

Formation of 2-(3'-Oxocyclohexyl)-2-cyclohexen-1-one via Reduction of 2-Cyclohexen-1-one with Electrogenerated Nickel(I) Salen

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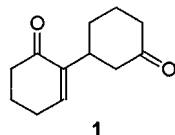
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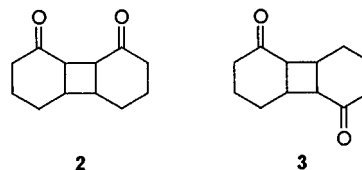
There have been relatively few previous reports¹ concerning the electrochemistry of 2-cyclohexen-1-one. Reduction of 2-cyclohexen-1-one by a sodium amalgam or by magnesium or zinc in acetic acid as well as by means of controlled-potential electrolysis has been shown by Touboul et al.^{2,3} to afford mixtures of cyclohexanone, 3,3'-dioxo-1,1'-bicyclohexyl, and three diethylenic ketones. In a series of papers by Ivcher and co-workers,^{4–7} various aspects of the polarographic behavior of 2-cyclohexen-1-one in aqueous media were probed, including the influence of pH on the protonation and reduction of the carbonyl moiety. Denney and Mooney⁸ examined the polarographic reduction of 2-cyclohexen-1-one in aqueous buffer solutions. In an investigation of the use of electrogenerated bases to promote Michael addition reactions, Baizer et al.⁹ observed that dimerization of 2-cyclohexen-1-one to afford 2-(3'-oxocyclohexyl)-2-cyclohexen-1-one (**1**) in a yield of 65% can be promoted via reduction



of only 0.13% of the starting material to its radical-anion (the electrogenerated base) at a mercury cathode in dimethylformamide containing tetra-*n*-propylammonium tetrafluoroborate. Apparently, however, the identification of **1** was based solely on earlier work by Leonard and Musliner,¹⁰ who employed only one-dimensional ¹H

NMR data to conclude that treatment of 2-cyclohexen-1-one with aqueous sodium hydroxide leads to **1**. In other electrochemical research, Tissot and co-workers¹¹ found that direct reduction of 2-cyclohexen-1-one at a mercury cathode in acetonitrile containing tetra-*n*-butylammonium tetrafluoroborate along with 5% water gives rise to 3-(3'-oxocyclohexyl)cyclohexanone in essentially quantitative yield.

In contrast to the paucity of information about the electroreductive dimerization of 2-cyclohexen-1-one, the photodimerization of this species has been the subject of numerous studies over the years,^{12–18} and irradiation of this compound yields principally a mixture of the head-to-head and head-to-tail dimers, **2** and **3**.



Recently, after investigating the addition of alkyl radicals, arising via the in situ catalytic reduction of primary alkyl monobromides and iodides by electrogenerated nickel(I) salen, to activated olefins such as ethyl acrylate and styrene, we decided to ascertain whether 2-cyclohexen-1-one might undergo similar alkylation reactions. In this study, we have examined the catalytic reduction of several alkyl iodides by nickel(I) salen electrogenerated at a glassy carbon cathode in the presence of 2-cyclohexen-1-one in dimethylformamide containing tetramethylammonium perchlorate as supporting electrolyte. Although we have observed the appearance of 3-alkylcyclohexanone and 3-alkyl-2-cyclohexen-1-one species in very low yields, a more significant finding is that **1** is formed in high yield. An important part of this research has been the use of various NMR techniques to identify **1** unambiguously as well as to exclude an isomer, 2-(2'-oxocyclohexyl)-2-cyclohexen-1-one, as a possible product. We propose that the formation of **1** is initiated by reaction of electrogenerated nickel(I) salen with 2-cyclohexen-1-one to give the radical-anion of the parent enone.

Experimental Section

Reagents. Dimethylformamide (DMF), which served as the solvent for all electrochemical experiments, was a Burdick and Jackson "distilled in glass" reagent and was used as received. Tetramethylammonium perchlorate (TMAP), from GFS Chemi-

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cals, Inc., was employed without further purification as the supporting electrolyte. Each of the following chemicals was used as received: 2-cyclohexen-1-one (Lancaster, 97%), [[2,2'-(1,2-ethanediy)bis(nitrilomethylidene)]bis[phenolato]]-*N,N,O,O'*-nickel(II) [nickel(II) salen, Aldrich, 98%], iodoethane (Aldrich, 99%), 1-iodopropane (Aldrich, 99%), 1-iodobutane (Aldrich, 99%), 1-iodopentane (Aldrich, 98%), and *n*-undecane (Aldrich, 99%). Deaeration procedures were carried out with Air Products zero-grade argon.

Authentic samples of 3-ethyl-, 3-*n*-propyl-, 3-*n*-butyl-, and 3-*n*-pentylcyclohexanone were synthesized according to a procedure published by House and Snoble,¹⁹ which involves treatment of a cold solution of the appropriate alkylmagnesium iodide with cuprous chloride and then 2-cyclohexen-1-one, with diethyl ether as solvent, followed by isolation and purification of the desired product.

Cells, Electrodes, Instrumentation, and Procedures.

Cells, instrumentation, and procedures for cyclic voltammetry and controlled-potential electrolysis are described in previous publications.^{20,21} For cyclic voltammetry, a short length of 3-mm-diameter glassy carbon rod (Grade GC-20, Tokai Electrode Manufacturing Co., Tokyo, Japan) was press-fitted into Teflon to give a planar, circular working electrode with a geometric area of 0.077 cm². For controlled-potential electrolyses, the working cathodes were disks of reticulated vitreous carbon (RVC 2X1-100S, Energy Research and Generation, Oakland, CA) with surface areas of approximately 200 cm²; these electrodes were fabricated, cleaned, and handled as described elsewhere.²² All potentials are quoted with respect to a reference electrode consisting of a cadmium/saturated mercury amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.76 V vs the aqueous saturated calomel electrode at 25 °C.^{23,24}

We acquired ¹H and ¹³C NMR spectra in CDCl₃, with TMS as an internal standard, by using 300-MHz Varian Gemini 200 and 400-MHz Varian Unity^{INOVA} spectrometers; chemical shifts are reported in parts per million (ppm).

Separation, Identification, and Quantitation of Products. Techniques and equipment for the separation, identification, and quantitation of electrolysis products by means of both gas chromatography and GC-MS are presented in earlier publications.^{20,25} To quantitate the products, we employed *n*-undecane as an electroinactive internal standard, which was added to each solution prior to the start of an electrolysis. Gas chromatographic response factors, relative to *n*-undecane, were determined experimentally for **1** and for the various 3-alkylcyclohexanones; response factors for the 3-alkyl-2-cyclohexen-1-ones were assumed to be the same as those for the corresponding 3-alkylcyclohexanones. All product yields reported in this paper are absolute; yields of the alkylated cyclohexanones and cyclohexenones are based on the initial quantity of the alkyl iodide, whereas the yield of **1** is based on the initial quantity of 2-cyclohexen-1-one.

We isolated **1** as a yellow oil by means of silica gel column chromatography with hexanes-ethyl acetate as the eluent; its purity was confirmed with the aid of GC and TLC: IR (CHCl₃) 1707, 1670 cm⁻¹; ¹H NMR (CDCl₃) δ 6.64 (t, 1H), 2.93 (m, 1H), 2.36 (m, 2H), 2.31 (m, 2H), 2.27 (m, 2H), 2.26 (m, 2H), 1.93 (m, 2H), 1.90 (m, 2H), 1.84 (d, 1H), 1.56 (d, 1H); ¹³C NMR (CDCl₃) δ 211.6, 198.7, 144.4, 141.9, 46.2, 41.2, 38.6, 37.5, 30.5, 25.9, 24.9, 22.6; HRMS *m/z* (M⁺) calcd (for C₁₂H₁₆O₂) 192.1150, found 192.1154.

It was essential to distinguish **1** from a possible isomer, namely 2-(2'-oxocyclohexyl)-2-cyclohexen-1-one, which cannot be

done by means of simple one-dimensional ¹H NMR data. Accordingly, we performed DEPT and two-dimensional HETCOR experiments to measure the chemical shift of the aliphatic methine hydrogen. A COSY NMR experiment revealed that at least three hydrogens are coupled to this aliphatic methine hydrogen; two of these methine-coupled hydrogens belong to the same methylene group, as determined from the HETCOR experiment. Results from one-dimensional NOE experiments were compared with molecular models (obtained with the aid of PC-MODEL and MMX-2 force field computations) to verify that the three methine-coupled hydrogens must be vicinal to the methine hydrogen. This evidence is singularly consistent with **1** and cannot arise from 2-(2'-oxocyclohexyl)-2-cyclohexen-1-one.

We identified 3-ethyl-, 3-*n*-propyl-, 3-*n*-butyl-, and 3-*n*-pentylcyclohexanone by means of GC-MS. Their gas chromatographic retention times and mass spectra were virtually identical with authentic compounds synthesized in our laboratory; in addition, our mass spectra for 3-ethylcyclohexanone and 3-*n*-propylcyclohexanone agree well with those reported, respectively, by House and Snoble¹⁹ and by House and Fischer.²⁶ Mass spectral data for the authentic compounds were acquired at 70 eV with the aid of a Hewlett-Packard 5890 Series II gas chromatograph coupled to a Hewlett-Packard Model 5971 mass-selective detector: (a) for 3-ethylcyclohexanone, *m/z* 126, M⁺ (33); 111, [M - CH₃]⁺ (9); 98, [M - C₂H₄]⁺ (18); 97, [M - C₂H₅]⁺ (55); 83, [M - C₃H₇]⁺ (100); 70, [M - C₄H₈]⁺ (40); 69, [M - C₄H₉]⁺ (34); 56, [M - C₅H₁₀]⁺ (22); 55, [M - C₅H₁₁]⁺ (89); (b) for 3-*n*-propylcyclohexanone, *m/z* 140, M⁺ (10); 112, [M - C₂H₄]⁺ (2); 111, [M - C₂H₅]⁺ (2); 98, [M - C₃H₆]⁺ (15); 97, [M - C₃H₇]⁺ (100); 81, [M - C₃H₇O]⁺ (5); 69, [M - C₅H₁₁]⁺ (15); 56, [M - C₆H₁₂]⁺ (18); 55, [M - C₆H₁₃]⁺ (53); (c) for 3-*n*-butylcyclohexanone, *m/z* 154, M⁺ (11); 126, [M - C₂H₄]⁺ (1); 111, [M - C₃H₇]⁺ (26); 110, [M - C₃H₈]⁺ (35); 97, [M - C₄H₉]⁺ (100); 83, [M - C₅H₁₁]⁺ (8); 82, [M - C₅H₁₂]⁺ (46); 69, [M - C₆H₁₃]⁺ (11); 56, [M - C₇H₁₄]⁺ (15); 55, [M - C₇H₁₅]⁺ (45); (d) for 3-*n*-pentylcyclohexanone, *m/z* 168, M⁺ (4); 125, [M - C₃H₇]⁺ (9); 111, [M - C₄H₉]⁺ (1); 98, [M - C₅H₁₀]⁺ (11); 97, [M - C₅H₁₁]⁺ (100); 83, [M - C₆H₁₃]⁺ (7); 69, [M - C₇H₁₅]⁺ (11); 56, [M - C₈H₁₆]⁺ (12); 55, [M - C₈H₁₇]⁺ (40).

Identities of unsaturated analogues of compounds mentioned in the preceding paragraph were established by means of GC-MS; their gas chromatographic retention times are slightly shorter than those for the corresponding saturated species: (a) for 3-ethyl-2-cyclohexen-1-one, *m/z* 124, M⁺ (47); 109, [M - CH₃]⁺ (11); 96, [M - C₂H₄]⁺ (100); 81, [M - C₃H₇]⁺ (28); 68, [M - C₄H₈]⁺ (20); 67, [M - C₄H₉]⁺ (54); 55, [M - C₅H₉]⁺ (11); 53, [M - C₅H₁₁]⁺ (26); (b) for 3-*n*-propyl-2-cyclohexen-1-one, *m/z* 138, M⁺ (83); 123, [M - CH₃]⁺ (41); 110, [M - C₂H₄]⁺ (100); 95, [M - C₃H₇]⁺ (76); 81, [M - C₄H₉]⁺ (82); 68, [M - C₅H₁₀]⁺ (24); 67, [M - C₅H₁₁]⁺ (73); 55, [M - C₆H₁₁]⁺ (28); 53, [M - C₆H₁₃]⁺ (72); (c) for 3-*n*-butyl-2-cyclohexen-1-one, *m/z* 152, M⁺ (67); 137, [M - CH₃]⁺ (29); 124, [M - C₂H₄]⁺ (47); 123, [M - C₂H₅]⁺ (68); 110, [M - C₃H₆]⁺ (65); 109, [M - C₃H₇]⁺ (75); 82, [M - C₅H₁₀]⁺ (93); 81, [M - C₅H₁₁]⁺ (100); 67, [M - C₆H₁₃]⁺ (93); 55, [M - C₇H₁₃]⁺ (79); 53, [M - C₇H₁₅]⁺ (99); (d) for 3-*n*-pentyl-2-cyclohexen-1-one, *m/z* 166, M⁺ (85); 151, [M - CH₃]⁺ (16); 137, [M - C₂H₅]⁺ (98); 123, [M - C₃H₇]⁺ (77); 111, [M - C₄H₇]⁺ (61); 110, [M - C₄H₈]⁺ (75); 109, [M - C₄H₉]⁺ (60); 95, [M - C₅H₁₁]⁺ (87); 82, [M - C₆H₁₂]⁺ (88); 81, [M - C₆H₁₃]⁺ (80); 68, [M - C₇H₁₄]⁺ (30); 67, [M - C₇H₁₅]⁺ (81); 55, [M - C₈H₁₅]⁺ (72); 53, [M - C₈H₁₇]⁺ (100).

Results and Discussion

Cyclic Voltammetry Studies of Individual Compounds. We have investigated the cyclic voltammetric behavior of each electroactive species employed in this work. For all experiments, the chosen compound was present at a concentration of 2 mM in DMF containing 0.10 M TMAP, a freshly polished glassy carbon electrode was used, and the scan rate was 100 mV s⁻¹. For the direct reduction of 2-cyclohexen-1-one, we observed a

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single irreversible wave with a peak potential of -1.24 V. As described in more detail in a previous paper,²⁷ the reduction of nickel(II) salen is a reversible process, and the cathodic and anodic peak potentials for the nickel(II) salen–nickel(I) salen redox couple are -0.85 and -0.78 V, respectively. Direct reduction of each of the alkyl iodides involved in this work gives rise to a single irreversible wave that is attributable to cleavage of the carbon–iodine bond, and the pertinent peak potentials are as follows: iodoethane, -1.50 V;²⁸ 1-iodopropane, -1.55 V;²⁹ 1-iodobutane, -1.45 V;³⁰ and 1-iodopentane, -1.42 V.³¹

Cyclic Voltammetric Behavior of 2-Cyclohexen-1-one–Nickel(II) Salen–Alkyl Iodide Systems. A cyclic voltammogram recorded at a scan rate of 100 mV s^{-1} for a solution consisting of a mixture of 1 mM nickel(II) salen and 20 mM 2-cyclohexen-1-one in DMF containing 0.10 M TMAP exhibited the reversible waves corresponding to the nickel(II) salen–nickel(I) salen couple (with cathodic and anodic peak potentials identical with those reported above) along with the irreversible wave for reduction of 2-cyclohexen-1-one (with the same cathodic peak potential listed earlier). Thus, a redox reaction between electrogenerated nickel(I) salen and 2-cyclohexen-1-one does not occur to an extent that is detectable under the conditions of our cyclic voltammetric measurements.

Remarkable behavior is seen when cyclic voltammograms are recorded for mixtures of nickel(II) salen and an alkyl iodide. First, there is an enhancement of the cathodic current at -0.85 V for reduction of nickel(II) salen as well as a disappearance of the anodic current for reoxidation of the electrogenerated nickel(I) salen, both features indicating catalytic reduction of the alkyl iodide by nickel(I) salen; moreover, the cathodic current increases in size as the concentration of alkyl iodide is raised. Second, a new irreversible cathodic wave appears at a potential 100 – 200 mV more negative than that for reduction of nickel(II) salen; the height of this wave also increases with the concentration of the alkyl iodide. It is pertinent to mention here that a wave for the direct (uncatalyzed) reduction of an alkyl iodide is observed at a much more negative potential than these two waves. Tentatively, we believe that the second wave might be attributable to reduction of an alkylnickel(III) salen intermediate, but more extensive studies must be done to prove this hypothesis.

When increasing concentrations of 2-cyclohexen-1-one are introduced into DMF– 0.10 M TMAP solutions containing 1 mM nickel(II) salen and 10 mM alkyl iodide (either iodoethane or 1-iodopentane), the height of the first wave (attributed to reduction of nickel(II) salen in the presence of the alkyl iodide) is unaffected. However, for increasing concentrations of 2-cyclohexen-1-one, the height of the second wave decreases gradually when iodoethane is present but increases considerably when 1-iodopentane is present; we cannot yet explain the cause of such behavior.

Table 1. Adducts Obtained from Nickel(I) Salen-Catalyzed Reduction of Alkyl Iodides in the Presence of 2-Cyclohexen-1-one in DMF Containing 0.10 M TMAP^a

| alkyl iodide | concn of 2-cyclohexen-1-one, mM | adducts, % ^b | | |
|---------------|---------------------------------|-------------------------|----------|----------|
| | | 1 | 8 | 9 |
| iodoethane | 10 | 75 | 6 | 3 |
| iodoethane | 20 | 77 | 6 | 2 |
| 1-iodopropane | 20 | 80 | 7 | 3 |
| 1-iodobutane | 5 | 72 | 5 | 3 |
| 1-iodobutane | 10 | 76 | 6 | 2 |
| 1-iodobutane | 20 | 80 | 6 | 4 |
| 1-iodobutane | 30 | 79 | 6 | 3 |
| 1-iodopentane | 30 | 74 | 7 | 3 |

^aFor all experiments, the initial concentrations of nickel(II) salen and alkyl iodide were 1.0 and 5.0 mM, respectively, and the potential of the cathode used to electrogenerate nickel(I) salen was -0.95 V. ^b**1** = 2-(3'-oxocyclohexyl)-2-cyclohexen-1-one, **8** = 3-alkylcyclohexanone, and **9** = 3-alkyl-2-cyclohexen-1-one.

Controlled-Potential Electrolytic Production of 2-(3'-Oxocyclohexyl)-2-cyclohexen-1-one (1). A series of electrolyses was carried out in which four different alkyl iodides were catalytically reduced by nickel(I) salen electrogenerated at a reticulated vitreous carbon cathode in the presence of 2-cyclohexen-1-one. Table 1 lists the results of these experiments. Each entry represents the average of two duplicate electrolyses; in all instances, the coulometric n value was essentially 1, all of the alkyl iodide was catalytically reduced, the total electrolysis time was less than 30 min, and the yields of the products were reproducible to $\pm 3\%$. As revealed in Table 1, **1** is obtained in yields ranging from 72% to 80%, whereas 3-alkylcyclohexanones and 3-alkyl-2-cyclohexen-1-ones are formed in small quantities. Furthermore, we observed smaller amounts of other products, including cyclohexanone along with alkanes and alkenes arising via disproportionation, coupling, and hydrogen atom abstraction (from DMF) of alkyl radicals.

Several experiments were carried out with systems containing nickel(II) salen and 2-cyclohexen-1-one, but in the absence of an alkyl iodide. First, a 1 mM solution of nickel(II) salen in DMF containing 0.10 M TMAP was exhaustively reduced at a reticulated vitreous carbon cathode held at -0.95 V in order to generate nickel(I) salen. Then, with the cathode potential kept at -0.95 V, 2-cyclohexen-1-one was added to give a concentration of 5 mM and the solution was stirred under argon for 1 h; no current flowed, the solution retained the green color characteristic of nickel(I) salen, and **1** was formed in 71% yield. Second, when the preceding experiment was repeated, except that the concentration of 2-cyclohexen-1-one was 20 mM, **1** was produced in 64% yield. Third, a 1 mM solution of nickel(II) salen was once again reduced to generate nickel(I) salen. Then, the electrolysis circuit was opened, 2-cyclohexen-1-one was introduced to give a concentration of 10 mM, and the solution was stirred under argon for 1 h; after only 5 min of stirring, the color of the solution changed from green to red, and **1** was obtained in 46% yield at the end of the experiment. Fourth, in a control experiment, in which a solution containing 1 mM nickel(II) salen and 20 mM 2-cyclohexen-1-one was stirred under argon for 1 h without any electrolysis being performed, we observed that **1** was not formed. In addition, it should be mentioned that direct reduction of a 20 mM solution of 2-cyclohexen-1-one alone in solvent-supporting electrolyte at a reticulated vitreous carbon cathode held at -0.95 V (approximately 300 mV

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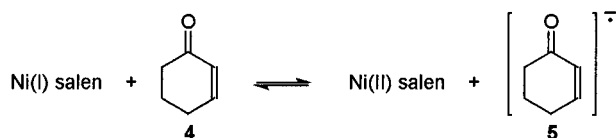
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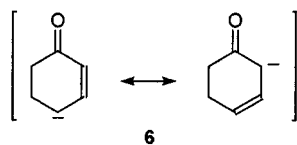
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more positive than the cyclic voltammetric peak potential for reduction of 2-cyclohexen-1-one) for 1 h led to the formation of **1** in a yield estimated to be no higher than 8%, although no current flow was observed. Thus, the use of nickel(I) salen is essential to obtaining **1** in high yields and in a short time.

Mechanistic Features of the Formation of 2-(3'-Oxocyclohexyl)-2-cyclohexen-1-one (1) and of the Alkylated Cyclohexanones and 2-Cyclohexen-1-ones. On the basis of our experimental observations, we conclude that **1** must arise via the interaction between 2-cyclohexen-1-one and electrogenerated nickel(I) salen. However, it appears that this reaction only serves to initiate the production of **1**, because the experiments described in the preceding section reveal that no significant amount of electrogenerated nickel(I) salen is consumed by reaction with 2-cyclohexen-1-one. Thus, we are led to propose a pathway for the production of **1** that involves an outer-sphere one-electron transfer between nickel(I) salen and 2-cyclohexen-1-one (**4**) to give a radical-anion (**5**).



Once formed, **5** acts as an electrogenerated base to deprotonate unreacted **4** to give the conjugate base of the starting material (**6**), and **6** can attack another molecule

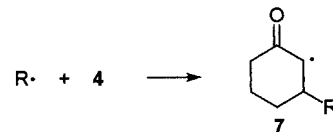


of **4** to yield a dimeric species that eventually becomes **1**; this last sequence of relatively rapid self-propagating

reactions is identical with that described earlier and more fully by Baizer et al.⁹ Although, on the basis of our cyclic voltammetric studies, the reduction of **4** by electrogenerated nickel(I) salen is strongly disfavored, we believe (as concluded by Baizer et al.⁹) that only a very small amount of an electrogenerated base (radical-anion **5**) is needed to trigger the formation of **1**.

Inasmuch as **6** can be formulated with a negative charge at either its 2- or 4-position, it is conceivable that, in addition to **1**, one might observe the presence of 4-(3'-oxocyclohexyl)-2-cyclohexen-1-one as a product. However, only a single gas chromatographic peak corresponding to **1** was seen. Moreover, 4-(3'-oxocyclohexyl)-2-cyclohexen-1-one possesses two methine hydrogen atoms, whereas our NMR experiments revealed the existence of only a single methine hydrogen atom, as occurs in **1**. Thus, we have no evidence for the formation of 4-(3'-oxocyclohexyl)-2-cyclohexen-1-one or any other dimer derived from **4**, except for **1** itself.

To account for the formation of the alkylated products, we propose that electrogenerated nickel(I) salen interacts with an alkyl iodide (possibly via a transient alkylnickel(III) salen intermediate) to yield an alkyl radical which can add to **4** to afford an alkylated radical (**7**).



In turn, **7** can abstract a hydrogen atom from the solvent (DMF) to give 3-alkylcyclohexanone (**8**). Formation of 3-alkyl-2-cyclohexen-1-one (**9**) might take place via disproportionation of **7** to afford both **8** and **9**.

Finally, the nickel(I) salen-promoted reductive dimerization of 2-cyclohexen-1-one may be unique, because our efforts to cause an analogous reaction with 2-cyclopenten-1-one were unsuccessful.

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