.; Camaioni, D. M. *J. Org. Chem.* **1980**, *45*, 5247–5255.

chloride (0.9 M × 150 mL, 135 mmol). All of the Mg metal must be removed from the Grignard solution before addition of the bromide reagent for optimum yields. After addition was completed, the solution was refluxed for 1.5 h. Excess Grignard reagent was quenched with 10% $H_2SO_4$ (50 mL). The butene was extracted with diethyl ether, washed with saturated NaCl, and dried over $MgSO_4$. Removal of solvent followed by vacuum distillation (bp 114 °C (17 mm)) yielded 4.74 g of clear liquid (22.5 mmol, 89% yield) that exhibits the following: $^1$H NMR ($CDCl_3$) $\delta$ 6.80–7.60 (m, 4 H), 5.50–6.10 (m, 1 H), 5.05 (d, $J$ = 8 Hz), 4.80 (s, 1 H), 2.80 (t, $J$ = 7 Hz, 2 H), 2.25 (q, $J$ = 7 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 141.06, 137.61, 132.81, 130.40, 127.61, 127.35, 124.55, 115.26, 35.67, 33.80; mass spectrum (GC—MS) $m/z$ (relative intensity) 212 ($M^{+\cdot}$ $^{81}$Br, 2), 210 ($M^{+\cdot}$ $^{79}$Br, 3), 171 (100), 169 (97), 131 (54), 130 (31), 90 (23), 89 (22), 63 (13), 51 (11).

Diisopropyl ether (Aldrich) was deoxygenated on the vacuum line (freeze–pump–thaw) and dried by passage through a column of activated alumina in the glovebox. 2-Propanol-*d* (98+ atom % D) and deuterium oxide (99.8 atom % D, Gold Label) were purchased from Aldrich and used as received. Sodium isopropylate was prepared by combining sodium metal (0.04 g-atom) with spectroscopic-grade 2-propanol (50 mL) (J. T. Baker) under $N_2$, heated (40–60 °C), and stirred until all of the metal had reacted. Excess alcohol was removed by heating (100–110 °C) under vacuum to yield the alcoholate, which was transferred and stored in the glovebox.

**Controlled-Potential Electrolysis and Product Analysis.** Controlled-potential electrolyses of bromobenzene and **3** were conducted at −2.65 and −2.25 V vs. SCE for direct electrode and mediated reductions, respectively. Electrolyses were terminated after the addition of 1 F mol$^{-1}$, unless otherwise indicated (Tables I–III). Upon completion of an electrolysis, $HClO_4$ was added to the solution under a positive argon atmosphere.

Products from electrolyzed solutions of **3** were quantitatively extracted into diethyl ether in the following manner. An internal standard nnaphthalene) and an aliquot of electrolyzed solution (10 mL) were added to water (20 mL) and ether (20 mL). The aqueous and organic layers were cooled (ice bath), filtered, acidified (5% HCl, pH <2 for aqueous phase), and separated. The aqueous phase was extracted with ether (3 × 5 mL) and all organic extracts were combined. The ether extract was washed with 5% HCl (3 × 5 mL), dried ($MgSO_4$), and filtered. The extracted solutions were qualitatively and quantitatively analyzed by gas chromatography on a Shimadzu GC-6AM GC equipped with $^1/_8$-in., all-glass packed columns (3% Dexsil 300 on Supelcoport, 100/120 mesh, 6-m) and FID detectors. The GC was coupled to a Hewlett-Packard (3390A) recording integrator. Qualitative identification was accomplished by spiking techniques. Quantitation of products was achieved by using response factors obtained for standard solutions of the observed products with respect to naphthalene. Product quantitation by GC analysis was periodically cross-checked by high-pressure liquid chromatographic analysis on a Waters Associates 6000A HPLC equipped with a Model 660 solvent programmer. The electrolyzed solutions of **3** were injected directly onto a 0.25 in. × 25 cm Alltech C18 column with a 10-$\mu$m mean particle-size packing. Products were identified by spiking techniques and were separated under isocratic eluent conditions (50% acetonitrile/50% water; flow rate = 1 mL min$^{-1}$). Calibration curves were prepared and employed for product quantitation.

Quantitation of products from the bromobenzene electrolyses was accomplished by HPLC analysis using similar methodology. Electrolyzed solutions were directly injected onto the C18 column and products were separated under the aforementioned eluent conditions. Electrolyzed solutions were extracted with diethyl ether (vide ante) for qualitative GC analysis.

Additional qualitative product analyses and deuterium-incorporation measurements were performed on extracted electrolysis solutions of **3** and bromobenzene by gas chromatography–mass spectroscopy (GC–MS). The extracted solutions were injected onto a Hewlett-Packard GC (Model 5790A) (25 m, OV-17 WCOT capillary column) equipped with a Hewlett-Packard mass-selective detector (Model 5970A). Chromatographic peaks were assigned to products by comparison of the resultant spectra with published spectra[65] or characteristic spectral fragmentation patterns. Deuterium-incorporation measurements for benzene, 3-butenylbenzene, and 1-methylindan were obtained from mass-spectral data analysis (GC–MS) using a procedure that has been described in detail.[66] Evidence for multiple deuterium atom incorporation was not observed for the electrolysis products of benzene, **1**, or **2**. In addition, deuterium incorporation for **1** and **2** was only observed in the methyl group for the former and in the ring for the latter compound.

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**Registry No. 1**, 767-58-8; **2**, 768-56-9; **3**, 71813-50-8; **4**, 100312-11-6; **5**, 57056-96-9; **6**, 75421-38-4; $D_2O$, 7789-20-0; Pt, 7440-06-4; Hg, 7439-97-6; bromobenzene, 108-86-1; benzene, 71-43-2; benzene-*d*, 1120-89-4; *m*-tolunitrile, 620-22-4; diisopropyl ether, 108-20-3; sodium isopropylate, 683-60-3; 2-propanol-*d*, 3979-51-9; phenyl anion, 30922-78-2; phenyl radical, 2396-01-2; *o*-bromobenzyl bromide, 3433-80-5; allylmagnesium chloride, 2622-05-1.

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