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Conversion of Benzal Chloride to Stilbene by Electrogenerated Cobalt(I)(Salen) A Doubly Electrocatalytic Process

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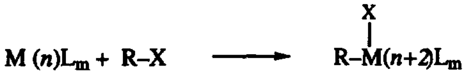
Abstract: Benzal chloride is converted to a mixture consisting primarily of *cis*- and *trans*-stilbene by the action of electrochemically-generated cobalt(I)(salen). The process involves a sequence involving electrocatalytic conversion of benzal chloride to a mixture of *meso*- and *dl*-1,2-dichloro-1,2-diphenylethane, followed by electrocatalyzed conversion of the latter to the stilbenes. Each of the diastereomeric dichlorides affords the same mixture of stilbenes under the reaction conditions.

A number of low-valent transition metal complexes have been found to react readily with alkyl halides ("oxidative addition") to afford adducts (eq 1).[1] Though often sensitive to heat and light, such adducts are frequently stable enough to be isolated and characterized. However, they are much less stable upon reduction to a lower valence state. Among the most widely studied examples of the latter phenomenon are adducts of alkyl halides with square planar cobalt(I) complexes such as those derived by reaction of reduced vitamin B_{12} and related substances.[2] It has been shown, for example, that reduction of methylcobalamin(III) to the cobalt(II) state is associated with a 10^{15} increase in the rate constant for bond cleavage.[3] The high reactivity of Co(I) complexes toward alkyl halides and the instability of the initial adducts upon reduction permit the construction of electrocatalytic cycles which involve a) electrochemical reduction of a Co(III) or Co(II) complex to the Co(I) state, b) oxidative insertion of the latter into a carbon-halogen bond to afford the Co(III) complex, and c) reduction of the latter to give a lower-valent cobalt species which then decomposes to a radical or carbanion plus the metal complex, which is then available to repeat the cycle. Scheffold has used such cycles to effect a variety of organic transformations.[2]



$$M(n)L_m + R\text{–}X \longrightarrow R\text{–}\overset{\overset{\displaystyle X}{|}}{M}(n{+}2)L_m \qquad (1)$$

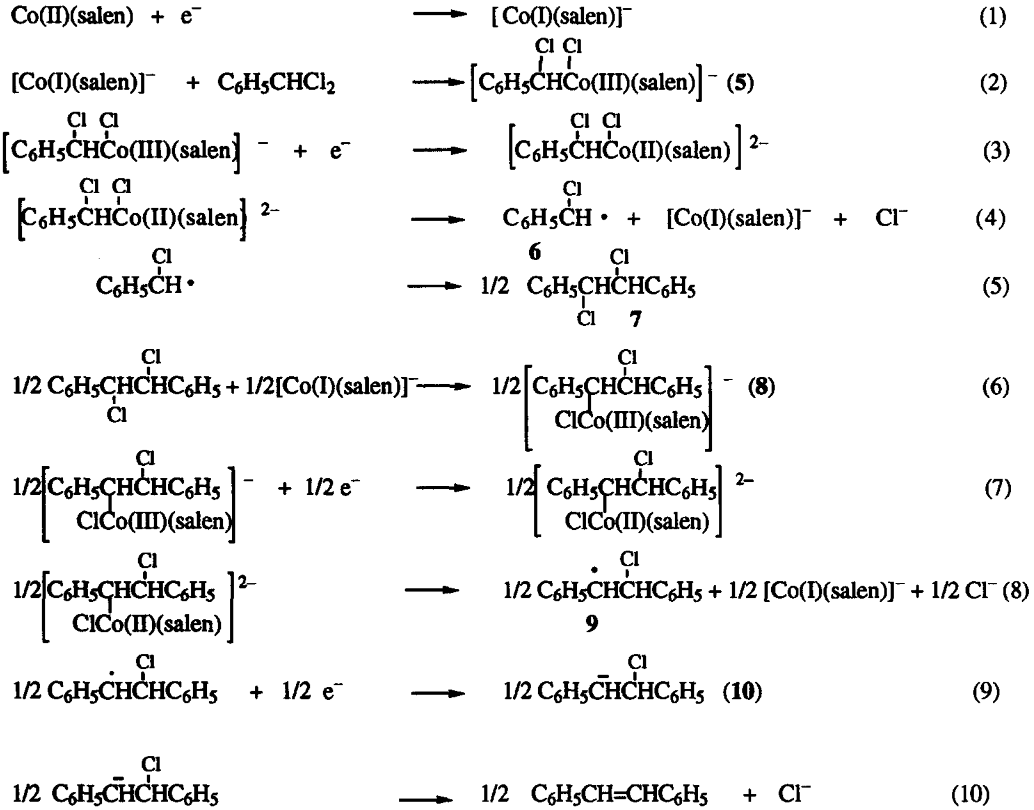
We have found that electrochemical reduction of catalytic quantities of cobalt(II)(salen) [salen = *bis*-salicylideneethylenediamine] in the presence of benzal chloride ($C_6H_5CHCl_2$, **1**) affords a mixture consisting predominantly of stilbenes (**2**)(*cis*:*trans* = 1.1:1), together with small amounts of bibenzyl (**3**), 1,2,3-triphenylpropane (**4**) and an unidentified isomer of **4** :

$$\underset{\mathbf{1}}{C_6H_5CHCl_2} \xrightarrow[\text{Co(II)(salen)}]{e^-} \underset{\mathbf{2},\ 87\ \%}{C_6H_5CH{=}CHC_6H_5} + \underset{\mathbf{3},\ 5\ \%}{C_6H_5CH_2CH_2C_6H_5}$$

$$+ \underset{\mathbf{4},\ 5\ \%}{(C_6H_5CH_2)_2CHC_6H_5} + \underset{3\ \%}{m/e\ 272}$$

We propose the following mechanistic Scheme, involving a novel doubly electrocatalytic sequence, to account for this conversion:

SCHEME I



$$Co(II)(salen) + e^- \longrightarrow [Co(I)(salen)]^- \quad (1)$$

$$[Co(I)(salen)]^- + C_6H_5CHCl_2 \longrightarrow \left[C_6H_5\overset{Cl}{C}H\overset{Cl}{C}o(III)(salen)\right]^- \ (\mathbf{5}) \quad (2)$$

$$\left[C_6H_5\overset{Cl}{C}H\overset{Cl}{C}o(III)(salen)\right]^- + e^- \longrightarrow \left[C_6H_5\overset{Cl}{C}H\overset{Cl}{C}o(II)(salen)\right]^{2-} \quad (3)$$

$$\left[C_6H_5\overset{Cl}{C}H\overset{Cl}{C}o(II)(salen)\right]^{2-} \longrightarrow \underset{\mathbf{6}}{C_6H_5\overset{Cl}{C}H\bullet} + [Co(I)(salen)]^- + Cl^- \quad (4)$$

$$C_6H_5\overset{Cl}{C}H\bullet \longrightarrow 1/2\ C_6H_5\underset{Cl}{C}H\overset{Cl}{C}HC_6H_5\ \mathbf{7} \quad (5)$$

$$1/2\ C_6H_5\underset{Cl}{C}H\overset{Cl}{C}HC_6H_5 + 1/2[Co(I)(salen)]^- \longrightarrow 1/2\left[\begin{array}{l} C_6H_5CH\overset{Cl}{C}HC_6H_5 \\ \ \ ClCo(III)(salen) \end{array}\right]^- \ (\mathbf{8}) \quad (6)$$

$$1/2\left[\begin{array}{l} C_6H_5CH\overset{Cl}{C}HC_6H_5 \\ \ \ ClCo(III)(salen) \end{array}\right]^- + 1/2\ e^- \longrightarrow 1/2\left[\begin{array}{l} C_6H_5CH\overset{Cl}{C}HC_6H_5 \\ \ \ ClCo(II)(salen) \end{array}\right]^{2-} \quad (7)$$

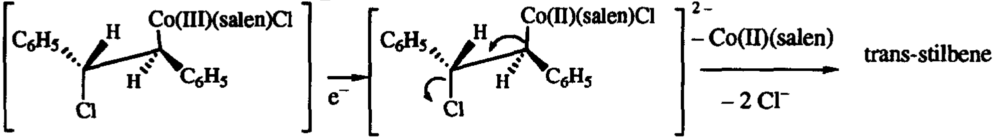
$$1/2\left[\begin{array}{l} C_6H_5CH\overset{Cl}{C}HC_6H_5 \\ \ \ ClCo(II)(salen) \end{array}\right]^{2-} \longrightarrow 1/2\ \underset{\mathbf{9}}{C_6H_5\dot{C}H\overset{Cl}{C}HC_6H_5} + 1/2\ [Co(I)(salen)]^- + 1/2\ Cl^- \quad (8)$$

$$1/2\ C_6H_5\dot{C}H\overset{Cl}{C}HC_6H_5 + 1/2\ e^- \longrightarrow 1/2\ C_6H_5\bar{C}H\overset{Cl}{C}HC_6H_5\ (\mathbf{10}) \quad (9)$$

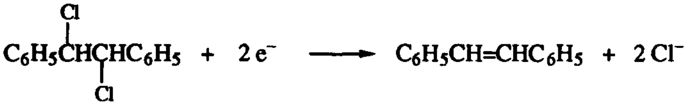
$$1/2\ C_6H_5\bar{C}H\overset{Cl}{C}HC_6H_5 \longrightarrow 1/2\ C_6H_5CH{=}CHC_6H_5 + Cl^- \quad (10)$$

The reaction cascade is initiated by reduction of cobalt(II)(salen) to the reactive cobalt(I) form at -1.8 V (*vs* Ag/AgNO3).[4] This is immediately followed by rapid oxidative insertion of electrochemically-generated Co(I)salen into a carbon-chlorine bond of **1** to form adduct **5**. The linear sweep voltammetric peak current of a Co(I)salen solution increases markedly upon addition of **1**,[5] demonstrating that **5** is formed rapidly on the voltammetric time scale and that it is easier to reduce than Co(II)salen. This is in marked contrast to the behavior of the corresponding adducts of aliphatic monohalides with Co(I) complexes, which have generally been found to be reduced at more negative potentials than the original Co(I) complex itself. This is a result of the electron-withdrawing ability of the remaining carbon-chlorine bond in **5**, together with the relatively positive potentials of benzylic radicals generally.[6] Alkylcobalt(II) species are much less stable than the corresponding Co(III) species,[3] and hence reduced **5** should immediately decompose, ejecting the α-chlorobenzyl radical **6** and regenerating Co(I)(salen). Dimerization of radical **6** then affords a mixture of *dl-* and *meso-1,2*-dichloro-1,2-diphenylethanes (**7**). Consistent with this interpretation, small amounts of **7** can be detected in samples taken during the electrolysis. These halides are benzylic, however, and presumably undergo rapid oxidative insertion with Co(I)(salen) to afford a new adduct (**8**), which immediately undergoes a second reduction-thermolysis sequence (Eqns. 7 and 8). The resulting radical (**9**) is then reduced to a carbanion (**10**) which then ejects chloride ion to afford the observed stilbenes. Bibenzyl (**3**) could arise by several routes, e.g., a side reaction involving hydrogen atom abstraction by radical **6** from the solvent and subsequent reductive coupling of benzyl chloride.[7] The two trimeric materials probably arise by attack on stilbene by **6** or benzyl radical (an intermediate on the way to **3**).

Several features of this proposed mechanism require comment. A number of 1,2-disubstituted materials, e.g., bromohydrins and β-halo ethers, undergo stereospecific *anti*-elimination to form alkenes,[2] and hence we expected a similar process, i.e., stereospecific elimination of the two heteroatoms from **8** (as, e.g., in Eqn 11) to afford the stilbenes directly. However, this is not the case. The diastereomeric *dl*- and *meso*-dichlorodiphenylethanes **7** were synthesized independently by chlorination of *trans*-stilbene and subsequent separation of the diastereomers by fractional crystallization.[8] It was found that each diastereomer is converted into a mixture of *cis* and *trans*-stilbenes in the presence of Co(I)(salen) under our electrolysis conditions, demonstrating that an intermediate which can lose stereochemical integrity, presumably radical **9**, is involved on the path to stilbenes.



(11)



$$C_6H_5CH(Cl)CH(Cl)C_6H_5 + 2e^- \longrightarrow C_6H_5CH{=}CHC_6H_5 + 2Cl^- \quad (12)$$

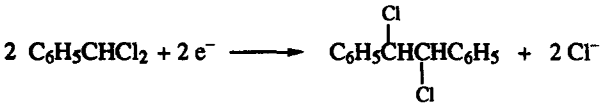
7

By summing equations 6-10, we obtain the net reaction shown in eqn. 12. It may be seen that the dichlorides **7** are converted to stilbenes without consumption of Co(I). The catalytic nature of the conversion can be verified by coulometry. Conversion of *n* moles of **7** to stilbenes in the presence of 1 mole of Co(II) catalyst should consume $2n + 1$ Faradays of current per mole of **7**, where the extra Faraday is required for the initial conversion of Co(II) to Co(I). The experimental data for a number of electrolyses are presented as runs 1 - 8 in Table I and nicely support the proposed stoichiometry.

Table I

Run	Substrate	# moles dihalide/mole of Co(II)(salen)	# of Faradays consumed/Co(II)(salen) Theor.	Experimental
1	*meso*-**7**	1.0	3.0	2.7
2	*meso*-**7**	2.0	5.0	5.3
3	*meso*-**7**	3.0	7.0	7.0
4	*meso*-**7**	4.0	9.0	9.9
5	*dl*-**7**	1.0	3.0	3.0
6	*dl*-**7**	2.0	5.0	5.0
7	*dl*-**7**	3.0	7.0	7.1
8	*dl*-**7**	4.0	9.0	9.6
9	**1**	1.0	3.0	2.6
10	**1**	2.0	5.0	3.9
11	**1**	4.0	9.0	6.5

Furthermore, summation of equations 2- 5 affords the net reaction shown in Eqn. 13. It is again clear that the only role of the cobalt species is to electrocatalyze the formation of **7**. Coulometric determination



$$2\ C_6H_5CHCl_2 + 2\,e^- \longrightarrow C_6H_5CH(Cl)CH(Cl)C_6H_5 + 2\,Cl^- \qquad (13)$$

7

of the catalytic character of this portion of the overall sequence is complicated by consumption of 7 by eqns 6-10 about as fast as it is formed. However, we can readily measure the amount of current consumed in the overall conversion of benzal chloride to stilbene. The overall stoichiometry can be obtained by summing either Eqns 1 - 10 (or Eqns 12 - 13) obtain the net overall electrode process, shown in Eqn 14:

$$2\ C_6H_5CHCl_2 + 4\,e^- \longrightarrow C_6H_5CH{=}CHC_6H_5 + 4\,Cl^- \qquad (14)$$

Eqn 14 predicts that conversion of *n* moles of benzal chloride to stilbenes should consume $2n + 1$ Faradays of current/mole of **1**. Entries 9-11 in Table I support the proposed catalytic mechanism, though the coulometric *n*-values are low, apparently because of incursion of the side reactions.

The source of electrons in eqns 3, 7, and 9 of Scheme I is almost certainly not the electrode but rather cobalt(I)(salen). Solution electron-transfers in multistep electrode processes are far more common than electron-transfer from the electrode itself.[9]

The sequence of reactions shown in Scheme I constitutes a doubly electrocatalytic process, in which, described in its most general terms, a substance A is converted catalytically to an intermediate B which in turn is converted, again catalytically, to the final product C (here, 1 → 7 → 2).[10] It is intriguing to consider whether similar concepts can be used to construct other doubly and even triply electrocatalytic cycles. We are exploring these possibilities.

Acknowledgments.

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Footnotes and References

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2. Scheffold, R. in *Modern Synthetic Methods,* vol. 3, Wiley, New York, 1983, p. 355 ff.
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4. (a) The Ag/0.1 M $AgNO_3$ reference electrode is +0.35 V positive of S.C.E.; (b) Benzal chloride (**1**) is not reduced before -2.4 V.
5. The complex voltammetric behavior of the Co(II)-benzal chloride system will be described elsewhere: Fry, A. J. and Sirisoma, N., manuscript in preparation.
6. Fry, A. J., Powers, T. A. *J. Org. Chem.* **1987**, *52,* 2498.
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8. (a) Buckles, R. E.; Steinmetz, W. E.; Wheeler, N. G. *J. Amer. Chem. Soc.* **1950**, *72,* 2496 (b) The progress of the fractional crystallization was followed by the relative heights of the methine singlets of the *meso* and *dl* diastereomers at δ 5.20 and 5.25, respectively. The *meso* diastereomer is the less soluble of the two.
9. 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.
10. The term "doubly electrocatalytic" can be used in another sense to describe processes in which a reagent formed at the electrode reacts with another component of the medium to generate a third species which then reacts with the organic substrate. Examples include the bromide–alkyl sulfide and chloride–ruthenium oxide systems devised by Shono[11a] and Torii,[11b] respectively, for the electrocatalytic oxidation of alcohols.
11. (a) Shono, T.; Matsumura, Y.; Hayashi, J.; Mizoguchi, M. *Tetrahedron Lett.* **1980**, *21,* 1867; (b) Torii, S.; Inokuchi, T.; Sugiura, T. *J. Org. Chem.* **1986**, *51,* 155.

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