

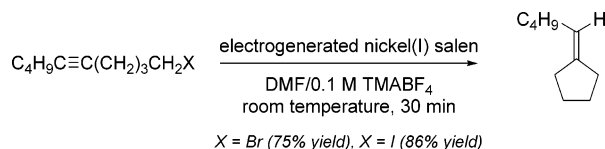
Catalytic Reduction and Intramolecular Cyclization of Haloalkynes in the Presence of Nickel(I) Salen Electrogenerated at Carbon Cathodes in Dimethylformamide

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Pentylidenecyclopentane can be conveniently prepared in up to 86% yield via the catalytic reduction of 1-iodo- or 1-bromo-5-decyne by [[2,2'-[1,2-ethanediylbis(nitrilomethylidene)]bis[phenolato]]-N,N',O,O'-nickelate(I) electrogenerated at a carbon cathode in dimethylformamide containing tetramethylammonium tetrafluoroborate. This electrosynthesis can be accomplished at potentials for which the haloalkynes are electroinactive, and it can be completed within 30 min at room temperature. Attempts to synthesize pentylidenecyclobutane and pentylidenecyclohexane from 1-halo-4-nonynes and 11-halo-5-undecynes, respectively, under similar conditions afford the carbocycles in very low yields (2% and 6%, respectively). Other products derived from the various haloalkynes are dimers, alkynes, and 1-alkenyne. Dimers (alkadiynes) arising from 1-halo-4-nonynes and 11-halo-5-undecynes are formed in yields ranging from 80% to 89%, whereas icos-5,15-diyne (the dimer obtained from a 1-halo-5-decyne) is found in significantly lower yield ($\leq 13\%$). Alkynes and 1-alkenyne are produced in yields of 3–10% and 2–3%, respectively. A mechanistic scheme, involving alkyn-1-yl radicals arising from nickel(I) salen catalyzed cleavage of the carbon–halogen bond of each haloalkyne, is proposed to account for the formation of all products.

Introduction

Crandall and Keyton¹ reported in 1969 that refluxing a mixture of 1-bromo-5-decyne and tri-*n*-butyltin hydride in benzene for 36 h, in the presence of 2,2'-azobis(2-methylpropionitrile) (AIBN) as a radical initiator, produces pentylidenecyclopentane in 99% yield. In the same research, benzylidenecyclopentane was obtained virtually quantitatively when 6-bromo-1-phenyl-1-hexyne was employed as the starting haloalkyne. These workers also sought to promote the intramolecular cyclizations of 1-bromo-4-nonyne and 11-bromo-5-undecyne, for which on the basis of other information^{2,3} the resulting carbocyclic products would be expected to be pentyl-

idenecyclobutane and pentylidenecyclohexane, respectively; unfortunately, no intramolecular cyclization was observed for these two haloalkynes.

Direct electrochemical reduction and intramolecular cyclization of haloacetylenes have been subjects of several investigations. In dimethylformamide (DMF) containing tetraalkylammonium salts, electrolyses of 6-bromo- and 6-iodo-1-phenyl-1-hexyne⁴ and 1-bromo- and 1-iodo-5-decyne⁵ at mercury pool cathodes do afford the expected five-membered carbocycles, but only in relatively low yields (<25%) because the dominant process is formation of diorganomercury compounds. When a

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reticulated vitreous carbon electrode is used to carry out the direct reductions of 1-bromo- and 1-iodo-5-decyne⁶ and of 6-iodo-1-phenyl-1-hexyne,⁷ there is a marked improvement in the amounts of desired carbocycles; pentylidencyclopentane and benzylidencyclopentane can be produced in yields of up to approximately 60%, and there is a general tendency for a phenyl-conjugated haloalkyne to undergo more extensive cyclization.

In recent years, our laboratory has become interested in the use of electrogenerated nickel(I) complexes as catalysts to effect the reductive intramolecular cyclizations of halogenated alkynes and alkenes. For example, electrogenerated [[2,2'-(1,2-ethanediyl-bis(nitrilomethylidene)]bis[phenolato]]-N,N',O,O']nickelate(I), referred to hereafter as nickel(I) salen, catalyzes the reductive cyclization of 6-bromo- and 6-iodo-1-phenyl-1-hexyne to give benzylidencyclopentane in up to 95% yield.⁸ On the other hand, catalytic reduction of 6-bromo-1-hexene by nickel(I) salen leads to the formation of mixtures of methylcyclopentane, 7-cyclopentylhept-1-ene, 1,2-dicyclopentylethane, 1-hexene, and 1,11-dodecadiene.⁹ Several bromo propargyloxy and allyloxy esters, e.g., ethyl 2-bromo-3-(3',4'-methylenedioxyphenyl)-3-(propargyloxy)propanoate, have been catalytically reduced by nickel(I) tetramethylcyclam electrogenerated at a carbon cathode in DMF to afford functionalized tetrahydrofurans in yields ranging from 80% to essentially quantitative.^{10,11} These last two publications provide some comparisons between the use of electrogenerated transition metal catalysts and of more classic techniques involving organometallic hydrides. A recent comprehensive review by Duñach and co-workers¹² provides ample evidence for the utility and diversity of carbon-carbon bond-forming syntheses that can be accomplished catalytically through the use of electrogenerated low-valent nickel species.

In the present work, we have employed cyclic voltammetry and controlled-potential electrolysis to examine the use of electrogenerated nickel(I) salen as a catalyst for the reductive intramolecular cyclization of six different halogenated alkynes (1-bromo- and 1-iodo-4-nonyne, 1-bromo- and 1-iodo-5-decyne, and 11-bromo- and 11-iodo-5-undecyne). No studies of the nickel(I) salen catalyzed reductions of these haloalkynes have been reported previously. We observed that the extent of cyclization is greatest (at least 75%) for 1-bromo- and 1-iodo-5-decyne. On the other hand, 1-bromo- and 1-iodo-4-nonyne as well as 11-bromo- and 11-iodo-5-undecyne display a significantly lesser propensity ($\leq 6\%$) to afford carbocycles; instead, coupling of alkyne-1-yl radicals to form alkadiynes is dominant. Other minor products derived from the nickel(I) salen catalyzed reductions of the haloalkynes are alkynes and 1-alkynes. A mechanistic scheme involving intramolecular radical cyclization, radical coupling and disproportionation, and hydrogen-atom abstraction from the solvent is offered to account for the formation of the various products.

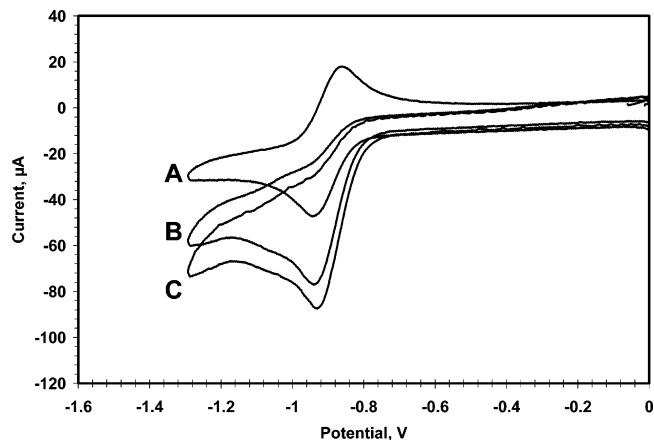


FIGURE 1. Cyclic voltammograms recorded with a glassy carbon electrode (area = 0.077 cm²) at 100 mV s⁻¹ in DMF containing 0.10 M TMABF₄ and (A) 2.0 mM nickel(II) salen, (B) 2.0 mM nickel(II) salen and 10.0 mM 1-bromo-5-decyne, and (C) 2.0 mM nickel(II) salen and 20.0 mM 1-bromo-5-decyne.

Results and Discussion

Cyclic Voltammetric Behavior of Haloalkynes. Cyclic voltammograms were recorded at a scan rate of 100 mV s⁻¹ for direct reduction of a 2.0 mM solution of each of the six haloalkynes at a glassy carbon electrode in DMF containing 0.10 M tetramethylammonium tetrafluoroborate (TMABF₄) under an argon atmosphere. For each compound, a single irreversible peak was seen that corresponds to two-electron reductive cleavage of the carbon-halogen bond; the cyclic voltammograms were very similar in appearance to those pictured in an earlier publication¹³ pertaining to the cathodic behavior of alkyl halides at glassy carbon electrodes. In the present work, the cathodic peak potentials (E_{pc}) for 1-iodo-4-nonyne, 1-iodo-5-decyne, and 11-iodo-5-undecyne were found to be virtually identical (-1.36 ± 0.01 V) and in reasonable agreement with values previously obtained for reduction of 1-iodo-5-decyne (-1.42 V)⁶ and 1-iododecane (-1.41 V)¹³ under comparable experimental conditions. Because a carbon-iodine bond is more fragile than a carbon-bromine bond, the latter is reduced at a more negative potential. Accordingly, cathodic peak potentials (E_{pc}) for 1-bromo-4-nonyne, 1-bromo-5-decyne, and 11-bromo-5-undecyne were -1.78 ± 0.01 V, these findings being consistent with earlier research that dealt with the reductions of 1-bromo-5-decyne (-1.90 V)⁶ and 1-bromodecane (-1.85 V).¹³ Our results demonstrate that the carbon-chain length of these haloalkynes has no significant influence on the reduction potential for either the carbon-iodine or carbon-bromine bond. This latter set of observations is reasonable in view of the fact that at least three methylene moieties separate the electroactive carbon-halogen bond from the alkyne site.

Cyclic Voltammetric Behavior of Nickel(II) Salen in the Absence and Presence of Haloalkynes. Shown as curve A in both Figures 1 and 2 is a cyclic voltammogram recorded at 100 mV s⁻¹ for reduction of 2.0 mM nickel(II) salen at a glassy carbon electrode in DMF containing 0.10 M TMABF₄ in the absence of a haloalkyne. A reversible nickel(II) salen-nickel(I) salen couple is seen, for which the cathodic peak potential (E_{pc})

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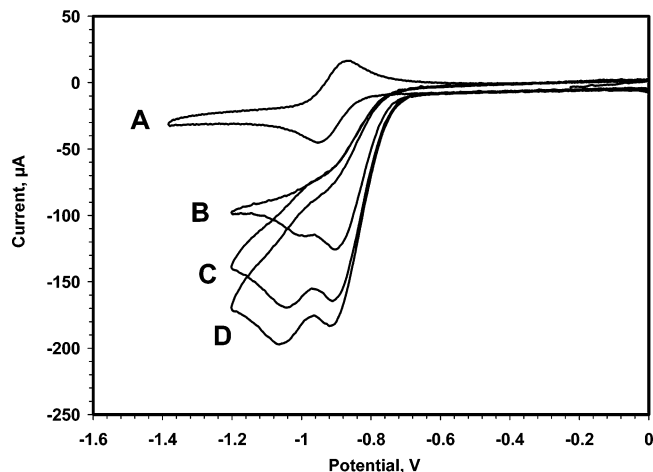


FIGURE 2. Cyclic voltammograms recorded with a glassy carbon electrode (area = 0.077 cm²) at 100 mV s⁻¹ in DMF containing 0.10 M TMABF₄ and (A) 2.0 mM nickel(II) salen, (B) 2.0 mM nickel(II) salen and 5.0 mM 1-iodo-5-decyne, (C) 2.0 mM nickel(II) salen and 10.0 mM 1-iodo-5-decyne, and (D) 2.0 mM nickel(II) salen and 20.0 mM 1-iodo-5-decyne.

is -0.95 V, the anodic peak potential (E_{pa}) is -0.86 V, and the ratio of the peak currents (I_{pa}/I_{pc}) is close to unity. These observations are in substantial agreement with the results of earlier investigations.^{14,15}

In the presence of a haloalkyne, the cyclic voltammetric behavior of nickel(II) salen is altered dramatically. For example, with 1-bromo- and 1-iodo-5-decyne, as seen in curves B and C of Figure 1 and curves B–D of Figure 2, there is an increase in the cathodic peak current for reduction of nickel(II) salen as it is recycled catalytically; this current enhancement is more pronounced for the iodoalkyne than for the bromoalkyne, because the rate of the catalyst–substrate reaction is greater for the former compound. In addition, the anodic peak for reoxidation of nickel(I) salen disappears as a result of the catalyst–substrate reaction. Several other features of the cyclic voltammograms in Figures 1 and 2 deserve mention. First, there is a positive shift in the cathodic peak potential for reduction of nickel(II) salen that is larger with the iodoalkyne than with the bromoalkyne, a difference again attributable to the fact that the electron-transfer reaction between nickel(I) salen and 1-iodo-5-decyne is faster. Second, a new cathodic peak is seen at approximately -1.04 ± 0.03 V for curves B–D of Figure 2 (and a much less conspicuous hump is seen in the same potential region for curves B and C of Figure 1); we now believe that this voltammetric feature is a signal that the imino bond of the salen ligand is attacked by an alkyl radical to afford a modified, catalytically less efficient, and more-difficult-to-reduce nickel salen species.¹⁶ Third, as the concentration of haloalkyne is raised, the cathodic peak current for reduction of nickel(II) salen does not increase in proportion to the amount of added substrate; such behavior has been seen before and has been attributed to sluggish regeneration of the catalyst precursor,^{10,11} a phenomenon that might be linked to the just-described formation of modified nickel salen species. All of the preceding trends were

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TABLE 1. Coulometric Data and Product Distributions for Catalytic Reduction of 20.0 mM Haloalkynes by 2.0 mM Nickel(I) Salen Electrogenerated at Reticulated Vitreous Carbon Cathodes in DMF Containing 0.10 M TMABF₄

entry	haloalkyne	n^b	product distribution, % ^a				
			1	2	3	4	total
1	1-bromo-4-nonyne	0.91	2	81	7	tr	90
2	1-iodo-4-nonyne	0.95	2	85	10	2	99
3	1-bromo-5-decyne	0.89	75	13	3	2	93
4	1-iodo-5-decyne	1.07	86	5	4	2	97
5	11-bromo-5-undecyne	0.93	5	89	6	3	103
6	11-iodo-5-undecyne	0.95	6	80	7	3	96

^a Yield expressed as the percentage of haloalkyne incorporated into each product; 1 = carbocycle; 2 = dimer; 3 = alkyne; 4 = 1-alkenyne. ^b Number of electrons per molecule of haloalkyne.

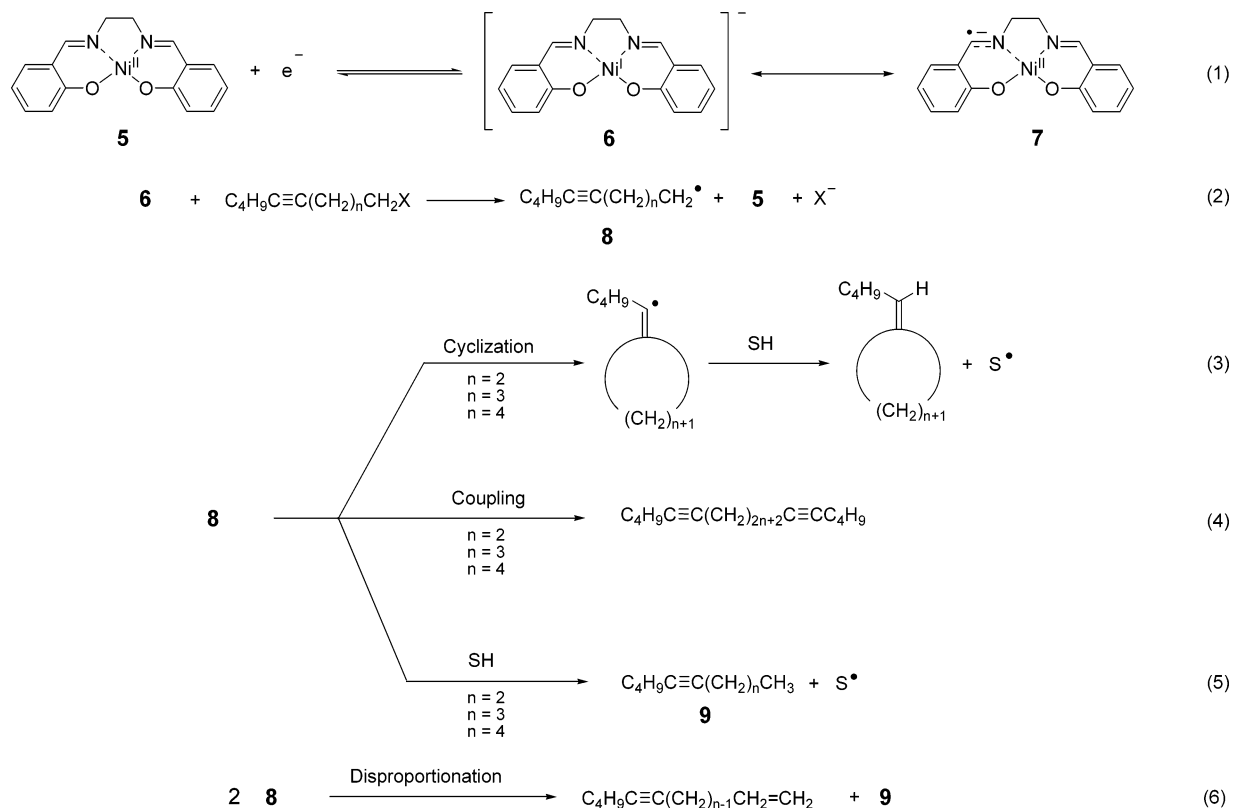
also observed for the 1-bromo- and 1-iodo-4-nonyne and for the 11-bromo- and 11-iodo-5-undecyne systems.

Controlled-Potential (Bulk) Electrolyses of Nickel(II) Salen in the Presence of Haloalkynes. Bulk electrolyses were performed at reticulated vitreous carbon cathodes in DMF containing 0.10 M TMABF₄, 2.0 mM nickel(II) salen, and 20.0 mM haloalkyne at -1.10 V, which is significantly more positive than the potential for direct reduction of any haloalkyne. Compiled in Table 1 are coulometric n values and product distributions obtained for these experiments; each entry represents the average of two separate runs. Coulometric n values indicate that the nickel(I) salen catalyzed reduction of a haloalkyne involves one-electron cleavage of the carbon–halogen bond to give an alkyl radical intermediate. Product yields represent the absolute amount of starting material incorporated into each species and are accurate to $\pm 3\%$; none of the starting haloalkyne remained unreduced and, within experimental error, the total yield of products is essentially 100%. Four products (carbocycle, dimer, alkyne, and 1-alkenyne) were separated, identified, and quantitated with the aid of GC and GC–MS.

As seen in entries 3 and 4 of Table 1, the desired carbocyclic species (pentylidenecyclopentane) was produced from 1-bromo- and 1-iodo-5-decyne in yields of 75% and 86%, respectively. These results compare reasonably well with those reported by Crandall and Keyton,¹ who observed that pentylidenecyclopentane is formed in 99% yield from the tri-*n*-butyltin hydride promoted intramolecular cyclization of 1-bromo-5-decyne. However, a distinct advantage of the electrochemical synthesis described here is that the process can be accomplished at room temperature within 30 min. Moreover, the use, removal, and disposal of toxic tri-*n*-butyltin hydride (and its byproducts) are avoided. Although the scale of our electrochemical procedure is relatively small (see Experimental Section), nothing should preclude adjusting the amounts of haloalkyne and nickel(II) salen, as well as the solution volume, to prepare the carbocycle in larger quantities. Another product derived from the nickel(I) salen catalyzed reductions of 1-bromo- and 1-iodo-5-decyne is a dimer (icosa-5,15-diyne), formed in yields of 13% and 5%, respectively, together with 5-decyne and 1-decen-5-yne, which are obtained in small amounts (2–4%).

In comparison with earlier work,⁸ for which interaction of electrogenerated nickel(I) salen with 6-halo-1-phenyl-1-hexynes was shown to afford the phenyl-conjugated carbocycle in up to 95% yield, the highest yield of pentylidenecyclopentane for the nickel(II) salen–1-halo-5-decyne system is 86% (Table 1, entry 4). These findings are consistent with the observation by

SCHEME 1



Crandall and Michaely¹⁷ that relative rates of reductive intramolecular cyclization of a phenyl-conjugated haloalkyne and an alkyl-substituted haloalkyne are approximately 40:1.

It is interesting to compare results for the nickel(I) salen catalyzed reductions of 1-bromo- and 1-iodo-5-decyne with those obtained from two earlier investigations^{5,6} in our laboratory. Direct reduction of 1-bromo- and 1-iodo-5-decyne at a mercury pool cathode in DMF containing tetramethylammonium perchlorate leads primarily to a diorganomercury species in yields as high as 89%, whereas pentylidenecyclopentane is formed in no higher than 9% yield.⁵ On the other hand, a subsequent study⁶ of the direct reduction of 1-bromo- and 1-iodo-5-decyne at a reticulated vitreous carbon cathode in DMF containing tetraalkylammonium perchlorates revealed that the carbocycle is produced in up to 60% yield if 1,1,1,1,3,3,3-hexafluoro-2-propanol is present as a proton donor.

As shown by entries 1 and 2 (for 1-bromo- and 1-iodo-4-nonyne, respectively) and entries 5 and 6 (for 11-bromo- and 11-iodo-5-undecyne, respectively) in Table 1, efforts to synthesize pentylidenecyclobutane and pentylidenecyclohexane electrochemically result largely in the formation of dimers; we obtained octadeca-5,13-diynes in yields of 81% and 85% from 1-bromo- and 1-iodo-4-nonyne, respectively, and docosa-5,17-diynes in yields of 89% and 80% from 11-bromo- and 11-iodo-5-undecyne, respectively. Unfortunately, the desired carbocycles are produced in only minor amounts; pentylidenecyclobutane was formed in only 2% yield from both 1-bromo- and 1-iodo-4-nonyne, whereas pentylidenecyclohexane was obtained in 5% and 6% yields, respectively, from 11-bromo- and 11-iodo-5-undecyne. Crandall and Keyton¹ did not achieve any reductive

intramolecular cyclization of either 1-bromo-4-nonyne or 11-bromo-5-undecyne through the use of tri-*n*-butyltin hydride. As seen in Table 1, formation of 1-nonen-5-yne from a 1-halo-4-nonyne and of 1-undecen-5-yne from an 11-halo-5-undecyne (via hydrogen atom abstraction from the medium by a catalytically generated primary alkyl radical) occurs to a greater extent than intramolecular cyclization. Finally, the 1-alkenyne, arising from disproportionation, is seen in yields lower than 3%.

Mechanistic Aspects of the Catalytic Reduction of Haloalkynes. Scheme 1 displays the routes by which we believe the products are formed via the nickel(I) salen catalyzed reactions. Earlier, in discussing the cyclic voltammetric characteristics of nickel(II) salen-haloalkyne systems, we indicated that there is evidence (Figure 2, curves B–D) for modification (alkylation) of nickel(II) salen during the catalytic reduction of an alkyl halide (or haloalkyne) by electrogenerated nickel(I) salen. Indeed, several alkylated nickel(II) salen complexes have been isolated and identified in our laboratory, and it has been suggested that one-electron reduction of nickel(II) salen gives rise to a species for which some electron density resides on the imino bonds of the salen ligand (although the nickel center bears the majority of electron density), rendering the imino bonds susceptible to attack by an alkyl radical.¹⁶ Support for the latter hypothesis is seen in a recent publication by Miranda, Wade, and Little,¹⁸ where the electrocatalytic cyclization of (*E*)-8-oxo-oct-2-enoic acid methyl ester to *trans*-(2-hydroxycyclohexyl)-acetic acid methyl ester is reported to require a reduced form of nickel(II) salen with electron density on the imino moieties.

In reaction 1, we represent the one-electron reduction of nickel(II) salen (**5**) as both a metal-centered and ligand-centered

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process to give species **6** and **7**, respectively. However, for purposes of the present study, the electroreductive intramolecular cyclization of haloalkynes can be readily understood in terms of **6** alone as the active catalyst. Accordingly, after the one-electron reduction of **5** to **6** [reaction 1], the latter transfers an electron to a haloalkyne, causing cleavage of the carbon–halogen bond to give a halide ion and an alkyn-1-yl radical (**8**) and to regenerate **5** [reaction 2]. As quickly as **8** appears, it can undergo cyclization, coupling, hydrogen-atom abstraction from the medium (SH), or disproportionation as depicted in reactions 3–6.

Experimental Section

Instrumentation, Electrodes, Cells, and Procedures. Instrumentation used for controlled-potential electrolyses is described elsewhere.^{19,20} For cyclic voltammetry, we utilized a scanning potentiostat; experiments were performed and manipulated via a companion computer program installed on a personal computer. A circular, planar working electrode (area = 0.077 cm²) was constructed by press-fitting a 3-mm-diameter glassy carbon rod into a Teflon shroud. Reticulated vitreous carbon disk working electrodes (approximately 2.4 cm in diameter, 0.4 cm in thickness, and having an approximate geometric area of 200 cm²) for controlled-potential electrolyses were cut from material (RVC 2X1-100S) supplied by Energy Research & Generation, Inc. (Oakland, CA); cleaning, preparing, and handling of these electrodes are described in an earlier publication.²¹ Descriptions of electrochemical cells for cyclic voltammetry and controlled-potential electrolysis can be found elsewhere.^{22,23} For each controlled-potential electrolysis, the solution volume was approximately 40 mL, the initial concentration of nickel(II) salen was 2.0 mM, and the concentration of haloalkyne was 20.0 mM. All potentials reported in this study are 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 reference electrode has a potential of –0.76 V versus an aqueous saturated calomel electrode (SCE) at 25 °C.^{24,25}

Separation, Identification, and Quantitation of Electrolysis Products. Electrolysis products in DMF–0.10 TMABF₄ were partitioned between diethyl ether and water, and the ether phase was dried over anhydrous sodium sulfate and concentrated by means of rotary evaporation. Separation, identification, and quantitation were performed by means of gas chromatography. Quantitation methods have been described in a previous paper.²⁶ Peak areas for the various products were determined with respect to that of an internal standard (*n*-dodecane) added to the solution at the beginning of an electrolysis. Additionally, gas chromatography–mass spectrometry was used to confirm the identities of all products through comparison of their retention times and mass spectra with those of commercially available and chemically synthesized authentic samples. High-resolution mass spectrometry employing either chemical ionization or electron impact was performed to aid in the identification of products.

Reagents. Each of the following compounds was purchased from commercial sources and was used without further purification: 1-bromopentane (97%), 1,4-dibromobutane (99%), 1,5-dibromopentane (99%), 1-hexyne (97%), 1,4-diiodobutane (99+%), 1,5-diiodopentane (97%), 1,3-dibromopropane (99%), 1,3-diiodopropane (99%), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%), tri-*n*-butyltin hydride (97%), dodecane (99+%), 1.6 M *n*-butyllithium in hexanes, 5-decyne (98%), and 4-nonyne (98%). Argon was used to deaerate solutions for all electrochemical experiments. Dimethylformamide (DMF, 99.9%) was used without further purification as the solvent for cyclic voltammetry and controlled-potential electrolysis; the concentration of residual water in the solvent is typically 40 mM.²⁷ Tetramethylammonium tetrafluoroborate (TMABF₄) was employed as the supporting electrolyte.

Synthesis of Bromo- and Iodoalkynes. We prepared 1-bromo-4-nonyne, 1-iodo-4-nonyne, 1-bromo-5-decyne, 1-iodo-5-decyne, 11-bromo-5-undecyne, and 11-iodo-5-undecyne by means of a previously published general procedure¹ that involves addition of 10 g of 1-hexyne in 80 mL of dry THF to 66 mL of 1.6 M *n*-butyllithium in hexane, followed by injection of the appropriate amount of an α,ω -dibromo- or α,ω -diiodoalkane into the solution. After being refluxed overnight, the mixture was hydrolyzed by addition of 2 mL of water. After drying with anhydrous sodium sulfate, the solvent was removed under reduced pressure and the residue was vacuum distilled to give the desired product.²⁷

Synthesis of Pentylicycloalkanes. Pentylicyclopentane was prepared according to a published procedure;^{1,5} equivalent quantities of a 10% solution of tri-*n*-butyltin hydride in benzene and a 0.07 M solution of 1-bromo-5-decyne in benzene (containing 1.8 mol % of AIBN as initiator) were mixed. Then the resulting solution was refluxed for 36 h, after which the product was purified by distillation: *m/z* (70 eV) 138, M⁺ (44); 95, [M – 43]⁺ (100); 67, [M – 71]⁺ (81).⁵

Pentylicyclobutane and pentylicyclohexane were identified as electrolysis products by a comparison of their gas chromatographic retention times and mass spectra with those of authentic compounds synthesized according to a published procedure.²⁸ For pentylicyclobutane: *m/z* (70 eV) 124, M⁺ (58); 95, [M – 29]⁺ (76); 81, [M – 43]⁺ (98); 67, [M – 57]⁺ (100). For pentylicyclohexane: *m/z* 152, M⁺ (49); 109, [M – 43]⁺ (73); 81, [M – 71]⁺ (69); 67, [M – 85]⁺ (100).

Synthesis of Alkadiynes. We identified docosa-5,17-diyne as an electrolysis product by comparison of its gas chromatographic retention time and mass spectrum with those of an authentic sample. This compound was prepared by overnight refluxing of 0.92 g of sodium (0.04 mol) and 4.62 g (0.02 mol) of 11-bromo-5-undecyne dissolved in anhydrous diethyl ether. Unreacted sodium was destroyed by addition of methanol to the reaction mixture. Then the ether phase was washed twice with water and dried over anhydrous magnesium sulfate. After the ether was evaporated, the residue was distilled to remove unreacted starting material and low-boiling side products. Mass spectra yielded the following results: *m/z* (70 eV) 302, M⁺ (trace); 273, [M – 29]⁺ (10); 259, [M – 43]⁺ (28); 245, [M – 57]⁺ (47); 147, [M – 155]⁺ (38); 95, [M – 207]⁺ (62); 81, [M – 221]⁺ (100); 67, [M – 235]⁺ (95); high-resolution electron impact mass spectrometry (HRMS) exact mass calculated for C₂₂H₃₈ (M⁺) 302.2974, found 302.2977.

We employed the same procedure to synthesize authentic samples of icoso-5,15-diyne and octadeca-5,13-diyne. For icoso-5,15-diyne: *m/z* (70 eV) 274, M⁺ (trace); 245, [M – 29]⁺ (8); 231, [M – 43]⁺ (16); 217, [M – 57]⁺ (62); 175, [M – 99]⁺ (25); 147, [M – 127]⁺ (42); 81, [M – 193]⁺ (100); 67, [M – 207]⁺ (100); high-resolution chemical ionization mass spectrometry (HRMS) exact mass calculated for C₂₀H₃₅ (M + 1)⁺ 275.2739, found 275.2733.

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For octadeca-5,13-diyne: m/z (70 eV) 246, M^+ (trace); 203, $[M - 43]^+$ (46); 189, $[M - 57]^+$ (51); 161, $[M - 85]^+$ (43); 147, $[M - 99]^+$ (63); 133, $[M - 113]^+$ (65); 105, $[M - 141]^+$ (75); 91, $[M - 155]^+$ (95); 79, $[M - 167]^+$ (100); 67, $[M - 179]^+$ (100); high-resolution electron impact mass spectrometry (HRMS) exact mass calculated for $C_{18}H_{30}$ (M^+) 246.2348, found 246.2338.

Other Electrolysis Products. We prepared another electrolysis product (5-undecyne) by combining 66 mL of 1.6 M *n*-butyllithium in hexane with 10 g of 1-hexyne in 80 mL of dry THF. To this solution was added 22 g of 1-bromopentane, and the mixture was refluxed overnight. After the solvents were removed under reduced pressure, the desired product was obtained by distillation (bp 195–196 °C) of the residue. Mass spectral data for the product matched those for 5-undecyne in the AIST database.²⁹

Other minor electrolysis products were 1-nonen-4-yne, 1-decen-5-yne, and 1-undecen-5-yne. These compounds were identified on the basis of gas chromatographic retention times and mass spectra.

(29) SDBSWeb: <http://www.aist.go.jp/RIODB/SDBS/> (National Institute of Advanced Industrial Science and Technology, September 22, 2005).

Their retention times are very close to those of the corresponding alkynes; for example, with our DB-5 capillary column (initial temperature, 50 °C; initial time, 2 min; rate, 8 °C min⁻¹), the retention time for 5-decyne was 8.54 min and that of 1-decen-5-yne was 8.32 min. Mass spectral data for these compounds are as follows: (a) for 1-nonen-4-yne, m/z (70 eV) 122, M^+ (50); 107, $[M - 15]^+$ (40); 79, $[M - 43]^+$ (100); (b) for 1-decen-5-yne, m/z (70 eV) 121, $[M - 15]^+$ (22); 107, $[M - 29]^+$ (13); 93, $[M - 43]^+$ (35); 79, $[M - 57]^+$ (100); 67, $[M - 69]^+$ (33); (c) for 1-undecen-5-yne, m/z (70 eV) 135, $[M - 15]^+$ (17); 121, $[M - 29]^+$ (15); 93, $[M - 57]^+$ (100); 79, $[M - 71]^+$ (70); 67, $[M - 83]^+$ (33).

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