J. Org. Chem. 1989, 54, 526–529

# Reduction of Organic Compounds at Lead Cathodes and Mediation by Dimethylpyrrolidinium Ion

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*Received July 28, 1988*

Reduction of several organic compounds at Pb cathodes was studied and the use of dimethylpyrrolidinium ($DMP^+$) as a mediator for such reactions was evaluated. Following previous reports that have shown that the reduction product of $DMP^+$ at Pb deposits as a monolayer and bulk $DMP(Pb_5)$, the catalytic properties of both phases for organic electroreduction were investigated. Of the organic compounds investigated, the monolayer catalyzes the reduction of alkyl chlorides only. Bulk $DMP(Pb_5)$ mediates electron transfer also to several ketones, allylbenzene, and difluorobenzene. Of particular interest is the fact that the reduction of 6-hepten-2-one (**5**), 6-heptyn-2-one, and 5-phenylpentan-2-one can be catalyzed whereas other ketones are unaffected. Preparative electrolyses at Pb were performed with 6-chloro-1-hexene (**4**) and 6-hepten-2-one (**5**). The main product of **4** was 1-hexene, whereas **5** yielded 1,2-dimethylcyclopentanol exclusively. The reduction of **4** and **5** in the presence of catalytic amounts of $DMP^+$ can be achieved at potentials 400–500-mV positive of the reduction potentials when $DMP^+$ is absent. The mechanism of the reductive cyclization of **5** is discussed.

Cathodic reduction of organic compounds has commonly been accomplished with mercury, platinum, or carbon electrodes. Other electrode materials are of interest, especially because recent studies have shown that metal cathodes are not always inert but can be chemically involved in the reduction process. Some behavior of lead cathodes suggests such involvement and this paper recounts our experience with lead cathodes in the presence of tetraalkylammonium ions for organic reductions. In several cases it appears that (tetraalkylammonium)lead intermediates are involved.

(Tetraalkylammonium)metals can be generated by cathodic reduction of tetraalkylammonium cations ($R_4N^+$) at several metals.[1] These (tetraalkylammonium)metals incorporate $R_4N^+$, electrons, and metal from the electrode. For several $R_4N^+$ reduced at mercury the composition has been determined[2] to be $R_4N(Hg_5)$. $R_4N(Hg_5)$ species are reducing agents. The dimethylpyrrolidinium ($DMP^+$) derivative $DMP(Hg_5)$ has been used[3] as a mediator, generated in situ, to achieve the cathodic reduction of a series of difficult-to-reduce organic substrates. These experiments involved the use of catalytic amounts of $DMP^+$ for electrolyses at Hg cathodes. Under these conditions the organic compounds reacted at the reduction potential of $DMP^+$. The reactants were electroinactive at this potential when $DMP^+$ was absent. In many cases the products of the $DMP^+$-mediated reduction were different than those obtained from direct electrolysis. The proposed mechanism for these mediated reductions is as follows:

$$DMP^+[\text{soln}] + 1e^- + 5Hg[\text{electrode}] \rightleftharpoons DMP(Hg_5)[\text{solid}]$$

$$DMP(Hg_5) + \text{reactant} \rightarrow \text{product} + DMP^+ + 5Hg$$

Recently, the reduction of $DMP^+$ at Pb cathodes was studied in some detail. The composition of the stable product was found[4] to be $DMP(Pb_5)$. The kinetics of the process were elucidated[5] and compared to the kinetics of $R_4N(Hg_5)$ formation.

**Table I. CV Data, at a Pb Wire Cathode, DMF, 0.05 M $(C_4H_9)_4NBF_4$**

| compd (concn, mM) | $E_p$ [−V(SCE)][a] |
|---|---|
| anthracene (1) | 1.99 (rev), 2.59 |
| phenanthrene (1) | 2.48 (rev) |
| naphthalene (5) | 2.60 (rev) |
| 1-methylnaphthalene (1) | 2.60 (rev) |
| 4-(1-naphthyl)-1-butene (1) | 2.58 (rev) |
| benzonitrile (1) | 2.37 (rev) |
| 2-allylbiphenyl (1) | 2.76[b] |
| fluorene (1) | 2.71 |
| **1** (1) | 2.24 |
| **2** (2) | 2.34 |
| **3** (1) | 2.60 |
| 1-phenyl-2-butanone (3) | 2.70[b] |
| 1,3-difluorobenzene (4) | 2.81[b] |

[a] Measured at 50 mV $s^{-1}$; (rev) means reversible couple. [b] Only a shoulder on rising background current.

The goals of the present study were to evaluate the possibility of mediating organic electroreductions by means of $DMP(Pb_5)$ and, if successful, to study the products of $DMP^+$-mediated organic reductions at Pb.

## Results and Discussion

Information on cathodic reductions at Pb is sparse, particularly when organic solvents are used.[6] We therefore employed cyclic voltammetry to learn about the cathodic behavior of a number of organic molecules at Pb. Cyclic voltammograms (CV's) were recorded at Pb wire electrodes, first with the electrolyte solution (0.05 M $(C_4H_9)_4NBF_4$ in DMF) only and then with increasing concentrations (0.001–0.006 M) of several reactants. Compounds that exhibited cathodic CV peaks are listed in Table I.

The range of potentials available is limited by the formation of the uncharacterized (tetrabutylammonium)lead at −2.8 V. Within this range several aromatic hydrocarbons show reversible couples (peak separation ~60 mV) at the expected potentials.[6] Thus a lead wire can be used just as well as the more common cathode materials. Also shown in Table I are data for several compounds that show

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[1] Kariv-Miller, E.; Lawin, P. B.; Vajtner, Z. *J. Electroanal. Chem.* **1985**, *195*, 435.

[2] (a) Kariv-Miller, E.; Svetličić, V. *J. Electroanal. Chem.* **1986**, *205*, 319. (b) Ryan, C. R.; Svetličić, V.; Kariv-Miller, E. *J. Electroanal. Chem.* **1987**, *219*, 247.

[3] (a) Kariv-Miller, E.; Andruzzi, R. *J. Electroanal. Chem.* **1985**, *187*, 175. (b) Kariv-Miller, E.; Vajtner, Z. *J. Org. Chem.* **1985**, *50*, 1394. (c) Kariv-Miller, E.; Mahachi, T. J. *J. Org. Chem.* **1986**, *51*, 1041.

[4] Kariv-Miller, E.; Lawin, P. B. *J. Electroanal. Chem.* **1988**, *247*, 345.

[5] Lawin, P. B.; Svetličić, V.; Kariv-Miller, E., unpublished results.

[6] Meites, L.; Zuman, P. *CRC Handbook Series in Organic Electrochemistry*; CRC Press: Boca Ratan, FL, 1983; Vol. 1–6.

0022-3263/89/1954-0526$01.50/0

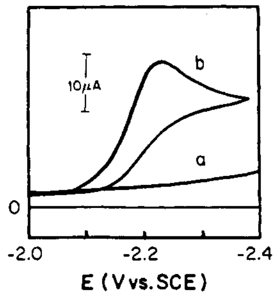


**Figure 1.** CV for 1 at a Pb wire cathode, $v$ = 50 mV $s^{-1}$: (a) electrolyte solution DMF, 0.05 M $(C_4H_9)_4NBF_4$; (b) 0.001 M 1 in (a).

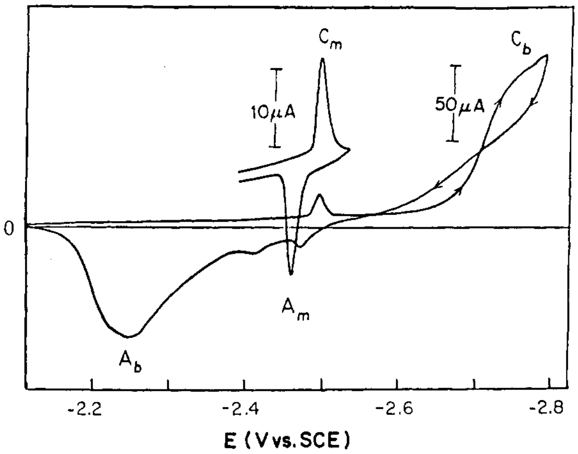
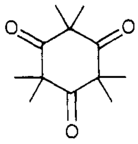


**Figure 2.** CV for $DMP^+$ at a Pb wire cathode: 0.005 M DMP$(BF_4)$ in DMF, 0.05 M $(C_4H_9)_4NBF_4$; $v$ = 50 mV $s^{-1}$.

cathodic peaks but no anodic peak on the reverse scan (Figure 1). Most interesting among these are the cyclic triketone 1 and the diketones 2 and 3. It has been previously proposed[7] from results using a dropping mercury electrode that anion-radicals of compounds like 1, 2, and 3 have strong interactions between the carbonyl groups which lead to fast follow-up reactions and reduction potentials which are more positive than those for simple ketones. A large number of other compounds were studied under these conditions and showed no cathodic peaks. These compounds were also studied with $DMP^+$ as a mediator and many were shown to be reactive at lead in the presence of this catalyst.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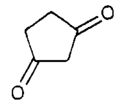
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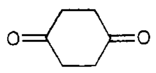
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Studies[4,5] of the reduction of $DMP^+$ at Pb have shown that $DMP(Pb_5)$ is a solid and two processes are involved, deposition of a monolayer followed by deposition of the bulk product. The two processes are detectible by means of cyclic voltammetry (Figure 2), which exhibits two pairs of deposition/stripping peaks, $C_m/A_m$ for the monolayer and $C_b/A_b$ for the bulk species. Since the catalytic properties of the monolayer and the bulk $DMP(Pb_5)$ could be different, the interaction of each with the organic molecules was investigated. The organic substrates used were the

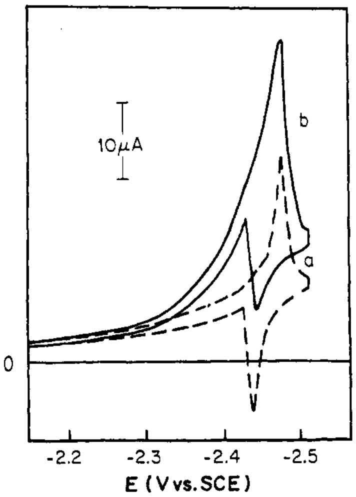

**Figure 3.** CV for the $DMP^+$-catalyzed reduction of 4, $v$ = 50 mV $s^{-1}$: (a) 0.005 M $DMP(BF_4)$ in DMF, 0.05 M $(C_4H_9)_4NBF_4$; (b) 0.001 M 4 in (a).

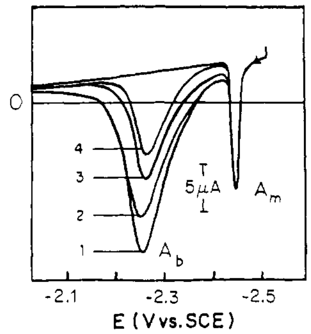

**Figure 4.** Anodic LSV's for the catalyzed reduction of 5. LSV's (50 mV $s^{-1}$) following constant potential electrolysis at −2.52 V for 60 s of 0.005 M $DMP(BF_4)$ in DMF, 0.05 M $(C_4H_9)_4NBF_4$. Concentration of 5: (1) none, (2) 1 mM, (3) 3 mM, (4) 4 mM.

ones with $E_p$ more negative than −2.80 V, to avoid interference with the reduction of $DMP^+$.

Catalysis of the reduction of organic compounds by the monolayer was detected by cyclic voltammetry. Instead of the cathodic/anodic pair of peaks ($C_m/A_m$) with equal size, catalysis leads to an increased cathodic peak and a decreased anodic peak.[3a] A series of CV's in the potential region for production of the $DMP(Pb_5)$ monolayer (−2.00 to −2.52 V) was recorded, first with 0.005 M $DMP^+$ only followed by increasing concentrations (0.001 to 0.006 M) of each of the organic compounds. Only the alkyl chlorides (Table II, first three entries) caused an increase in the cathodic current ($C_m$) and a decrease in the anodic current ($A_m$). The CV's for 6-chloro-1-hexene are shown as an example in Figure 3.

For investigation of catalysis by bulk $DMP(Pb_5)$, a study of the bulk CV peaks ($C_b/A_b$), like that used for $C_m/A_m$, was inappropriate because the cathodic peak ($C_b$) overlaps with the background and exhibits hysteresis when the potential is reversed (Figure 2). However, bulk $DMP(Pb_5)$ can be formed by constant-potential electrolysis at a potential negative of −2.50 V and can be consequently stripped anodically.[4,5] Testing for catalysis by bulk $(DMP(Pb_5)$ could, therefore, be accomplished with constant-potential electrolysis (CPE), followed by anodic linear sweep voltammetry (LSV) to see how much DMP$(Pb_5)$ remained. In practice the potential was held constant at −2.52 V for 60 s; the deposit was then stripped by means of LSV at $v$ = 50 mV $s^{-1}$ and its amount was determined from the anodic charge $Q_b$ (the area of peak $A_b$).

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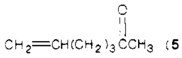
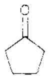
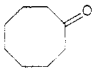
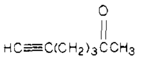
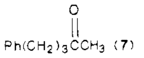
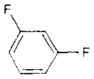
(7) (a) Kariv-Miller, E.; Cohen, B. J.; Gileadi, E. *Tetrahedron* **1971**, *27*, 805. (b) Kariv-Miller, E.; Hermolin, J.; Rubinstein, I.; Gileadi, E. *Tetrahedron* **1971**, *27*, 1303. (c) Kariv-Miller, E.; Cohen, B. J. *J. Chem. Soc. Perkin Trans. II* **1972**, 509.

Table II. Data from Anodic LSV Recorded Following CPE (Pb Wire Cathode; 0.005 M $DMP^+$; 0.003 M Organic Compound in DMF, 0.05 M $(C_4H_9)_4NBF_4$; CPE at −2.52 V for 60 s; LSV at $v$ = 50 mV $s^{-1}$)

| compd | decrease in $Q_b$, % |
|---|---|
| $CH_2{=}CH(CH_2)_3CH_2Cl$ (4) | 100 |
| $CH_3(CH_2)_4CH_2Cl$ | 100 |
| $CH_3(CH_2)_6CH_2Cl$ | 100 |
|  $CH_2{=}CH(CH_2)_3\overset{\overset{O}{\parallel}}{C}CH_3$ (5) | 37 |
|  | 28 |
|  | 24 |
|  $HC{\equiv}C(CH_2)_3\overset{\overset{O}{\parallel}}{C}CH_3$ (6) | 20 |
|  $Ph(CH_2)_3\overset{\overset{O}{\parallel}}{C}CH_3$ (7) | 13 |
| $PhCH_2CH{=}CH_2$ | 32[a] |
|  | 16[a] |

[a] The concentration of the organic compound was 0.004 M.

Experiments were carried out with 0.005 M $DMP^+$ only, and with $DMP^+$ solutions containing each of the organic compounds. All the compounds listed in Table II caused a decrease of $Q_b$. They behaved similarly and the LSV's recorded with 6-hepten-2-one (5) following CPE are shown as examples in Figure 4. The decrease in $Q_b$ depends on the concentration of the organic compound and is larger at higher concentrations. Except for alkyl chlorides, the stripping peak for the monolayer ($A_m$) is unaffected by the organic compounds. As expected from the CV studies of the alkyl chlorides the peak $A_b$ is completely absent, even at the lowest concentration [RCl] = 0.001 M, indicating that all the bulk $DMP(Pb_5)$ generated at the CPE step is consumed. In addition, $A_m$ decreased (the shape of the LSV was identical with the anodic scan of the CV, as shown in Figure 3, confirming the catalytic properties of the monolayer for alkyl chlorides.

In contrast to these examples of successful catalysis, several compounds shown to be reduced at Hg are inactive with $DMP^+$ at Pb. Both methods, CV and the CPE (−2.52 V) followed by LSV, were used in attempt to detect catalysis. Compounds whose reductions are uncatalyzed (concentration, mM) were 2-pentanone (3), 1-hexyne (3), 1-hexene (3), benzene (7), 5-hexen-2-one (12), fluorobenzene (6), 2,4-dimethyl-1,3-pentadiene (9), and diphenyl ether (9). Of these, 2-pentanone, 5-hexen-2-one, fluorobenzene, and 2,4-dimethyl-1,3-pentadiene can be catalyzed[3a] by $DMP^+$ at Hg. This shows that monolayer or bulk $DMP(Pb_5)$ is less reactive than $DMP(Hg_5)$.

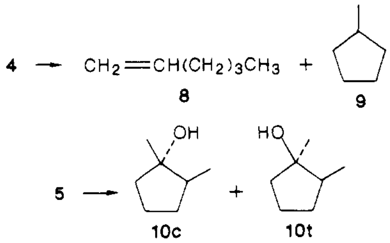
The experiments described indicate that electron transfer to the organic compounds listed in Table II can be mediated by $DMP(Pb_5)$. Although the mechanisms are yet unknown, and it is reasonable that they will differ for different functional groups, it is possible to make a crude comparison of some overall reaction rates from the available data. The percent decrease of $Q_b$ caused by the same concentration of the different substrates (Table II), as a measure, shows that the rate of catalysis is highest for alkyl chlorides. A "safer" comparison is among substrates with the same functional group, which are likely to follow a similar mechanism. Comparing the percent decrease of $Q_b$ for the various ketones studied shows that the rate of catalysis is cyclopentanone > cyclooctanone, whereas 2-pentanone and 5-hexen-2-one are not catalyzed. This is in accord with the expected reactivities of the carbonyls. Reductions of 6-hepten-2-one (5), 6-heptyn-2-one (6), and 5-phenylpentan-2-one (7), all of which contain an unstrained carbonyl, are catalyzed in the order 5 > 6 > 7. The fact that catalysis is observed for 5, 6, and 7 but not for the comparable dialkyl ketone, 2-pentanone, is remarkable. It could originate from the unsaturated moiety of the molecules; but, since 1-hexene, 1-hexyne, and benzene are unreactive, it seems that both the carbonyl and the unsaturated moiety are necessary for catalysis. The difference between 5, 6, and 7 in comparison with 5-hexen-2-one (which is not catalyzed) probably arises because 5, 6, and 7 undergo radical cyclization, whereas 5-hexen-2-one does not. It is noteworthy that electrogenerated $DMP(Hg_5)$ catalyzes intramolecular reductive cyclization of 5, 6, and 7. In addition the rates of catalysis[8] by $DMP^+$ at Hg as at Pb are 5 > 6 > 7, and 5-hexen-2-one does not cyclize.

Table III. Composition of Preparative Reduction Mixtures after Transfer of 2 F $mol^{-1}$ (1 mmol of Reactant in 25 mL of DMF, 0.1 $M(C_4H_9)_4NBF_4$)

| reactant | $[DMP^+]$ | $E$ [−V(SCE)] | composition of electrolysis mixture |
|---|---|---|---|
| 4[a] | 0 | 3.05[c] | 8 (87%); 9 (6%); 4 (7%) |
| 4[a] | 0.005 M | 2.55[c] | 8 (78%); 9 (7%); 4 (15%) |
| 5[b] | 0 | 2.95[d] | 10 (73%);[e] 5 (27%) |
| 5[b] | 0.005 M | 2.55[d] | 10 (36%);[f] 5 (64%) |

[a] The mass yield was 60–70% (comment in Experimental Section). [b] The mass yield was 80–95%. [c] The reaction current was 60 mA. [d] The reaction current was 30 mA. [e] The ratio 10c/(10c + 10t) was 0.75. [f] The ratio 10c/(10c + 10t) was 0.86.

To investigate the catalytic effect of $DMP(Pb_5)$ on a preparative scale, we chose to study 6-chloro-1-hexene (4) and 6-hepten-2-one (5). We performed preparative electrolyses of each substrate, in solutions containing $DMP^+$ and without it. Products were identified and their yields determined (Table III). In a typical experiment 0.001 mol of organic substrate in 25 mL of DMF (0.1 M $(C_4H_9)_4NBF_4$) was electrolyzed at a Pb plate cathode. Formation of products and the consumption of reactants were monitored by calibrated GC analysis of aliquots withdrawn from the electrolysis cell. Upon completion, the electrolysis mixtures were worked up and the major products were compared with authentic samples. The major product of 6-chloro-1-hexene (4) was 1-hexene (8) accompanied by small amounts of methylcyclopentane (9). 1,2-Dimethylcyclopentanol (10) was the exlcusive product of 5. In solutions containing $DMP^+$ reduction was achieved at −2.55 V, a potential at which neither 4 nor 5 is electroactive. In the absence of $DMP^+$, the currents at −2.55 V were negligible (~2 mA) and reductions were carried out at −3.05 V for 4 and −2.95 V for 5. Thus, the potentials for preparative reduction of 4 and 5 are shifted positively by 500 mV and 400 mV, respectively. Values of the reduction currents measured in the presence of $DMP^+$, 60 mA for 4, and 30 mA for 5, confirmed the CV



observation that the overall reaction of **4** under these conditions is faster than that of **5**.

Reduction of **5** yields two stereoisomeric alcohols **10c** and **10t**. The cis isomer **10c** predominates, whether or not DMP$^+$ is used, and the yields **10c**/(**10c** + **10t**) are 86% in the presence of DMP$^+$ and 75% without it. The effect of DMP$^+$ at Pb cathodes on the stereochemistry of **10** is not understood. It is noteworthy that it resembles the DMP$^+$-catalyzed reduction of **5** at Hg cathodes. In this case, which has been studied in more detail,[8] the cyclic **10** is exclusively formed and the cis isomer **10c** predominates. However, at a Hg cathode without DMP$^+$, the only product of **5** is the simple straight-chain 6-hepten-2-ol. Cyclic voltammetry has shown that **5** has a cathodic reduction peak at Hg, indicating direct electron transfer from this cathode to **5**. Exclusive formation of cyclic **10** in the presence of DMP$^+$ vs the simple reduction to 6-hepten-2-ol when DMP$^+$ is absent can be rationalized if we assume 2e$^-$ transfer in the direct reduction vs 1e$^-$ transfer and cyclization of the radical anion in the DMP(Hg$_5$)-mediated process. Since at the Pb cathode **5** does not exhibit a reduction peak and only the cyclic product **10** is observed, it is possible that at this cathode, with or without DMP$^+$, the reduction of **5** is mediated. Preparative reduction of **5** at Pb (when DMP$^+$ is absent) takes place at potentials at which the electrolyte is electroactive and it could be that a $(C_4H_9)_4$-lead product participates in the reaction sequence.

Reviewing the preparative results in Table III, we believe that reductive elimination of chloride from alkyl chlorides and reductive intramolecular cyclization of 6-en-2-ones can be achieved by cathodic reduction at Pb electrodes. Both types of reactions can be mediated by DMP$^+$ and can be performed at the reduction potential of the catalyst at which the organic compounds themselves are electroinactive. The catalyst slightly decreases the efficiency of reduction of alkyl chlorides (after transfer of 2 F mol$^{-1}$, 15% unreacted **4** remains as compared to 7% when DMP$^+$ is absent). It significantly lowers the rate of reduction of ketones (the yield of **10** in the presence of DMP$^+$ is half of that obtained when DMP$^+$ is absent). This indicates that the catalytic system DMP$^+$/Pb cathode may be useful for selective cleavage of C–Cl bonds when ketone is also present.

## Experimental Section

**Materials.** (DMP)BF$_4$ was prepared by a reported procedure.[3a] $(C_4H_9)_4NBF_4$ was prepared by the reaction of $(C_4H_9)_4NBr$ (Southwestern Analytical) with HBF$_4$[9] and by recrystallization from ethyl acetate–pentane. The cathode was a Pb plate (Alfa, 99.9%). The solvent, DMF (Burdick and Jackson, high purity), was distilled in vacuo and the middle 60% were stored over activated alumina (Fisher Scientific). 6-Chloro-1-hexene (**4**) was prepared[10] by reaction of 5-hexen-1-ol (Aldrich) with thionyl chloride. 6-Hepten-2-one (**5**) and 5-phenylpentan-2-one (**7**) were prepared by condensation of the corresponding alkyl bromide with ethyl acetoacetate[11] followed by decarboxylation.[12] 6-Heptyn-2-one (**6**) was obtained from 3-methyl-2-cyclohexenone (Aldrich) by epoxidation followed by treatment with (*p*-tolylsulfonyl)hydrazine.[13]

**Cyclic Voltammetry.** Measurements were performed with a PAR 173 potentiostat, a PAR 175 universal programmer, and an omnigraphic 2000 x-y recorder. The working electrode was a Pb wire ($d$ = 0.75 mm) purchased from Alfa products (99.9995%). The geometric area of the Pb wire submerged in the solution was 0.1 ± 0.01 cm$^2$. The electrode was pretreated by scanning the potential negatively up to ca. −3.0V, prior to each set of experiments. The reference electrode was a SCE.[3a] The counter electrode was a platinum wire and the cell was a five-necked flask (25 mL). The experiments were performed at 25 °C under an argon atmosphere.

**Preparative Electrolysis.** Electrolyses were carried out at constant potential with an Electronic Instruments power supply coupled with an Electrosynthesis 412 potentiostatic controller equipped with an Electrosynthesis 640 digital coulometer. The cathode was a Pb plate (25 cm$^2$) and the reference electrode was a SCE.[3a] All potentials reported are vs SCE. The counter electrode was a platinum flag (4 cm$^2$). It was enclosed in an alundum cup (Fisher Scientific), which was immersed in the cell and served as the anode compartment. The cell was a 15-cm-high cylinder with a 30-cm$^2$ base. It was kept in an ice bath throughout the experiments. Nitrogen was bubbled through the catholyte solution for 10 min prior to electrolysis and above it during the experiment.

Electrolyses were performed at constant potential. The values of the initial currents were 60 mA for **4** and 30 mA for **5**. In a typical experiment 0.1–0.2 g of substrate was dissolved in 25 mL of the appropriate electrolyte solution. The anolyte (5–10 mL) consisted of electrolyte solution only.

The spectrometer for $^1$H NMR was an IBM AC-200. Mass and IR spectra were recorded with a Finnigan 4000 and a Beckman IR 4250 spectrometer, respectively.

**Electrolysis of 6-Chloro-1-hexene (4).** Samples were taken at various times and analyzed by means of GC with *n*-nonane as the internal standard. Gas chromatographic analyses were performed with a 20 ft × $^1/_8$ in. 20% OV-17 on Chromosorb W-AW column and a Varian 3740 gas chromatograph with a flame ionization detector. The slightly low mass balance of the reaction may be due to the low boiling points of the compounds involved. Significant amounts of products **8** of **9** and of starting material **4** were found in a dry ice trap connected to the cell. The formation of organolead compounds[14] cannot be excluded but due to the above observations seems unlikely.

The product 1-hexene (**8**) was identified by comparison of GC and GC-MS with a sample purchased from Aldrich. Methylcyclopentane (**9**) was identified by GC comparison with a sample purchased from Aldrich.

**Electrolysis of 6-Hepten-2-one (5).** The electrolysis mixture was worked up and the product composition was determined by GC with cyclopentanol as the internal standard. Internal standard and 2 mL of 0.1 M acetic acid were added to the catholyte immediately upon disconnection of the current. The catholyte was then poured into 100 mL of saturated sodium chloride solution. For optimal isolation of the cyclic alcohols **10c** and **10t**, the aqueous solution was extracted with diethyl ether. The extract was washed with brine, dried, and analyzed with a Varian 3740 gas chromatograph modified with a J & W Scientific megabore kit and a 30 m × 0.32 mm heliflex-bonded superox 0.5-μm column.

A pure mixture of *cis*- and *trans*-1,2-dimethylcyclopentanol (**10c** and **10t**) was obtained by distillation (60 °C, 17 mm) of the electrolysis product. Components **10c** and **10t** were identified by comparison with reported[3c] GC and $^1$H NMR data. The ratio of **10c** to **10t** was determined by both GC and $^1$H NMR analyses.

**Acknowledgment.** We are grateful to the National Science Foundation for support of this research. A. C. Hutson received a UROP fellowship from the University of Minnesota.

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