3496 *J. Org. Chem.* **1993,** *58,* 3496–3501

Nickel(I)(Salen)-Electrocatalyzed Reduction of Benzal Chloride

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Received January 19, 1993

Electrochemical reduction of nickel(II)(salen) (5) in the presence of benzal chloride (1) in dimethylformamide at a carbon cathode results in catalytic conversion of 1 into a variety of monomeric and dimeric products, depending upon experimental conditions. The mechanism of formation of the various products and the results of experiments designed to clarify these mechanisms are discussed.

The electrochemical reduction of alkyl halides has been shown to be mediated by a variety of transition metal complexes. Typically, the process involves reduction of the metal complex to a reactive low-valent form, followed by oxidative addition of the latter into the carbon–halogen bond to generate an organometallic intermediate (eq 1).

$$\mathrm{RHal} + \mathrm{M}(n)\mathrm{L}_x \rightarrow \mathrm{RM}(n+2)\mathrm{L}_x\mathrm{Hal} \qquad (1)$$

Subsequent steps depend on the relative values of the electrolysis potential, the reduction potentials of the alkyl halide and the organometallic, the stability of the latter on the electrolysis time scale, and other experimental variables.[1] We recently examined the cobalt(I)(salen)[2] electrocatalyzed reduction of benzal chloride (1) (Scheme I).[3] The reaction differs in several significant respects from the analogous processes involving cobalt(salen) and simple alkyl monohalides.[4] In particular, the initial organometallic intermediate (2) is more easily reduced than 1. This causes the overall reduction to be electrocatalytic: 2 is reduced as soon as it is formed, and the resulting alkylCo(II) species rapidly decomposes to Co(I)(salen)$^{-1}$, which then continues the cycle. The other product of the decomposition is the α-chlorobenzyl radical (3), which suffers dimerization and eventual conversion to stilbene (4). A critical feature of this process is the fact, which we have deduced from both product analysis and voltammetric evidence, that 3 is not reducible at the potential at which the reduction of Co(II)(salen) is carried out, thus explaining the isolation of dimeric products (the stereoisomers of 4) derived from 3.

We were interested in examining the effect on this reaction of a change in the metal complex with an eye to finding a mediator which might produce radical 3 even more readily than in the cobalt series. Ni(II)(salen) (5) appeared to be an attractive choice in this respect. A number of investigators have reported that the electrochemical reduction of alkyl halides is mediated by complexes of nickel, including 5,[5] and there is evidence that the initial adducts decompose to radicals very readily. Geminal dihalides have, however, not been examined previously in studies of this type. We were also interested in the possible mechanistic consequences of the fact that the reduction potential of 5 is substantially negative of that of both Co(II)(salen) and 3. We report here the results of a study of the electrochemical reduction of 5 in the presence of 1 and the considerably different behavior of this system from the Co(salen)–benzal chloride system.

Scheme I

$$\mathrm{Co(II)(salen)} + e^- \longrightarrow \mathrm{Co(I)(salen)^{-1}}$$

$$\mathrm{Co(I)(salen)^{-1}} + \underset{\mathbf{1}}{\mathrm{C_6H_5CHCl_2}} \longrightarrow \underset{\mathbf{2}}{\mathrm{C_6H_5CH(Cl)Co(III)(salen)Cl^{-1}}}$$

$$\mathbf{2} + e^- \longrightarrow \mathrm{C_6H_5CH(Cl)Co(II)(salen)Cl^{-1}}$$

$$\mathrm{C_6H_5CH(Cl)Co(II)(salen)Cl^{-1}} \longrightarrow \underset{\mathbf{3}}{\mathrm{C_6H_5CHCl^{\bullet}}} + \mathrm{Co(I)(salen)^{-1}}$$

$$2\ \mathbf{3} \longrightarrow \mathrm{C_6H_5CHClCHClC_6H_5} \longrightarrow\longrightarrow \underset{\mathbf{4}}{\mathrm{C_6H_5CHC{=}CHC_6H_5}}$$

Results

Voltammetry. The electrochemical behavior of Ni(II)(salen) (5) was examined by cyclic voltammetry at a platinum electrode in dimethylformamide (DMF) containing tetrabutylammonium hexafluorophosphate. Complex 5 exhibits a single reversible wave at −2.08 V vs Ag/0.1 M $\mathrm{AgNO_3}$.[6] Addition of an 8-fold equivalent amount of 1 to the medium causes major changes in the voltammogram (Figure 1); the cathodic peak increases substantially in size and moves to more positive potentials and the anodic peak disappears, demonstrating that reaction of 1 with the reduced nickel intermediate 5^{-1} is fast on the voltammetry time scale.

Controlled-Potential Electrolysis. A series of controlled potential electrolyses were carried out under different conditions on mixtures of 1 and Ni(II)(salen) (5) at a potential (−2.2 V) sufficient to reduce 5 but not 1. The results of these electrolyses are given in Table I. Except where noted, electrolysis was carried out on mixtures containing 1 mmol of 5 and 10 mmol of 1. In all cases, material balances in the electrolyses were in the range of 88–95%.

Electrolysis of a mixture of 1 and 5 with no other components added to the medium (run 1) afforded approximately equal quantities of toluene (6), bibenzyl (7), and trans-stilbene (4). Coulometry indicated that 2.85 $m\mathcal{F}$ ($m\mathcal{F}$ = millifaraday) were consumed per mmol of 1 in the electrolysis. (This is in addition to the 1 $m\mathcal{F}$ necessary

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[1] Scheffold, R. In *Modern Synthetic Methods;* Wiley: New York, 1983; Vol. 3, p 355 .

[2] Salen = bis(salicylidene)ethylenediamine.

[3] (a) Fry, A. J.; Sirisoma, U. N.; Lee, A. S. *Tetrahedron Lett.* **1993,** *34,* 809. (b) Fry , A. J.; Sirisoma, U. N., submitted for publication.

[4] (a) Costa, G.; Puxeddu, A.; Reisenhofer, E. *J. Chem. Soc., Dalton Trans.* **1973,** 2034. (b) Puxeddu, A.; Costa, G.; Marsich, N. *J. Chem. Soc., Dalton Trans.* **1980,** 1489.

[5] (a) Gosden, C.; Kerr, J. B.; Pletcher, D.; Rosas, R. *J. Electroanal. Chem.* **1981,** *117,* 101. (b) Mubarak, M. S.; Peters, D. G. *J. Electroanal. Chem.* **1992,** *332,* 127. (c) Fauvarque, J. F.; Chevrot, C.; Jutand, A.; François, M.; Perichon, J. *J. Organomet. Chem.* **1984,** *264,* 273.

[6] (a) The Ag/0.1 M $\mathrm{AgNO_3}$ reference electrode is +0.35 V positive of SCE. (b) Benzal chloride (1) is not reduced before −2.4 V.

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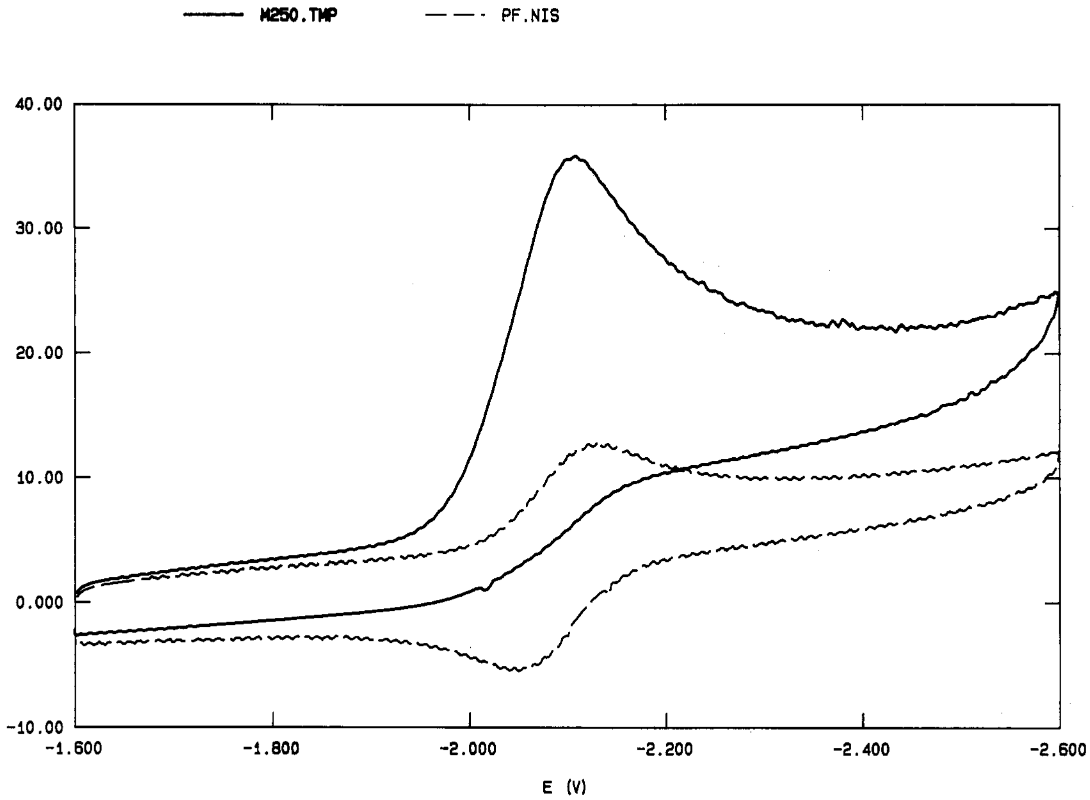

Figure 1. Cyclic voltammograms measured in DMF/0.1 M Bu_4NPF_6 at a platinum disk electrode. Scan rate 100 mV s^{-1}. Solid line: 1 mM Ni(II)(salen). Dashed line: 1 mM Ni(II)(salen) plus benzal chloride (8 mM).

Table I. Products from Direct and Ni(salen) Catalyzed Electrochemical Reduction of Benzal Chloride and Related Substances

run	reactants	products[a] (%)	m$\mathcal{F}$ consumed[b]	*n* exptl[c]	*n* calcd[d]
1	5 (1 mmol); 1 (20 mmol)	4 (30); 6 (36); 7 (34)	57.04	2.85	3.09
2	5 (1 mmol); 1 (10 mmol); H_2O (5 mmol)	4 (3); 7 (10); 8 (67); 9 (20); 10 (41)	19.04	1.90	1.90
3	5 (1 mmol); 1 (10 mmol); D_2O (100 mmol)	4 (18); 6 (24); 7 (16); 11 (1)	45.34	4.53	2.62
4	5 (1 mmol); 1 (10 mmol); diethyl malonate (10 mmol)	4 (14); 6 (26); 7 (49); 12 (11)			
5	5 (1 mmol); 4 (5.55 mmol)	4 (40); 7 (60)			
6	4 (5.55 mmol)	4 (92); 7 (8)	0.83	1.87	2.00
7	5 (1 mmol); 9 (10 mmol)	9 (100)			
8	5 (1 mmol); 1 (10 mmol); cyclopentene (150 mmol)	4 (30); 6 (33); 7 (37)			

[a] Yields represent the composition of the final electrolysis medium. [b] Total current consumed less that necessary (1.0 m$\mathcal{F}$) to reduce the Ni(II) complex to Ni(I); m$\mathcal{F}$ = milliFaradays. [c] No. of m$\mathcal{F}$ consumed per mmol of 1 or 4 consumed. [d] Computed coulometric *n* value, based on product composition.

to reduce 5 to 5^{-1} to initiate the catalytic cycle). Significantly, an electrolysis carried out under similar conditions, but on a more dilute solution (run 2), afforded substantially greater quantities of the monomeric products 6 and dibenzyl ether (8). Also notable in this experiment are

$C_6H_5CH_2OCH_2C_6H_5$ **8** $C_6H_5CH_2N(CH_3)_2$ **10**

$(C_6H_5CH_2)_2CHC_6H_5$ **11** $C_6H_5CH_2CH(CO_2C_2H_5)_2$ **12**

the formation of diphenylacetylene (9) and the consumption of considerably less current (1.90 m$\mathcal{F}$ per mmol of 1). Run 3 was carried out in the presence of a 10-fold excess of D_2O because of our suspicion (see Discussion) that these reactions involve carbanion intermediates. Indeed, the toluene produced in the reaction consisted (mass spectrometry) of a mixture containing primarily $C_6H_5CHD_2$ and $C_6H_5CD_3$. The 4, 6, 7, and benzyldimethylamine (10) produced in this reaction were also deuterated. 10 is apparently produced as a consequence of hydrolysis of the solvent by D_2O to afford dimethylamine. The latter can react with benzyl chloride, an intermediate in the electrolysis (see Discussion) to produce 10. A trace of 1,2,3-triphenylpropane (11) was formed in this reaction. This substance was also isolated in small quantities in the Co(salen) mediated-reactions.[3]

Diethyl malonate has been used frequently as a proton trap for electrogenerated carbanions.[7] Electrolysis in the presence of an equivalent amount of diethyl malonate (run 4) resulted in formation of a reduced amount of stilbene compared to run 1, together with production of a roughly equivalent amount of diethyl benzylmalonate (12).

Runs 5–7 were carried out to obtain information on the mechanistic origin of bibenzyl (7) in these reactions. Electrochemical reduction of a mixture of *trans*-stilbene (4) and 5 for the same length on time as a typical electrolysis (~24 h) afforded a mixture consisting of about 60% 7 and 40% unreacted 4 (run 5). A large amount of tributylamine was produced in this reaction by attack of electrogenerated

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[7] (a) Little, R. D.; Fox, D. P.; Hijfte, L. V.; Dannecker, R.; Sowell, G.; Wolin, R.; Moëns, Baizer, M. M. *J. Org. Chem.* **1988**, *53*, 2287. (b) Mbarak, M. S.; Peters, D. G. *J. Org. Chem.* **1982**, *47*, 3397.

hydroxide ion (see Discussion) on the supporting electrolyte. On the other hand, the current in an electrolysis of stilbene at −2.2 V in the absence of **5** was very low, and after 24 h electrolysis had resulted in only *ca.* 5% reduction of stilbene to bibenzyl (run 6). In contrast with run 5, very little tributylamine was produced in this electrolysis. These facts are consistent with slow but efficient direct electrochemical reduction of **4** at −2.2 V, which is somewhat positive of the reduction potential of **4**.[8] Run 7 involved electrochemical reduction of **5** in the presence of diphenylacetylene (**9**). Unreacted **9** was isolated from this electrolysis, along with a considerable amount of tributylamine.

Run 8, which included a 15:1 ratio of cyclopentene to benzal chloride (**1**), produced products which were almost identical to those from run 1. Analysis by GC–mass spectrometry showed the absence of any other products. In particular, the stereoisomeric 6-phenylbicyclo[3.1.0]pentanes (**13**) were not formed in this reaction.

Scheme II

Path A:

$\underset{14}{\mathrm{Ni(I)(salen)}^{-1}} + \underset{1}{\mathrm{C_6H_5CHCl_2}} \rightarrow \underset{15}{\mathrm{C_6H_5CH(Cl)Ni(III)(salen)Cl}^{-1}}$

$15 + e^- \rightarrow \underset{16}{\mathrm{C_6H_5CH(Cl)Ni(II)(salen)Cl}^{-2}}$

$16 \rightarrow 14 + 3 + Cl^-$

Path B:

$14 + 1 \rightarrow 15$

$15 \rightarrow 3 + 5 + Cl^-$

$5 + e^- \rightarrow 14$

Path C:

$14 + 1 \rightarrow 3 + 5 + Cl^-$

$5 + e^- \rightarrow 14$

Net reaction for all three paths:

$$1 + e^- \rightarrow 3 + Cl^- \quad (2)$$

Discussion

These processes are obviously complex: a variety of products are produced, the nature of the products is greatly dependent upon experimental conditions, and there are clearly several different electrocatalytic reaction sequences involved. However, we believe that relatively simple principles govern the course of these reactions. Our previous investigations on the electrochemical reduction of cobalt(II)(salen) in the presence of **1**[3] have provided a number of facts which have been helpful in understanding the reactions under discussion here.

While the active form of nickel in some electrocatalytic processes involving phosphine complexes appears to be Ni(0),[9] the first step in our reactions is undoubtedly reduction of Ni(II)(salen) (**5**) to the Ni(I) stage.[5] Controlled-potential coulometry of a solution of **5** consumes one electron and produces the stable Ni(I)(salen)$^{-1}$ ion (**14**).[5a] The details of the next steps, although not their ultimate consequences, are a matter of conjecture. There are three distinctly different processes which might occur upon collision between electrogenerated **14** and **1** (Scheme II). Paths A and B both begin by oxidative addition of **14** into a carbon–halogen bond of **1** to afford the Ni(III) complex **15**. We have previously established with certainty that cobalt(I)(salen)$^{-1}$ does undergo oxidative addition to **1**.[3] Intermediate **15** might be reduced to an σ-alkylnickel(II) species (**16**) which would be expected to undergo facile thermal decomposition to the α-chlorobenzyl radical (**3**) and **14** (path A). Alternatively, **15** might decompose spontaneously to **3** and **5**, which would then be reduced to **14** (path B). Castro has suggested a sequence akin to path B for the Ni(I)(octaethylisobacteriochlorin)-catalyzed reduction of alkyl halides.[10] Finally, direct electron transfer from **5** to **1** could produce **3** directly. Espenson has suggested that reaction between any of several Ni(I)(cyclam) complexes and alkyl halides occurs by inner-sphere electron transfer.[11] Since paths A–C all result in formation of **3** and **14**, they are equivalent (see eq 2 in Scheme II). They all explain the need for only catalytic quantities of **5** in these reactions.

We learned in our studies on the cobalt analog of this process[3] that the reduction potential of radical **3** is *ca.* −2.0 V (relative to our reference electrode). Other substituted benzyl radicals exhibit similar reduction potentials.[12,13] Thus, under the electrolysis conditions **3** is produced at a potential negative of its reduction potential. One might expect it to be reduced immediately to the corresponding carbanion (**17**) (Scheme III). Isolation of dimeric products derived from **3**, e.g., **4**, may seem surprising. However, it is necessary to recognize that no matter by which path (of Scheme II) **3** is produced, its formation takes place in homogeneous solution, near but not necessarily at the electrode surface. It must either return to the electrode surface or encounter a molecule of **14** in order for reduction to **17** to take place. Since the electrolysis solution is stirred, diffusion of **3** to the electrode is competing with convection, a powerful force acting to remove **3** from the vicinity of the electrode. Even the reduction of **3** by **14** in homogeneous solution has to compete with dimerization of **3**, which should be rapid.[13] Similar arguments may be made with respect to the reduction of **19** vis-a-vis its reduction to **20**. For all of these reasons, some **3** might escape reduction. From the products we observe, it appears that this is indeed so. Nevertheless, the relatively negative potential (−2.2 V) at which these electrolyses are carried out does have clear consequences: the corresponding electrolyses using Co(II)(salen) and carried out at −1.7 V (positive of the reduction potential of **3**), do not produce any products derived from carbanion **17**. Previous electrocatalytic reactions of alkyl halides involving **14** afforded radical-derived products because the electrolyses were carried out

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Scheme III

$$3 + e^- \longrightarrow \underset{17}{C_6H_5CHCl^-} \tag{3}$$

$$17 + H_2O \longrightarrow \underset{18}{C_6H_5CH_2Cl^-} + OH^- \tag{4}$$

$$18 + e^- \longrightarrow \underset{19}{C_6H_5CH_2^\bullet} + Cl^- \tag{5}$$

$$2\ 19 \longrightarrow \underset{7}{C_6H_5CH_2CH_2C_6H_5} \tag{6}$$

$$2\ 1 + 6e^- + 2H_2O \longrightarrow 7 \tag{7}$$

$$19 + e^- \longrightarrow \underset{20}{C_6H_5CH_2^-} \tag{8}$$

$$20 + H_2O \longrightarrow \underset{6}{C_6H_5CH_3} + OH^- \tag{9}$$

$$2\ 18 + 2OH^- \longrightarrow \underset{8}{C_6H_5CH_2OCH_2C_6H_5} + 2H_2O + 2Cl^-$$

$$17 + CH_2(CO_2C_2H_5)^- \longrightarrow 18 + {}^-CH(CO_2Et)_2$$

$$18 + {}^-CH(CO_2Et)_2 \longrightarrow \underset{12}{C_6H_5CH_2CH(CO_2Et)_2}$$

$$2\ 3 \longrightarrow \underset{21}{C_6H_5CHClCHClC_6H_5}$$

$$21 + 2e^- \longrightarrow 4 + 2Cl^-$$

$$1 + OH^- \longrightarrow \underset{24}{C_6H_5CCl_2^-} \tag{10}$$

$$24 \longrightarrow \underset{25}{C_6H_5CCl^{2\bullet}} + Cl^- \tag{11}$$

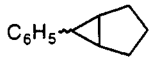
$$24 + 25 + [C_6H_5CCl_2C(Cl)C_6H_5]^- \longrightarrow \underset{26}{C_6H_5C(Cl){=}C(Cl)C_6H_5} \tag{12}$$

$$26 + 2e^- \longrightarrow 9 + 2Cl^- \tag{13}$$

at potentials positive of the reduction potential of the radical intermediates.[5a] We interpret the course of these reactions in terms of the reactions illustrated in Scheme III.

Formation of Toluene and Dibenzyl Ether. That fraction of 3 which is reduced to carbanion 17 will be protonated by adventitious water (which is extremely difficult to remove from DMF)[14] to produce benzyl chloride (18). 18 can be converted to benzyl anion (20) and then toluene (6) by a second cycle initiated by 14 (and proceeding by path A, B, or C). Overall, this is a doubly electrocatalytic process[3] (1 → 18 → 6). On the other hand, hydroxide ion produced by protonation of 17 can attack 18 in an S_N2 reaction to produce benzyl alcohol; deprotonation of the latter and a second alkylation would afford 8. Analogous products have been isolated from the electrochemical reduction of some alkyl halides in DMF.[15] The considerably increased proportion of monomeric products[16] in dilute solution (77% in run 2 vs 36% in run 1) where dimerization should be less competitive (the rate of radical dimerization depends on the square of the concentration) are consistent with this interpretation. Isolation of benzylmalonic ester (12) in run 4 demonstrates that 17 is indeed a reaction intermediate. Protonation of 17 by malonic ester affords 18 and malonate ion, which then back-react to afford 12 (see Scheme III).

Formation of Bibenzyl and Stilbene. That portion of 3 which escapes reduction dimerizes to afford the stereoisomeric 1,2-dichloro-1,2-diphenylethanes (21). We have shown[3] that the isomers of 21 are converted nonstereoselectively to stilbenes (4) by Co(I)(salen)$^{-1}$. Production of 4 probably occurs by an analogous path in the present work. We considered the possibility that 4 might be formed by a carbene route, i.e., decomposition of 17 to phenylcarbene (22). 22 would be expected to react with another molecule of 17 to afford 4 by a well-precedented path.[17] However, addition of a large excess of cyclopentene, a good carbene trap, failed to produce even a trace of the bicyclic material 13. This eliminates 22 from consideration as an intermediate in the electrolysis. Formation of 4 by either direct or nickel(I)(salen)-catalyzed reduction of diphenylacetylene (9) was excluded by the stability of 9 under the electrolysis conditions (run 7). It is harder to exclude 4 as a precursor of bibenzyl (7), however, since a substantial amount of 7 was produced in run 6. Some of the 7 formed may come through 4. It is likely, however, that most of the 7 produced comes from reductive coupling of 18 via benzyl radical 19 for the following reasons. (a) An isomer of 7, probably 23, is formed in very small amounts (<1%; detectable by gas chromatography–mass spectrometry but not isolable); this type of coupling is common in reactions affording benzyl radicals.[12a] (b) Reduction of stilbene (4) is slow under our conditions: almost half the starting 4 still remained after 24 h in run 5, whereas electrolysis runs 1–4 were complete by this time. The formation of substantial quantities of tributylamine in run 5 also shows that reduction of stilbene by 14 is slow. Tributylamine is formed by a two-step sequence: electrogenerated 14 reduces water to hydrogen and hydroxide ion,[4a] and tributylamine is produced by subsequent attack of hydroxide on the supporting electrolyte. A substantial quantity of tributylamine is formed in run 7 for the same reason. Since 14 does not react with 9, it is available to react with water in the medium to produce the amine. Very little tributylamine was produced in run 6 because *direct* reduction of water is very slow at −2.2 V.



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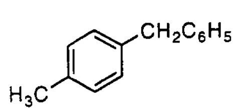

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The trimer 11 is probably produced by attack of benzyl radical 19 on 4. This process was observed during the cobalt(salen)-catalyzed reduction of 1.[3]

Formation of Diphenylacetylene. The most surprising product in these electrochemical reactions is diphenylacetylene (9). This substance is at the highest oxidation state relative to 1 of any of the observed products. We suggest the sequence of reactions in eqs 10–13 to account for formation of 9. Deprotonation of starting material 1 by hydroxide ion would afford anion 24. The formation of fully deuterated toluene, $C_6H_5CD_3$, in run 3 is strong

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[14] (a) Fry, A. J. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P., Heineman, W., Eds.; in press. (b) de la Torre, R. A.; Sease, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 1687.

[15] La Perriere, D. M.; Carroll, W. F., Jr.; Willett, B. C.; Torp, E. C.; Peters, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 7561.

[16] Ether 8 is included in this category because it is derived from benzyl alcohol, a monomeric intermediate.

[17] (a) Kirmse, W. *Carbene Chemistry*, Academic: New York, 1964; Chapter 8. (b) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964; Chapter 6.

evidence for formation of **24**. Ejection of chloride ion from **24** would afford phenylchlorocarbene **25**, and reaction of **25** with **24**, followed by ejection of chloride ion from the resulting adduct, would produce dichlorostilbene (**26**). Electrocatalytic vicinal dechlorination of **26** would finally produce **9**.[18] Carbanion **24** should eject chloride to form a carbene more readily than would **17** because of the additional chlorine atom in **24**.[17,19] Inasmuch as S_N2 substitution is slowed by halogen substitution,[19] we consider as unlikely an alternative route to **9** involving S_N2 attack on **1** by **24** to afford 1,1,2-trichloro-1,2-diphenylethane, followed by a combination of dehydrochlorination and dechlorination. Run 2 is the only electrolysis which produced **9**. It is likely that **9** can only be produced under fairly special conditions, i.e., in dilute, relatively dry solution where competition with dimerization of radical **3** is minimal and where hydroxide ion is most active. The latter is necessary in order to convert **1** to its conjugate base. (As a consequence of hydrogen bonding, hydroxide is much less basic in DMF containing considerable amounts of water,[14] explaining why **9** is not produced in run 3).

Runs 5 and 6 demonstrate that at −2.2 V stilbenes (**4**) are reduced slowly to bibenzyl but that diphenylacetylene (**9**) is not reducible to **4**. This raises an interesting question. The reduction potentials of *cis*- and *trans*-**4** and **9** are −2.42, −2.43, and −2.46, respectively.[8] Thus, **4** and **9** have almost the same reduction potentials, yet only **4** is reduced (and it is reduced slowly directly but more rapidly in the presence of **5**). The difference in reduction potentials between **4** and **9** is not large, but we are operating under marginal conditions, i.e., at an electrolysis potential which is positive of the reduction potentials of **4** and **9**. Because electron-transfer rates increase approximately exponentially with potential, the slightly greater ease of reduction of **4** might well make enough of a difference to permit **4** to undergo the observed very slow direct reduction while **9** is unaffected. Another contributing factor may be a specific interaction between **14** and **4** (but not **9**) which facilitates the reduction of **4**. The pronounced difference between runs 5 and 6 provides support for this suggestion.

Although we write a number of the steps in Schemes II and III, e.g., eqs 3, 7, and 9 of Scheme III, as electron-transfer reactions, the source of the electrons is almost certainly not the electrode but rather $Ni(I)(salen)^{-1}$ (**14**). Since these reactions presumably take place because their reduction potentials are positive of that of **5**, reduction by **14** is thermodynamically favorable. In general, solution electron transfers of this type have been found to be far more common in multistep electrode processes than electron transfer from the electrode itself.[20]

Coulometry. Coulometric measurements made on several electrolyses are consistent with the mechanistic inferences we have made here. It is useful to classify each product according to the value *n*, defined as the number of millifaradays of current per mmol of **1** which should be required to produce that particular substance. For example, summation of eqs 2–6 leads to eq 7, the equation describing the overall conversion of **1** to **7**, from which it can be seen that *n* for this conversion should be 3. Similarly, summation of eqs 2–5 with eqs 8 and 9 shows that *n* should be 4 for conversion of **1** to **4**. Table II summarizes computed *n* values for formation of all of the various electrolysis products. Note that Ni(I) is not consumed in any of these conversions. All are multiply catalytic[3] in Ni(I)(salen). The electrolyses generally produce several products, each with a different *n* value. Nonintegral *n* values are therefore to be expected. On the basis of the observed product distributions, the coulometry results are in good agreement with the expected amounts of current. For example, run 1 produced almost equal quantities of **6**, **7**, and **4**. These products require consumption of 4, 3, and 2 m$\mathcal{F}$/mmol of **1**, respectively. On the basis of the actual product composition, the overall consumption of current (apparent *n*-value based on **1**) should be 3.06 m$\mathcal{F}$/mmol of **1** (after subtraction of the current required for the initial conversion of the Ni(II) complex to the Ni(I) stage); the actual experimental value was 2.85. The corresponding calculated current consumption values for runs 2 and 3 are 2.12 and 2.62, respectively; the experimental coulometric values are 1.90 and 4.53, respectively. The higher coulometric value in run 3 is probably because of increased turnover of Ni(I)(salen) by reaction with the substantial excess of D_2O present in this experiment.

Table II. Calculated Coulometric Demand and Net Reactions for Production of Products from the Ni(salen)-Catalyzed Reduction of Benzal Chloride

product	*n*[a]	net reaction
9	1	$2\,\mathbf{1} + 2\,e^- + 2\,OH^- \rightarrow \mathbf{9} + 2\,H_2O + 4\,Cl^-$
8	2	$2\,\mathbf{1} + 4\,e^- + H_2O \rightarrow \mathbf{8} + 4\,Cl^-$
4	2	$2\,\mathbf{1} + 4\,e^- \rightarrow \mathbf{4} + 4\,Cl^-$
7	3	$2\,\mathbf{1} + 6\,e^- + 2\,H_2O \rightarrow \mathbf{7} + 2\,OH^- + 4\,Cl^-$
6	4	$\mathbf{1} + 4\,e^- + 2\,H_2O \rightarrow \mathbf{6} + 4\,Cl^-$

[a] Number of faradays required to produce the given product per mole of benzal chloride consumed.

The apparent *n* value in run 6 was 1.88 after correction for the fact that reduction had proceeded to only 8% completion. This is reasonable, since reduction of **4** to **7** should consume 2.0 faradays per mol of **4**.

Conclusions. As we noted above, the results of electrochemical reduction of nickel(II)(salen) in the presence of benzal chloride are complex. A variety of products are produced, depending upon the experimental conditions; each product is the result of at least two catalytic cycles. The isolation of dimeric products (**4**, **7**, **9**) at potentials which are negative of the reduction potentials of **3** and **19** is a useful reminder of the fact that, in processes such as these involving chemical reactions coupled to the electron-transfer step, intermediates are generated at some distance from the electrode and may more readily escape reduction than when they are generated by direct electrolysis.

Experimental Section

General. Dimethylformamide was distilled at aspirator vacuum from CaH_2 and stored over 3-Å molecular sieves. Bu_4NPF_6 was prepared by reaction between an aqueous HPF_6 and an acetone solution of Bu_4NI, followed by recrystallization from ethanol. Benzal chloride was obtained from Aldrich Chemical Co. and used as received after verification of its purity by NMR spectroscopy and analysis using an Hewlett-Packard Model 5988 gas chromatograph–mass spectrometer. Ni(II)(salen) was prepared by a literature procedure.[21]

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[18] We have recently found that **26** is converted into **9** by Co(I)(salen): Kaufman, S.; Fry, A. J. Unpublished observation.

[19] Reference 17b, Chapter 3.

[20] E.g.: (a) Parker, V. D. *Acta Chem. Scand.* **1981**, *35B*, 149. (b) Andrieux, C. P.; Savéant, J. M. *J. Electroanal. Chem.* **1974**, *53*, 165.

[21] Gilbert, W. C.; Taylor, L. T.; Dillard, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 2477.

Cyclic voltammetry was carried out with the aid of a computerized system consisting of a Princeton Applied Research (PAR) VersaStat interfaced to a Gateway Systems 386SX computer, using the PAR Model 250 software to generate waveforms and to acquire and manipulate data. Voltammograms were plotted on a Hewlett-Packard ColorPro plotter.

The electrolysis cell was supplied by The Electrochemicals Co., Middletown, CT, and consisted of a glass bottom and Teflon top machined to accept the counter electrode compartment and all cell utilities, including electrodes, nitrogen inlet, and sampling port; the cell utilities were contained in standard 14/20 adapters for ease of cell assembly. The counter electrode compartment consisted of a coarse porosity fritted disk set in a glass tube and containing a methylcellulose gel containing 0.1 M Bu_4NPF_6 [22] to reduce mass transport between the working and counter electrode compartments. The cathode and anode were composed of reticulated vitreous carbon (RVC) and carbon cloth, respectively. The reference electrode has been described previously.[23] A standard taper adapter equipped with a large serum cap was installed in one of the cell ports, and two needles (one for nitrogen introduction and one for nitrogen escape) were inserted through the serum cap.

Electrolysis Procedure. The cell was assembled with counter electrode compartment, cathode, reference electrode, and magnetic stir bar, and 100 mL of a 0.1 M solution of Bu_4NPF_6 in DMF was added. Fifty mL of the same solution was added to the anode compartment. Reactants were added, and the solution was degassed by bubbling nitrogen through the solution for 20 min. The solution was stirred and electrolyzed at −2.2 V until the current had decayed to less than 1–2% of its original value. The catholyte was then extracted three times with pentane, which was then washed twice with water and dried over Na_2SO_4. The pentane solution was concentrated to a known volume by distillation of the solvent through a packed column, and the products were analyzed by GC–mass spectrometry. All products were identified by comparison of gas chromatographic retention times and mass spectral cracking patterns with those of authentic samples.

Acknowledgment. Financial support for this research was provided by National Science Foundation grant no. CHE-91-00943. Seth Kaufman supplied the supporting electrolyte used in these experiments.

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(22) Fry, A. J. *Synthetic Organic Electrochemistry*, 2nd ed.; Wiley: New York, 1989; pp 318–323.

(23) Fry, A. J.; Touster, J. *J. Org. Chem.* **1986**, *51*, 3905.