

Electroreductive Cyclization Reactions of 6-Chloro-1-phenyl-1-hexyne and 6-Chloro-1-phenyl-1,2-hexadiene at a Mercury Cathode in Dimethylformamide

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Abstract: A study of the electrochemical behavior of 6-chloro-1-phenyl-1-hexyne at a mercury cathode in dimethylformamide containing 0.1 *F* tetra-*n*-butylammonium perchlorate has been undertaken. Two polarographic waves are observed for this compound; the first wave is due to reduction of the carbon-carbon triple bond, whereas the second step results from simultaneous reductions of the carbon-chlorine bond of the starting material and benzyldenecyclopentane, a prior electrolysis product. For a sufficiently low concentration of 6-chloro-1-phenyl-1-hexyne (2.5×10^{-4} *M*), large-scale controlled-potential reduction of the carbon-carbon triple bond produces a radical anion which mainly undergoes intramolecular cyclization to yield benzyldenecyclopentane; alternatively, this radical anion exhibits a unique intramolecular electron-transfer reaction leading to chemical reduction of the carbon-chlorine bond. For larger concentrations (>0.002 *M*), electrolytically induced isomerization of the acetylene causes formation of 6-chloro-1-phenyl-1,2-hexadiene which upon reduction yields five-membered carbocycles (1-benzylcyclopentene, benzyldenecyclopentane, and benzylcyclopentane), a four-membered carbocycle (*trans*-1-phenyl-2-cyclobutylethylene), six-membered carbocycles (3-phenylcyclohexene and 1-phenylcyclohexene), and various straight-chain compounds.

Recently, we investigated the electrochemical reduction of 1-phenyl-1-hexyne at a mercury cathode in anhydrous dimethylformamide containing 0.1 *F* tetra-*n*-butylammonium perchlorate as supporting electrolyte.¹ It was discovered that the acetylene forms 1-phenyl-1,2-hexadiene by a bimolecular base-catalyzed rearrangement, and that reduction of the allene isomer is the predominant process for initial concentrations of 1-phenyl-1-hexyne greater than 0.002 *M*. Whereas 1-phenyl-1-hexyne undergoes a direct four-electron reduction to 1-phenylhexane, the 1-phenyl-1,2-hexadiene is reduced in stepwise fashion, first to *trans*-1-phenyl-1-hexene, *trans*-1-phenyl-2-hexene, and *cis*-1-phenyl-1-hexene, and then to 1-phenylhexane. Tetra-*n*-butylammonium cation is the ultimate source of protons for the reduction and, following deprotonation, yields tri-*n*-butylamine and 1-butene via a Hofmann elimination reaction.

As part of continuing efforts to understand the mechanisms of electrochemically induced intramolecular cyclizations of 6-halo-1-phenyl-1-hexynes,² a thorough examination of the behavior of 6-chloro-1-phenyl-1-hexyne has been undertaken. Because reduction of the phenyl-activated carbon-carbon triple bond occurs more easily than that of the carbon-chlorine moiety, this system provides the opportunity for a study of nucleophilic displacement reactions involving intramolecular attack of electrochemically generated radical anions on the terminal alkyl chloride site. From a knowledge of the product distribution, it was hoped that the nature of the highly reactive, electrolytically generated intermediates could be established. What has been found for 6-chloro-1-phenyl-1-hexyne is that the course of the reduction and the distribution of products depend on the concentration of the starting material. At concentrations in the neighborhood of 2.5×10^{-4} *M*, reduction of the acetylene and intramolecular cyclization of the resulting radical anion to benzyldenecyclopentane are predominant. At higher concentrations, isomerization of the acetylene to the corresponding allene, as observed for 1-phenyl-1-hexyne,¹ is very important; thus, the electrochemical process becomes more complicated and, in addition to five-membered rings, the products include four- and six-membered carbocycles.

There is a similarity between the results of our electrochemical experiments and those seen with polynuclear aro-

matic radical anions. Crandall and Keyton³ proposed that reduction of 5-chloro-1-phenyl-1-pentyne by lithium biphenyl in tetrahydrofuran proceeds by initial transfer of an electron to the phenyl-activated carbon-carbon triple bond, and that the resulting radical anion displaces chloride ion intramolecularly to yield benzyldenecyclobutane. This mechanism is consistent with the electrochemical behavior of 6-chloro-1-phenyl-1-hexyne at relatively low concentrations. However, our observations with higher concentrations of 6-chloro-1-phenyl-1-hexyne indicate that isomerization of the acetylene to an allene and subsequent reduction of the latter species could be an important process when chemical reducing agents are employed.

Experimental Section

Instrumentation and Procedures. Dimethylformamide employed as solvent and tetra-*n*-butylammonium perchlorate used as supporting electrolyte were handled as described previously.¹ Also discussed in this earlier reference are the electrochemical cell, the associated hardware including the polarograph and potentiostat, and the procedures for performing the electrochemical experiments and product analyses.

A Hewlett-Packard Model 5700A dual-column gas chromatograph equipped with a thermal-conductivity detector was used for routine analysis of the electrolysis products. A 10 ft $\times$ $\frac{1}{8}$ in. column, packed with 3% UCON Polar on 80-100 Chromosorb W and operated at 127° and a helium flow rate of 25 ml/min, was utilized to separate and determine the chlorine-containing species in electrolysis mixtures; this column did not resolve individual hydrocarbon products well, but it was possible to measure the total percentage of these compounds. Hydrocarbons were resolved and determined through the use of a 14 ft $\times$ $\frac{1}{8}$ in. column packed with 16% UCON Polar on 60-80 Chromosorb W and operated at 155° and a carrier-gas flow rate of 30 ml/min.

Major components (benzyldenecyclopentane, benzylcyclopentane, 1-benzylcyclopentene, *trans*-1-phenyl-2-cyclobutylethylene, and tri-*n*-butylamine) of electrolyzed solutions were obtained pure by means of preparative-scale gas chromatography. A stainless steel Swagelok $\frac{1}{8}$ to 0.25 in. adapter, which accommodated glass sample collection tubes, was attached with Teflon ferrules to the $\frac{1}{8}$ in. carrier-gas exit port of the Hewlett-Packard chromatograph. Electrical heating tape was wrapped around the adapter, and its temperature was kept at 150° so that no condensation of products would occur inside the adapter. Two columns were utilized for preparative-scale gas chromatography, a 5 ft $\times$ 0.25 in. column

packed with 10% UCON Polar on 80-100 Chromosorb W and a similar column prepared from Carbowax 20M, each operated at 125° and a helium flow rate of 125 ml/min.

Infrared and NMR spectra as well as gas chromatographic retention times for the major products were compared with corresponding data for authentic compounds synthesized as described below. A Varian EM-360 spectrometer was utilized to record NMR spectra, tetramethylsilane being used as internal standard; infrared spectra were obtained with the aid of a Perkin-Elmer Model 137 instrument. Mass spectra were obtained with either a Varian CH-7 or AEI MS-9 spectrometer operated at 70 eV.

A number of minor products, each present to the extent of less than 5%, could not be isolated in a pure state. These species were identified through comparison of their retention times with those of known compounds, either purchased or synthesized, and through our knowledge of the electrochemical behavior of these species.

All product yields reported in this study are based on the amount of recovered material. In a separate experiment involving use of an electroinactive internal standard (phenylcyclohexane), measurements of the areas of chromatographic peaks for the standard and the various electrolysis products indicated that the recovery was at least 92% of the theoretical yield.

Synthesis of Starting Material. To prepare 6-chloro-1-phenyl-1-hexyne, we treated 4-chlorobutyl *p*-toluenesulfonate (synthesized according to the method published by Pattison and Millington⁴) with lithium phenylacetylide in tetrahydrofuran. After removal of phenylacetylene, a vacuum distillation yielded the desired compound as a pale-yellow liquid: bp 94-95° (0.2 mm); ir (neat) 2220 (m, C≡C), 757 and 690 cm⁻¹ (s, phenyl); NMR (CDCl₃) δ 7.32 (m, 5, aromatic H), 3.57 (t, CH₂Cl, *J* = 6 Hz), 2.41 (t, C≡CCH₂, *J* = 6 Hz), and 1.85 (m, 4, CH₂). Anal. Calcd for C₁₂H₁₃Cl: C, 74.80; H, 6.80; Cl, 18.40. Found: C, 74.38; H, 6.77; Cl, 18.22.

Five-Membered Carbocycles. Benzylidenecyclopentane [NMR (CDCl₃) δ 7.28 (m, 5, aromatic H), 6.34 (m, 1, vinylic H), 2.50 (m, 4, allylic H), and 1.74 (m, 4, CH₂)] and 1-benzylcyclopentene [NMR (CCl₄) δ 7.13 (m, 5, aromatic H), 5.31 (m, 1, vinylic H), 3.34 (m, 2, benzylic H), and 1.4-2.6 (m, 6, CH₂)] were prepared as described by Michaely.⁵ Benzylcyclopentane was obtained by hydrogenation of benzylidenecyclopentane in a Parr apparatus containing a palladium/charcoal catalyst: NMR (CDCl₃) δ 7.12 (m, 5, aromatic H), 2.61 (m, 2, benzylic H), and 0.9-2.2 (m, 9).

Four-Membered Carbocycles. A modified Wittig reaction⁶ involving diethyl benzylphosphonate and cyclobutanecarboxylate was utilized for the synthesis of *trans*-1-phenyl-2-cyclobutylethylene: bp 117-118° (1.5 mm); ir (neat) 1650 (w, C=C), 970 (s, *trans*-CH=CH), 749 and 698 cm⁻¹ (s, phenyl); NMR (CCl₄) δ 7.20 (m, 5, aromatic H), 6.23 (m, 2, CH=CH), 2.7-3.5 (m, 1, cyclobutyl H), 1.6-2.4 (m, 6, CH₂).⁷ Anal. Calcd for C₁₂H₁₄: C, 91.08; H, 8.92. Found: C, 91.06; H, 9.13. A portion of this olefin was hydrogenated to give 1-phenyl-2-cyclobutylethane, a previously unreported compound, and a trace product found upon electrolytic reduction of 6-chloro-1-phenyl-1-hexyne: NMR (CCl₄) δ 7.13 (m, 5, aromatic H), 2.45 (t, 2, *J* = 7 Hz, benzylic H), 1.4-2.5 (m, 9).

Six-Membered Carbocycles. Commercially available 1-phenylcyclohexene and phenylcyclohexane exhibited gas chromatographic retention times identical with those for two minor electrolysis products. In addition, it was found that 1-phenylcyclohexene undergoes reduction, with a polarographic half-wave potential of -2.0 V,⁸ to phenylcyclohexane; this behavior is consistent with the observation that 1-phenylcyclohexene is formed upon electrolytic reduction of 6-chloro-1-phenyl-1-hexyne at potentials near -1.75 V, whereas phenylcyclohexane is obtained from electrolyses performed at potentials close to -2.0 V. A third six-membered carbocyclic product, 3-phenylcyclohexene, was obtained independently by the preparative-scale gas chromatographic separation of the mixture of four species (3-phenylcyclohexene, 1-phenylcyclohexene, benzylidenecyclopentane, and 1-benzylcyclopentene) resulting from dehydration of *trans*-2-phenylcyclohexanol,^{9,10} with *p*-toluenesulfonic acid monohydrate in benzene in a Dean-Stark apparatus. Characterization of 3-phenylcyclohexene was based on the following spectral data: NMR (CCl₄) δ 7.12 (m, 5, aromatic H), 5.74 (m, 2, olefinic H), 3.34 (m, 1, methine H), 2.08 (m, 2, allylic H), and 1.77 (m, 4, CH₂).

Straight-Chain Species. Among the minor electrolysis products are 1-phenyl-1-hexyne, *trans*-1-phenyl-1-hexene, *trans*-1-phenyl-2-hexene, *cis*-1-phenyl-1-hexene, and 1-phenylhexane. Information about the preparation and identification of these compounds has been reported earlier.¹

Another component of electrolyzed solutions is 1-phenyl-1-hexyn-5-ene. This compound was prepared according to the general method used by Michaely⁵ to synthesize a variety of substituted phenylacetylenes. Into a 300-ml, three-necked, round-bottomed flask purged with argon and fitted with a dropping funnel and condenser was syringed 70 ml of 1.5 *F* *n*-butyllithium (0.115 mol) in hexane. Then 12 g (0.118 mol) of phenylacetylene (dried overnight before use with Linde 4A molecular sieves) in 80 ml of freshly distilled tetrahydrofuran was added, and the mixture was refluxed for 3 hr. After evolution of gas ceased, 18 g (0.133 mol) of 4-bromo-1-butene was introduced, and the solution was refluxed overnight. After a normal work-up procedure, distillation gave 11 g (60%) of the desired pale-yellow liquid: bp 77-78° (1.0 mm); NMR (CDCl₃) δ 7.25 (m, 5, aromatic H), 5.6-6.3 (m, 1, vinylic H), 5.20 and 4.94 (m, 2, terminal CH₂), and 2.40 (m, 4, CH₂). A partial electrochemical reduction of 1-phenyl-1-hexyn-5-ene was performed in order to prepare *trans*-1-phenyl-1,5-hexadiene,¹¹ which was found to have a gas chromatographic retention time identical with that of a product obtained in small yield from the electrolysis of 6-chloro-1-phenyl-1-hexyne.

To prepare 1-phenyl-1,3-hexadiene, triphenyl-*n*-propylphosphonium iodide was condensed with *trans*-cinnamaldehyde in dimethylformamide containing sodium methoxide.¹² Using preparative-scale gas chromatography, we isolated the major component and identified it by the following spectral data: NMR (CDCl₃) δ 7.30 (m, 5, aromatic H), 5.3-7.1 (m, 4, olefinic H), 2.12 (m, 2, *J* = 6 Hz, CH₂), and 1.03 (t, 3, *J* = 6 Hz, CH₃). The most intense band in the infrared spectrum is the carbon-hydrogen bending mode at 982 cm⁻¹. These data strongly suggest that this diene (which has a gas chromatographic retention time identical with that of a minor electrolysis product) is *trans,trans*-1-phenyl-1,3-hexadiene.¹¹

To obtain gas chromatographic data for 6-chloro-1-phenyl-1-hexene and 6-chloro-1-phenylhexane, a sample of 6-chloro-1-phenyl-1-hexyne was partially hydrogenated. Retention times were determined and compared with those for products derived from the electrochemical reduction of 6-chloro-1-phenyl-1-hexyne. A product obtained in low yield was found to have the same retention time as 6-chloro-1-phenyl-1-hexene,¹³ but 6-chloro-1-phenylhexane was absent from the list of electrolysis products.

One trace component present among the electrolysis products was obtained pure by means of preparative-scale gas chromatography. An exact mass of 174.1046 indicates that C₁₂H₁₄O is its molecular formula, but sufficient material was not available for NMR or infrared studies.

Results and Discussion

Polarographic Behavior of 6-Chloro-1-phenyl-1-hexyne. If a polarogram is recorded for a 0.005 *M* solution of 6-chloro-1-phenyl-1-hexyne in dimethylformamide containing 0.1 *F* tetra-*n*-butylammonium perchlorate, two waves are observed with half-wave potentials of -1.77 and -2.05 V⁸ and with respective diffusion currents in an approximate 2:1 ratio.

We attribute the first wave to reduction of the carbon-carbon triple bond. It is interesting that the half-wave potential for this process is 110 mV more positive than that (-1.88 V) for the reduction of 1-phenyl-1-hexyne.¹ There are two ways to account for this positive shift in the half-wave potential. First, a molecular model of 6-chloro-1-phenyl-1-hexyne shows that the alkyl chloride group can approach the triple bond very closely; thus, it is conceivable that the electronegative alkyl chloride center polarizes the triple bond, causing it to be more easily reduced than the acetylenic bond in 1-phenyl-1-hexyne. Second, if chemical reactions which follow the initial electron-transfer process are faster for 6-chloro-1-phenyl-1-hexyne than for 1-phenyl-1-hexyne, one should see a positive shift in the polaro-

graphic half-wave potential and the cyclic voltammetric peak potential for the former species; rate constants differing by a factor of at least 1000 would be required to cause a shift of 110 mV.¹⁴ As described subsequently, the radical anion of 6-chloro-1-phenyl-1-hexyne undergoes protonation and intramolecular cyclization; based on the observed product distribution, the rate of cyclization does not appear to be more than 20 times faster than the rate of protonation. Assuming that the rates of protonation of the radical anions of 6-chloro-1-phenyl-1-hexyne and 1-phenyl-1-hexyne are similar, we cannot attribute the positive shift in potential solely to differences in rate constants. Therefore, we conclude that the polar effect of the alkyl chloride group and the differing rate constants for the following reactions both contribute to the observed shift in half-wave potential.

Although the half-wave potential for the second polarographic wave is close to -2.05 V, exact measurement is difficult because of the final current rise due to reduction of the tetra-*n*-butylammonium cation just beyond -2.1 V. It appears that two different reactions—reduction of benzyldenecyclopentane and reduction of the carbon-halogen bond of 6-chloro-1-phenyl-1-hexyne—are responsible for the second wave. Benzyldenecyclopentane, which results from cyclization of an intermediate formed during the process corresponding to the first polarographic wave, exhibits its own two-electron reduction wave with a half-wave potential of -2.05 V. To test the possibility that reduction of the alkyl chloride group contributes to the second polarographic wave, the electrochemical behavior of 6-chloro-1-phenylhexane was examined. A single cathodic wave was observed with a half-wave potential near -2.1 V; when a controlled-potential electrolytic reduction of 6-chloro-1-phenylhexane was performed at -2.10 V, the products were 1-phenylhexane (95%) and 6-phenyl-1-hexene (5%).

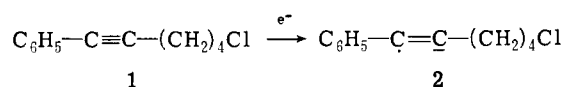
Undoubtedly, the second polarographic wave for 6-chloro-1-phenyl-1-hexyne does result from the superimposed reactions of the carbon-chlorine bond of the starting material and the electrolytically formed benzyldenecyclopentane; however, there is good evidence that reduction of the latter is predominant. Electrolyses performed at potentials on the second polarographic wave for 6-chloro-1-phenyl-1-hexyne show nearly the same distribution of four-, five-, and six-membered carbocycles and straight-chain products as electrolyses done at potentials on the first polarographic wave, as discussed later in this paper. If the carbon-chlorine bond did undergo appreciable direct electrolytic reduction, one should see an increase in the amounts of straight-chain products. Therefore, the logical conclusion is that, instead of direct reduction of the carbon-chlorine bond, chloride ion is displaced mainly upon cyclization of the radical anion formed by reduction of the triple bond. In addition, preliminary cyclic voltammetric studies of 6-chloro-1-phenyl-1-hexyne with a sessile mercury drop electrode have revealed an anodic wave for the presumed reoxidation of the radical anion of benzyldenecyclopentane which is almost as large as the second cathodic wave.

Controlled-Potential Electrolyses of 6-Chloro-1-phenyl-1-hexyne. Electrolyses performed at potentials in the region of the first polarographic wave for 6-chloro-1-phenyl-1-hexyne offer an excellent opportunity to study intramolecular nucleophilic displacement reactions of electrochemically produced radical anions. On the other hand, processes which occur during electrolyses at potentials corresponding to the second polarographic wave are more difficult to interpret mechanistically because of the concomitant reduction of the alkyl chloride moiety. Accordingly, most controlled-potential electrolyses of 6-chloro-1-phenyl-1-hexyne were carried out at -1.75 V or more positive potentials, but the potential region in the vicinity of the second polaro-

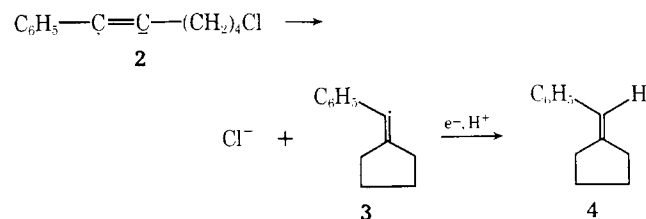
graphic wave has been examined briefly. However, the most interesting variable is the concentration of starting material. At sufficiently low concentrations, 6-chloro-1-phenyl-1-hexyne can be reduced without isomerizing to 6-chloro-1-phenyl-1,2-hexadiene. At concentrations larger than approximately 0.002 M, isomerization to and reduction of 6-chloro-1-phenyl-1,2-hexadiene become important, and the product distribution changes markedly.

An exhaustive controlled-potential electrolysis of a 2.5×10^{-4} M solution of 6-chloro-1-phenyl-1-hexyne in dimethylformamide containing 0.1 F tetra-*n*-butylammonium perchlorate was performed at -1.75 V. No evidence for isomerization of acetylene to allene was observed; the electrolysis current exhibited a normal exponential decrease with time, and polarograms recorded at intermediate stages of the electrolysis showed no wave for reduction of the allene.¹ At the end of the electrolysis, there was an abundance of benzyldenecyclopentane (81%) as well as smaller amounts of benzylcyclopentane (6%), 1-phenyl-1-hexyne (4%), *trans*-1-phenyl-1-hexene (3%), *cis*-1-phenyl-1-hexene (2%), *trans*-1-phenyl-2-hexene (2%), 1-phenylhexane (1%), and 1-benzylcyclopentene (<1%). Also present among the electrolysis products was tri-*n*-butylamine. As demonstrated previously for the reduction of 1-phenyl-1-hexyne,¹ the tetra-*n*-butylammonium cation is the ultimate source of protons for electrolytically generated carbanions, and tri-*n*-butylamine and 1-butene are produced by a Hofmann elimination process.

For the reduction of 6-chloro-1-phenyl-1-hexyne (**1**) at -1.75 V, we propose that all the hydrocarbon products result from secondary reactions of the radical anion **2** formed by addition of one electron to the carbon-carbon triple bond:



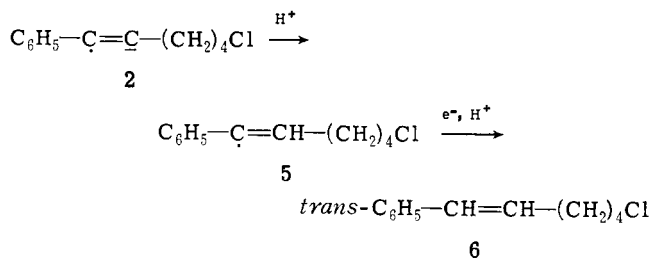
Intramolecular cyclization of **2** gives rise to benzyldenecyclopentane (**4**). However, for the low concentrations of 6-chloro-1-phenyl-1-hexyne required to prevent electrolytically induced isomerization of the acetylene to the allene isomer, the quantity of electricity passed is so small that it is difficult to determine unambiguously whether benzyldenecyclopentane is produced by addition of an electron to the cyclic radical precursor (**3**) followed by protonation



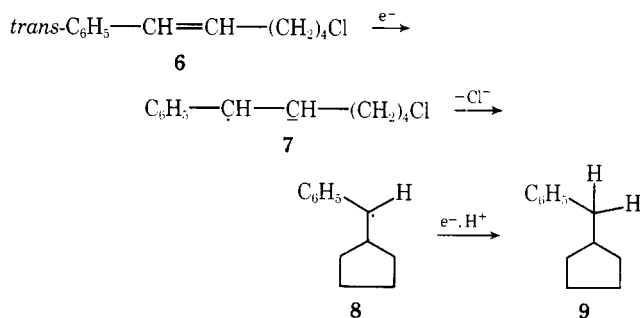
or whether benzyldenecyclopentane is formed upon abstraction of a hydrogen atom from a solvent molecule by the cyclic radical.¹⁵

There are two ways by which a small quantity (6%) of benzylcyclopentane could be formed—it might arise from electrochemical reduction of benzyldenecyclopentane, or it might result from an intramolecular reductive cyclization reaction involving *trans*-6-chloro-1-phenyl-1-hexene. Although the polarographic half-wave potential for benzyldenecyclopentane is approximately -2.05 V, it is conceivable that a slight amount of reduction occurs during a prolonged electrolysis at -1.75 V. To probe this possibility, a 0.003 M solution of benzyldenecyclopentane in dimethylformamide containing 0.1 F tetra-*n*-butylammonium perchlorate was stirred over a mercury pool at -1.75 V for sev-

eral hours; *no* benzylcyclopentane appeared, and benzylidenecyclopentane was quantitatively recovered. In competition with intramolecular cyclization of **2** is protonation of this species which, after addition of a second electron and proton, yields *trans*-6-chloro-1-phenyl-1-hexene (**6**):

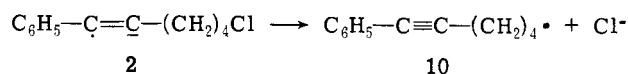


We have found *trans*-6-chloro-1-phenyl-1-hexene in samples taken *during* electrolyses of 6-chloro-1-phenyl-1-hexyne, although it is absent from the final roster of products. Subsequent reduction of *trans*-6-chloro-1-phenyl-1-hexene results in the formation of benzylcyclopentane (**9**) via intramolecular cyclization:



Inasmuch as benzylidenecyclopentane is formed to a much greater extent (81%) than benzylcyclopentane (6%), the rate of intramolecular cyclization of **2** appears to be approximately 13 times larger than its rate of protonation under the conditions of an electrolysis.

Other products obtained from the electrochemical reduction of 6-chloro-1-phenyl-1-hexyne at -1.75 V are 1-phenyl-1-hexyne, *trans*-1-phenyl-1-hexene, *trans*-1-phenyl-2-hexene, *cis*-1-phenyl-1-hexene, and 1-phenylhexane. However, at a potential of -1.75 V, direct electrochemical reduction of the carbon-chlorine bond is not possible. What process is responsible for the formation of 1-phenyl-1-hexyne and its characteristic reduction products? It is important to note that 1-phenyl-1-hexyne and its reduction products account for 12% of all species derived from 6-chloro-1-phenyl-1-hexyne at a concentration of starting material sufficiently low to render negligible bimolecular processes such as the isomerization of acetylene to allene discussed later. We suggest that intramolecular *chemical* reduction of the carbon-chlorine bond by the acetylenic radical anion takes place, resulting in formation of a primary alkyl radical (**10**) and chloride ion:¹⁶



Primary radical **10** is readily converted to 1-phenyl-1-hexyne whose pattern of electrochemical reduction is well established.¹ Intramolecular electron-transfer reactions have been observed previously.¹⁷⁻²⁰ For the electrochemical reduction of triphenylbromoethylene in dimethylformamide, Miller and Riekena¹⁷ proposed that chemical reduction of the carbon-bromine bond follows initial transfer of an electron to the lowest energy vacant π molecular orbital of the ethylene moiety.

Chemical reductions of alkyl halides by polynuclear aromatic radical-anions have been studied in detail,²¹⁻²³ however, no report of a corresponding reduction by an acetylenic radical anion has appeared. To examine the possibility of such a chemical process, 6-chloro-1-phenylhexane was treated with the radical anion of diphenylacetylene. A 0.005 *M* solution of diphenylacetylene was electrolyzed at -1.65 V, a potential on the first polarographic wave for the compound.²⁴ After 15 min, the dimethylformamide solution had acquired the deep-green color characteristic of the radical anion; then 50 μl of 6-chloro-1-phenylhexane was syringed into the working-electrode compartment. Within 10 to 15 sec, the green color changed dramatically to a deep purple, and the electrolysis current increased slightly, both effects indicating a reaction between the acetylenic radical anion and the alkyl chloride. Electrolysis was allowed to proceed for 1.5 hr, after which time gas chromatographic analysis showed that 1-phenylhexane (78%) and 6-phenyl-1-hexene (22%) were derived from 6-chloro-1-phenylhexane (of which approximately 50% was recovered unchanged). Thus, chemical reduction of an alkyl chloride by an acetylenic radical anion is a feasible process. This experiment lends credibility to the proposed mechanism of intramolecular electron transfer from the acetylenic radical anion to the alkyl chloride center upon electrochemical reduction of 6-chloro-1-phenyl-1-hexyne.

Formation and Reduction of 6-Chloro-1-phenyl-1,2-hexadiene. A large-scale controlled-potential electrolysis of a 0.0025 *M* solution of 6-chloro-1-phenyl-1-hexyne in dimethylformamide was performed at -1.75 V. As in our earlier study of the electrochemical reduction of 1-phenyl-1-hexyne,¹ rapid isomerization of the starting material to an allene (6-chloro-1-phenyl-1,2-hexadiene) was indicated by the appearance of a pronounced maximum in the current-time curve; this was accompanied by development of a dark-green color. Gas chromatographic analysis of the products after exhaustive electrolysis showed the presence of 1-benzylcyclopentene (36%), benzylidenecyclopentane (30%), benzylcyclopentane (13%), *trans*-1-phenyl-2-cyclobutylethylene (8%), 1-phenylcyclohexene (4%), *trans*-1-phenyl-1-hexene (3%), *trans*-1-phenyl-2-hexene (3%), *trans*-1-phenyl-1,5-hexadiene (2%), and 3-phenylcyclohexene (1%).

To confirm the presence of the allene, a 0.01 *M* solution of 6-chloro-1-phenyl-1-hexyne was electrolyzed at -1.75 V for 10 min until the characteristic current maximum was reached. Polarography revealed the presence of a new wave with a half-wave potential of -1.55 V due to reduction of 6-chloro-1-phenyl-1,2-hexadiene. Infrared and NMR spectroscopic evidence for the allene was identical with that seen in our previous work.¹ Gas chromatographic analysis showed that 6-chloro-1-phenyl-1,2-hexadiene and 6-chloro-1-phenyl-1-hexyne are partially but adequately resolved on a 10 ft column packed with 3% UCON Polar on 80-100 Chromosorb W. This made it possible to determine the amounts of allene (43%) and acetylene (42%) as well as the yields of the various reduction products comprising the remaining 15% of the material. Hence, 6-chloro-1-phenyl-1-hexyne is rapidly converted into 6-chloro-1-phenyl-1,2-hexadiene, and the quantities of the acetylene and allene isomers are nearly equal at the current maximum.

In another experiment, a 0.01 *M* solution of 6-chloro-1-phenyl-1-hexyne was electrolyzed at -1.75 V. Throughout the course of the reduction, aliquots of the solution were removed from the cell and were analyzed completely for all compounds present. In Table I are summarized analytical data taken at four different stages of electrolysis corresponding to 8, 44, 94, and 100% consumption of starting material. Striking differences are observed in the final prod-

Table I. Percentage Distribution of Species during Controlled-Potential Reduction of 0.01 *M* 6-Chloro-1-phenyl-1-hexyne at -1.75 V

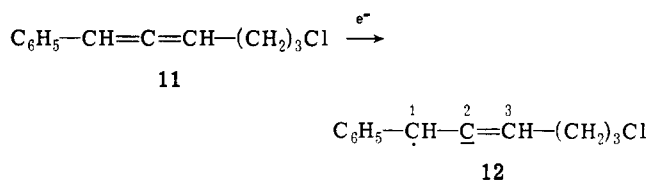
Species	Sample ^a			
	1	2	3	4
6-Chloro-1-phenyl-1-hexyne	39	26	3	
6-Chloro-1-phenyl-1,2-hexadiene	53	30	3	
1-Benzylcyclopentene	3	17	33	37
Benzylidenecyclopentane	3	14	29	29
Benzylcyclopentane		1	6	14
<i>trans</i> -1-Phenyl-2-cyclobutylethylene		2	7	9
1-Phenylcyclohexene			1	3
3-Phenylcyclohexene		2	3	2
<i>trans</i> -1-Phenyl-1,5-hexadiene		1	3	3
<i>trans</i> -1-Phenyl-2-hexene				2
<i>trans</i> -1-Phenyl-1-hexene				1

^a The following products were present in some samples (but not the final aliquot) in amounts indicated in parentheses: *trans*, *trans*-1-phenyl-1,3-hexadiene (<4%), *trans*-6-chloro-1-phenyl-1-hexene (<3%), $C_{12}H_{14}O$ (<2%), 1-phenyl-1-hexyne (<1%), 1-phenyl-1-hexyn-5-ene (<1%), *cis*-1-phenyl-1-hexene (trace), 1-phenyl-2-cyclobutylethane (trace).

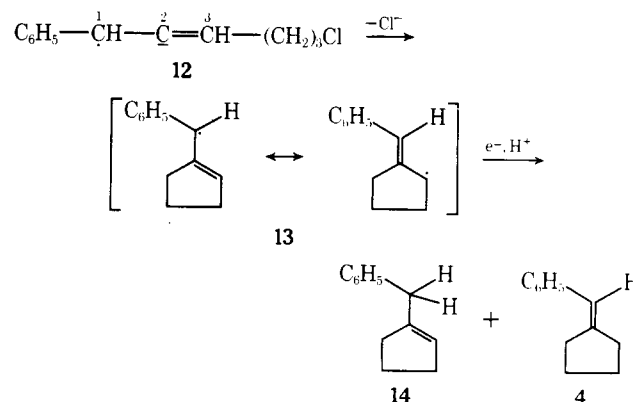
uct distributions obtained with 2.5×10^{-4} *M* starting material (for which there is no formation of allene) and with 0.01 *M* starting material (for which formation and reduction of the allene are prominent). For the higher concentration of starting material, notable differences are the presence of both four- and six-membered carbocycles and the tremendous increase in the amount of 1-benzylcyclopentene (from 1 to 37%) coupled with the corresponding decrease in the yield of benzylidenecyclopentane (from 81 to 29%).

To acquire a better understanding of the electrochemical processes, it was imperative to ascertain what products are formed when only 6-chloro-1-phenyl-1,2-hexadiene is reduced. Accordingly, electrolysis of a 0.0065 *M* solution of 6-chloro-1-phenyl-1-hexyne was begun at -1.75 V. Within minutes, when appearance of the current maximum indicated that the acetylene-to-allene isomerization had reached its greatest extent, the potential was readjusted to -1.57 V (at which only the allene undergoes reduction), and the electrolysis was continued until the current decayed to 0.5 mA. Although the final distribution of products was similar to that found upon exhaustive reduction of 0.01 *M* 6-chloro-1-phenyl-1-hexyne at -1.75 V (Table I), there was an increase in the amount of *trans*-1-phenyl-2-cyclobutylethylene (13%), a small increase in six-membered carbocyclic products (7%), and a decrease in the yield of five-membered carbocycles (66%), although the relative amounts of 1-benzylcyclopentene, benzylidenecyclopentane, and benzylcyclopentane were nearly the same. This similarity in the product distributions for electrolyses at -1.57 and -1.75 V suggests that, for initial concentrations of 6-chloro-1-phenyl-1-hexyne higher than approximately 0.0025 *M*, reduction proceeds largely through the allene isomer. Slightly increased yields of four- and six-membered carbocycles can be expected for the reduction of the allene at -1.57 V, because reduction of 6-chloro-1-phenyl-1-hexyne (which cannot occur at this potential) gives only five-membered carbocycles and straight-chain products.

Mechanism for Reduction of 6-Chloro-1-phenyl-1,2-hexadiene. The base-catalyzed isomerization responsible for production of 6-chloro-1-phenyl-1,2-hexadiene begins soon after the start of an electrolysis and is analogous to the isomerization of 1-phenyl-1-hexyne described earlier.¹ Once formed, 6-chloro-1-phenyl-1,2-hexadiene (**11**) is reduced by addition of one electron to the phenyl-conjugated double bond:

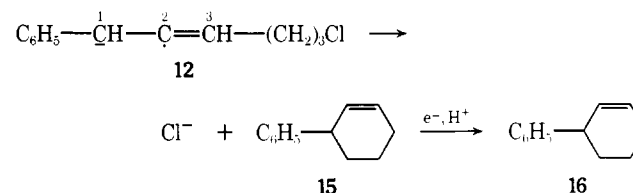


Radical anion **12** can undergo a relatively facile intramolecular cyclization with displacement of chloride, and the resulting cyclic allyl radical (**13**) is then further reduced and protonated to yield both 1-benzylcyclopentene (**14**) and benzylidenecyclopentane (**4**):



As a consequence of the formation of cyclic allyl radical **13**, an equilibrium distribution of 1-benzylcyclopentene and benzylidenecyclopentane is obtained. In fact, the 1-benzylcyclopentene-to-benzylidenecyclopentane ratio was always close to 1.3, in sharp contrast to reduction of a low concentration of 6-chloro-1-phenyl-1-hexyne which yields benzylidenecyclopentane almost exclusively.²⁵

Experimental evidence indicates that a small fraction of the negative charge on **12** resides on C₁. Though formation of both four- and six-membered carbocycles is associated with reduction of the allene isomer, analyses of samples withdrawn during early stages of several electrolyses have shown that production of 3-phenylcyclohexene definitely precedes the formation of *trans*-1-phenyl-2-cyclobutylethylene. In fact, the rapid appearance of 3-phenylcyclohexene (**16**) strongly suggests that it arises by the following intramolecular cyclization reaction:



This situation differs from that of the acetylenic radical anion **2** which yields benzylidenecyclopentane as the only cyclic product and which can therefore be accurately represented by a single resonance form. However, because the yield of five-membered carbocycles derived from 6-chloro-1-phenyl-1,2-hexadiene greatly exceeds that of six-membered rings, the radical anion initially formed from 6-chloro-1-phenyl-1,2-hexadiene is best represented by the resonance structure in which the negative charge is located on C₂.

After radical anion **12** is formed, there is competition between intramolecular cyclization and protonation similar to that previously described for radical anion **2**. Protonation of **12** at C₂ yields an allyl radical (**17**) which is further reduced to an allylic anion:

clopente is difficult to refute on the basis of work done only with 6-chloro-1-phenyl-1-hexyne. However, our recent studies of the reductions of 6-bromo- and 6-iodo-1-phenyl-1-hexyne, for which **10** is generated at potentials near -1.75 V, indicate that 1-phenyl-1-hexyne is the major product; therefore, it is quite unlikely that conversion of **10** to **3** takes place to any appreciable extent.

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 (25) An alternate pathway can be suggested for the formation of **4** and **14** from **12** which is mechanistically similar to that mentioned in ref 16 for the conversion of **10** to **3**. Thus, **12** could yield the species $C_6H_5CH=C=CH(CH_2)_3$ that cyclizes intramolecularly to give **13** which leads to **4** and **14**. If this process did occur, one should obtain more $C_6H_5CH=C=CH(CH_2)_2CH_3$ and its reduction products as the concentration of starting material increases; however, the yield of these reduction products definitely decreases with increasing involvement of the allene at higher starting-material concentrations, indicating that this alternate pathway is unimportant.

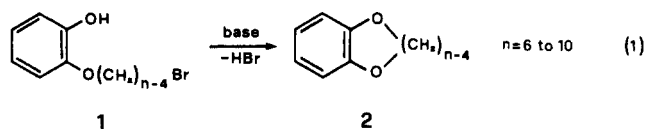
Ring-Closure Reactions. V.¹ Kinetics of Five- to Ten-Membered Ring Formation from *o*- ω -Bromoalkylphenoxides. The Influence of the O-Heteroatom

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Abstract: Rates and activation parameters have been determined for the intramolecular Williamson synthesis of coumaran, chroman, and their higher homologs up to ring size ten, starting from the corresponding *o*- ω -bromoalkylphenoxides in 75% ethanol solution. Interestingly, the entropy of activation was found to decrease linearly with increasing chain length, with an average drop of 4 eu per added methylene group. Eight- and nine-membered ring closures are accompanied by significant amounts of the isomeric open-chained alkenylphenols, which are believed to result from a peculiar intramolecular β -elimination reaction of the E2 type. Enthalpy of activation data indicate that strain in the cyclic transition states is highest for ring sizes eight and nine. Therefore, the side reaction becomes favored as a consequence of a steric factor responsible for the increase in the elimination/substitution ratio. Comparison of the present data with those previously established for a closely related system, i.e., the formation of catechol polymethylene ethers from *o*- ω -bromoalkoxyphenoxides has allowed an assessment of the influence of the oxygen atom on ease of ring closure. Replacement of a methylene group by an oxygen atom causes a rate enhancement which is largest for the most strained eight- and nine-membered rings. This effect is discussed in terms of strain and other factors.

It is well known that medium ring compounds (8- to 11-membered) exhibit special features when compared with rings of either smaller or greater ring size. The structural effects responsible for a special behavior are angular distortions, eclipsing interactions, and van der Waals repulsions of atoms across the rings.² A dissection into the different contributions has been recently effected on a theoretical basis by Allinger et al. for the series of cycloalkanes.³ It was shown that angle deformation and van der Waals interaction are particularly severe for the medium rings and are responsible for most of the total strain energy. When the variation of both physical and chemical properties of ring compounds as a function of ring size are considered, extrema are often found in the medium ring region. In particular, one of such extrema, namely a deep minimum in ring-closure tendency, was apparent in the early history of the many-membered rings on attempted medium ring formation by Ruzicka's cyclization reaction of dicarboxylic acids salts^{2,4} and is generally regarded as the most characteristic feature of the medium rings. However, the rates of cyclization of conjugate bases of *o*- ω -bromoalkoxyphenols **1** to the corresponding catechol polymethylene ethers **2** were found by us⁵ to display no minimum but, rather, to decrease con-



tinuously with increasing chain length, in agreement with Ziegler's early semiquantitative work.⁶ In macro ring chemistry, the presence of rigid groups and/or oxygen atoms in place of one or more methylene groups has long been known to enhance ring-closure tendency.² More recently, calculations by Allinger et al.⁷ showed that medium ring ketones and *cis*-alkenes are significantly less strained (by 2.5–5.4 kcal/mol) than the corresponding cycloalkanes. Accordingly, the presence of the O—C=C—O moiety in the cyclic ethers **2** was held responsible for the lack of a minimum in ring-closure reactivity.⁶ In order to assess the relative contributions of the double bond and oxygen atoms, rate data for the formation of the homocyclic rings **3** would

