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References and Notes

(1) Part XXVII of a series on Transfer Reactions Involving Boron; for part XXVI, see D. J. Pasto and P. E. Timony, *J. Organometal. Chem.*, 19, (1973).

(2) D. J. Pasto and P. E. Timony, *Org. Mass Spectrom.*, in press.

(3) The almost total lack of boron-containing cationic species in the icr spectrum of **1** unfortunately precluded a study of the reactions of such species, which might have provided information concerning their structures.

(4) See J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, **4**, 114 (1971); G. A. Gray, *Advan. Chem. Phys.*, **19**, 141 (1971), and references therein.

(5) F. P. Abramson and J. H. Futrell, *J. Chem. Phys.*, **45**, 1925 (1966); J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

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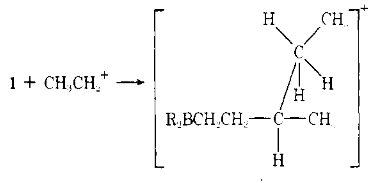
(9) The possibility of hydrogen migration in **2**, *i.e.*, leading to equilibration between the possible protonated 1 structures, cannot be dismissed. Information relating to this possibility is not available.

(10) An alternative mechanistic possibility involves the insertion of a cationic species into C–H or C–C bonds to form "addition" products[5,6,8] such as structure i which may then undergo fragmentation. However, such addition products were not detected in the present study, and, based on the reported formation of C_3 and C_4 ions from the ethane "addition" intermediates,[8] ions containing more than four carbon atoms were not formed. If intermediates similar to i had been formed, it is not obvious why product ions containing more than four carbon atoms should not have been produced.



i

Electrochemical Reduction of 1-Phenyl-1-hexyne at a Mercury Cathode in Dimethylformamide

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Abstract: In dimethylformamide containing 0.1 *F* tetra-*n*-butylammonium perchlorate as supporting electrolyte, 1-phenyl-1-hexyne gives a single polarographic wave corresponding to the four-electron reduction to 1-phenylhexane, the other products being tri-*n*-butylamine and 1-butene. Under certain conditions during a large-scale electrolysis, 1-phenyl-1-hexyne can rapidly isomerize to yield 1-phenyl-1,2-hexadiene. Once formed, the allene is easier to reduce than the acetylene and undergoes stepwise conversion, first to an olefin (*trans*-1-phenyl-1-hexene, *trans*-1-phenyl-2-hexene, or *cis*-1-phenyl-1-hexene) and then to 1-phenylhexane. For concentrations of 1-phenyl-1-hexyne between 0.002 and 0.01 *M*, the bimolecular acetylene-to-allene rearrangement is a dominant reaction, and the reduction of the acetylene proceeds largely *via* the allene species. For much lower concentrations of the acetylene, there is no observable formation of allene, and the electrochemical process is almost entirely the reduction of 1-phenyl-1-hexyne to 1-phenylhexane.

Relatively few investigations of the electrochemical reduction of acetylenic compounds have been reported. Diphenylacetylene and phenylacetylene have been studied polarographically in a dioxane–water solvent system[1] and in anhydrous dimethylformamide.[2] Sioda, Cowan, and Koski[3] examined the electrochemistry of phenylacetylene, diphenylacetylene, and several substituted diphenylacetylenes in dimethylformamide and presented evidence based on epr spectroscopy for the formation of relatively stable radical-anion intermediates upon reduction of these compounds. Recently, it has been confirmed by House and Kinloch[4] that nonconjugated acetylenes are polarographically inactive in dimethylformamide.

Benkeser and Tincher[5] prepared a number of trans olefins by prolonged electrolysis at a platinum cathode of methylamine–lithium chloride solutions containing different acetylenic compounds. These authors suggested that the reduction involves a homogeneous reaction between the acetylenic compound and elemental lithium formed at the cathode.

Studies of the electrochemical reduction of certain cyclizable halogen-substituted acetylene compounds at mercury electrodes in dimethylformamide have been underway in this laboratory for some time.[6] Reduction of 1-phenyl-1-hexyne was originally performed in order to prepare *cis*- and *trans*-1-phenyl-1-hexene for use as comparison samples for other investigations. A partial controlled-potential electrolysis near the half-wave potential of 1-phenyl-1-hexyne yielded the two expected olefinic products plus a small amount of 1-phenylhexane which resulted from total reduction of the triple bond. Surprisingly, a third olefin (*trans*-1-phenyl-2-hexene) was obtained, raising the possibility of an interesting rearrangement or isomerization process. In addition, the current-time behavior during the electrolysis was unusual in that, after decreasing exponentially for 10 to 15 min, the current rose to a maximum before resuming a normal decay.

Thus, the present study was undertaken to explain these intriguing observations about the electrochemical reduction of 1-phenyl-1-hexyne. Our results complement previous knowledge of the reduction of phenyl acetylenes in aprotic media and point out the important role played by the allenic isomer of a 1-phenyl-1-alkyne in the electrochemical process.

Experimental Section

Reagents. Dimethylformamide employed as solvent throughout this research was Fisher Spectranalyzed material. It was determined that the moisture content of dimethylformamide stored over Linde 4A molecular sieves ranged from 200 to 400 ppm. For most experiments, the sieve-dried solvent was used without further treatment. To determine the effect of additional purification, an experiment was performed with dimethylformamide containing less than 100 ppm of water; the distribution of electrolysis products was essentially the same as that obtained with less stringently dried solvent.

Starting material, 1-phenyl-1-hexyne, was purchased from K & K Laboratories and was determined to be 99.5% pure by means of gas chromatography. Tetra-*n*-butylammonium perchlorate, obtained from the G. Frederick Smith Chemical Co., was employed as the supporting electrolyte. This reagent was sufficiently pure to be utilized without recrystallization. Pure nitrogen (99.98%) served for the deaeration of all solutions. It was passed through copper turnings at 800° to remove any oxygen and through a column of 8-mesh Drierite to remove residual water.

Apparatus. Figure 1 shows the cell designed for large-scale electrolyses at a mercury pool cathode as well as for polarographic monitoring of the reduction processes. The working-electrode compartment has a diameter of 6 cm and a height of 12 cm and is topped by a 71/60 female standard-taper joint into which the auxiliary-electrode compartment fits. Reference-electrode ports are tilted downward about 30° to permit the tips of the reference electrodes to be positioned close to the mercury pool. Electrical contact to the mercury pool is made by means of a platinum wire sealed through the bottom of the cell. We fabricated the auxiliary-electrode compartment by cutting off the top of a 150-ml fine-porosity fritted-glass Büchner funnel and by making a ring-seal to position the stem and the fritted disk concentrically within a 71/60 male standard-taper joint. Inside the auxiliary-electrode compartment was a 0.1 *F* solution of tetra-*n*-butylammonium perchlorate into which was dipped a 0.080-in. diameter platinum wire anode. To prevent the solution in the auxiliary-electrode compartment from leaking into the working-electrode compartment, the platinum wire anode was pushed through a rubber septum, and the auxiliary-electrode compartment was partially evacuated.

Because of the large diameter (6 cm) of the fritted disk, there is no practical resistive limit on the maximum cell current attainable. In addition, the parallel placement of the fritted disk above the mercury pool guarantees that the cathode is a sufficiently equipotential surface.[7-9] By placing two identical reference electrodes across the pool from each other, one electrode serving as the controlling reference and the other as a probe, we found that the variation in the potential across the cathode did not exceed 50 mV even for the maximum currents attained in this work.

All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride.[10] This electrode has a potential of −0.750 V *vs.* the saturated calomel electrode; furthermore, the potential is relatively insensitive to the presence of small amounts of water. Each reference electrode was prepared in a stoppered compartment[11] terminated by a cracked-glass tip[12] and was positioned directly above the mercury pool at a distance of 3 mm. Using a method described by Lauer and Osteryoung,[13] we found the uncompensated cell resistance to be approximately 4 ohms.

Controlled-potential electrolyses were performed with a Princeton Applied Research Model 173 potentiostat-galvanostat equipped with a Model 176 current-to-voltage converter to permit monitoring of the cell current on a strip-chart recorder. Use of the *iR* compensation capability of the current-to-voltage converter rendered the uncompensated ohmic potential drop negligible during the large-scale electrolyses.

Polarograms were obtained with a controlled-potential and derivative voltammeter, Model ORNL-1988A (Indiana Instrument and Chemical Corp.), and a Sargent-Welch Model SRG recorder. A Sargent-Welch 6-12-sec capillary was used at a mercury column height of 45 cm; the drop time was 3.1 sec, and $m^{2/3}t^{1/6}$ was 0.64 mg$^{2/3}$ sec$^{-1/2}$ at a potential of −2.00 V.

A Hewlett-Packard Model 5700A dual-column gas chromatograph with a thermal-conductivity detector was used for routine product analysis and for determination of solvent purity. Product analysis was achieved with a 15 ft × ⅛ in. column packed with 15% UCON Polar on 80-100 Chromosorb W. A 6 ft × ⅛ in. column packed with Porapak Q was utilized for the measurement of moisture in dimethylformamide. A preparative-scale gas chromatograph (F & M Model 720) was used with a 8 ft × 0.25 in. TCEP column to isolate individual electrolysis products for spectral analysis and identification. Individual mass spectra of products were obtained with a tandem gas chromatograph-mass spectrometer arrangement consisting of a Varian Aerograph Series 1200 gas chromatograph interfaced through a Watson-Biemann separator to a Varian CH-7 mass spectrometer operated at 70 eV. A Varian EM-360 spectrometer was used to obtain nmr spectra, and infrared spectra were recorded with a Perkin-Elmer Model 137 instrument.

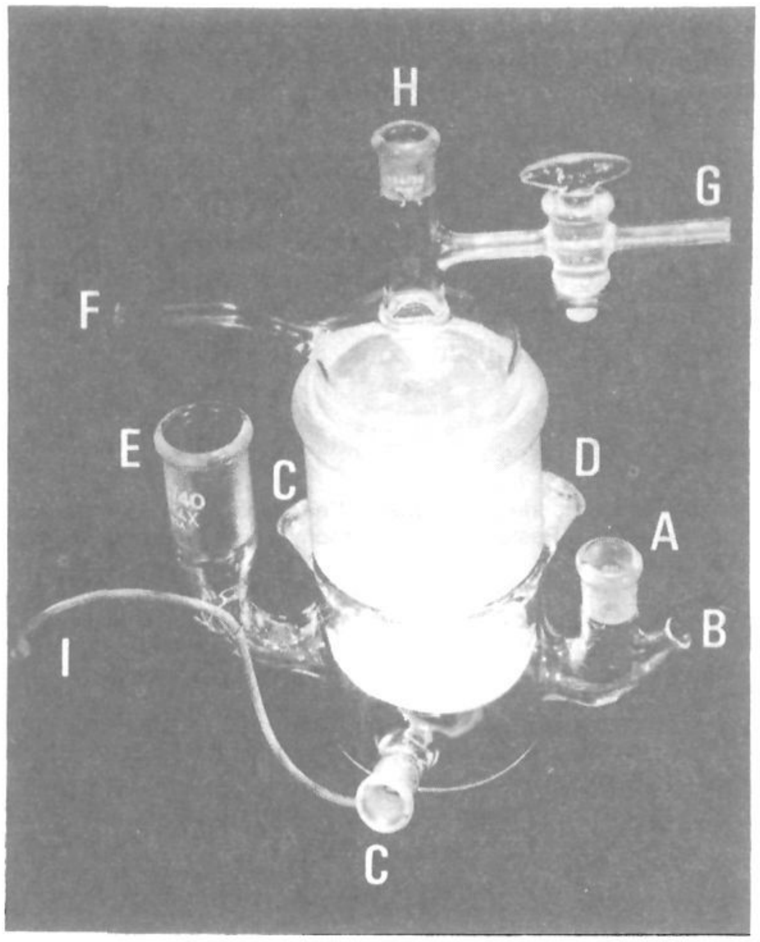


Figure 1. Electrolysis cell: (A) port into which dropping mercury electrode fits; (B) port (covered with rubber septum) for addition and removal of samples; (C) ports for reference electrodes; (D) port for sintered-glass bubbler for deaeration; (E) port for solvent introduction; (F) nitrogen outlet; (G) tube used for partial evacuation of auxiliary-electrode compartment; (H) port (covered with rubber septum) through which auxiliary electrode is inserted; (I) connection to platinum wire sealed through bottom of cell.

Procedures. Each controlled-potential electrolysis of 1-phenyl-1-hexyne was preceded by a blank electrolysis. With 0.1 *F* tetra-*n*-butylammonium perchlorate in dimethylformamide in the working-electrode compartment and with the potential of the mercury pool at least 50 mV more negative than for an actual experiment, the blank electrolysis was continued until the current decayed essentially to zero. Then 1-phenyl-1-hexyne was syringed into the working-electrode compartment, and a polarogram was recorded. A potential for the electrolysis was chosen by inspection of this polarogram. During the electrolysis, aliquots of the solution were removed for analysis, and polarograms were recorded periodically. An electrolysis was stopped when the current dropped to approximately 0.5 mA.

Water and diethyl ether were added to each aliquot of the electrolyzed solution. Desired species were extracted into the ether layer, which was then washed with water and dried with anhydrous magnesium sulfate. Excess ether was removed with a reduced-pressure rotary evaporator before analysis by means of gas chromatography.

Product Identification. Gas chromatography (involving spiking with authentic reference samples) coupled with mass spectrometry sufficed for positive identification of tri-*n*-butylamine, 1-phenylhexane, and unreduced 1-phenyl-1-hexyne. Three olefinic reduction products having molecular ions at *m/e* 160 could not be differ-

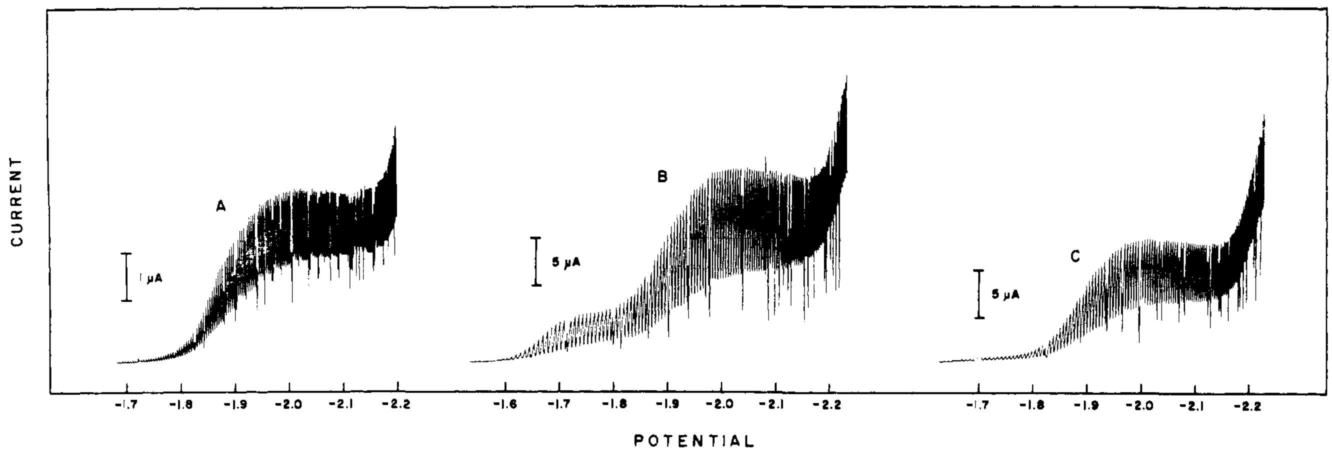


Figure 2. (A) Polarogram for 5.2×10^{-4} *M* 1-phenyl-1-hexyne in dimethylformamide containing 0.1 *F* tetra-*n*-butylammonium perchlorate. (B) Polarogram corresponding to the current maximum (Figure 3, point B) during controlled-potential electrolysis of 2.6×10^{-3} *M* 1-phenyl-1-hexyne. (C) Polarogram recorded during late stage (Figure 3, point C) of controlled-potential electrolysis of 2.6×10^{-3} *M* 1-phenyl-1-hexyne.

entiated by means of mass spectrometry.

Both the most and least predominant of these olefins are completely reducible at potentials employed for reduction of 1-phenyl-1-hexyne, suggesting that the two compounds are *cis*-and *trans*-1-phenyl-1-hexene. When the most abundant olefin was isolated by means of preparative-scale gas chromatography, the following spectral data were obtained: ir (neat) 690, 740, 960, and 1595 cm^{-1}; nmr (CCl_4) δ 0.90 (t, 3), 1.39 (m, 4), 2.12 (q, 2), 6.15 (m, 2), and 7.12 (m, 5). These spectral data matched those for *trans*-1-phenyl-1-hexene synthesized by means of the modified Wittig reaction[14] between valeraldehyde and diethyl benzylphosphonate. In addition, a mixture of the two olefins was prepared by partial hydrogenation of 1-phenyl-1-hexyne. Since partial hydrogenation favors the cis product overwhelmingly, peaks for the cis and trans isomers on a gas chromatogram are readily distinguishable; retention times for the synthesized *cis*- and *trans*-1-phenyl-1-hexene matched those of the so-assigned products in electrolyzed solutions of 1-phenyl-1-hexyne.

Identification of *trans*-1-phenyl-2-hexene as the third olefin was based on the following spectral data: ir (neat) 695, 740, 960, and 1535 cm^{-1}; nmr (CCl_4) δ 0.40 (t, 3), 1.37 (m, 2), 1.98 (q, 2), 3.30 (d, 2), 5.45 (m, 2), and 7.10 (m, 5). To substantiate this assignment, 1-phenyl-2-hexyne was hydrogenated under controlled conditions to yield a mixture of *cis*- and *trans*-1-phenyl-2-hexene; the retention time for the third olefinic electrolysis product was the same as that for *trans*-1-phenyl-2-hexene in the mixture.

Volatile species from the reduction of 1-phenyl-1-hexyne were trapped from the nitrogen stream at −198°. The trapped material was purified by passage through a bath at −45° to remove dimethylformamide and water, and was recondensed in another trap at −198°. When the purified condensate was volatilized, its infrared spectrum was identical with the Sadtler reference spectrum for 1-butene.

Results and Discussion

Polarography and Current-Time Curves. As shown in Figure 2A, a polarogram for a 5.2×10^{-4} *M* solution of 1-phenyl-1-hexyne in dimethylformamide containing 0.1 *F* tetra-*n*-butylammonium perchlorate exhibits a single reduction wave with a half-wave potential of −1.88 V. This wave corresponds to an irreversible process, as indicated by the Tomeš criterion of reversibility,[15] the value of $E_{1/4} - E_{3/4}$ being 86 mV. Based on evidence discussed later, the polarographic wave can be attributed formally to the four-electron reduction of 1-phenyl-1-hexyne to 1-phenylhexane.

Large-scale controlled-potential reductions of 1-phenyl-1-hexyne were performed at −1.95 V (on the rising portion of the polarographic wave) and at −2.07 V (on the plateau of the polarogram). For electrolyses at −2.07 V, the current shows a normal exponential decrease with time. On the other hand, an unusual feature of controlled-potential electrolyses at −1.95 V is the pronounced maximum in the current-time traces, as shown in Figure 3. This phenomenon is noticeably enhanced at higher concentrations of 1-phenyl-1-hexyne and is also affected by the reduction potential and the solvent purity. For example, electrolysis of a 2.1×10^{-3} *M* solution of 1-phenyl-1-hexyne at −1.95 V resulted in a gentle current rise from 14 to 18 mA, whereas electrolysis of a 0.010 *M* solution at the same potential yielded a more exaggerated maximum with the current increasing from 22 to 50 mA. Near the current maximum in the latter experiment, the solution acquired a deep red color; this coloration persisted until the end of the steep current decline (Figure 3, point C). It was observed that the current starts up faster at more negative potentials on the rising portion of the 1-phenyl-1-hexyne wave as well as in a drier solvent. For freshly distilled and very dry dimethylformamide (H_2O < 100 ppm), the electrolysis current rises almost immediately.

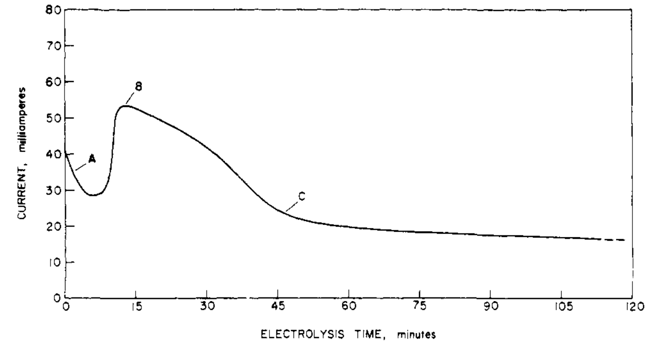


Figure 3. Current-time curve for the controlled-potential reduction of 6.2×10^{-3} *M* 1-phenyl-1-hexyne in dimethylformamide containing 0.1 *F* tetra-*n*-butylammonium perchlorate at −1.95 V.

Polarograms corresponding to various stages of controlled-potential reductions at −1.95 V provided further insight into the nature of the electrochemical process. A polarogram recorded during the initial current decay (Figure 3, point A) differs little from that depicted in Figure 2A. However, a polarogram obtained near the current maximum (Figure 3, point B) consists of two waves as seen in Figure 2B; the half-wave potential for the first wave is −1.67 V, whereas that for the second is the same as for the original 1-phenyl-1-hexyne wave. As the electrolysis progresses past the current maximum, the first wave decreases and finally disappears near the point where the current-time curve changes slope (Figure 3, point C); the remaining polarographic wave with a half-wave potential of −1.89 V (Figure 2C) diminishes and eventually vanishes as the electrolysis current decays to zero. Thus, the maximum in current-time curves for electrolyses performed at potentials on the rising portion of the polarographic wave for 1-phenyl-1-hexyne is due to the rapid formation of a substance which is easier to reduce (Figure 2B) than 1-phenyl-1-hexyne itself.

What species causes the new polarographic wave seen at −1.67 V in Figure 2B as well as the maximum in the current-time curve? It was suspected that 1-phenyl-1-hexyne might be undergoing an electrochemically induced isomerization to a more readily reducible species. To probe this possibility, a solution of 1-phenyl-1-hexyne was electrolyzed until the current maximum was reached; rapid quenching with water and isolation of products followed. An infrared spectrum exhibited a medium-intensity band at 1950 cm^{-1} characteristic of an allene. Examination of an nmr spectrum revealed a complex multiplet at δ 5.70–6.35 and a quartet centered at δ 5.42, showing the presence of a compound having allenic hydrogen atoms. Integration of the nmr spectrum indicated that the allene, presumed to be 1-phenyl-1,2-hexadiene, comprised nearly 50% of all compounds (including 1-phenyl-1-hexyne) present in solution at the current maximum.

To confirm the presence of 1-phenyl-1,2-hexadiene, the allenic species was chemically prepared by treatment of 1-phenyl-1-hexyne with potassium *tert*-butoxide in *tert*-butyl alcohol, a base-catalyzed propargylic rearrangement yielding an allene–acetylene mixture.[16] An infrared spectrum of this mixture exhibited the allene absorption at 1950 cm^{-1}, and the pattern of allenic hydrogen lines in the nmr spectrum was identical with that obtained upon electrochemical reduction of 1-phenyl-1-hexyne. In addition, a polarogram for the synthetic allene–acetylene mixture showed two waves with the same half-wave potentials as those shown by polarograms obtained during early stages (Figure 2B) of the reduction of 1-phenyl-1-hexyne. Thus, during an electrolysis, 1-phenyl-1-hexyne does isomerize to the more easily reducible 1-phenyl-1,2-hexadiene.

Additional information was obtained from inspection of the polarogram for the synthetically prepared allene–acetylene mixture. From the relative heights of the two polarographic waves and from knowledge of the concentrations of the two isomers based on nmr spectroscopy, it was established that 1-phenyl-1,2-hexadiene undergoes a pair of two-electron reductions. In the first step, having a half-wave potential of −1.67 V, the allene is reduced to *trans*-1-phenyl-1-hexene, *cis*-1-phenyl-1-hexene, or *trans*-1-phenyl-2-hexene; the second step, having the same half-wave potential (−1.89 V) as the four-electron reduction of 1-phenyl-1-hexyne, corresponds formally to the conversion of the phenyl-conjugated olefins to 1-phenylhexane. Although *trans*-1-phenyl-2-hexene is not a phenyl-conjugated olefin and cannot be electrochemically reduced, evidence presented later indicates that it isomerizes to a reducible olefin.

Distribution of Products and Overall Reaction Stoichiometry. To follow the progress of the reduction of 1-phenyl-1-hexyne, aliquots of the solution were removed periodically during an electrolysis, and the composition of the solution was determined by means of gas chromatography. Figure 4 illustrates how the composition of a solution during an electrolysis varies with the number of electrons (n) transferred per molecule of 1-phenyl-1-hexyne. These results pertain to controlled-potential electrolyses performed at potentials on the rising portion of the polarographic wave for 1-phenyl-1-hexyne and to solutions ranging from 0.0021 to 0.010 M in the starting material. Product distributions were reproducible to within ±10% on a relative basis. All n values were determined by integration of current–time curves and were essentially identical with the n values based on the distribution of products; such agreement demonstrated that we accounted for all products derived from the starting material.

With reference to Figure 4, several aspects of the electrochemical process deserve further emphasis. Because the retention times for 1-phenyl-1-hexyne and 1-phenyl-1,2-hexadiene are identical on a variety of columns, only the sum of the percentages of the acetylene and allene is shown. However, the individual amounts of the two isomers were estimated for some samples of the solution by integration of the nmr spectrum. Near the beginning of an electrolysis, 1-phenyl-1-hexyne quickly isomerizes to 1-phenyl-1,2-hexadiene, and the current increases rapidly as reduction of the allene becomes important. Throughout nearly the entire first half of an electrolysis, the quantities of acetylene and allene remain equal within experimental error until the two isomers are both completely reduced ($n = 2$). In order of decreasing abundance, the reduction products initially formed are *trans*-1-phenyl-1-hexene, *trans*-1-phenyl-2-hexene, and *cis*-1-phenyl-1-hexene. Just beyond $n = 2$, *cis*- and *trans*-1-phenyl-1-hexene reach maximum yields (based on starting material) of approximately 3 and 75%, respectively, but both compounds are completely reduced to 1-phenylhexane in an exhaustive electrolysis ($n = 4$). As shown in Figure 4, the quantity of *trans*-1-phenyl-2-hexene attains its highest value of almost 20% at $n = 1.5$; thereafter, the amount of this species decreases to and remains constant at approximately 2%. Interestingly, the completely reduced product, 1-phenylhexane, is formed to a slight extent for $n < 2$; however, the yield of 1-phenylhexane rapidly rises for $n > 2$, eventually climbing to 98% at $n = 4$.

Note that the polarogram in Figure 2C corresponds to a stage of the electrolysis beyond the disappearance of 1-phenyl-1-hexyne; therefore, although the polarographic wave in Figure 2C might appear to be due to the reduction of starting material, it is actually attributable to the two-electron reductions of *cis*- and *trans*-1-phenyl-1-hexene.

In addition to the compounds identified in Figure 4, 1-butene was detected in the nitrogen stream leaving the working-electrode compartment, and a gas chromatographic peak for tri-*n*-butylamine was observed. Apparently, the tetra-*n*-butylammonium cation is the ultimate source of protons for carbanions, and a Hofmann elimination reaction immediately ensues to give tri-*n*-butylamine and 1-butene. Hence, the conversion of 1-phenyl-1-hexyne to 1-phenylhexane can be written as

$$C_6H_5C{\equiv}CC_4H_9 + 4N(C_4H_9)_4^+ + 4e^- \longrightarrow C_6H_5C_6H_{13} + 4N(C_4H_9)_3 + 4CH_2{=}CHC_2H_5$$

if the small quantity of unreduced *trans*-1-phenyl-2-hexene is ignored. Actually, the recovered amounts of 1-butene and tri-*n*-butylamine were only 65–75% of those predicted from the stoichiometry of the preceding reaction, because some protons were supplied by water present in the dimethylformamide. Calculations revealed that the average quantity (200–400 ppm) of water in the solvent was of the correct magnitude to produce the deviation observed.

Mechanism of the Reaction. Isomerization of 1-phenyl-1-hexyne begins within minutes after the start of the electrolysis. Presumably, only enough time is required to exhaust residual water which, if present, rapidly protonates any carbanionic species. This isomerization is a base-catalyzed propargylic rearrangement[17] triggered through the abstraction of an α proton from 1-phenyl-1-hexyne by an electrolytically formed radical-anion (**1**).[18] Reabstraction of a proton by the propargylic anion (**3**) can result in the formation of either 1-phenyl-1,2-hexadiene or starting ma-

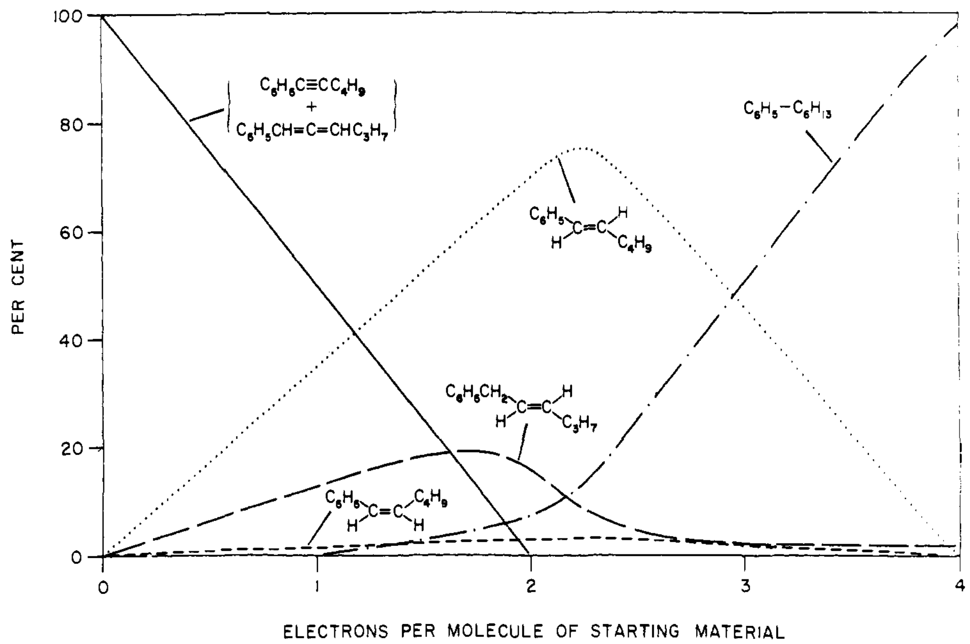
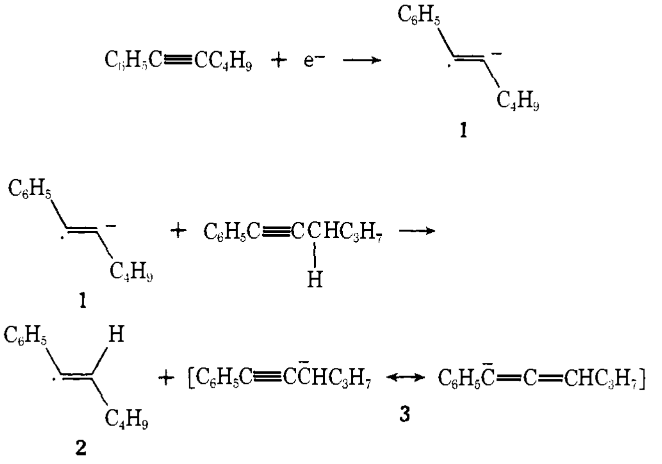
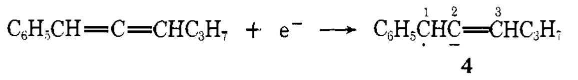


Figure 4. Composition of a solution as a function of the number of electrons (n) transferred per molecule of starting material during the controlled-potential reduction of 1-phenyl-1-hexyne at −1.95 V.



terial; thus, a pseudo equilibrium between the isomers is quickly established. Then the neutral free radical (**2**) is further reduced to yield mainly *trans*-1-phenyl-1-hexene.

Reduction of 1-phenyl-1,2-hexadiene, which occurs more readily than its acetylenic precursor, probably involves the addition of an electron to the phenyl-conjugated double bond



$$C_6H_5CH=C=CHC_3H_7 + e^- \longrightarrow C_6H_5\overset{1}{C}H\underset{-}{\overset{2}{C}}=\overset{3}{C}HC_3H_7$$

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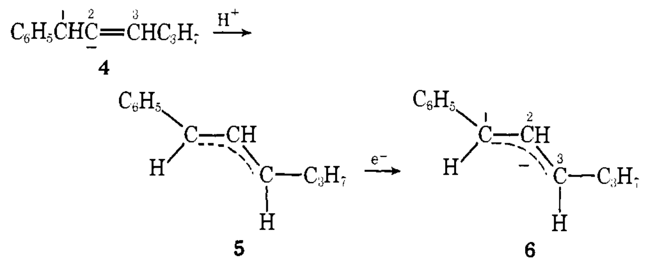
the negative charge residing primarily on C_2 in order to yield the favored trigonal carbanion.[19] Proton abstraction by the carbanion (**4**) produces an allyl radical (**5**) which is further reduced electrochemically to an allylic anion (**6**):



Protonation of the latter anion (**6**) leads to *trans*-1-phenyl-1-hexene, *trans*-1-phenyl-2-hexene, and *cis*-1-phenyl-1-hexene. At potentials employed for the electrolyses, the two phenyl-conjugated olefins are directly reducible to 1-phenylhexane. Furthermore, loss of a benzylic proton from *trans*-1-phenyl-2-hexene regenerates the allylic anion (**6**) which can accept a hydrogen ion to yield one of the reducible olefins.

That formation of the thermodynamically more stable trans olefins is favored to a large extent probably reflects the most stable configuration of the allyl radical precursor (**5**). Protonation of the allylic anion (**6**) at C_3 seems to be preferred, as evidenced by the majority of phenyl-conjugated olefins which are formed, but this conclusion must be drawn with caution because *trans*-1-phenyl-2-hexene formed by protonation at C_1 appears to undergo reasonably rapid isomerization. In fact, in the absence of isomerization, the percentage of *trans*-1-phenyl-2-hexene would be expected to attain a constant value because the nonconjugated double bond is not electroactive. However, as shown in Figure 4, the quantity of *trans*-1-phenyl-2-hexene passes through a maximum and decreases, because its rate of isomerization exceeds its rate of generation.

Although it should be possible for the four-electron reduction of 1-phenyl-1-hexyne to 1-phenylhexane to occur in a single step, the process takes place in two stages under conditions of most electrolyses performed in this investigation. If a one-step process were involved, 50% 1-phenylhexane and 50% 1-phenyl-1-hexyne should be present after the equivalent of two electrons is transferred to the starting material; however, as revealed in Figure 4, olefins comprise 87% of the products for $n = 2$.

Inasmuch as the formation of 1-phenyl-1,2-hexadiene is a bimolecular reaction, electrolysis of a sufficiently dilute solution of 1-phenyl-1-hexyne should proceed without isomerization to the allene. Accordingly, the electrochemical reduction of a 2.6×10^{-4} M solution of 1-phenyl-1-hexyne was examined. In contrast to experiments done with solutions 20–40 times more concentrated, the electrolysis current decayed normally and polarography revealed the formation of no allene. This electrolysis was terminated after the equivalent of two electrons had been transferred to the starting material; the species present were 1-phenylhexane

(47%), 1-phenyl-1-hexyne (37%), *trans*-1-phenyl-1-hexene (11%), *cis*-1-phenyl-1-hexene (4%), and *trans*-1-phenyl-2-hexene (1%). Such an extremely small amount of the nonconjugated olefin is expected, because the migrated double bond can result only from reduction of 1-phenyl-1,2-hexadiene. In addition, in the absence of the allene, the electrochemical reduction tends to proceed more in one step. This is because the reduction potentials for 1-phenyl-1-hexyne and *cis*- and *trans*-1-phenyl-1-hexene are nearly identical.

It was of interest to observe the products derived solely from the electrochemical reduction of 1-phenyl-1,2-hexadiene and to compare the results with those for the reduction of 1-phenyl-1-hexyne. A relatively high concentration of the allene was prepared by the controlled-potential electrolysis of a 0.010 *M* solution of 1-phenyl-1-hexyne at −2.00 V until the current reached its maximum value (Figure 3, point B). Analysis of an aliquot of the solution revealed 67% allene, 8% olefinic species, and 25% starting material. Then the potential was adjusted to −1.60 V, at which only 1-phenyl-1,2-hexadiene undergoes reduction, and an exhaustive electrolysis was performed. At the end of the electrolysis, the solution contained *trans*-1-phenyl-1-hexene (73%), *trans*-1-phenyl-2-hexene (19%), *cis*-1-phenyl-1-hexene (4%), 1-phenyl-1-hexyne (3%), and 1-phenylhexane (1%). This distribution of compounds closely resembles the situation depicted in Figure 4 in which two electrons have been transferred to 1-phenyl-1-hexyne. Such a similarity suggests that, for concentrations of 1-phenyl-1-hexyne used in the majority of experiments (0.002-0.010 *M*), the pathway for the electrochemical reduction at −1.95 V actually proceeds almost entirely through the allene species. Thus, for electrolyses done at −1.95 V, the rate of isomerization of 1-phenyl-1-hexyne greatly exceeds the rate of its direct reduction, and the olefinic products are largely derived from the allene isomer.

A controlled-potential electrolysis of a 0.005 *M* solution of 1-phenyl-1-hexyne was performed at −2.07 V, a potential on the plateau of the polarographic wave for the starting material (Figure 2A). There was a normal, exponential decay of current with time, although formation of the allene was evident from polarograms recorded during the electrolysis. Aliquots of the solution were analyzed at intervals corresponding to the addition of 1.0, 2.3, and 4.0 electrons to each molecule of starting material. It can be seen from Table I that 1-phenylhexane is present to a significant extent before the starting material disappears. This result reflects the lesser discrimination between allene and olefin reduction at −2.07 V. In addition, the direct reduction of 1-phenyl-1-hexyne is more competitive with the process of isomerization to 1-phenyl-1,2-hexadiene. Interestingly, substantial amounts of the olefinic products are present at intermediate stages in the electrolysis; apparently, this situation arises because the carbanionic intermediates are not protonated sufficiently fast and are repelled by the cathode into the solution before total reduction can occur.

Table I. Percentage Distribution of Species during Controlled-Potential Reduction of 0.005 *M* 1-Phenyl-1-hexyne at −2.07 V

	Electrons/molecule of starting material		
Species	1.0	2.3	4.0
trans-1-Phenyl-1-hexene	40	58	
trans-1-Phenyl-2-hexene	8	9	4
cis-1-Phenyl-1-hexene	2	3	
1-Phenylhexane		22	96
1-Phenyl-1-hexyne + 1-phenyl-1,2-hexadiene	50	8	

Intensive investigations of the electrochemical reduction and intramolecular cyclization of 6-halo-1-phenyl-1-hexynes are in progress.[6] It is now clear that isomerization of the acetylene to the allene and stepwise reduction of the latter are key steps in the detailed mechanisms of these processes.

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(18) In preliminary cyclic voltammetric experiments with a sessile mercury drop electrode and a 0.005 *M* solution of 1-phenyl-1-hexyne, sweep rates of at least 100 V sec^{-1} were needed to observe reoxidation of the initially formed radical-anion **1**, indicating that its lifetime is on the order of 1 msec.
(19) There is other evidence in our work that the negative charge is located mainly at C_2. In an investigation of the electrochemical reduction of 6-chloro-1-phenyl-1-hexyne, we have obtained large yields (*ca.* 80%) of five-membered carbocycles. Because the allene isomer is definitely formed during the course of the reduction, we believe that the species $C_6H_5\dot{C}H\bar{C}{=}CHC_3H_6Cl$ undergoes intramolecular cyclization to give (after either hydrogen atom abstraction or further reduction and protonation) the carbocycles.