Electrolytically Induced Allene-Alkyne Isomerizations

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Preparative-scale electrolyses at mercury cathodes in dimethylformamide containing tetra-*n*-butylammonium perchlorate have revealed that 1-phenyl-1,2-hexadiene exhibits no evidence of isomerization to form 1-phenyl-1-hexyne via an electrolytically induced, base-catalyzed rearrangement; similarly, 1-phenyl-1,2-butadiene exhibits only a slight tendency (1-2%) to form 1-phenyl-1-butyne. In contrast, voltammetric and electrolytic experiments demonstrate that isomerization of 1-phenyl-1-butyne, 1-phenyl-1-pentyne, and 1-phenyl-1-hexyne to the corresponding allenes occurs much more readily. Observations from several investigations show that the extent of allene-to-alkyne rearrangement increases from 1-phenyl-1,2-hexadiene to 1-phenyl-1,2-butadiene to phenylpropadiene, whereas the reverse alkyne-to-allene isomerization decreases in significance from 1-phenyl-1-hexyne to 1-phenyl-1-pentyne to 1-phenyl-1-butyne to 1-phenyl-1-propyne. Steric and electronic factors, which affect protonation of the conjugate bases of the various starting materials at carbons 1 and 3, can be invoked to explain these trends.

For a number of years, we have been interested in the electrochemistry of phenyl-conjugated unsaturated hydrocarbons.[1-5] Indeed, the present article stems from our desire to elucidate more thoroughly the kinetics of the electrolytically induced isomerization of 1-phenyl-1-hexyne to 1-phenyl-1,2-hexadiene[1] through the use of rotating ring-disk electrodes and digital simulation.[6] In a recent study[5] of the electrochemical reduction of phenylpropadiene at mercury cathodes in dimethylformamide containing tetra-*n*-butylammonium perchlorate, it was demonstrated by means of polarography, cyclic voltammetry, and controlled-potential electrolysis that phenylpropadiene undergoes rapid and substantial isomerization to 1-phenyl-1-propyne; however, under the same conditions, reduction of 1-phenyl-1-propyne yields no phenylpropadiene. An earlier publication[1] described a similar electrochemically induced isomerization of 1-phenyl-1-hexyne to 1-phenyl-1,2-hexadiene at mercury cathodes in dimethylformamide containing tetra-*n*-butylammonium perchlorate. For each of these systems, mechanisms for the isomerizations have been proposed that involve deprotonation of the parent compound by the electrogenerated radical anion of the parent species. Base-catalyzed alkyne-allene isomerizations are well-known,[7,8] and on the basis of the above-mentioned studies, we anticipated that 1-phenyl-1-hexyne would result from the electrolysis of 1-phenyl-1,2-hexadiene. However, in this investigation we have found that electrolytic reduction of 1-phenyl-1,2-hexadiene at mercury pool cathodes in dimethylformamide containing tetra-*n*-butylammonium perchlorate affords only a mixture of the cis and trans isomers of 1-phenyl-1-hexene and 1-phenyl-2-hexene. In addition to observing the contrasting behavior of 1-phenyl-1,2-hexadiene and phenylpropadiene, we have undertaken preliminary studies of 1-phenyl-1-butyne and 1-phenyl-1,2-butadiene and have shown that there is electrolytically induced isomerization in both directions. Finally, we have examined the voltammetric behavior of 1-phenyl-1-pentyne; its rearrangement process is similar to that of 1-phenyl-1-hexyne.

Experimental Section

Reagents. Dimethylformamide (DMF) used as solvent and tetra-*n*-butylammonium perchlorate (TBAP) employed as supporting electrolyte were handled as described in a previous paper.[3] Commercially available 1-phenyl-1-butyne and 1-phenyl-1-pentyne (both from Chemical Samples Co.) and 1-phenyl-1-hexyne (Farchan Laboratories) were determined by means of gas chromatography to be at least 98% pure and therefore were used as received. Diethyl malonate (Fisher Chemical Co.) was employed as a proton donor and was used as received. All deaeration operations were carried out with Air Products UHP argon.

Instrumentation and Procedures. Cells and procedures for polarography, cyclic voltammetry, and controlled-potential electrolyses were similar to those described in earlier publications.[9,10] Working electrodes were prepared from either triply distilled mercury (Troy Chemical Corp., Wood Ridge Chemical Division) or a glassy carbon rod (Tokai Electrode Manufacturing Company, Tokyo, Japan, Grade GC-20) that was press fitted into a shroud of Kel-F. All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride;[11,12] this electrode has a potential of -0.76 V vs the aqueous saturated calomel electrode at 25 °C.

Controlled-potential electrolyses were performed with the aid of a Princeton Applied Research Corp. (PARC) Model 173 potentiostat-galvanostat equipped with a PARC Model 176 current-to-voltage converter capable of providing *iR* compensation. Current-time curves were monitored with an Esterline Angus L1101S strip-chart recorder, and current-time integrals were determined with a house-built digital coulometer.[13] Polarograms and cyclic voltammograms were obtained by use of a PARC Model 175 universal programmer coupled to the potentiostat-galvanostat and were recorded with a Houston Instruments Model 2000-5-5 *X-Y* plotter.

Infrared spectra were acquired with a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were recorded with a Varian Model EM-390 90-MHz instrument; all chemical shifts are reported in ppm downfield from tetramethylsilane. Gas chromatographic analyses were performed through the use of a Varian Model 3700 instrument equipped with dual flame-ionization detectors and coupled to a Hewlett-Packard Model 3380S inte-

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grator. Products were separated on either an Alltech RSL-150 or RSL-300 wide-bore capillary column (10 m × 0.53 mm); the stationary phase of the former is similar to OV-101, whereas that of the latter is similar to OV-17. Mass spectra were obtained with a Kratos Model MS80 RFQQ gas chromatograph–mass spectrometer system. Product identity was verified by comparison of gas chromatographic retention times of electrolysis products with those of authentic samples. Further verification of the products was established by analysis of GC MS data. Decane or dodecane was used as internal standard in the bulk electrolyses so that absolute product yields could be determined; however, relative yields are reported for the electrolyses of 1-phenyl-1,2-butadiene.

Synthesis of 1-Phenyl-1,2-hexadiene. All reactions were carried out in flame-dried glassware, under argon, and with freshly distilled reagents. We prepared 1-phenyl-2-propynyl ethanoate by acetylation[14] of 1-phenyl-2-propyn-1-ol, which was either synthesized from acetylene, *n*-butyllithium, and benzaldehyde[15] or purchased from Fairfield Chemical Co., Inc., Blythewood, SC.

A solution of 1-bromopropane (0.010 mol) in 2 mL of anhydrous diethyl ether was slowly dripped into a mixture of magnesium metal turnings (0.020 mol) in 5 mL of anhydrous diethyl ether; once the reaction mixture was refluxing, an additional 5 mL of anhydrous diethyl ether was added. Upon completion of the reaction, the grayish-black solution was syringed into a flask that contained anhydrous cuprous iodide (0.010 mol) and anhydrous lithium bromide (0.010 mol) dissolved in 50 mL of tetrahydrofuran and that was kept in an ice–salt bath;[16] the solution was stirred for 30 min. Next, 1-phenyl-2-propynyl ethanoate (0.0017 mol), dissolved in 4 mL of tetrahydrofuran, was slowly dripped into the navy-blue solution; the resulting slurry became dark green. Then the mixture was allowed to stir for several hours at 0 °C. Saturated ammonium chloride solution was added to the reaction mixture, and the organic layer was washed with brine, separated, and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the remaining viscous orange–red liquid was purified by passage through a silica gel column, hexane being used as eluent. Upon removal of hexane, the product was confirmed to be 1-phenyl-1,2-hexadiene: ^{1}H NMR ($CDCl_3$) δ 7.22 (s, 5 H), 6.03 (quintet, 1 H, J = 3 Hz), 5.47 (q, 1 H, J = 7 Hz), 2.07 (m, 2 H), 1.50 (sextet, 2 H, J = 7 Hz), 0.93 (t, 3 H, J = 8 Hz); IR (neat) 3015, 2960, 2860, 1950, 1600, 1490, 1450 cm^{-1}; mass spectrum (30 eV), *m/e* (rel. intensity) 158 (19), 143 (15), 129 (100), 115 (49), 102 (11), 91 (11), 77 (11).

Synthesis of 1-Phenyl-1,2-butadiene. To a solution of anhydrous cuprous iodide (0.010 mol) and anhydrous lithium bromide (0.010 mol) in 50 mL of tetrahydrofuran at 0 °C was added methylmagnesium bromide (Aldrich, 3.4 mL of 3.0 M ethereal solution, 0.010 mol); the resulting lime-green solution was stirred for 30 min. Then 1-phenyl-2-propynyl ethanoate (0.0017 mol), dissolved in 4 mL of tetrahydrofuran, was slowly dripped into the cuprate solution; the dark green solution was stirred for several hours at 0 °C. Product workup and purification procedures were identical with those for preparation of 1-phenyl-1,2-hexadiene. Spectroscopic data for 1-phenyl-1,2-butadiene are as follows: ^{1}H NMR ($CDCl_3$) δ 7.22 (s, 5 H), 6.03 (quintet, 1 H, J = 3 Hz), 5.47 (quintet, 1 H, J = 7 Hz), 1.80 (q, 3 H, J = 3 Hz); IR (neat) 3015, 2980, 2920, 2830, 1950, 1600, 1490, 1460, 1440 cm^{-1}; mass spectrum (35 eV), *m/e* (rel. intensity) 130 (100), 115 (95), 102 (11), 89 (13), 77 (16).

Results and Discussion

Polarographic and Cyclic Voltammetric Behavior of 1-Phenyl-1,2-hexadiene. A polarogram for the reduction of 5.0 mM 1-phenyl-1,2-hexadiene in DMF containing 0.1 M TBAP exhibits two waves with half-wave potentials of −1.73 and −1.98 V; the height of the second wave is approximately one-third that of the first. As will be demonstrated later from the results of preparative-scale electrolyses, the first wave is due to a two-electron reduction of 1-phenyl-1,2-hexadiene to form *cis*- and *trans*-1-phenyl-1-hexene, as well as *cis*- and *trans*-1-phenyl-2-hexene; the second wave is attributable to two-electron reduction of 1-phenyl-1-hexene and is smaller than the first wave because 1-phenyl-2-hexene is not electroactive. When a proton donor is added (20 mM diethyl malonate), the second wave disappears (because conversion of the initially formed 1-phenyl-2-hexene to the electroactive 1-phenyl-1-hexene is blocked) and the half-wave potential for the remaining (first) wave is −1.74 V.

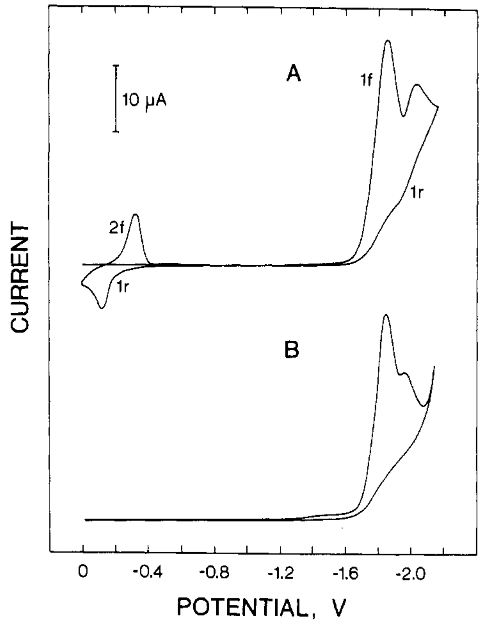

Figure 1. Cyclic voltammograms for 5.0 mM 1-phenyl-1,2-hexadiene obtained at a scan rate of 0.2 V s^{-1} and with a hanging mercury drop in DMF containing 0.1 M TBAP. A: first forward (negative-going) scan (1f) is from 0 to −2.2 V; first reverse (positive-going) scan (1r) is from −2.2 to 0 V; second forward (negative-going) scan (2f) is from 0 to −0.6 V. B: solution contains 20 mM diethyl malonate as proton donor.

As shown in Figure 1A, the cyclic voltammetric behavior of 5.0 mM 1-phenyl-1,2-hexadiene at a hanging mercury drop electrode in DMF containing 0.1 M TBAP at a scan rate of 0.2 V s^{-1} reveals two reduction processes with peak potentials of −1.84 and −2.04 V. As in the polarographic experiments, the first peak is due to the two-electron reduction of 1-phenyl-1,2-hexadiene and the second peak is due to the two-electron reduction of 1-phenyl-1-hexene. Both 1-phenyl-1-hexene and 1-phenyl-2-hexene are products of the reduction of 1-phenyl-1,2-hexadiene, and the ratio of the two olefins formed during a cyclic voltammetric scan is sensitive to the presence of adventitious proton donors in the solvent-supporting electrolyte; consequently, on the first negative-going scan from 0 V, the height of the second peak varies from one-third to one-half that of the first peak when correction is made for the current decay of the first wave. If the potential is repeatedly cycled between 0 and −2.2 V, the heights of the two waves in Figure 1A show normal depletion effects for electron-transfer processes controlled only by diffusional mass transport;[17] this behavior differs dramatically from that of phenylpropadiene,[5] for which the first wave disappears after just three scans due to the electrolytically induced

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[17] Repetitive cycling of the potential results in a steady-state concentration of the parent electroactive species at the electrode surface that is approximately 80% of that in the bulk of the solution.

Table I. Coulometric Data and Product Distributions for Electrolytic Reduction of 1-Phenyl-1,2-hexadiene at Mercury in Dimethylformamide Containing 0.1 M Tetra-*n*-butylammonium Perchlorate

			product distribution, %			
concn of allene, mM	potential, V	n	*cis*-1-phenyl-2-hexene	*trans*-1-phenyl-2-hexene	*cis*-1-phenyl-1-hexene	*trans*-1-phenyl-1-hexene
4.5[a]	−2.00	3.8				
5.8	−1.70	2.1	6	30	5	57
8.4	−1.70	2.0	1	10	5	84
5.7[b]	−1.70	2.1		52	31	15

[a] Gas chromatographic analysis revealed the formation of 1-phenylhexane and tri-*n*-butylamine as the major products. [b] Electrolysis performed in the presence of 20 mM diethyl malonate.

isomerization of phenylpropadiene to 1-phenyl-1-propyne. In addition, when the potential is scanned to 0 V, an oxidation wave is observed (Figure 1A) at −0.12 V; reversal of the direction of potential scan results in a new Gaussian-shaped reduction wave with a peak potential of −0.32 V.

In our previous investigation of the electrochemical behavior of phenylpropadiene,[5] it was found that an increase in the concentration of the allene leads to a greater extent of isomerization to 1-phenyl-1-propyne. Therefore, in the present study, we examined the effect of the initial concentration of 1-phenyl-1,2-hexadiene on its cyclic voltammetric behavior; for a 15 mM solution of the hexadiene in DMF containing 0.1 M TBAP, the characteristics of the cyclic voltammogram, except for the magnitude of the currents, are indistinguishable from those for lower concentrations of 1-phenyl-1,2-hexadiene. Thus, there is no cyclic voltammetric evidence that 1-phenyl-1,2-hexadiene undergoes isomerization to 1-phenyl-1-hexyne—a finding supported by results of large-scale electrolyses of the allene described below.

Figure 1B illustrates the cyclic voltammetric behavior if a proton donor (20 mM diethyl malonate) is added to a solution of 1-phenyl-1,2-hexadiene; a wave due to the two-electron reduction of this allene is seen with a peak potential of −1.85 V. In addition, on the side of this large wave is a small shoulder with a peak potential of −1.96 V, which can be assigned to reduction of the small amount of 1-phenyl-1-hexene formed within the diffusion layer during the cyclic voltammetric experiment. Note that the oxidation and reduction processes in the potential region between 0 and −1.0 V in Figure 1A are absent when a proton donor is present.

Controlled-Potential Electrolyses of 1-Phenyl-1,2-hexadiene. Summarized in Table I are results obtained from preparative-scale electrolyses of 1-phenyl-1,2-hexadiene in DMF containing 0.1 M TBAP. Electrolysis of a 4.5 mM solution of the allene at −2.00 V, which corresponds to a potential on the second voltammetric wave (Figure 1A), involved the passage of 3.8 faradays/mol of starting material and led to the appearance of two major products, 1-phenylhexane and tri-*n*-butylamine. Formation of the latter species arises when supporting electrolyte cation is deprotonated by electrogenerated bases (Hofmann elimination reaction).[9,10]

For reduction of 1-phenyl-1,2-hexadiene at potentials on the first voltammetric wave, the choice of electrolysis potential (−1.70 V) deserves explanation. When electrolyses are carried out at potentials corresponding to the limiting-current region for the first wave, a prolonged current decay results, the number of electrons transferred to each molecule of starting material approaches three, and, most importantly, 1-phenylhexane is observed as a product. Evidently, if the potential is on the limiting-current region for the first wave, it is negative enough to be on the foot of the second voltammetric wave. Because −1.70 V is more positive than the half-wave potential for the first wave, the electrolysis current takes more time to decay than is ideal, but potentials that correspond to the second wave are avoided. Electrolysis of a 5.8 mM solution of 1-phenyl-1,2-hexadiene at −1.70 V resulted in the transfer of 2.1 electrons/molecule of starting material; neither 1-phenyl-1-hexyne (derived from the base-catalyzed rearrangement of starting material) nor 1-phenylhexane is seen as a product when reduction takes place at −1.70 V. Product analysis revealed the formation of *cis*-1-phenyl-2-hexene (6%), *trans*-1-phenyl-2-hexene (30%), *cis*-1-phenyl-1-hexene (5%), and *trans*-1-phenyl-1-hexene (57%); tri-*n*-butylamine was again observed as a byproduct.

Exhaustive electrolysis of a higher concentration (8.4 mM) of 1-phenyl-1,2-hexadiene at −1.70 V resulted in the passage of 2.0 faradays/mol of parent molecule and in the formation of *cis*-1-phenyl-2-hexene (1%), *trans*-1-phenyl-2-hexene (10%), *cis*-1-phenyl-1-hexene (5%), and *trans*-1-phenyl-1-hexene (84%); note again the absence of 1-phenyl-1-hexyne and also the approximately 30% increase in the yield of 1-phenyl-1-hexene. Some comments about the current–time (i–t) curve should be made. Approximately 20 min after the start of the electrolysis, the current, which had been decaying in an ordinary exponential manner, leveled off and began to increase slightly; the color of the solution (clear to slightly yellow at the start of the electrolysis) turned dark red during the initial current decay and then dark purple as the current began to rise. This purple color persisted throughout the time that the current increased, as well as past its maximum, and then the color became green as the current resumed its normal decay. Such current–time behavior, though not nearly so obvious, was observed during the electrolysis of 5.8 mM hexadiene and has been seen previously for preparative-scale electrolysis of 1-phenyl-1-hexyne;[1] this behavior is indicative of the formation of a species more easily reduced than the parent compound. Note that this unusual current–time behavior is not seen when electrolyses are performed at −2.00 V.

Preparative-scale electrolysis of 5.7 mM 1-phenyl-1,2-hexadiene in the presence of a proton donor (20 mM diethyl malonate) resulted in the uptake of 2.1 electrons/molecule of starting material; the products were 1-phenyl-2-hexene (52%), *cis*-1-phenyl-1-hexene (31%), and *trans*-1-phenyl-1-hexene (15%). Note that tri-*n*-butylamine is not observed when excess diethyl malonate is employed as proton donor and also that the electrolysis current decays in an ordinary manner and no color changes are observed during the course of the experiment.

Although no attempt was made to identify the species responsible for the abnormal current–time behavior described above, it is noteworthy that (i) the anomalous current decay and color changes become much more pronounced when the initial concentration of 1-phenyl-1,2-hexadiene is increased and (ii) a normal decay results when electrolyses are carried out at more negative potentials or in the presence of diethyl malonate, regardless of the allene

Table II. Coulometric Data and Product Distributions for Electrolytic Reduction of 1-Phenyl-1,2-butadiene at Mercury in Dimethylformamide Containing 0.1 M Tetra-*n*-butylammonium Perchlorate

			product distribution, %			
concn of allene, mM	potential, V	*n*	1-phenyl-2-butene	*cis*-1-phenyl-1-butene	*trans*-1-phenyl-1-butene	1-phenyl-1-butyne
5.1	−1.70	1.9	23	5	70	2
10.3	−1.70	1.8	11	5	83	1
5.1[a]	−1.70	2.0	54	30	16	

[a] Electrolysis performed in the presence of 20 mM diethyl malonate.

concentration. These same phenomena are observed during the electrolyses of 1-phenyl-1,2-butadiene discussed below.

It was previously found[1] that 1-phenyl-2-hexene is present as a product at intermediate stages of a large-scale electrolysis of 1-phenyl-1-hexyne in the absence of a proton donor. However, this olefin is not present at the end of an electrolysis; apparently, nonelectroactive 1-phenyl-2-hexene loses a benzylic proton, which then allows for its rearrangement to electroactive 1-phenyl-1-hexene. In light of these former observations, the results from our preparative-scale electrolyses of 1-phenyl-1,2-hexadiene at −1.70 V merit further discussion. With reference to Table I and the electrolysis of a 5.8 mM solution of 1-phenyl-1,2-hexadiene in the *absence* of a proton donor, one notes that *cis*- and *trans*-1-phenyl-2-hexene account for 36% of all products, whereas in the *presence* of the proton donor, these species account for 52% of all products in the electrolysis of a 5.7 mM solution of the hexadiene; loss of the benzylic proton from 1-phenyl-2-hexene is less probable in the latter situation, which leads to a higher yield of the 2-alkene. For electrolysis of an 8.4 mM solution of 1-phenyl-1,2-hexadiene in the absence of a proton donor, *cis*- and *trans*-1-phenyl-2-hexene account for only 11% of all products. It is evident that loss of the benzylic proton (and, hence, isomerization to the 1-alkene) occurs more readily when strong proton donors are absent and when the initial concentration of 1-phenyl-1,2-hexadiene is higher; this latter condition promotes rearrangement because the concentration of electrogenerated base is higher.

Preparative-Scale Reduction of 1-Phenyl-1,2-butadiene. Table II shows data obtained from bulk electrolyses of 1-phenyl-1,2-butadiene at −1.70 V in DMF containing 0.1 M TBAP. Note that the potential employed for these experiments is the same as that used for electrolyses of 1-phenyl-1,2-hexadiene on its first reduction wave, because the polarographic and cyclic voltammetric behavior of 1-phenyl-1,2-butadiene is indistinguishable from that of 1-phenyl-1,2-hexadiene. For a 5.1 mM solution of the butadiene, electrolysis resulted in the transfer of 1.9 electrons/molecule of starting material and in the appearance of the following products: 1-phenyl-2-butene (23%), *cis*-1-phenyl-1-butene (5%), *trans*-1-phenyl-1-butene (70%), and 1-phenyl-1-butyne (2%).

Next, we examined the products obtained from electrolysis of a 10.3 mM solution of 1-phenyl-1,2-butadiene under the same conditions outlined above; 1.8 electrons/molecule of starting material were transferred, and 1-phenyl-2-butene (11%), *cis*-1-phenyl-1-butene (5%), *trans*-1-phenyl-1-butene (83%), and 1-phenyl-1-butyne (1%) were formed. For the higher concentration of 1-phenyl-1,2-butadiene, (i) the yield of 1-phenyl-1-butyne remains the same within experimental error, (ii) the yield of 1-phenyl-1-butene rises, and (iii) the same abnormal current–time behavior is observed as in electrolyses of 1-phenyl-1,2-hexadiene in the absence of a proton donor.

An electrolysis of a 5.1 mM solution of 1-phenyl-1,2-butadiene, in the presence of 20 mM diethyl malonate, resulted in the passage of 2.0 electrons/molecule of parent and in the formation of 1-phenyl-2-butene (54%), *cis*-1-phenyl-1-butene (30%), and *trans*-1-phenyl-1-butene (16%); the electrolysis current was observed to decay in an ordinary manner, as in the electrolysis of 1-phenyl-1,2-hexadiene in the presence of a proton donor.

Trends for the formation of 1-phenyl-2-butene are consistent with those for production of 1-phenyl-2-hexene from electrolyses of 1-phenyl-1,2-hexadiene; the yield of the 2-alkene decreases with an increase in the parent concentration and increases if a proton donor is present. Another example of this behavior can be found in an earlier investigation[5] of the isomerization of phenylpropadiene to 1-phenyl-1-propyne.[18]

Voltammetry of 1-Phenyl-1-hexyne, 1-Phenyl-1-pentyne, and 1-Phenyl-1-butyne. Voltammetric and preparative-scale electrolytic experiments with mercury electrodes have shown (i) that 1-phenyl-1,2-hexadiene does not undergo electrolytically induced rearrangement and (ii) that 1-phenyl-1,2-butadiene demonstrates only a slight tendency (1–2%) for isomerization to 1-phenyl-1-butyne. In contrast, there is evidence that 1-phenyl-1-hexyne, 1-phenyl-1-pentyne, and 1-phenyl-1-butyne all rearrange to form allenic analogues that are more easily reduced than the parent alkynes. Therefore, detection of the isomerization process on a shorter time scale—by means of voltammetry, for example—is possible. For comparative purposes, it should be pointed out that the voltammetric response for the three phenyl-conjugated acetylenes is equivalent at mercury and carbon electrodes with two exceptions. First, at carbon, the Gaussian-shaped reduction wave at −0.32 V (Figure 1A) that accompanies the oxidation wave at −0.12 V for mercury is never seen. Second, the amount of isomerization that occurs during the voltammetric experiment is less at a *spherical* mercury electrode than at a *planar* carbon electrode because these two geometries lead to different concentration–distance profiles[19] for the electrogenerated bases that catalyze the alkyne-to-allene rearrangement.

In comparing the electrochemistry which occurs at mercury electrodes with that which occurs at carbon electrodes, one must exercise some caution. For all of our investigations of the electrochemical behavior of alkynes and allenes at mercury electrodes, there is no evidence that any of the starting materials, intermediates, or products undergoes chemical or physical interaction with the mercury surface. Indeed, we believe that the identities of the electrolysis products (although not necessarily the yields of the products) at mercury are the same as those that arise at carbon. Moreover, we are not attempting to elucidate mechanisms from the voltammetry to be described below;

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(18) Electrolyses of phenylpropadiene in the absence of a proton donor result in the formation of 1-phenyl-1-propyne and 1-phenyl-1-propene. In the presence of a proton donor, the products include 1-phenyl-1-propene and 1-phenyl-2-propene, although the former is found in higher concentration.

(19) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; Wiley: New York, 1980; pp 142–146.

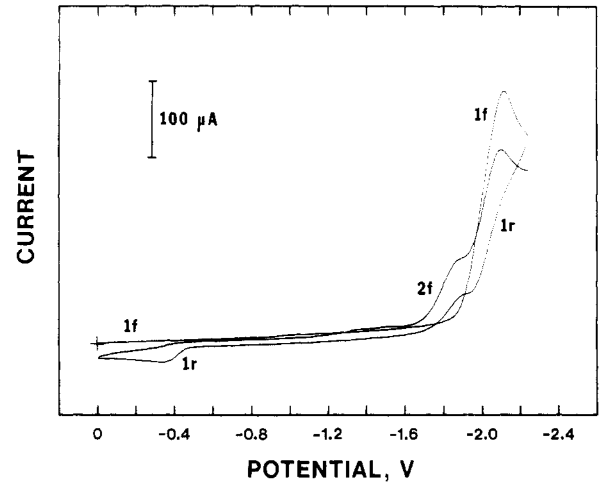


Figure 2. Cyclic voltammogram for 4.6 mM 1-phenyl-1-hexyne obtained at a scan rate of 0.2 V s^{-1} and with a glassy carbon disk in DMF containing 0.1 M TBAP and 14.5 mM H_2O; 1f denotes the first forward (negative-going) scan, 1r denotes the first reverse (positive-going) scan, 2f denotes the second forward (negative-going) scan.

instead, our intent is to make comparisons of the direction and extent of electrolytically induced isomerization on the shorter time scale of the voltammetric experiment.

A representative voltammogram recorded at a scan rate of 0.2 V s^{-1} that provides evidence for rearrangement of 5 mM 1-phenyl-1-hexyne in DMF containing 0.1 M TBAP at a glassy carbon electrode is shown in Figure 2. Note that (i) a current crossover at approximately −1.80 V is observed, (ii) a new peak, which is approximately 20% the height of the main reduction wave for the alkyne, appears in the region of the current crossover, and (iii) an oxidation wave is seen at approximately −0.33 V; these observations are due to the formation of 1-phenyl-1,2-hexadiene. Voltammograms for 1-phenyl-1-butyne and 1-phenyl-1-pentyne were recorded under identical conditions, and both were practically indistinguishable from that of 1-phenyl-1-hexyne shown in Figure 2—a result that suggests either that the extent of isomerization for all three alkynes is equivalent or, more likely, that the conditions of the experiment do not allow different rates of rearrangement to be distinguished readily.

Shown in Figure 3, parts A–C, are voltammograms obtained at a slower scan rate of 0.02 V s^{-1} with a glassy carbon electrode for approximately 5 mM solutions of 1-phenyl-1-hexyne, 1-phenyl-1-pentyne, and 1-phenyl-1-butyne, respectively, in DMF containing 0.1 M TBAP. There are several important features to observe for these voltammograms: (i) on the first negative-going scan, a prepeak is observed at approximately −1.95 V in Figure 3A,B but not in Figure 3C, and this prepeak *appears only on the first scan*; (ii) there is a current crossover in all three cases; (iii) a new peak appears, corresponding to the region of the current crossover, on the second and succeeding negative-going scans for all three alkynes. From these results, it is obvious that isomerization occurs in all systems; however, research, utilizing digital simulation, soon to be published from this laboratory provides evidence that the prepeak is a measure of the extent of the rearrangement process. Therefore, as seen in Figure 3, the hexyne and pentyne systems are nearly identical in terms of their prepeak behavior, whereas no prepeak is observed for the butyne system; rearrangement of 1-phenyl-1-butyne to 1-phenyl-1,2-butadiene is less facile than the isomerization of either 1-phenyl-1-hexyne to 1-phenyl-1,2-hexadiene or 1-phenyl-1-pentyne to 1-phenyl-1,2-pentadiene.

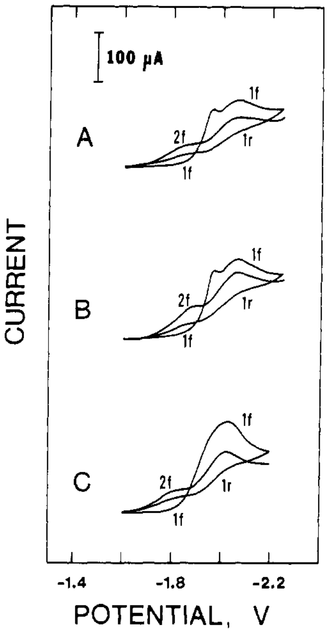


Figure 3. Cyclic voltammograms for phenyl-conjugated alkynes obtained at a scan rate of 0.02 V s^{-1} and with a glassy carbon disk in DMF containing 0.1 M TBAP; 1f denotes the first forward (negative-going) scan, 1r denotes the first reverse (positive-going) scan, 2f denotes the second forward (negative-going) scan. A: 4.6 mM 1-phenyl-1-hexyne, 14.5 mM H_2O. B: 5.0 mM 1-phenyl-1-pentyne, 24.9 mM H_2O. C: 5.5 mM 1-phenyl-1-butyne, 24.9 mM H_2O.

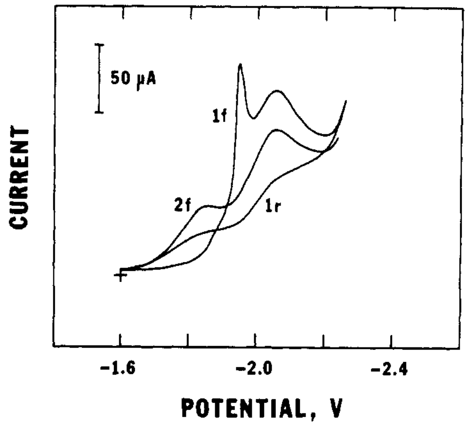
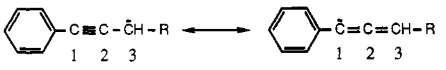


Figure 4. Cyclic voltammogram for 5.0 mM 1-phenyl-1-hexyne obtained at a scan rate of 0.02 V s^{-1} and with a glassy carbon disk in DMF containing 0.1 M TBAP and 8.3 mM H_2O; 1f denotes the first forward (negative-going) scan, 1r denotes the first reverse (positive-going) scan, 2f denotes the second forward (negative-going) scan.

It is crucial to point out that the appearance of the prepeak, due to the kinetically controlled reduction of the allene formed by the isomerization process, is dependent upon the rate of potential scan and the concentration of residual water in the sample solution. For the hexyne system (Figure 3A) the water level determined by means of gas chromatography was approximately 15 mM, whereas the concentration of water for the other two systems had the same value of approximately 25 mM. If the water level or the rate of potential scan is increased, the prepeak is attenuated; therefore, one may conclude that if the water level or the rate of potential scan is lowered, the prepeak (and hence isomerization) will be more pronounced. Figure 4 is the voltammetric response for a 5.0 mM solution of 1-phenyl-1-hexyne in DMF containing 0.1 M TBAP (compare with Figure 3A) with a residual water concentration of 8.3 mM—the prepeak is indeed more prominent.



R	Preferred Product	Favored Protonation Site
H	alkyne	C_3
CH_3	-----[a]	-----[a]
C_2H_5	allene	C_1
C_3H_7	allene	C_1

[a] Electrolytic reduction of 1-phenyl-1-butyne or 1-phenyl-1,2-butadiene has little tendency to cause rearrangement to the other isomer.

Figure 5. Resonance-stabilized propargylic anion. Formation of an acetylene or an allene depends upon the site of protonation.

Summary and Interpretation of Observed Differences for Electrolytically Induced Allene–Alkyne Rearrangements. On the basis of cyclic voltammetric experiments, it is obvious from previous work[5] that phenylpropadiene undergoes rapid rearrangement to 1-phenyl-1-propyne, whereas, in the present investigation, the conversion of 1-phenyl-1,2-hexadiene and 1-phenyl-1,2-butadiene to their alkyne analogues is impossible to detect. On the other hand, when the cyclic voltammetric behavior of the alkynes is compared, especially at slow scan rates, it is apparent that 1-phenyl-1-propyne does not exhibit any tendency to isomerize to the corresponding allene and that 1-phenyl-1-hexyne and 1-phenyl-1-pentyne undergo more facile rearrangement than does 1-phenyl-1-butyne. Results of preparative-scale electrolyses of phenylpropadiene, 1-phenyl-1,2-butadiene, and 1-phenyl-1,2-hexadiene as well as 1-phenyl-1-propyne and 1-phenyl-1-hexyne are in agreement with those obtained by means of cyclic voltammetry.

In previous publications,[1-5] we proposed mechanistic schemes for electrolytically induced allene–alkyne isomerizations that involve protonation of resonance forms of the conjugate base of the parent molecule at one site in preference to another. Shown in Figure 5 is the deprotonated form (conjugate base) of the parent species which arises when the starting material is either a phenyl-conjugated 1-alkyne or a phenyl-conjugated 1,2-allene; R represents hydrogen, methyl, ethyl, or propyl. Listed with these substituents are the isomeric products that result from electrolytically induced rearrangement along with the site at which protonation of the conjugate base must occur to yield these isomers. Accordingly, protonation at C_1 will result in an allene and protonation at C_3 will result in the acetylene.

In the system involving propadiene and 1-phenyl-1-propyne (R = H), protonation of the conjugate base must be more extensive at C_3 than at C_1. Such a conclusion is explicable if one considers that (i) the phenyl group withdraws negative charge density from C_1 and offers slight steric hindrance to protonation at C_1 and (ii) there is no electron-donating alkyl group attached to C_3 to shift negative charge density from C_3 to C_1 or to hinder sterically the addition of a proton at C_3. Turning to the system of 1-phenyl-1,2-hexadiene and 1-phenyl-1-hexyne (R = C_3H_7), we can rationalize the preference for rearrangement of the alkyne to the allene by noting that introduction of the propyl group at C_3 acts inductively to decrease the negative charge density at C_3 and sterically to hinder protonation at C_3; both factors act to favor protonation at C_1 to an extent greater than what is seen with the conjugate base of phenylpropadiene and 1-phenyl-1-propyne. Likewise, the system of 1-phenyl-1-pentyne and 1-phenyl-1,2-pentadiene (R = C_2H_5) should behave similarly to the previous hexyne–hexadiene case due to the fact that the ethyl group attached to C_3 has inductive and steric properties similar to those of the propyl group. Finally, when a methyl group is attached to C_3, we are dealing with a system having characteristics between the preceding situations; the methyl group should induce a shift of negative charge density from C_3 to C_1 that would favor formation of the allene, whereas protonation at C_3 and consequent production of the alkyne would not be hindered sterically nearly as much as by an ethyl or propyl group.

On the basis of digital simulations of the cyclic voltammetric behavior of 1-phenyl-1-hexyne at carbon cathodes in DMF containing 0.1 M TBAP, we have discovered (i) that the rate-determining step in the isomerization of the alkyne to the allene is protonation of the electrogenerated radical anion of the alkyne by unreduced parent (to yield the conjugate base shown in Figure 5) and (ii) that protonation of the conjugate base by another parent molecule is a necessary and fast step in the process. A report of these digital simulations is being prepared for publication.

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