

on the NMR time scale because the ^{31}P coupling to the protons of the β -methyl group in Va and Vb was clearly observed. Furthermore, the gated proton decoupled ^{13}C NMR spectrum of Va in $\text{DMSO}-d_6$ showed a dd at δ 61.2 with $^1J_{^{13}\text{C}-\text{H}} = 148$ Hz and $^1J_{^{13}\text{C}-\text{P}} = 61$ Hz for the hydroxylic carbon. This resembles the parameters reported¹⁰ for the "ylid carbon" resonance of $\text{Cp}(\text{NO})(\text{I})\text{Mo}[\eta^2\text{-OC}(\text{PMe}_3)\text{-}(p\text{-C}_6\text{H}_4\text{Me})]$ at δ 72.2 with $^1J_{^{13}\text{C}-\text{P}} = 60.3$ Hz. The silaacyl adduct $\text{Cp}^*\text{Cl}_3\text{Ta}[\eta^2\text{-OC}(\text{PEt}_3)\text{SiMe}_3]$ differs from the preceding examples with a δ 78.0 doublet ($^1J_{^{13}\text{C}-\text{P}} = 7.5$ Hz) observed for the acyl derived carbon; however, P-C couplings to metal bound carbons show a high variability.⁹ A dq at δ 4.6 with $^1J_{^{13}\text{C}-\text{H}} = 133$ Hz and $^1J_{^{13}\text{C}-\text{P}} = 51$ Hz in the spectrum of Va may be assigned to the phosphine methyl groups and a quartet at δ 16.5 with $^1J_{^{13}\text{C}-\text{H}} = 128$ Hz to the remaining methyl group.

Scheme II displays a suggested mechanism for the formation of I-V. It is not clear whether HX or PR_3 addition

to the carbonyl group occurs first, so both possibilities are included in the scheme. Although it is likely that the synthesis of the 1-OTMS derivative occurs by the right-hand path of Scheme II, the possibility of acid catalysis (left path) cannot be excluded.

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Supplementary Material Available: Tables of positional parameters of hydrogen atoms and anisotropic thermal parameters for the phosphorus atom (2 pages); listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Electrochemical Reduction and Intramolecular Cyclization of 6-Iodo-1-phenyl-1-hexyne at Vitreous Carbon Cathodes in Dimethylformamide

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In dimethylformamide containing a tetraalkylammonium perchlorate, a cyclic voltammogram for reduction of 6-iodo-1-phenyl-1-hexyne at a glassy carbon electrode exhibits three prominent waves corresponding to cleavage of the carbon-iodine bond and to subsequent reductions of 1-phenyl-1-hexyne and benzyldenecyclopentane. At potentials for which only reduction of the carbon-iodine bond occurs, large-scale electrolyses of 6-iodo-1-phenyl-1-hexyne afford benzyldenecyclopentane and 1-phenyl-1-hexyne; the yield of the carbocycle, averaging 36%, is insensitive to potential, but the quantity of 1-phenyl-1-hexyne varies from 28 to 48% as the potential is chosen to be more negative. In the presence of diethyl malonate as a proton donor, the quantity of benzyldenecyclopentane changes little, the yield of 1-phenyl-1-hexyne decreases, and substantial (>33%) diethyl (1-phenyl-1-hexyn-6-yl)malonate is obtained. With 1,1,1,3,3,3-hexafluoroisopropyl alcohol as proton source, the yield of benzyldenecyclopentane increases to approximately 60%, whereas the quantity of 1-phenyl-1-hexyne decreases somewhat. It appears that each of the major hydrocarbon products is formed via a combination of one- and two-electron processes.

For a number of years, we have been interested in the electrochemical reduction and intramolecular cyclization of acetylenic halides.¹⁻⁴ In dimethylformamide containing tetra-*n*-butylammonium perchlorate, electrolysis of a low concentration (<1 mM) of 6-chloro-1-phenyl-1-hexyne at a mercury cathode¹ proceeds via reduction of the carbon-carbon triple bond to yield a radical anion that cyclizes with displacement of chloride to afford predominantly benzyldenecyclopentane; however, at a higher concentration (>2 mM), the acetylenic chloride undergoes extensive electrolytically induced, base-catalyzed rearrangement to 6-chloro-1-phenyl-1,2-hexadiene, and reduction of the allene leads to formation of a number of carbocyclic and acyclic species, the two principal products being 1-benzylcyclopentane and benzyldenecyclopentane.

Unlike the behavior of 6-chloro-1-phenyl-1-hexyne, the reductions of 6-iodo- and 6-bromo-1-phenyl-1-hexyne at

mercury in dimethylformamide containing tetra-*n*-butylammonium perchlorate² initially involve one-electron scission of the carbon-halogen bond and are complicated by the formation of substantial amounts of diorganomercury compounds. Benzyldenecyclopentane, the desired product, can be obtained in a yield no higher than 24% from the acetylenic iodide, and the quantity of this carbocycle declines as the potential is made more negative.

Reduction of 1-iodo- and 1-bromo-5-decyne has been examined with the aid of both mercury³ and carbon⁴ electrodes in dimethylformamide containing several different tetraalkylammonium perchlorates. Because these starting materials possess no phenyl-conjugated acetylenic bond, the only electrochemically reducible site is the carbon-halogen moiety. At potentials for which the 5-

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decyn-1-yl radical is generated at a mercury cathode, bis(5-decyn-1-yl)mercury is the major product, although 5-decyne and pentylidenecyclopentane can each be obtained in low yield (<10%); if the potential of a mercury electrode is sufficiently negative to produce the 5-decyn-1-yl carbanion, the amount of diorganomercury compound decreases at the expense of both 5-decyne and 1-decen-5-yne, whereas the quantity of pentylidenecyclopentane falls to approximately 1%. At a vitreous carbon cathode, 1-iodo- and 1-bromo-5-decyne both undergo net two-electron reduction to the 5-decyn-1-yl anion. However, the transient 5-decyn-1-yl radical, when formed by electrolysis of the acetylenic iodide at a carbon surface, persists long enough to cyclize, thereby affording pentylidenecyclopentane in a yield of up to 46%, together with 5-decyne and 1-decen-5-yne; the last two compounds are the major products derived from 1-bromo-5-decyne. If one adds a proton donor (1,1,1,3,3,3-hexafluoroisopropyl alcohol) that can block dehydrohalogenation of 1-iodo-5-decyne and that can make more of the starting material available for electrolytic reduction, pentylidenecyclopentane is obtained in at least 60% yield.

In the research reported in this paper, we have studied the electrochemical reduction of 6-iodo-1-phenyl-1-hexyne at carbon instead of mercury electrodes in order to avoid the formation of diorganomercury species and in an effort to enhance the production of benzylidenecyclopentane. In addition, during the course of this work, we have investigated the cyclic voltammetric behavior of benzylidenecyclopentane, we have observed that 1-phenyl-1-hexyne (an electrolysis product) undergoes electrolytically induced isomerization to 1-phenyl-1,2-hexadiene, and we have discovered that, in contrast to what has been seen previously with a mercury cathode, the potential for reduction of the carbon-iodine bond of 6-iodo-1-phenyl-1-hexyne at carbon in dimethylformamide is unaffected by the identity of the supporting electrolyte.

Experimental Section

Reagents. Dimethylformamide employed as solvent was "distilled in glass" material purchased from American Burdick & Jackson Laboratories, Inc.; it was stored over 4-Å molecular sieves for at least 24 h prior to any electrochemical experiment. Tetramethylammonium perchlorate and tetra-*n*-butylammonium perchlorate, which served as supporting electrolytes, were obtained from the G. Frederick Smith Chemical Co. and were used without further purification. Diethyl malonate (Fisher) and 1,1,1,3,3,3-hexafluoroisopropyl alcohol (Aldrich) utilized as proton donors were used as received. Deaeration of all solutions for electrochemical experiments was accomplished with the aid of Air Products zero-grade argon.

Synthesis of 6-Iodo-1-phenyl-1-hexyne. This starting material was synthesized, as described in an earlier publication,² from *n*-butyllithium, phenylacetylene, and 1,4-diodobutane and was recovered in approximately 97% purity by means of vacuum distillation, bp 140–143 °C (0.3 Torr): mass spectrum (obtained with a Kratos Model MS80 RFQQ instrument) *m/e* 284, M⁺ (8.9); 157, M⁺ - I (25.6); 129, M⁺ - C₂H₄I (39.9); 115, M⁺ - C₃H₆I (100); 91, M⁺ - C₃H₆I (44.6); 77, M⁺ - C₆H₈I (16.7).

Instrumentation and Procedures. A description of the cells and general techniques for cyclic voltammetry and controlled-potential coulometry can be found in previous publications.⁵⁻⁷ Vitreous carbon electrodes for the cyclic voltammetric experiments consisted of short lengths of 3-mm-diameter glassy carbon rods (grade GC-20, Tokai Electrode Manufacturing Co., Tokyo, Japan)

press fitted into Teflon shrouds. Electrodes for controlled-potential electrolyses were disks cut from blocks of reticulated vitreous carbon (RVC 2X1-45S, Energy Research and Generation, Inc., Oakland, CA). Procedures for polishing, cleaning, and handling the carbon electrodes appear in a previous publication.⁸

Cyclic voltammetric experiments were performed with the aid of a Princeton Applied Research Corporation (PARC) Model 175 Universal Programmer coupled to a PARC Model 173 potentiostat-galvanostat, and current-potential curves were recorded with a Houston Instruments Model 2000-5-5 X-Y plotter. Controlled-potential electrolyses were done through the use of the potentiostat-galvanostat equipped with a PARC Model 176 current-to-voltage converter that provided *iR* compensation. Each preparative-scale electrolysis was controlled by means of an IBM personal computer interfaced to the potentiostat via a home-built analog-to-digital converter; the current-time curve was monitored, stored, and integrated to provide the coulometric *n* value for the electrolysis. All potentials in this paper 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;^{8,9} this electrode has a potential of -0.76 V vs the aqueous saturated calomel electrode at 25 °C.

Gas chromatographic analyses were accomplished with the aid of a Varian Model 3700 dual-column instrument equipped with flame ionization detectors and coupled to a Spectra Physics Model SP 4400 integrator. Products were separated with a 10 m × 0.53 mm, wide-bore, capillary column (RSL-300, Alltech Associates) that uses poly(phenylmethylsiloxane) as the stationary phase. A known amount of a nonelectroactive internal standard (*n*-decane) was added to the solution before each experiment to quantitate the various compounds obtained from a large-scale electrolysis. Gas chromatographic response factors were measured experimentally with authentic samples of each product, and all yields tabulated in this paper represent the absolute percentage of 6-iodo-1-phenyl-1-hexyne incorporated into a particular species.

Product Identification. We identified 1-phenyl-1-hexyne as an electrolysis product by comparing its gas chromatographic retention time with that of an authentic, commercially obtained sample. Benzylidenecyclopentane was similarly verified as a product because its properties matched those of an independently synthesized¹⁰ sample. A third product, found only when diethyl malonate is employed as a proton donor in electrolyses of 6-iodo-1-phenyl-1-hexyne, is diethyl (1-phenyl-1-hexyn-6-yl)-malonate. For the synthesis of this last compound, 18.1 mL (0.12 mol) of diethyl malonate was added, slowly and with stirring, to a solution of 2.3 g (0.10 mol) of sodium in 60 mL of absolute ethanol; this step was followed by the addition of 23.7 g (0.10 mol) of 6-bromo-1-phenyl-1-hexyne, prepared according to the procedure used for 6-iodo-1-phenyl-1-hexyne. This mixture was stirred for 1 h and then partitioned between diethyl ether and water; the ether phase was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated by evaporation. Pure (>96%) diethyl (1-phenyl-1-hexyn-6-yl)malonate was collected by means of vacuum distillation: bp 182–185 °C (0.3 Torr); electron-impact mass spectrum (70 eV) *m/e* 316, M⁺ (0.5); 271, M⁺ - C₂H₅O (13.5); 243, M⁺ - C₃H₅O₂ (16.4); 115, M⁺ - C₁₀H₁₇O₄ (100); chemical-ionization mass spectrum *m/e* 317, M⁺ + 1 (2.7); 271, M⁺ - C₂H₅O (21.0); 243, M⁺ - C₃H₅O₂ (32.2); 157, M⁺ - C₇H₁₁O₄ (34.5); 115, M⁺ - C₁₀H₁₇O₄ (100); 91, M⁺ - C₁₂H₁₇O₄ (76.9); 77, M⁺ - C₁₃H₁₉O₄ (11.2).

Results and Discussion

Cyclic Voltammetric Behavior of 6-Iodo-1-phenyl-1-hexyne and Its Electrolysis Products. Shown in Figure 1 are two cyclic voltammograms obtained with a freshly polished glassy carbon electrode at a scan rate of 100 mV s⁻¹ for a 2.5 mM solution of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing either tetramethylammonium perchlorate or tetra-*n*-butylammonium

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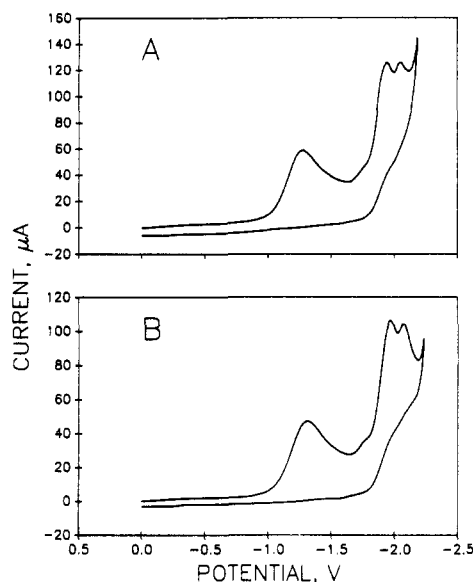


Figure 1. Cyclic voltammograms for a 2.5 mM solution of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate (curve A) and 0.1 M tetra-*n*-butylammonium perchlorate (curve B) recorded with a glassy carbon electrode (area = 0.077 cm²) at a scan rate of 100 mV s⁻¹.

perchlorate as supporting electrolyte. Each of the cyclic voltammograms exhibits three well-defined waves; with 0.1 M tetramethylammonium perchlorate (Figure 1A), the peak potentials are -1.29, -1.96, and -2.07 V, whereas the corresponding peak potentials are -1.31, -1.97, and -2.08 V in the presence of 0.1 M tetra-*n*-butylammonium perchlorate (Figure 1B). In addition, at the foot of the second wave for each cyclic voltammogram is a poorly defined small shoulder at approximately -1.76 V. On the basis of an earlier investigation⁶ of the cyclic voltammetric behavior of 1-iododecane at a glassy carbon electrode, the first wave for reduction of 6-iodo-1-phenyl-1-hexyne is ascribed to electrolytic cleavage of the carbon-iodine bond. It is evident from research¹¹⁻¹³ pertaining to the electrochemistry of 1-phenyl-1-hexyne that the second wave is caused by reduction of the alkyne and that the small shoulder at -1.76 V is most likely due to reduction of 1-phenyl-1,2-hexadiene arising from electrolytically induced, base-catalyzed isomerization of the alkyne; when cyclic voltammograms are recorded for solutions of 6-iodo-1-phenyl-1-hexyne containing a proton donor (diethyl malonate), the alkyne-to-allene rearrangement is blocked and the small wave at -1.76 V does not appear. Finally, from our own studies of the electrochemical characteristics of authentic benzylidenecyclopentane, we have established that the third major cathodic wave for each cyclic voltammogram in Figure 1 arises from reduction of the carbocycle.

A surprising observation revealed in Figure 1 is that the peak potential for reduction of the carbon-iodine bond of 6-iodo-1-phenyl-1-hexyne is virtually unaffected by the identity of the supporting electrolyte; as mentioned in the preceding paragraph, the peak potentials are -1.29 and -1.31 V, respectively, in the presence of tetramethylammonium perchlorate and tetra-*n*-butylammonium perchlorate. Moreover, in a separate investigation of the cyclic voltammetric behavior of 1-iododecane at a freshly polished glassy carbon electrode in dimethylformamide, we found that the peak potential for reductive cleavage

Table I. Coulometric Data and Product Distributions for Electrolytic Reduction of 6-Iodo-1-phenyl-1-hexyne at Carbon in Dimethylformamide Containing Tetraalkylammonium Perchlorates

| condtn ^a | potntl, V | <i>n</i> | product distribution, % | | |
|---------------------|-----------|----------|-----------------------------------|-----------------------|------------------------|
| | | | benzylid- enecyclo- pentane | 1-phenyl- 1-hexyne | unredcd startg matl |
| TMAP | -1.40 | 0.75 | 38 | 28 | 11 |
| TMAP | -1.60 | 0.89 | 33 | 48 | |
| TBAP | -1.70 | 1.01 | 37 | 43 | |

^aTMAP = 0.1 M tetramethylammonium perchlorate, TBAP = 0.1 M tetra-*n*-butylammonium perchlorate.

of the carbon-iodine bond is -1.36 V with 0.1 M tetramethylammonium perchlorate and -1.40 V with 0.1 M tetra-*n*-butylammonium perchlorate. These results contrast dramatically with those found in earlier investigations^{2,14} of the polarographic behavior of 6-iodo-1-phenyl-1-hexyne and 1-iododecane; half-wave potentials for the first, one-electron step in the reduction of the carbon-iodine bond for each compound at mercury in dimethylformamide are -0.88 and -0.86 V, respectively, in the presence of 0.1 M tetramethylammonium perchlorate and are -1.25 and -1.19 V, respectively, in the presence of 0.1 M tetra-*n*-butylammonium perchlorate. Similar large shifts in half-wave and peak potentials due to changes in supporting electrolyte have been seen in other studies^{3,5,15-18} of the electrolytic reduction of alkyl iodides and bromides at mercury cathodes. We hope to examine this phenomenon more thoroughly in some future work.

Controlled-Potential Electrolysis of 6-Iodo-1-phenyl-1-hexyne. To avoid possible electrolytically induced isomerization of 1-phenyl-1-hexyne to 1-phenyl-1,2-hexadiene¹⁹ and to prevent any reduction of benzylidenecyclopentane, we performed preparative-scale electrolyses of 6-iodo-1-phenyl-1-hexyne only at potentials in the region of the first cyclic voltammetric wave, which corresponds to reduction of the carbon-iodine bond. As a result, just two readily identifiable products, 1-phenyl-1-hexyne and benzylidenecyclopentane, are formed.

Summarized in Table I are coulometric data and product distributions obtained from electrolyses of 2.5 mM solutions of starting material in dimethylformamide containing either tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate. At the least negative potential employed, namely -1.40 V, we noticed that the electrolysis was incomplete, as indicated by the recovery of approximately 11% of the starting material and by a relatively low coulometric *n* value (0.75), although the potential chosen is more negative than the peak potential for the first cyclic voltammetric wave and although the current did decay to the background level during the course of the electrolysis.

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(19) If the potential is negative enough to electrolyze 1-phenyl-1-hexyne at the concentration levels of 6-iodo-1-phenyl-1-hexyne used in these experiments, the alkyne-to-allene isomerization will occur and reduction of 1-phenyl-1,2-hexadiene will lead to the production of *cis*- and *trans*-1-phenyl-1-hexene and *trans*-1-phenyl-2-hexene as demonstrated in ref 11; moreover, the alkyne-to-allene isomerization is signaled by an unusual maximum in the current-time curve recorded during an electrolysis and by the appearance of a red-colored species (probably an allylic anion) in solution.

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Table II. Coulometric Data and Product Distributions for Electrolytic Reduction of 6-Iodo-1-phenyl-1-hexyne at Carbon in Dimethylformamide Containing Tetraalkylammonium Perchlorates and Proton Donors

| condtns ^a | potntl, V | <i>n</i> | product distribution, % | | | |
|----------------------|-----------|----------|-------------------------|-------------------|---|---------------------|
| | | | benzylidenecyclopentane | 1-phenyl-1-hexyne | diethyl (1-phenyl-1-hexyn-6-yl)malonate | unredcd startg matl |
| TMAP, DEM | -1.40 | 0.84 | 42 | 11 | 42 | 6 |
| TMAP, HFIP | -1.40 | 0.72 | 37 | 13 | | 50 |
| TMAP, DEM | -1.60 | 1.50 | 41 | 31 | 33 | |
| TMAP, HFIP | -1.60 | 1.61 | 59 | 36 | | |
| TBAP, DEM | -1.70 | 1.05 | 29 | 20 | 46 | |
| TBAP, HFIP | -1.70 | 1.64 | 61 | 31 | | 4 |

^aTMAP = 0.1 M tetramethylammonium perchlorate, TBAP = 0.1 M tetra-*n*-butylammonium perchlorate, DEM = 10 mM diethyl malonate, HFIP = 10 mM 1,1,1,3,3,3-hexafluoroisopropyl alcohol.

With the preceding facts in mind, we obtained a set of cyclic voltammograms with an initially freshly polished glassy carbon electrode for a 2.5 mM solution of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate at a scan rate of 20 mV s⁻¹. We observed that, after 10 cyclic voltammograms were recorded, the peak potential for the first wave had shifted approximately 200 mV in the negative direction. Similar behavior has been previously encountered in an investigation of the reduction of 1-iododecane at a carbon cathode in dimethylformamide containing tetramethylammonium perchlorate.⁶ This shift in the peak potential implies that, although the electrolysis is begun at a potential more negative than the peak potential, there may come a time during the electrolysis when the initially chosen potential may correspond only to the rising portion of the wave for reduction of the carbon-iodine bond or even to a value too positive for any significant electrolysis of the starting material. It is conceivable that the peak potential shifts and the electrolysis fails to reach completion because a product is adsorbed onto the surface of the cathode. Indeed, when we performed an electrolysis of a 10 mM solution of 6-iodo-1-phenyl-1-hexyne at -1.60 V in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate, the coulometric *n* value was only 0.04 and approximately 89% of the starting material remained unreduced. On the basis of these findings, we have conducted the majority of our electrolyses with 2.5 mM solutions of 6-iodo-1-phenyl-1-hexyne and at potentials considerably more negative than the peak of the first cyclic voltammetric wave.

Inspection of Table I reveals that, at less negative potentials, benzylidenecyclopentane is obtained in higher yield than 1-phenyl-1-hexyne; on the other hand, the alkyne is produced in greater abundance than the carbocycle at more negative potentials. This is precisely the same trend seen in our earlier investigation of the reduction of 1-iodo-5-decyne at carbon electrodes.⁴ Another observation in the present work is the absence of 1-phenyl-5-hexen-1-yne and 1-phenyl-1-hexyn-6-ol, products that result, respectively, from the E2 and S_N2 attack of hydroxide ion (arising from deprotonation of adventitious water in the supporting electrolyte-solvent by electrogenerated carbanions) on the starting material. For the electrolysis of 6-iodo-1-phenyl-1-hexyne at mercury cathodes,² such elimination and displacement reactions do occur, though only to a small extent (5% or less). For the reductions of both 1-iodo- and 1-bromo-5-decyne at mercury³ and carbon⁴ electrodes, the E2 process can lead to the formation of 1-decen-5-yne in yields as high as 33%, but 5-decyn-1-ol is produced in no more than 2% yield via the S_N2 reaction. It should be noted in Table I that we have not accounted for approximately 20% of the starting material. In previous work dealing with electrochemical

reductions of 6-iodo-1-phenyl-1-hexyne,² 1-iodo-5-decyne,^{3,4} 1-iododecane,¹⁴ and 1,10-diiododecane,²⁰ we have postulated and, in two papers, experimentally demonstrated that a family of telomers is formed, most likely via processes that involve attack of a solvent-derived radical on an olefinic moiety; such reactions, if highly efficient, can account for the missing starting material as well as for the total absence of 1-phenyl-5-hexen-1-yne.

Electrolysis of 6-Iodo-1-phenyl-1-hexyne in the Presence of Added Proton Donors. To gain more information about the mechanism for the electrochemical reduction of the carbon-iodine bond of 6-iodo-1-phenyl-1-hexyne, electrolyses were undertaken in the presence of species capable of protonating electrogenerated carbanions; previous work^{3,4,6,17,20,21} has shown that diethyl malonate and 1,1,1,3,3,3-hexafluoroisopropyl alcohol are effective proton donors that, in addition, prevent the base-catalyzed isomerization of 1-phenyl-1-hexyne to 1-phenyl-1,2-hexadiene. Table II lists coulometric data and product distributions for electrolyses of 2.5 mM solutions of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetraalkylammonium perchlorates and 10 mM proton donor. When 6-iodo-1-phenyl-1-hexyne is electrolyzed in the presence of either diethyl malonate or 1,1,1,3,3,3-hexafluoroisopropyl alcohol, it is notable that, within the limits of experimental uncertainty, we can account for *all* of the starting material; unlike electrolyses done without a proton donor, no 1-phenyl-5-hexen-1-yne should form because dehydrohalogenation is blocked by a proton donor and, as a consequence, it appears that no telomers are produced.

At more negative potentials, the coulometric *n* values are generally higher in the presence (Table II) than in the absence of a proton donor (Table I). When diethyl malonate is employed as a source of protons, substantial amounts of diethyl (1-phenyl-1-hexyn-6-yl)malonate are formed via attack of the diethyl malonate anion on unreduced starting material, as suggested in earlier work^{3,4,6,17,20,21}—a result demonstrating the intermediacy of carbanions. Whereas the use of diethyl malonate has no beneficial effect on the production of benzylidenecyclopentane, the yield of the carbocycle reaches approximately 60% when 1,1,1,3,3,3-hexafluoroisopropyl alcohol is the proton donor. Both proton donors cause a decrease in the quantity of 1-phenyl-1-hexyne that is formed.

Mechanistic Aspects of the Reduction of 6-Iodo-1-phenyl-1-hexyne at Carbon. Although previous voltammetric evidence^{4,5} indicates that reductive cleavage of the carbon-iodine bond of 6-iodo-1-phenyl-1-hexyne is a

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two-electron process at a vitreous carbon cathode, it is reasonable to expect the product of a one-electron transfer, namely, the 1-phenyl-1-hexyn-6-yl radical, to be at least a transient species. According to Crandall and Keyton,²² the 1-phenyl-1-hexyn-6-yl radical should undergo intramolecular cyclization preferentially *before* hydrogen atom abstraction from solvent; therefore, when derived from the radical intermediate, benzyldenecyclopentane, not 1-phenyl-1-hexyne, is the favored product. On the other hand, the 1-phenyl-1-hexyn-6-yl carbanion is more likely to accept a proton from water (present as an impurity in the supporting electrolyte-solvent) or some other donor to afford 1-phenyl-1-hexyne than it is to undergo intramolecular cyclization to give the anionic precursor of benzyldenecyclopentane. However, there is another pathway by which the carbocycle can be produced; *after* the 1-phenyl-1-hexyn-6-yl radical cyclizes, the cyclized radical could accept an electron and then a proton to yield benzyldenecyclopentane.

To correlate the absolute yields of benzyldenecyclopentane and 1-phenyl-1-hexyne with the coulometric n values listed in Tables I and II, it is necessary to propose that each of these products arises through a combination of one- and two-electron processes. There are several pieces of evidence that support this conclusion. First, in our previous study of the electrochemical reduction of 1-iodo-5-decyne at carbon electrodes,⁴ electrolyses carried out in the presence of 1 M D₂O revealed that up to 10% of the resulting pentyldenecyclopentane was monodeuteriated at the vinyl position. Such a finding indicates that the cyclized 5-decyn-1-yl radical does undergo some reduction to yield, after protonation, the carbocycle. Crandall and Keyton²² concluded similarly in their investigation of the formation of benzyldenecyclopentane upon reduction of 6-bromo-1-phenyl-1-hexyne with excess lithium biphenyl in tetrahydrofuran. At the same time, these results demonstrate that the major pathway for intramolecular reductive cyclization of these acetylenic halides is a one-electron process. Second, when 1-iodo-5-decyne was electrolyzed at carbon in the presence of D₂O in our aforementioned study,⁴ at least 50% of the resulting 5-decyne was monodeuteriated. We actually interpreted this observation, along with other information, to mean that more than one-half of the 5-decyne was derived from a carbanion intermediate; however, the possibility that some 5-decyne forms by transfer of a hydrogen atom to the 5-decyn-1-yl radical is not precluded, and a similar situation should prevail (to a lesser extent) for the production of 1-phenyl-1-hexyne from the 1-phenyl-1-hexyn-6-yl radical in dimethylformamide. Third, the appearance of diethyl (1-phenyl-1-hexyn-6-yl)malonate in considerable yield, when 6-iodo-1-phenyl-1-hexyne is reduced at carbon in a system containing diethyl malonate (Table II), requires the intermediacy of the 1-phenyl-1-hexyn-6-yl carbanion.

A final point concerns the ability of 1,1,1,3,3,3-hexafluoroisopropyl alcohol to improve the yield of benzyldenecyclopentane, as seen from the data in Table II. We speculate that, at the more negative potentials for which

this enhancement of yield occurs, the alcohol is adsorbed onto the surface of the carbon cathode. Conceivably, this adsorbed material might (i) facilitate intramolecular cyclization of the initially formed 1-phenyl-1-hexyn-6-yl radical as well as further reduction of the cyclized radical to the anion at the electrode and (ii) serve as a local source of protons to afford benzyldenecyclopentane.

Synthetic Aspects of the Reduction of 6-Iodo-1-phenyl-1-hexyne at Carbon. At the outset of this work, our principal goal was to obtain benzyldenecyclopentane in maximal yield by electrochemical reduction of 6-iodo-1-phenyl-1-hexyne. As the data in Table II show, the desired carbocycle can be produced in 61% yield from an electrolysis done at -1.70 V in the presence of 10 mM 1,1,1,3,3,3-hexafluoroisopropyl alcohol in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate. Although the peculiar effect of this proton donor on the production of benzyldenecyclopentane is not readily explicable at this time, we sought to determine what result might accrue from the use of higher concentrations of the proton donor. Specifically, we have carried out electrolyses of a 2.5 mM solution of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate and 50 mM 1,1,1,3,3,3-hexafluoroisopropyl alcohol and at three different potentials. For these experiments, the potentials chosen and the product distributions were as follows: (1) at -1.70 V, benzyldenecyclopentane (55%), 1-phenyl-1-hexyne (13%), unreduced starting material (28%); (2) at -1.80 V, benzyldenecyclopentane (70%), 1-phenyl-1-hexyne (19%), unreduced starting material (14%); (3) at -1.90 V, benzyldenecyclopentane (57%), 1-phenyl-1-hexyne (25%), unreduced starting material (17%). For reasons that are not obvious at this time, the presence of a higher concentration of proton donor leads to incomplete electrolyses. Nevertheless, if we define an electrochemical efficiency for the production of benzyldenecyclopentane as the yield of the carbocycle with respect to just the electrolyzed starting material, we calculate that the carbocycle was formed with electrochemical efficiencies of approximately 80, 79, and 70%, respectively, for the three electrolyses listed.

Apparently, if one wishes to electrosynthesize benzyldenecyclopentane, the second experiment affords the carbocycle in maximal absolute yield (70%) and with close to 80% electrochemical efficiency. If the conditions of the second experiment are translated into a practical electrosynthesis, one concludes that, in less than 3 h, almost 140 mg of benzyldenecyclopentane could be obtained from a controlled-potential electrolysis of 500 mL of a 2.5 mM solution of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate and 50 mM 1,1,1,3,3,3-hexafluoroisopropyl alcohol with a reticulated vitreous carbon electrode (approximately 200 cm² in area) held at -1.80 V (or -2.55 V vs the aqueous saturated calomel electrode). To separate the desired benzyldenecyclopentane from 1-phenyl-1-hexyne (which, as shown in Tables I and II, is the principal side product), we have successfully employed¹ preparative-scale gas chromatography with a packed column containing 10% UCON Polar on 80-100-mesh Chromosorb W; benzyldenecyclopentane can be obtained in at least 99% purity.

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