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Catalytic Reduction of Phenyl-Conjugated Acetylenic Halides by Nickel(I) Salen: Cyclization versus Coupling

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Cyclic voltammetry and controlled-potential electrolysis were employed to study the catalytic reduction of five phenyl-conjugated haloalkynes by nickel(I) salen electrogenerated at carbon cathodes in dimethylformamide containing tetramethylammonium tetrafluoroborate. Electrocatalytic reduction of 7-bromo- and 7-iodo-1-phenyl-1-heptyne affords the carbocyclic product, benzylidenecyclohexane, in up to 41% yield, whereas under similar conditions reduction of 5-halo-1-phenyl-1-pentyne and 8-bromo-1-phenyl-1-octyne gives benzylidenecyclobutane and benzylidenecycloheptane, respectively, in very low yield (≤1%). Dimers, alkynes, and alkenynes are other products formed from the phenyl-conjugated haloalkynes. Dimers (diphenylalkadiynes) derived from 5-halo-1-phenyl-1-pentyne and 8-bromo-1-phenyl-1-octyne are obtained in yields ranging from 85 to 93%, whereas 1,14-diphenyltetradeca-1,13-diyne (the dimer produced from 7-halo-1-phenyl-1-heptyne) is found in yields of 45–51%. To account for the formation of the various products, a mechanistic scheme that involves phenyl-conjugated alkynyl radicals arising from nickel(I) salen catalyzed cleavage of the carbon–halogen bond of each substrate was formulated.

Introduction

Reductive intramolecular cyclization of acetylenic halides has been a subject of long-standing mechanistic and synthetic interest to organic chemists.[1–11] An excellent illustration of this process is provided by 6-bromo-1-phenyl-1-hexyne which, when treated with tri-*n*-butyltin hydride (Bu_3SnH) in the presence of a trace amount of 2,2′-azobis(2-methylpropionitrile) (AIBN) in refluxing benzene for 36 h, affords benzylidenecyclopentane in essentially quantitative yield.[4] As a complement to earlier research on the chemically promoted intramolecular cyclization of acetylenic halides, we demonstrated in our laboratory that direct electrochemical reduction of such compounds at both mercury and carbon cathodes results in cleavage of the carbon–halogen bond, which produces an alkyl radical that cyclizes to form an ylidenecycloalkane.[12–17]

In subsequent work, [{2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]bis(phenolato)}(*N*,*N*′,*O*,*O*′)]nickelate(I), better known as nickel(I) salen, electrogenerated at a glassy carbon electrode in dimethylformamide containing tetraalkylammonium salts, was shown to be a useful catalyst for the reductive intramolecular cyclization of haloalkynes.[18,19] Indeed the catalytic method gives the desired carbocycle in a higher yield than can be obtained by direct electrolysis. For example, electrogenerated nickel(I) salen catalytically reduced phenyl-conjugated haloalkynes such as 6-bromo- and 6-iodo-1-phenyl-1-hexyne to give benzylidenecyclopentane in up to 95% yield,[18] whereas direct reduction of the same compounds at a mercury pool or reticulated vitreous carbon cathode produced the carbocycle in maximum yields of only 24[14] and 61%,[17] respectively, mainly as a consequence of the formation of undesired acyclic side products such as alkynes and alkenynes.

In a recent investigation of the nickel(I) salen catalyzed reduction of a family of non-phenyl-conjugated acetylenic halides,[19] it was found that five-membered carbocycles were formed in higher yield than were the related six- and four-membered carbocycles. In quantitative terms, 1-bromo- and 1-iodo-5-decyne afforded pentylidenecyclopentane in yields as high as 75 and 86%, respectively, whereas pentylidenecyclohexane was obtained in a maximum yield of only 6% from 11-bromo- and 11-iodo-5-undecyne, and pentylidenecyclobutane was formed in no more than 2% yield from either 1-bromo- or 1-iodo-4-nonyne. This trend in yields is a reflection of the difference between the stability of the cyclized radical precursor (phenylmethylenylcycloalkane) of each carbocycle (before abstraction of a hydrogen atom from the solvent to form the final product) and the stability of the corresponding straight-chain radical $[C_4H_9C{\equiv}C(CH_2)_n^{\cdot}$, where n = 3, 4, or 5] formed initially by the nickel(I) salen-promoted cleavage of the carbon–halogen bond of each parent acetylenic halide.

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In the present work, cyclic voltammetry and controlled-potential electrolysis were employed to investigate further the extent of reductive intramolecular cyclization of five different phenyl-conjugated acetylenic halides when electrogenerated nickel(I) salen was employed as the catalyst. For the catalytic reductions of 7-bromo- and 7-iodo-1-phenyl-1-heptyne, a six-membered carbocycle (benzylidenecyclohexane) was obtained in up to 41% yield. In contrast, when 8-bromo-1-phenyl-1-octyne, 5-bromo-1-phenyl-1-pentyne, and 5-iodo-1-phenyl-1-pentyne were catalytically reduced, diphenylalkadiynes (dimeric products) were formed in up to 93% yield, whereas the desired carbocyclic compounds were found only in very small amounts.

Results and Discussion

Cyclic Voltammetric Behavior of Phenyl-Conjugated Haloalkynes

Cyclic voltammograms were recorded at 100 mV s^{-1} for the direct reduction at a glassy carbon disk electrode of separate 2.0 mM solutions of 5-bromo-1-phenyl-1-pentyne (**1**), 5-iodo-1-phenyl-1-pentyne (**2**), 7-bromo-1-phenyl-1-heptyne (**3**), 7-iodo-1-phenyl-1-heptyne (**4**), and 8-bromo-1-phenyl-1-octyne (**5**) in DMF containing 0.10 M $TMABF_4$ under an argon atmosphere; representative cyclic voltammograms for **1** and **2** are depicted in Figure 1.

As seen in curve A of Figure 1, the three closely spaced irreversible waves are associated with the reduction of **1**. First, the shoulder at approximately –1.6 V is attributable to the two-electron cleavage of the carbon–bromine bond. Second, on the basis of previous research in our laboratory,[20–22] the small peak at –1.85 V is undoubtedly due to reduction of 1-phenyl-1,2-pentadiene, which is formed in the diffusion layer by electrolytically induced, base-promoted isomerization of 1-phenyl-1-pentyne derived from the reduction of **1**. Third, the prominent peak at –2.05 V is due to the reduction of 1-phenyl-1-pentyne itself. Additionally, in situations where reduction of the phenyl-conjugated haloalkyne leads to substantial intramolecular cyclization to form a carbocyclic product − as is true for the reduction of **3** to afford benzylidenecyclohexane − another peak appears at –2.18 V that is caused by reduction of the carbocycle. In other respects, cyclic voltammograms for the reduction of **3** and **5** are virtually identical to that of **1**.

Curve B of Figure 1 shows a cyclic voltammogram for the reduction of **2**. At –1.40 V is a peak that can be assigned to irreversible two-electron scission of the carbon–iodine bond; this observation is in close agreement with results obtained previously under comparable experimental conditions for the reduction of 1-iodo-4-nonyne,[19] 1-iodo-5-decyne,[19] 11-iodo-5-undecyne,[19] 6-iodo-1-phenyl-1-hexyne,[18] and 1-iodo-5-decyne.[16] A barely discernible shoulder at –1.85 V signals the reduction of 1-phenyl-1,2-pentadiene, which again arises from the base-catalyzed isomerization of 1-phenyl-1-pentyne. In this instance, the current for reduction of the allene is very small because, unlike the situation for **1** (curve A, Figure 1), reductive

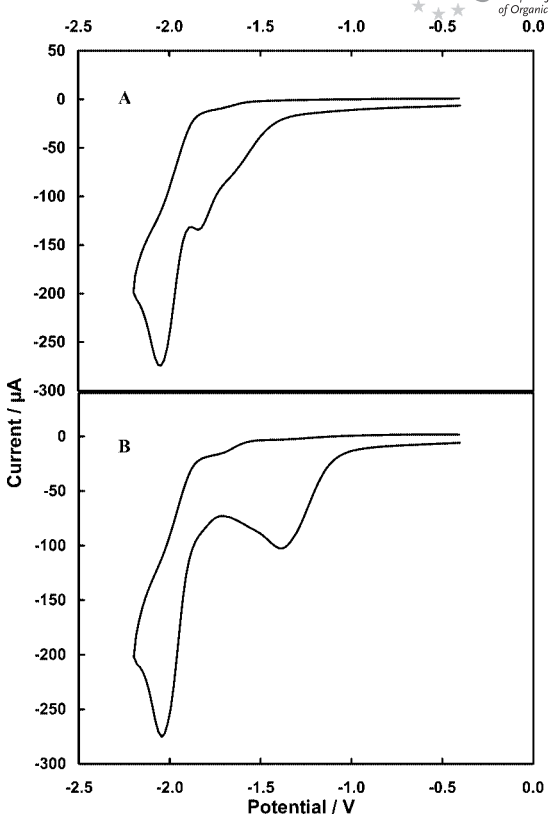


Figure 1. Cyclic voltammograms recorded with a glassy carbon disk electrode (area = 0.077 cm^2) at 100 mV s^{-1} in air-free DMF containing 0.10 M $TMABF_4$ and (A) 2.0 mM 5-bromo-1-phenyl-1-pentyne and (B) 2.0 mM 5-iodo-1-phenyl-1-pentyne. Scans go from –0.41 to –2.20 to –0.41 V.

cleavage of the carbon–iodine bond of **2** occurs to form 1-phenyl-1-pentyne at less negative potentials, so the alkyne-to-allene transformation has more time to take place; however, some of the allene leaves the diffusion layer without being reduced, which lowers the current. As expected, curve B of Figure 1 shows a large irreversible cathodic peak at –2.05 V that can be ascribed to the reduction of 1-phenyl-1-pentyne. Not surprisingly, a cyclic voltammogram for a solution of **4** in DMF/0.10 M $TMABF_4$ looks almost exactly like curve B of Figure 1, except that electrolysis of the parent haloacetylene gives rise (through reductive intramolecular cyclization) to benzylidenecyclohexane, which exhibits a cathodic peak at –2.18 V.

Cyclic Voltammetric Behavior of Nickel(II) Salen in the Absence and Presence of a Phenyl-Conjugated Haloalkyne

Displayed in Figures 2 and 3 are cyclic voltammograms recorded with a glassy carbon electrode at a scan rate of 100 mV s^{-1} for reduction of 2.0 mM nickel(II) salen in DMF containing 0.10 M $TMABF_4$ in the absence and presence of a haloalkyne. We show just the region of potentials where nickel(II) salen is electroactive. In the absence of a haloalkyne, the reversible one-electron nickel(II) salen–nickel(I) salen couple is observed (Figures 2 and 3, curves A), for which the cathodic peak potential (E_{pc}) is –0.95 V, the an-

odic peak potential (E_{pa}) is –0.86 V, and the peak-current ratio (I_{pa}/I_{pc}) is close to unity. These observations are consistent with the results of a recent study.[19]

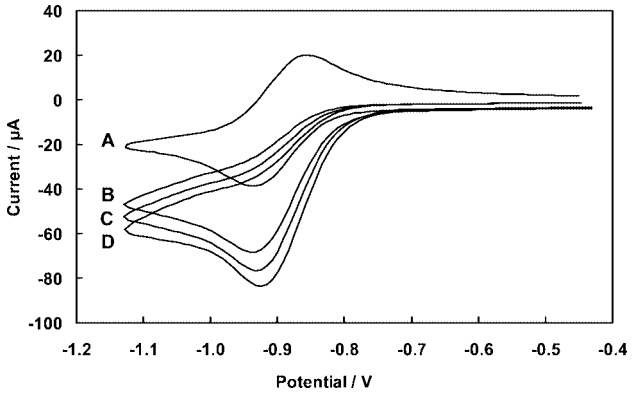


Figure 2. Cyclic voltammograms recorded with a glassy carbon disk electrode (area = 0.077 cm^2) at 100 $mV s^{-1}$ in air-free DMF containing 0.10 M $TMABF_4$ and (A) 2.0 mM nickel(II) salen, (B) 2.0 mM nickel(II) salen and 5.0 mM 7-bromo-1-phenyl-1-heptyne, (C) 2.0 mM nickel(II) salen and 10.0 mM 7-bromo-1-phenyl-1-heptyne, and (D) 2.0 mM nickel(II) salen and 20.0 mM 7-bromo-1-phenyl-1-heptyne. Scans go from –0.45 to –1.13 to –0.45 V.

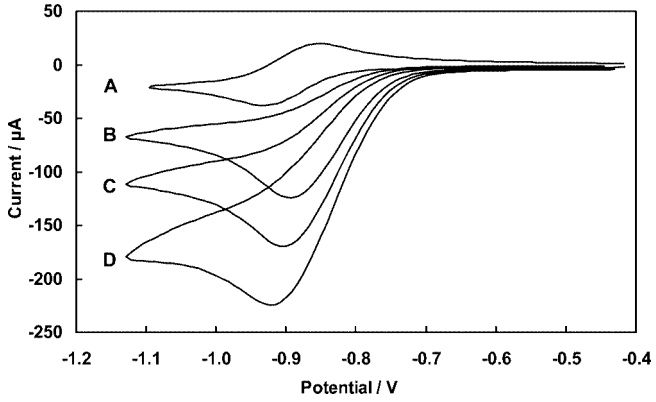


Figure 3. Cyclic voltammograms recorded with a glassy carbon disk electrode (area = 0.077 cm^2) at 100 $mV s^{-1}$ in air-free DMF containing 0.10 M $TMABF_4$ and (A) 2.0 mM nickel(II) salen, (B) 2.0 mM nickel(II) salen and 5.0 mM 7-iodo-1-phenyl-1-heptyne, (C) 2.0 mM nickel(II) salen and 10.0 mM 7-iodo-1-phenyl-1-heptyne, and (D) 2.0 mM nickel(II) salen and 20.0 mM 7-iodo-1-phenyl-1-heptyne. Scans go from –0.45 to –1.13 to –0.45 V.

When a haloalkyne is added to the system, the cyclic voltammetric behavior of nickel(II) salen is changed significantly. As shown in curves B–D of Figures 2 and 3, when a stoichiometric excess of either **3** or **4** is combined with nickel(II) salen, the cathodic peak current corresponding to reduction of nickel(II) salen increases and the anodic current due to oxidation of nickel(I) salen disappears; both features are predictable characteristics of the nickel(I) salen catalyzed reduction of a haloalkyne. Notice that the enhancement in the cathodic peak current is more pronounced with **4** than with **3** owing to the fact that the catalyst–substrate reaction is faster with the iodoalkyne than with the bromoalkyne; for example, when cathodic peak currents are compared for curve D in both Figures 2 and 3, I_{pc} is 83 μA for the catalytic reduction of 20.0 mM **3**, whereas I_{pc} is 220 μA for the catalytic reduction of 20.0 mM **4**. Another feature of the cyclic voltammograms (Figures 2 and 3) is that the cathodic peak currents do not increase in proportion to the concentration of added substrate. This latter behavior, seen in a number of earlier studies,[18,19,23–25] has been linked to sluggish regeneration of the precursor of the active catalyst. In at least some instances, evidence was obtained to suggest that this loss in catalytic efficiency of the nickel(II) salen–nickel(I) salen system may be caused by alkylation of the imino (C=N) bonds of the ligand by an alkyl radical derived from the reductive cleavage of a carbon–halogen bond of a substrate.[26,27]

Controlled-Potential (Bulk) Electrolyses of Nickel(II) Salen in the Presence of a Phenyl-Conjugated Haloalkyne

Bulk electrolyses were performed at reticulated vitreous carbon cathodes in DMF containing 0.10 M $TMABF_4$, 2.0 mM nickel(II) salen, and two different concentrations of each haloalkyne; the cathode potential was held at –1.00 V, which is significantly more positive than that for the direct reduction of any of the haloalkynes. Listed in Table 1 are the coulometric *n* values and product distributions obtained from these experiments; each entry represents the average of two separate runs. Coulometric *n* values (based on the number of electrons transferred to each molecule of haloalkyne) were reproducible to ±0.05; because *n* is essentially 1, the nickel(I) salen catalyzed reduction of each haloalkyne must involve one-electron cleavage of a carbon–halogen bond to give a reactive primary alkyl radical. Yields of individual products were in agreement to ±3% absolute, and none of the parent haloalkyne remained unreduced; within experimental error, the total yield of all products was close to 100%, which indicates that we have successfully accounted for all of the original substrate.

As revealed in Table 1, four products were obtained from the catalytic reduction of each phenyl-conjugated haloalkyne. Entries 1–4 show that the principal product (>85%) derived from both 5-bromo- and 5-iodo-1-phenyl-1-pentyne was a dimeric species (1,10-diphenyldeca-1,9-diyne), whereas the desired carbocyclic compound (benzylidenecyclobutane) was detected in no higher than 1% yield, along with small amounts of 1-phenyl-1-pentyne (5–8%) and 1-phenyl-4-penten-1-yne (2–3%).

In contrast to the preceding results, the catalytic reductions of 7-bromo- and 7-iodo-1-phenyl-1-heptyne afforded benzylidenecyclohexane in yields ranging from 33–41% as well as 1,14-diphenyltetradeca-1,13-diyne (45–51%), 1-phenyl-1-heptyne (6–9%), and 1-phenyl-6-hepten-1-yne (3–6%), as seen from entries 5–8 of Table 1. On the basis of the product distributions obtained from 5-halo-1-phenyl-1-pentynes and 7-halo-1-phenyl-1-heptynes, it is obvious that intramolecular cyclization of the catalytically formed 1-phenyl-1-heptyn-7-yl radical is greatly favored from stereochemical considerations over ring closure of the 1-phenyl-1-pentyn-5-yl radical.

Table 1. Coulometric data and product distributions for catalytic reduction of phenyl-conjugated haloalkynes by nickel(I) salen electrogenerated at reticulated vitreous carbon cathodes held at –1.00 V in DMF containing 0.10 M $TMABF_4$.

Entry	Haloalkyne [mM][b]	n[c]	Product distribution [%][a]				
			6	**7**	**8**	**9**	Total
1	5-bromo-1-phenyl-1-pentyne, **1** (10)	1.01	<1[d]	93[g]	8[j]	2[m]	103
2	5-bromo-1-phenyl-1-pentyne, **1** (20)	0.98	1[d]	88[g]	6[j]	3[m]	98
3	5-iodo-1-phenyl-1-pentyne, **2** (10)	1.02	<1[d]	85[g]	7[j]	2[m]	94
4	5-iodo-1-phenyl-1-pentyne, **2** (20)	0.98	1[d]	87[g]	5[j]	3[m]	96
5	7-bromo-1-phenyl-1-heptyne, **3** (10)	1.02	37[e]	45[h]	6[k]	4[n]	92
6	7-bromo-1-phenyl-1-heptyne, **3** (20)	0.96	33[e]	49[h]	7[k]	4[n]	93
7	7-iodo-1-phenyl-1-heptyne, **4** (10)	0.99	35[e]	51[h]	8[k]	3[n]	97
8	7-iodo-1-phenyl-1-heptyne, **4** (20)	0.95	41[e]	48[h]	9[k]	6[n]	104
9	8-bromo-1-phenyl-1-octyne, **5** (10)	1.00	<1[f]	86[i]	7[l]	2[o]	95
10	8-bromo-1-phenyl-1-octyne, **5** (20)	1.03	1[f]	81[i]	10[l]	2[o]	94

6 = carbocycle (benzylidenecycloalkane); **7** = dimer (diphenylalkadiyne); **8** = 1-phenyl-1-alkyne; **9** = 1-phenylalken-1-yne.

[a] % = Yield expressed as the percentage of original haloalkyne incorporated into each product. [b] Each number in parentheses is the millimolar concentration of haloalkyne. [c] Number of electrons per molecule of haloalkyne. [d] Benzylidenecyclobutane. [e] Benzylidenecyclohexane. [f] Benzylidenecycloheptane. [g] 1,10-Diphenyldeca-1,9-diyne. [h] 1,14-Diphenyltetradeca-1,13-diyne. [i] 1,16-Diphenylhexadeca-1,15-diyne. [j] 1-Phenyl-1-pentyne. [k] 1-Phenyl-1-heptyne. [l] 1-Phenyl-1-octyne. [m] 1-Phenyl-4-penten-1-yne. [n] 1-Phenyl-6-hepten-1-yne. [o] 1-Phenyl-7-octen-1-yne.

For the catalytic reduction of 8-bromo-1-phenyl-1-octyne (Table 1, Entries 9 and 10), the product distribution was quite similar to those for the analogous 5-halo-1-phenyl-1-pentynes; the dimeric species (1,16-diphenylhexadeca-1,15-diyne) was the major compound obtained (81–86%) and only small quantities of benzylidenecycloheptane (1%), 1-phenyl-1-octyne (7–10%), and 1-phenyl-7-octen-1-yne (2%) were found.

Comparison of the Electrogenerated Nickel(I) Salen and Other Chemical Reductants as Reagents for Effecting the Intramolecular Cyclization of Phenyl-Conjugated Haloacetylenes

It is interesting to compare some chemical procedures previously employed to carry out the reductive intramolecular cyclization of phenyl-conjugated acetylenic halides with respect to the electrochemical method described in the present study. Crandall and coworkers investigated the use of tri-*n*-butyltin hydride (Bu_3SnH),[4] lithium biphenylide,[4] Grignard chemistry,[5] chromium(II) in aqueous DMF containing ethylenediamine,[8] and lithium di-*n*-butylcuprate[7] as reductants to promote the intramolecular cyclization of haloacetylenes. With the use of Bu_3SnH (with AIBN as initiator), Crandall and Keyton[4] found that 5-bromo-1-phenyl-1-pentyne underwent no reductive cyclization, whereas 7-bromo-1-phenyl-1-heptyne was converted into benzylidenecyclohexane in up to 75% yield depending on the initial concentration of the starting material. In the same work,[4] the use of the lithium metal–biphenyl system led to formation of benzylidenecyclobutane in 26% yield from 5-bromo-1-phenyl-1-pentyne, and benzylidenecyclohexane was obtained in 15% yield from 7-bromo-1-phenyl-1-heptyne. When a tetrahydrofuran solution of the Grignard reagent derived from 5-bromo-1-phenyl-1-pentyne was heated at reflux for 30 days, the desired carbocycle was produced in 21% yield; a similar experiment with the Grignard reagent of 7-bromo-1-phenyl-1-heptyne afforded benzylidenecyclohexane in 35% yield, but attempts to obtain benzylidenecycloheptane from the Grignard reagent of 8-iodo-1-phenyl-1-octyne gave only 1-phenyl-1-octyne. By employing chromium(II) in DMF containing ethylenediamine as a reducing agent, Crandall and Michaely[8] reported that no carbocycle could be obtained from either 5-bromo-1-phenyl-1-pentyne or 8-iodo-1-phenyl-1-octyne; however, depending on the order in which the reactants were combined, benzylidenecyclohexane was formed in at least 79% yield from both 7-bromo- and 7-iodo-1-phenyl-1-heptyne. Treatment of 5-bromo-1-phenyl-1-pentyne and 7-iodo-1-phenyl-1-heptyne with lithium di-*n*-butylcuprate was found to afford benzylidenecyclobutane and benzylidenecyclohexane in yields up to 79 and 58%, respectively, but no carbocycle was obtained from 8-iodo-1-phenyl-1-octyne.[7]

In general, when compared with Bu_3SnH/AIBN, which is the most common system employed to effect intramolecular cyclizations based on the intermediacy of alkyl radicals, electrogenerated nickel(I) salen seems to be a viable alternative. Among the advantages of the latter reagent are that electrosyntheses can be conducted at room temperature and in relatively short time (<1 h) and that the environmental nuisance associated with the recovery and disposal of toxic tin-containing residues is eliminated. Another virtue of the nickel(I) salen catalyzed synthesis of carbocycles is that the carbon–halogen bond is effectively reduced at a much less negative potential, which thereby avoids the formation of carbanionic intermediates that do not cyclize. Thus, nickel(I) salen promoted reductive intramolecular cyclizations deserve serious attention as a tool for organic synthesis.

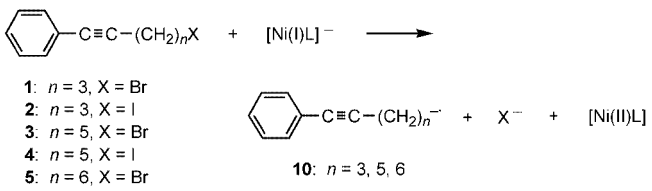
Mechanistic Aspects of the Nickel(I) Salen Catalyzed Reduction of Phenyl-Conjugated Haloalkynes

Shown in Equations (1) to (6) are the most plausible pathways for formation of the various products of the

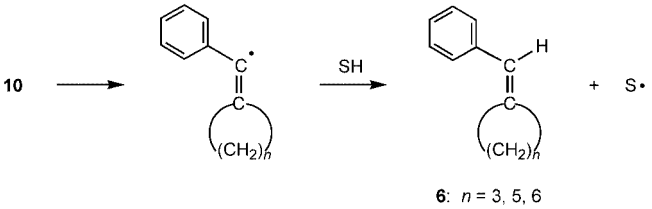
nickel(I) salen catalyzed reduction of a phenyl-conjugated haloalkyne. Recent investigations in our laboratory have indicated that the one-electron reduction of nickel(II) salen can be considered as either a metal- or a ligand-centered process. First, for the catalytic reduction of 1-haloalkanes by electrogenerated nickel(I) salen, we discovered that the imino (C=N) bonds of the ligand are alkylated, which suggests that reduction of nickel(II) salen places significant electron density on the imino bonds.[26] Second, by using density functional theory, we determined that for nickel(II) salen there are two unoccupied molecular orbitals − one metal-centered and one ligand-centered − differing in energy by 2–3 kcal mol^{-1} available to accommodate the electron added to generate the reduced form of nickel(II) salen.[27] However, for the present discussion, we offer a mechanistic scheme that involves only the one-electron, metal-centered reduction of nickel(II) salen to give catalytically active nickel(I) salen.

Accordingly, reversible one-electron reduction of nickel(II) salen to nickel(I) salen [Equation (1)] is the initial step in the catalytic process. As quickly as it is generated, nickel(I) salen transfers an electron to the carbon–halogen bond of a phenyl-conjugated acetylenic halide to afford a 1-phenyl-1-alkyn-ω-yl radical (**10**) and a free halide ion, and to regenerate nickel(II) salen [Equation (2)]. Once formed, **10** can engage in four product-forming processes. First, and most important to the present study, **10** can undergo intramolecular cyclization, followed by hydrogen atom abstraction from the solvent (SH), to give benzylidenecycloalkane **6** [Equation (3)]. Alternatively, **10** can engage in radical coupling with itself to yield **7** [Equation (4)]. In addition, **10** can abstract a hydrogen atom from the solvent (SH), prior to intramolecular cyclization, to give 1-phenyl-1-alkyne **8** [Equation (5)]. Finally, disproportionation of **10** leads to **8** and **9** [Equation (6)].

(1)



(2)



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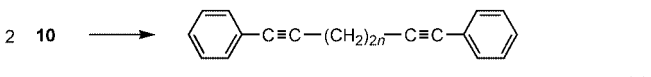

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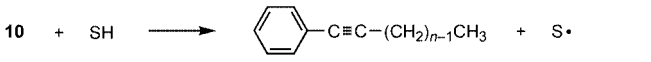

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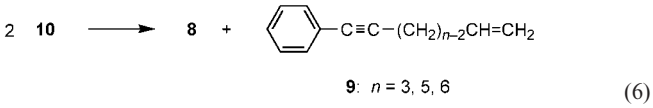

(6)

Experimental Section

Reagents: Each of the following compounds was purchased from Aldrich Chemical Company and was used without further purification: [{2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]bis(phenolato)}-(*N*,*N*′,*O*,*O*′)]nickel(II) {nickel(II) salen, 99%}, 1,3-dibromopropane (99%), 1,5-dibromopentane (99%), 1,6-dibromohexane (96%), 1,3-diiodopropane (99%), 1,5-diiodopentane (97%), phenylacetylene (98%), 1,10-dibromodecane (97%), 1,12-dibromododecane (98%), benzyltriphenylphosphonium chloride (99%), (4-bromobutyl)triphenylphosphonium bromide (98%), cyclohexanone (99+%), cycloheptanone (99%), 1-phenyl-1-pentyne (98%), 1.6 M *n*-butyllithium in hexanes, 2.0 M benzylmagnesium chloride in tetrahydrofuran, and *n*-decane (99%). We obtained 1-phenyl-1-heptyne (99%) and 1-phenyl-1-octyne (95%) from TCI America. Zero-grade argon (Air Products) was used to deaerate solutions for all electrochemical experiments. Dimethylformamide (DMF, ACS grade, 99.8%) from Fisher Scientific was used without further purification as the solvent for cyclic voltammetry and controlled-potential electrolysis; the concentration of residual water in the solvent was typically 40 mM.[28] Tetramethylammonium tetrafluoroborate ($TMABF_4$, 97%), employed as the supporting electrolyte, was obtained from GFS Chemicals and was recrystallized from water/methanol and stored in a vacuum oven at 80 °C to remove traces of water.

Instrumentation, Electrodes, and Cells: Instrumentation employed for cyclic voltammetry and controlled-potential electrolyses is described elsewhere.[29,30] For cyclic voltammetry, we constructed a planar, circular working electrode with an area of 0.077 cm^2 by press-fitting a 3-mm-diameter glassy carbon rod (Grade GC-20, Tokai Electrode Manufacturing Company, Tokyo, Japan) into a Teflon shroud. Before each cyclic voltammogram was recorded, the electrode was cleaned with an aqueous suspension of 0.05-μm alumina on a Master-Tex (Buehler) polishing pad, after which the electrode was rinsed ultrasonically in a water bath.

Reticulated vitreous carbon disks (RVC 2X1–100S, Energy Research and Generation, Inc., Oakland, CA), approximately 2.4 cm in diameter, 0.4 cm in thickness, and with an approximate geometric area of 200 cm^2, were employed as working electrodes for all controlled-potential (bulk) electrolyses. Procedures for preparing, cleaning, and handling of these electrodes are cited in the literature.[31]

Electrochemical cells for cyclic voltammetry and controlled-potential electrolysis have also been described previously.[32,33] All poten-

tials 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 (SCE) at 25 °C.[34,35]

Separation, Identification, and Quantitation of Electrolysis Products: At the end of each controlled-potential electrolysis, the catholyte containing the products was partitioned between diethyl ether and water, and then the ether phase was dried with anhydrous magnesium sulfate, concentrated by means of rotary evaporation, and analyzed with the aid of either GC–MS or GC. First, we used GC–MS to identify all of the electrolysis products through a comparison of their gas chromatographic retention times and mass spectra with those of authentic reference compounds; a Hewlett–Packard 6890N gas chromatograph coupled with a Hewlett–Packard 5973 inert mass-selective detector was employed. Second, the quantitation of products was accomplished with a Hewlett–Packard 5890 Series II gas chromatograph equipped with a flame-ionization detector, a Hewlett–Packard 3392A integrator, and a 30 m × 0.25 mm capillary column (J & W Scientific) with a DB-5 stationary phase consisting of 5% phenylpolysiloxane and 95% methylpolysiloxane. As described in an earlier publication,[36] peak areas and yields for the various products were determined with respect to that of an electroinactive internal standard (*n*-decane) added in known amount to the solution at the beginning of each electrolysis. Throughout this paper, all product yields are expressed as the percentage of starting material incorporated into each species.

Synthesis of Phenyl-Conjugated Bromo- and Iodoalkynes (1–5): We prepared 5-bromo-1-phenyl-1-pentyne (**1**), 5-iodo-1-phenyl-1-pentyne (**2**), 7-bromo-1-phenyl-1-heptyne (**3**), 7-iodo-1-phenyl-1-heptyne (**4**), and 8-bromo-1-phenyl-1-octyne (**5**) according to a previously published procedure[19] involving the addition of phenylacetylene (12.0 g, 0.117 mol, 12.9 mL) in dry THF (80 mL) to *n*-butyllithium (1.6 M in hexanes, 66 mL, 0.106 mol). This mixture was heated to reflux and, after cessation of gas evolution (2–4 h), the appropriate amount of an α,ω-dibromo- or α,ω-diiodoalkane was injected into the solution. Then, after heating at reflux overnight, the mixture was hydrolyzed by the addition of water (2 mL). Finally, the solution was dried with anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was vacuum distilled to give the desired product. For each of the five compounds, the boiling point and ^{1}H NMR spectrum were in agreement with previously published data.[5]

Synthesis of Carbocycles (Benzylidenecycloalkanes) (6)

Benzylidenecyclobutane: We obtained benzylidenecyclobutane through a Wittig reaction by adding *n*-butyllithium (1.6 M in hexanes, 60 mL, 0.094 mol) to (4-bromobutyl)triphenylphosphonium bromide (38.0 g, 0.080 mol) dissolved in anhydrous diethyl ether (300 mL). After this solution was heated at reflux for 24 h, additional *n*-butyllithium (1.6 M in hexanes, 60 mL, 0.094 mol) was added to the reaction mixture, which was then stirred for 1 h. Next, freshly distilled benzaldehyde (10.6 g, 0.100 mol) was added, and the solution was stirred for 1 h. The mixture was then filtered and concentrated, and triphenylphosphane oxide was precipitated by the addition of cold pentane. Finally, the pentane extract was concentrated and distilled under vacuum to give benzylidenecyclobutane. MS (70 eV): *m*/*z* (%) = 144 (42) $[M]^+$, 129 (100) $[M – 15]^+$, 115 (83) $[M – 29]^+$. The boiling point and ^{1}H NMR spectrum agreed with those recorded previously.[5]

Benzylidenecyclohexane: We synthesized benzylidenecyclohexane through a Wittig reaction by adding *n*-butyllithium (1.6 M in hexanes, 80 mL, 0.125 mol) to benzyltriphenylphosphonium chloride (39.5 g, 0.102 mol) dissolved in dry THF (250 mL). After the solution was stirred for 1 h, cyclohexanone (12.3 g, 0.125 mol) was added, and the mixture was heated at reflux for 4 h. The solution was then filtered and concentrated, and triphenylphosphane oxide was precipitated by the addition of cold pentane. Pentane was removed under reduced pressure, and the residue was vacuum distilled to afford benzylidenecyclohexane. MS (70 eV): *m*/*z* (%) = 172 (96) $[M]^+$, 143 (15) $[M – 29]^+$, 129 (63) $[M – 43]^+$, 104 (78) $[M – 68]^+$, 91 (68) $[C_7H_7]^+$, 81 (100) $[M – 91]^+$. The ^{1}H NMR spectrum agreed with that recorded previously.[5]

Benzylidenecycloheptane: We employed the procedure outlined in the preceding paragraph to prepare benzylidenecycloheptane (8-phenylheptafulvene), except that cycloheptanone (14.0 g, 0.125 mol) was used instead of cyclohexanone. MS (70 eV): *m*/*z* (%) = 186 (93) $[M]^+$, 143 (21) $[M – 43]^+$, 129 (58) $[M – 57]^+$, 115 (49) $[M – 71]^+$, 104 (100) $[M – 82]^+$, 91 (52) $[C_7H_7]^+$.

Synthesis of Dimers (Diphenylalkadiynes) (7)

1,10-Diphenyldeca-1,9-diyne: This compound was prepared according to a previously published procedure.[19] Mass spectral measurements yielded the following results. MS (70 eV): *m*/*z* (%) = 286 (14) $[M]^+$, 257 (32) $[M – 29]^+$, 243 (24) $[M – 43]^+$, 128 (44) $[M – 158]^+$, 115 (100) $[M – 171]^+$, 91 (40) $[C_7H_7]^+$. HRMS: calcd. for $C_{22}H_{22}$ $[M]^+$ 286.1722; found 286.1730.

1,14-Diphenyltetradeca-1,13-diyne: For the preparation of this compound, phenylacetylene (12.0 g, 0.117 mol, 12.9 mL) in dry THF (80 mL) was added to *n*-butyllithium (1.6 M in hexanes, 66 mL, 0.106 mol), and the mixture was heated at reflux for 3 h. Then, 1,10-dibromodecane (16.0 g, 0.053 mol, 12.0 mL) was added, and the solution was heated at reflux overnight. After treatment with water (2 mL), the organic layer was dried with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Finally, the residue was vacuum distilled to eliminate unreacted starting materials and low-boiling side products, after which the desired product was obtained. MS (70 eV): *m*/*z* (%) = 342 (42) $[M]^+$, 285 (14) $[M – 57]^+$, 209 (29) $[M – 133]^+$, 129 (84) $[M – 213]^+$, 115 (82) $[M – 227]^+$, 91 (100) $[C_7H_7]^+$. HRMS: calcd. for $C_{26}H_{30}$ $[M]^+$ 342.2342; found 342.2339. HRMS: calcd. for $C_{26}H_{29}$ $[M – H]^+$ 341.2264; found 341.2254.

1,16-Diphenylhexadeca-1,15-diyne: We used the procedure described in the preceding paragraph to synthesize an authentic sample of 1,16-diphenylhexadeca-1,15-diyne. MS (70 eV): *m*/*z* (%) = 370 (20) $[M]^+$, 243 (23) $[M – 127]^+$, 231 (40) $[M – 139]^+$, 121 (48) $[M – 249]^+$, 115 (100) $[M – 255]^+$, 91 (50) $[C_7H_7]^+$. HRMS: calcd. for $C_{28}H_{35}$ $[M + H]^+$ 371.2731; found 371.2733. HRMS: calcd. for $C_{28}H_{34}$ $[M]^+$ 370.2667; found 370.2665. HRMS: calcd. for $C_{28}H_{33}$ $[M – H]^+$ 369.2573; found 369.2577.

Identification of Minor Products 8 and 9

Phenyl-Conjugated Alkynes (8): We verified the presence of 1-phenyl-1-pentyne, 1-phenyl-1-heptyne, and 1-phenyl-1-octyne as electrolysis products by comparing gas chromatographic retention times and mass spectroscopic data of the suspected compounds with those of commercially available authentic samples.

Phenyl-Conjugated Eneynes (9): Eneynes, such as 1-phenyl-7-hepten-1-yne, were identified as minor electrolysis products on the basis of their gas chromatographic retention times and mass spectra. Retention times for the eneynes are very close to those for the corresponding alkynes; for example, with our DB-5 capillary column (initial temperature, 50 °C; initial time, 1 min; rate, 8 °C min^{-1}), the retention time for 1-phenyl-1-heptyne was 8.61 min, whereas that for 1-phenyl-7-hepten-1-yne was 8.41 min.

Data for 1-phenyl-4-penten-1-yne: MS (70 eV): *m*/*z* (%) = 142 (85) $[M]^+$, 141 (100) $[M - 1]^+$, 115 (55) $[M - 27]^+$. Data for 1-phenyl-6-hepten-1-yne: MS (70 eV): *m*/*z* (%) = 170 (16) $[M]^+$, 169 (28) $[M - 1]^+$, 155 (53) $[M - 15]^+$, 141 (94) $[M - 29]^+$, 115 (100) $[M - 55]^+$, 91 (26) $[C_7H_7]^+$. Data for 1-phenyl-7-octen-1-yne: MS (70 eV): *m*/*z* (%) = 184 (4) $[M]^+$, 183 (8) $[M - 1]^+$, 169 (21) $[M - 15]^+$, 155 (33) $[M - 29]^+$, 141 (73) $[M - 43]^+$, 115 (100) $[M - 69]^+$, 91 (25) $[C_7H_7]^+$.

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