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

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Abstract: Polarograms for 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne in dimethylformamide containing tetra-*n*-butylammonium perchlorate exhibit three waves, the first being due to reduction of the carbon–halogen bond. Superimposed upon the first wave for each compound is a large current maximum which is concentration dependent and much more pronounced for the iodo species. Large-scale electrolyses were carried out at potentials corresponding to the first wave to avoid reduction of the carbon–carbon triple bond and subsequent isomerization of the alkynes to their respective allenes; coulometric *n* values were found to be unity. At potentials on or before the polarographic maximum, controlled-potential electrolyses yield large quantities of diorganomercury compounds (containing both alicyclic and acyclic organic moieties) which indicate direct involvement of the mercury cathode in the reduction process. A variety of straight-chain and alicyclic monomers, derived from both radicals and carbanions, are included among the products, and the amounts of these species vary systematically with potential and the initial concentration of starting material. In addition, minor quantities of an alcohol and *N*-methylformamide adduct formed from the acetylenic halides are observed; these products arise by reaction of hydroxide ion with unreduced parent compound.

Following publication of a paper[1] dealing with the electrochemical reduction and intramolecular cyclization of 6-chloro-1-phenyl-1-hexyne at mercury cathodes in dimethylformamide containing tetra-*n*-butylammonium perchlorate, we undertook an examination of the behavior of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne under similar conditions because each of the latter two acetylenic halides has, in contradistinction to 6-chloro-1-phenyl-1-hexyne, a carbon–halogen bond which is easier to reduce than the phenyl-conjugated carbon–carbon triple bond. However, in preliminary studies of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne,[2] we were unable to account for all the products derived from selective reduction of the carbon–halogen bonds. Consequently, to obtain more information about the electrolytic reduction of simple alkyl halides, the behavior of 1-iododecane and 1-bromodecane at mercury electrodes in dimethylformamide containing either tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate was investigated.[3] It was found that net one-electron reduction of the alkyl halide prevails over the entire range of potentials explored; virtually quantitative yields of didecylmercury are formed at the least negative potentials, whereas production of decane, 1-decene, 1-decanol, *N*-decyl-*N*-methylformamide, and telomers occurs at more negative potentials.

Armed with knowledge resulting from the previous work with 6-chloro-1-phenyl-1-hexyne and the 1-halodecanes, we have now reinvestigated the electrochemical behavior of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne. Electrolysis products which have been isolated and identified include the same kinds of species previously observed for the 1-halodecanes[3] as well as benzylidenecyclopentane (formed by intramolecular cyclization) and diorganomercury compounds possessing alicyclic and acyclic moieties. In addition, significant differences are seen when the electrolytic reductions of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne are compared with chemical reductions of these substances.[4]

Experimental Section

Reagents. Tetra-*n*-butylammonium perchlorate and tetramethylammonium perchlorate, obtained from the G. Frederick Smith Chemical Co., were used without further purification as supporting electrolytes. Dimethylformamide utilized as solvent for electrochemical work was Fisher Spectranalyzed material (lot 751169) distilled at a reduced pressure from calcium hydride immediately prior to use. Gas chromatographic measurements with a 6 ft × 1/8 in. column packed with Porapak Q revealed that the water content of solutions to be electrolyzed was approximately 1000 ppm. In a previous paper[3] the significance of the presence of trace amounts (as high as 0.05 mol %) of *N*-methylformamide in solvent that was not redistilled has been discussed. By means of standard-addition experiments, employing gas chromatography with a 10 ft × 1/8 in. column packed with 15% Carbowax 20M on 80–100 mesh Chromosorb W, we found no more than 0.002 mol % and usually less than 0.001 mol % *N*-methylformamide in the redistilled dimethylformamide.

Preparation of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne was accomplished by addition of the appropriate 1,4-dihalobutane to a solution of lithium phenylacetylide, obtained from the reaction of *n*-butyllithium with phenylacetylene, in freshly distilled tetrahydrofuran. Vacuum distillation of 6-iodo-1-phenyl-1-hexyne yielded a clear liquid: bp 106–107 °C (0.1 mm); NMR ($CDCl_3$) δ 7.35 (m, 5, aromatic H), 3.21 (t, 2, CH_2I, $J = 6.5$ Hz), 2.43 (t, 2, $C{\equiv}CCH_2$, $J = 5.5$ Hz), and 1.5–2.3 (m, 4, CH_2). Anal. Calcd for $C_{12}H_{13}I$: C, 50.73; H, 4.61; I, 44.66. Found: C, 50.49; H, 4.46; I, 44.59. For 6-bromo-1-phenyl-1-hexyne, a clear liquid, the following

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data were obtained: bp 102–103 °C (0.1 mm); NMR ($CDCl_3$) δ 7.33 (m, 5, aromatic H), 3.45 (t, 2, CH_2Br, J = 6 Hz), 2.39 (t, 2, $C{\equiv}CCH_2$, J = 5 Hz), and 1.5–2.3 (m, 4, CH_2). Anal. Calcd for $C_{12}H_{13}Br$: C, 60.76; H, 5.48; Br, 33.76. Found: C, 61.03; H, 5.71; Br, 33.94. Gas chromatographic analysis of these acetylenic halides indicated that each material was at least 99% pure.

Instrumentation and Procedures. A previous paper[5] contains descriptions of the electrolysis cell, the instrumentation for polarography and controlled-potential coulometry, and the procedures for the electrochemical experiments. 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; this electrode has a potential of −0.750 V vs. the aqueous saturated calomel electrode.

After a controlled-potential electrolysis was terminated, the solution was divided into two equal portions. One portion was subjected to the same procedure for extraction of products that is outlined in the earlier paper.[5] However, to permit the determination of diorganomercury compounds, the second portion was treated for 10 min with 1 mL of glacial acetic acid saturated with iodine in order to convert the diorganomercury species quantitatively to organic iodides; after extraction of the organic products with diethyl ether, the ether phase was contacted with an aqueous solution of potassium thiosulfate to reduce the excess iodine. Finally, the ether phase was washed with water and was dried over magnesium sulfate. Ether extracts obtained from each portion of the electrolyzed solution were concentrated and then analyzed by means of gas chromatography.

Gas chromatographic measurements were performed with a Hewlett-Packard Model 5700A dual-column instrument equipped with a thermal conductivity detector; columns used included the previously mentioned Carbowax column, a 20 × $^1/_8$ in. column packed with 10% OV-101 on 80–100 mesh Gas Chrom P, a 20 × $^1/_8$ in. column packed with 10% UC W98 on 80–100 mesh Chromosorb W, and a 6 ft × $^1/_8$ in. column packed with 3% OV-17 on 100–120 mesh Gas Chrom Q. In addition, the chromatograph was adapted for preparative-scale work in a manner described elsewhere;[1] a 16 × $^1/_4$ in. column packed with 10% SE-30 on 80–100 mesh Chromosorb W was employed for the preparative-scale chromatography.

A Varian EM-360 spectrometer was utilized to record NMR spectra; chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectrometric data for individual electrolysis products were obtained with the aid of a Varian CH-7 mass spectrometer operated at 70 eV and coupled to a Varian Aerograph Series 1200 gas chromatograph through a Llewellyn separator. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and by Midwest Microlab, Ltd., Indianapolis, Ind.

A known quantity of an electroinactive internal standard (phenylcyclohexane) was added to every solution subjected to controlled-potential electrolysis. An experimentally measured gas chromatographic response factor for each major electrolysis product vs. phenylcyclohexane permitted the recovery of that compound to be determined; if we were unable to measure a response factor, it was taken to be unity. Accordingly, all product yields are absolute and are expressed as the percentage of starting material incorporated into a particular species.

Product Identification. Three monomeric products—1-phenyl-1-hexyne, 1-phenyl-5-hexen-1-yne, and benzylidenecyclopentane—were identified by comparison of their retention times and spectra with known samples of these materials, reported in an earlier communication.[1]

In the present study, diorganomercury products could not be reliably detected or quantitated directly by means of gas chromatography. However, treatment of the diorganomercury species with a saturated solution of iodine in glacial acetic acid resulted in quantitative destruction of these compounds into two organic iodides—6-iodo-1-phenyl-1-hexyne and 1-iodo-1-phenyl-2,2-tetramethylenethylene—both of which can be accurately measured with the aid of gas chromatography, thereby allowing quantification of diorganomercury products with acyclic and alicyclic constituents. Identification of 6-iodo-1-phenyl-1-hexyne and 1-iodo-1-phenyl-2,2-tetramethyleneethylene was based upon comparison of their gas chromatographic and mass spectrometric data with independently synthesized materials.

An authentic sample of 1-iodo-1-phenyl-2,2-tetramethylenethylene was prepared according to the following procedure. Cyclopentyl phenyl ketone was added dropwise to anhydrous hydrazine over a period of 2 h. Several drops of concentrated sulfuric acid were added and the solution was refluxed for 14 h, after which the resulting cyclopentylphenylhydrazone was isolated in chloroform solution. Then the solution of the hydrazone was concentrated and added to triethylamine in freshly distilled tetrahydrofuran. Next, over a period of 24 h, a saturated solution of iodine in tetrahydrofuran was added dropwise. Finally, the product was partitioned between diethyl ether and water, and the ether phase was washed several times with acidified water and once with water saturated with sodium thiosulfate. Although distillation of the crude product at 0.35 mm led to some decomposition, a sample of 90% pure 1-iodo-1-phenyl-2,2-tetramethylenethylene was obtained at 110–113 °C. Gas chromatography-mass spectrometry for both this fraction and the suspected product gave essentially the same results, relative mass abundances being reported in parentheses: m/e 285, $M^+ + 1$ (0.6%); 284, M^+ (13.0%); 157, $M^+ - I$ (100%); 129, $M^+ - C_2H_4I$ (97.2%).

Another compound found in all electrolyzed solutions was 1-phenyl-1-hexyn-6-ol, which was identified by gas chromatography-mass spectrometry of the suspected product: m/e 174, M^+ (7.9%); 173, $M^+ - 1$ (3.3%); 156, $M^+ - H_2O$ (3.7%); 115, $M^+ - C_3H_5OH$ (100%); 31, $CH_2{=}O^+H$ (8.7%). From earlier work with 1-iododecane and 1-bromodecane,[3] it was expected that an adduct derived from *N*-methylformamide (a trace impurity in the solvent) would be discovered among the electrolysis products. Identification of *N*-methyl-*N*-(6-phenyl-5-hexynyl)formamide was accomplished through gas chromatography-mass spectrometry: m/e 216, $M^+ + 1$ (0.5%); 215, M^+ (1.5%); 214, $M^+ - 1$ (1.7%); 187, $M^+ - CO$ (7.0%); 186, $M^+ - CHO$ (9.1%); 157, $M^+ - N(CH_3)CHO$ (10.3%); 130, base (100%). Confirmation of the identity of the formamide derivative came from the observation that the yield of the suspected product increased when 100 μL of *N*-methylformamide was deliberately added to a solution before a large-scale electrolysis was performed.

None of the possible dimers (containing alicyclic or acyclic moieties) resulting from radical-coupling reactions was found as a product in electrolyses at any potential. Authentic samples of the dimers were prepared through formation of a Grignard reagent by addition of magnesium turnings to 6-bromo-1-phenyl-1-hexyne in anhydrous diethyl ether under nitrogen. Next, the Grignard reagent was transferred to a flask which contained solid silver bromide dispersed in anhydrous diethyl ether under a nitrogen atmosphere and which was kept in an ice bath. After a 45-min reaction time, the black solution containing suspended elemental silver was refluxed for 2 h. Finally, the products were partitioned between water and diethyl ether. It was determined that more than 50% of the 6-bromo-1-phenyl-1-hexyne had been converted into the three possible dimers. Gas chromatographic and mass spectrometric data for these compounds indicated that they are absent from the roster of products for all large-scale electrolyses of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne.

Two other electrolysis products were detected by means of gas chromatography-mass spectrometry. However, identification of these species from such data alone proved impossible; and, because of their small yields, it was impractical to isolate enough material for other analytical tests.

Results and Discussion

Polarographic Behavior of 6-Iodo-1-phenyl-1-hexyne. Figure 1A illustrates a polarogram for a 0.0025 M solution of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate. A large maximum[6] which peaks at −1.65 V is superimposed upon the normal wave for reduction of the carbon–iodine bond. Following the maximum are a small current minimum at −1.67 V and a wave for reduction of the carbon–carbon triple bond which is at least partially masked by the maximum. At −2.0 V is a wave for benzylidenecyclopentane, a product resulting from electrolytic reduction and intramolecular cyclization of the starting material. If the maximum is assumed to be absent, the polarographic half-wave potential for reduction of the carbon–iodine bond can be estimated to be −1.25 V.

A polarogram for a 0.005 M solution of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate is shown in Figure 1B. In a number of studies of the electrochemistry of alkyl iodides, we

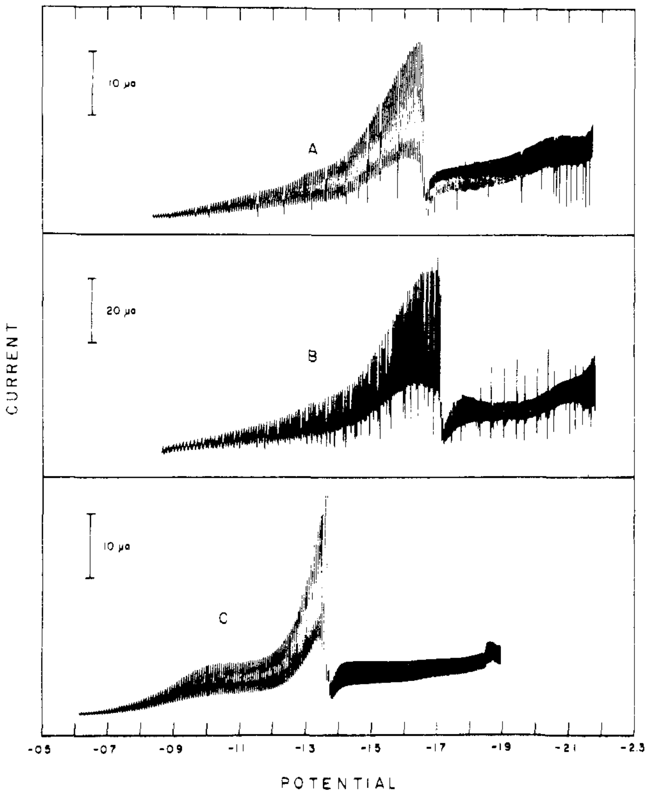


Figure 1. (A) Polarogram for 0.0025 M 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate. (B) Polarogram for 0.005 M 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate. (C) Polarogram for 0.0025 M 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate.

have discovered that the polarographic maximum characteristically shifts toward more negative potentials as the concentration of starting material is increased; for the present situation, the maximum reaches a peak at −1.71 V, which is 60 mV more negative than that seen in Figure 1A for a lower concentration of 6-iodo-1-phenyl-1-hexyne. Additionally, when the concentration of acetylenic iodide is raised, it can be noted that the absolute size of the maximum increases and that a sharper current decline occurs.

Figure 1C depicts a polarogram for a 0.0025 M solution of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate. As observed in earlier work,[3] the wave for reduction of the carbon-iodine bond is shifted approximately 400 mV more positive and the maximum is shifted 300 mV more positive than is the case for the same concentration of 6-iodo-1-phenyl-1-hexyne in the presence of 0.1 M tetra-*n*-butylammonium perchlorate. Shifts in reduction potentials for alkyl halides arising from the use of different tetraalkylammonium salts have been previously noted by us[3,7] and by others.[8,9] For progressively smaller tetraalkylammonium cations, the positive shift in the half-wave potential for reduction of the carbon–halogen bond has been attributed to an increase in the rate of electron transfer or in the ease of reduction owing to less steric hindrance at the electrode surface. Factors which affect this change are all interrelated, and no fully satisfactory explanation for the phenomenon has yet been reported. In the tetramethylammonium perchlorate–dimethylformamide system, the half-wave potential for reduction of the carbon–iodine bond of 6-iodo-1-phenyl-1-hexyne has a readily measurable value of −0.88 V; the polarogram itself consists of a diffusion-limited wave followed by a prominent maximum at −1.37 V, and a well-defined limiting-current plateau is reestablished after a current minimum at −1.38 V. There is no polarographic evidence for reduction of the phenyl-conjugated carbon–carbon triple bond in the presence of tetramethylammonium perchlorate.

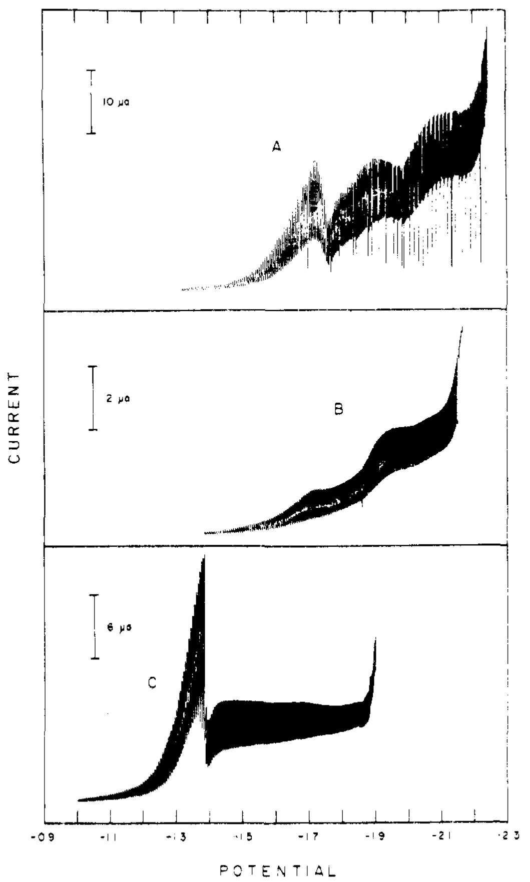


Figure 2. (A) Polarogram for 0.0025 M 6-bromo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate. (B) Polarogram for 0.0005 M 6-bromo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate. (C) Polarogram for 0.0025 M 6-bromo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate.

Polarographic Behavior of 6-Bromo-1-phenyl-1-hexyne. A polarogram for a 0.0005 M solution of 6-bromo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate is seen in Figure 2B. Because there is virtually no maximum to distort the first polarographic wave, which corresponds to reduction of the carbon–bromine bond, we can reliably report that the half-wave potential for this process is −1.63 V. Reduction of the carbon–carbon triple bond is responsible for the second wave at −1.87 V; and, preceding the final rise in current caused by decomposition of the supporting electrolyte, is a small wave at −2.05 V due to reduction of benzylidenecyclopentane.

As seen for 6-iodo-1-phenyl-1-hexyne, when the concentration of starting material is increased, the polarographic maximum becomes much more pronounced. Figure 2A depicts this situation for a 0.0025 M solution of 6-bromo-1-phenyl-1-hexyne in the presence of tetra-*n*-butylammonium perchlorate. In addition, the peak of the maximum is at −1.72 V, slightly more negative than that observed for the same concentration of 6-iodo-1-phenyl-1-hexyne (Figure 1A). Because of the maximum, the half-wave potential for reduction of the carbon–bromine bond is impossible to measure in this instance.

A polarogram for a 0.0025 M solution of 6-bromo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate is shown in Figure 2C. Once again, one sees shifts toward more positive values in the potentials both for reduction of the carbon–bromine bond and

Table I. Product Distribution and Coulometric Data for Electrolytic Reduction of 0.0025 M 6-Iodo-1-phenyl-1-hexyne in Dimethylformamide Containing 0.1 M Tetra-*n*-butylammonium Perchlorate

		product distribution, %[a]								
potential, V	*n* value	**1**	**2**	**3**	**4**	**5**	**6**	**7**	others	total recovery
−1.1	0.93	tr	24	1	66 (63, 3)	5			5	101
−1.2	1.07	tr	24	2	65 (62, 3)	4	tr		7	102
−1.3	0.99	2	23	3	49 (45, 4)	5	2		5	89
−1.4	1.03	9	19	4	42 (39, 3)	5	4		7	90
−1.5	1.12	16	16	3	28 (26, 2)	3	3		8	77
−1.6	1.02	28	12	5	21 (20, 1)	2	4		7	79
−1.7	1.23	18	11	3	10 (9, 1)	2	14	3	6	67
−1.8	*b*	9	13	8	6 (5, 1)	4	5	4	5	54

[a] Products referred to by number in the above table are as follows: **1**, 1-phenyl-1-hexyne; **2**, benzylidenecyclopentane; **3**, 1-phenyl-5-hexen-1-yne; **4**, R_2Hg (R = acyclic, R = alicyclic); **5**, 1-phenyl-1-hexyn-6-ol; **6**, *N*-methyl-*N*-(6-phenyl-5-hexynyl)formamide; **7**, allene-derived species. [b] Electrolysis was stopped early to minimize isomerization of acetylene to allene.

in the polarographic maximum than for 6-bromo-1-phenyl-1-hexyne in the presence of 0.1 M tetra-*n*-butylammonium perchlorate.

Another observation stemming from polarographic study of the acetylenic halides is that the carbon–iodine bond and the carbon–bromine bond of these species are easier to reduce by 150 mV than the respective carbon–halogen bonds for 1-iododecane and 1-bromodecane. This extra ease of reduction has been found for 1-halo-5-decynes as well.[10]

Controlled-Potential Electrolysis of 6-Iodo-1-phenyl-1-hexyne. Summarized in Table I are results of a series of controlled-potential electrolyses of 0.0025 M solutions of 6-iodo-1-phenyl-1-hexyne at mercury pool cathodes in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate. In order to probe only reduction of the carbon–iodine bond, electrolysis potentials were chosen to minimize isomerization of the acetylene to an allene, as has been previously observed for 1-phenyl-1-hexyne[5] and 6-chloro-1-phenyl-1-hexyne;[1] consequently, instead of ten or more monomeric products, only three main monomeric species are formed—1-phenyl-1-hexyne, benzylidenecyclopentane, and 1-phenyl-5-hexen-1-yne. Over the entire range of potentials studied, the coulometric *n* value is unity or slightly higher. This result indicates that 6-iodo-1-phenyl-1-hexyne undergoes a net one-electron reduction. However, at the most negative potentials employed, namely, −1.7 and −1.8 V, there is unquestionably some reduction of the carbon–carbon triple bond.

Many interesting observations emerge if the absolute percentages of the major electrolysis products reported in Table I are plotted as a function of potential (Figure 3A). At potentials positive of the polarographic maximum, the predominant product is the acyclic diorganomercury species, but the yield of all organomercury products decreases rapidly as the potential becomes more negative. This behavior is analogous to that observed for 1-iododecane,[3] for which quantitative yields of didecylmercury are found at potentials positive of the polarographic maximum, whereas very little diorganomercury species are obtained at potentials more negative than the maximum. Benzylidenecyclopentane is the most important monomeric product at potentials positive with respect to the polarographic maximum, decreasing in abundance as the potential is made more negative. At potentials corresponding to the polarographic maximum, the major monomeric product is 1-phenyl-1-hexyne; 1-phenyl-5-hexen-1-yne only becomes significant at the most negative potentials.

Results of chronocoulometric studies[11] of 6-iodo-1-phenyl-1-hexyne and 6-bromo-1-phenyl-1-hexyne indicate no adsorption of these species onto mercury. With this fact in mind, we propose that 6-iodo-1-phenyl-1-hexyne in solution is reduced at the electrode surface in a one-electron step to form a primary radical which may undergo any of several reactions depending upon the experimental conditions.

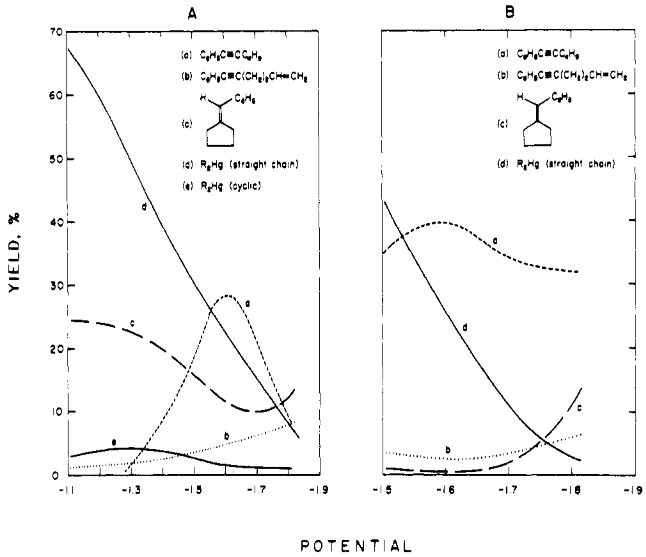


Figure 3. (A) Product distribution as a function of potential for electrolytic reduction of 0.0025 M 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate. (B) Product distribution as a function of potential for electrolytic reduction of 0.0025 M 6-bromo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate.

At potentials between −1.1 and −1.4 V in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate, the primary radical is adsorbed onto the mercury pool and incorporates an atom of mercury, a process which greatly increases the lifetime of the radical.[12] Diorganomercury products arise from the reaction of two adsorbed organomercury radicals with the expulsion of mercury.

$$C_6H_5C{\equiv}C(CH_2)_4I + e^- \rightarrow C_6H_5C{\equiv}C(CH_2)_4\cdot + I^-$$

$$C_6H_5C{\equiv}C(CH_2)_4\cdot \xrightarrow{\text{fast}} C_6H_5C{\equiv}C(CH_2)_4\cdot(\text{ads})$$

$$\xrightarrow{Hg} C_6H_5C{\equiv}C(CH_2)_4Hg\cdot(\text{ads})$$

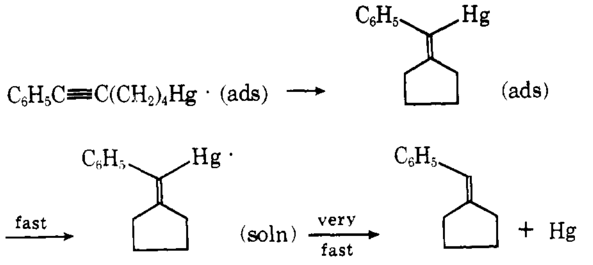
$$2C_6H_5C{\equiv}C(CH_2)_4Hg\cdot(\text{ads}) \rightarrow [C_6H_5C{\equiv}C(CH_2)_4]_2Hg + Hg$$

In addition, adsorbed organomercury radicals may cyclize intramolecularly[13] to produce an alicyclic organomercury radical, though, as evidenced by the low yield of alicyclic organomercury species, this process (eq 1) is not favored. If an acyclic or alicyclic organomercury radical is desorbed, it should immediately demercurate,[14] forming a radical which abstracts

Table II. Product Distribution and Coulometric Data for Electrolytic Reduction of 0.0025 M 6-Bromo-1-phenyl-1-hexyne in Dimethylformamide Containing 0.1 M Tetra-*n*-butylammonium Perchlorate

		product distribution, %[a]								
potential, V	*n* value	**1**	**2**	**3**	**4**	**5**	**6**	**7**	others	total recovery
−1.5	1.10	35	1	4	43 (43, −)	12	9		2	106
−1.6	1.26	40	1	3	26 (26, −)	8	10		3	91
−1.7	1.03	35	2	4	11 (11, −)	4	20	1	4	81
−1.8	*b*	32	11	6	3 (3, −)	2	17	3	12[c]	86

[a] Products referred to by number in the above table are as follows: **1**, 1-phenyl-1-hexyne; **2**, benzylidenecyclopentane; **3**, 1-phenyl-5-hexen-1-yne; **4**, R_2Hg (R = acyclic, R = alicyclic); **5**, 1-phenyl-1-hexyn-6-ol; **6**, *N*-methyl-*N*-(6-phenyl-5-hexynyl)formamide; **7**, allene-derived species. [b] Electrolysis was stopped early to minimize isomerization of acetylene to allene. [c] Includes 8% unreduced starting material.



(1)

a hydrogen atom (most likely from the solvent) to yield 1-phenyl-1-hexyne or benzylidenecyclopentane, respectively. However, intramolecular cyclization of the electrolytically formed primary radical in solution, followed by hydrogen atom abstraction, is believed to be the predominant pathway for the production of benzylidenecyclopentane, the major monomeric species obtained at potentials between −1.1 and −1.4 V. Thus, in solution the primary radical cyclizes more rapidly than it accepts a hydrogen atom to give 1-phenyl-1-hexyne.

At potentials corresponding to the polarographic maximum (−1.5 to −1.6 V for 0.0025 M 6-iodo-1-phenyl-1-hexyne in the presence of 0.1 M tetra-*n*-butylammonium perchlorate), two phenomena cause the yields of both diorganomercury species and benzylidenecyclopentane to decrease and the quantity of 1-phenyl-1-hexyne to increase. First, from our latest studies of the electrochemistry of 1-iododecane,[15] we now know that the polarographic maximum marks the onset of further reduction of the primary radical to a carbanion or of direct two-electron reduction of the alkyl halide moiety to the carbanion. Consequently, a smaller amount of diorganomercury species is formed because there is less of the primary radical available for adsorption onto mercury. In addition, the primary carbanion is more likely to gain a proton from the solvent or from water (present as an impurity) to give 1-phenyl-1-hexyne than it is to undergo intramolecular cyclization to the anionic precursor of benzylidenecyclopentane; such behavior is consistent with observations previously made by Crandall and Keyton[4] concerning the reaction of 6-bromo-1-phenyl-1-hexyne with lithium biphenyl. Second, besides the production of carbanionic intermediates at more negative potentials, it is reasonable to expect that primary radicals will be less strongly adsorbed onto mercury because of more competitive adsorption of tetraalkylammonium salts employed as supporting electrolytes.

Recent investigations[15] of the electrochemical behavior of 1-iododecane in dimethylformamide containing tetraalkylammonium salts have shown that 1-decene and 1-decanol, two of the observed electrolysis products, are formed by chemical reaction of the alkyl iodide with hydroxide ion and that *N*-decyl-*N*-methylformamide, a side product, arises because the anion resulting from deprotonation of *N*-methylformamide (an impurity in the solvent) by hydroxide attacks the alkyl iodide. Contrary to the mechanisms proposed in an earlier paper,[3] we believe that hydroxide ion is generated by abstraction of a proton from water by a carbanion produced via two-electron reduction of the carbon–halogen bond and that subsequent attack of hydroxide on unreduced alkyl iodide can result in an apparent one-electron reduction of 1-iododecane. At potentials on or more negative than the polarographic maximum, there is competition between reaction of radicals derived from one-electron reduction of the carbon–halogen bond and uptake of a second electron. To account for the appearance of 1-phenyl-5-hexen-1-yne, 1-phenyl-1-hexyn-6-ol, and *N*-methyl-*N*-(6-phenyl-5-hexynyl)formamide upon reduction of 6-iodo-1-phenyl-1-hexyne at potentials positive of the polarographic maximum, it is possible that even at these potentials some carbanions are produced or that hydroxide ions are formed during preelectrolysis of the supporting electrolyte–solvent. A more complete discussion of this topic will be presented in a future paper.[15]

Low total recovery of products quantifiable by means of gas chromatography at the most negative electrolysis potentials (Table I) is attributable to extensive telomerization. Evidence in support of this conclusion is our detection of several 2:1 telomers as well as our strong suspicion that species of higher molecular weight are present, a situation analogous to that previously encountered for the 1-halodecanes;[3] however, the behavior of the acetylenic halides is more complicated because of the availability of more sites for radicals and carbanions to attack.

Controlled-Potential Electrolysis of 6-Bromo-1-phenyl-1-hexyne. In contrast to the situation observed for 1-bromodecane,[3] where no didecylmercury is produced, substantial quantities of diorganomercury species are found for large-scale controlled-potential reductions of 6-bromo-1-phenyl-1-hexyne at potentials on or positive of the polarographic maximum. This result was anticipated because of the correlation we have found between the appearance of polarographic maxima (as well as inverted cyclic voltammetric waves) for alkyl halides and the formation of large amounts of diorganomercury product.[3] Both of the preceding voltammetric phenomena are observed for 6-bromo-1-phenyl-1-hexyne,[16] but are not seen for 1-bromodecane.[3]

If the yields of the major products listed in Table II for reduction of 6-bromo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate are plotted vs. potential, one notes (Figure 3B) essentially the same trends as those observed for 6-iodo-1-phenyl-1-hexyne (Figure 3A). However, if absolute yields of products obtained from 6-bromo-1-phenyl-1-hexyne and 6-iodo-1-phenyl-1-hexyne are compared at the same potential, there are several significant differences; higher yields of both 1-phenyl-1-hexyne and the *N*-methylformamide adduct as well as lower yields of benzylidenecyclopentane are found for the former compound. No explanations for these differences have been formulated, though additional work with 1-halo-5-decynes may provide an answer.[10]

Effects of Starting-Material Concentration and of Supporting-Electrolyte Identity. Electrolyses at several different potentials were performed in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate with concentrations of the acetylenic halides varying from 0.0005 to 0.005 M. When the concentration of acetylenic halide is increased, the yields of 1-phenyl-5-hexen-1-yne, benzylidenecyclopentane, and (to a lesser extent) diorganomercury species are higher, whereas the yield of 1-phenyl-1-hexyne is lower. As expected, the apparent coulometric *n* value remains unity despite an increase in the concentration of acetylenic halide.

Results of large-scale controlled-potential electrolyses performed with 0.0025 M solutions of the acetylenic halides in dimethylformamide containing 0.1 M tetramethylammonium perchlorate are analogous to those found when tetra-*n*-butylammonium perchlorate is utilized as supporting electrolyte, if the shift in reduction potentials toward more positive values in the presence of tetramethylammonium perchlorate is taken into consideration; in other words, one should compare electrolyses at potentials in tetra-*n*-butylammonium perchlorate solutions with electrolyses at potentials 300-400 mV more positive in the tetramethylammonium perchlorate solutions. For the reduction of 6-iodo-1-phenyl-1-hexyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate at potentials (−0.9 to −1.2 V) corresponding to the current plateau before the polarographic maximum, we have observed that the absolute yields of all products remain the same throughout this potential region. Such behavior, which has also been seen for 5-iodo-1-phenyl-1-pentyne in the same supporting electrolyte–solvent system,[16] is attributed to strong adsorption of the primary radical onto mercury at these potentials.

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