in *tert*-butyl alcohol–potassium *tert*-butoxide[53] (31%): bp 63 °C (0.4 mm); IR (film) 2120 cm^{-1}. Anal. Calcd for $C_{11}H_{13}N$: C, 83.02; H, 8.18; N, 8.80. Found: C, 82.98; H, 8.30; N, 8.75.

Rate Measurements. Solutions (0.05–0.12 M) of the isonitriles, an *n*-alkane standard for GLC,[34] and a 1.6 molar excess of 1,1-diphenylethylene or 3-cyanopyridine were treated with ultrasound and nitrogen (99.99% pure) for removing oxygen. Samples of this solution (0.15 mL) were distributed over a series of 2-mL glass ampules[33a] and again degassed by repeated freezing in liquid nitrogen, evacuating, aerating with pure nitrogen, and thawing. Finally, the ampules were sealed under nitrogen and (10–15/experiment) thermostated at the indicated temperature (±0.2 °C).[33a] For analysis, the ampules were removed at definite times and chilled. The reactions were followed up at least to 80% completeness and analyzed either by GLC[55] or IR.[33b] The first-order rate constants were obtained by least-squares fitting of the concentration data.[35] Details and a listing of the rate constants are found in ref 55 and 56, and the activation parameters are recorded in Table I.

Product analysis was conducted by GLC (2 m, 15% silicone, SE 30) with *n*-alkanes as integration standards.[34] The products were identified by retention-time comparison with authentic samples or by GLC–MS.

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Electrochemical Reduction and Intramolecular Cyclization of 1-Iodo-5-decyne and 1-Bromo-5-decyne at Vitreous Carbon Cathodes in Dimethylformamide

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In dimethylformamide containing tetramethylammonium perchlorate, cyclic voltammograms for reduction of 1-iodo-5-decyne and 1-bromo-5-decyne at a vitreous carbon electrode each consist of a single irreversible wave due to two-electron scission of the carbon–halogen bond. Preparative-scale electrolyses of 1-iodo-5-decyne yield pentylidenecyclopentane, 5-decyne, 1-decen-5-yne, and a small amount of 5-decyn-1-ol, whereas reduction of 1-bromo-5-decyne affords mainly 5-decyne and 1-decen-5-yne along with a modest quantity of pentylidenecyclopentane. Differences in product distributions correlate with the extent to which the 5-decyn-1-yl radical persists as a transient species. Pentylidenecyclopentane arises via intramolecular cyclization of the 5-decyn-1-yl radical followed by hydrogen atom abstraction, 5-decyne is formed via protonation of the 5-decyn-1-yl carbanion by either water or the tetramethylammonium cation, and 1-decen-5-yne and 5-decyn-1-ol are obtained, respectively, via E2 and S_N2 reactions between unreduced starting material and hydroxide ion (generated by deprotonation of water). In the presence of a proton donor (diethyl malonate or hexafluoroisopropyl alcohol), the quantities of pentylidenecyclopentane and 5-decyne rise noticeably and the yield of 1-decen-5-yne falls dramatically.

In a previous paper[1] we described the electrochemical behavior of 1-iodo-5-decyne and 1-bromo-5-decyne at mercury cathodes in dimethylformamide containing tetraalkylammonium salts as supporting electrolytes. It was found that 1-iodo-5-decyne undergoes stepwise reduction (first to the 5-decyn-1-yl radical and then to the corresponding carbanion) and that the distribution of products depends on the potential of the cathode. At potentials that give rise to the 5-decyn-1-yl radical, the principal product is di-5-decynylmercury (>85%), and only a small quantity of pentylidenecyclopentane (<5%) is obtained. At potentials for which the carbanion intermediate is predominant, the major species formed are 5-decyne (>40%) and 1-decen-5-yne (>20%), whereas the yields of di-5-decynylmercury (<15%) and pentylidenecyclopentane (<1%) decrease as the potential is made more negative.

In studying the electrochemistry of 1-bromo-5-decyne, we discovered that this compound exhibits just a *single* polarographic wave corresponding to generation of the 5-decyn-1-yl anion. However, the product distribution reflects the existence of *two* regimes of behavior. At potentials on the *rising part* of the polarographic wave, the major products are di-5-decynylmercury (>65%) and 5-decyne (>17%); but the lack of any change in yields when a proton donor is added to the system indicates that these two compounds are derived from a transient *radical* intermediate. On the other hand, when 1-bromo-5-decyne is electrolyzed at potentials on the *plateau* of the polarographic wave, the main products are 5-decyne (>47%) and 1-decen-5-yne (>23%); if a proton donor (diethyl malonate) is introduced, the amount of 5-decyne rises (>80%) and the quantity of 1-decen-5-yne falls (<1%)—results which clearly implicate a *carbanion* intermediate.

In the present research, we have examined the electrochemical reduction of 1-iodo-5-decyne and 1-bromo-5-decyne at vitreous carbon electrodes in dimethylformamide containing tetramethylammonium perchlorate. We have sought to complement our recent work[2] on the reduction of alkyl halides in such systems and, in particular, to probe

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Table I. Coulometric Data and Product Distributions for Electrolytic Reduction of 2.5 mM Solutions of 1-Iodo-5-decyne and 1-Bromo-5-decyne at Reticulated Vitreous Carbon in Dimethylformamide Containing Tetraalkylammonium Perchlorates

			product distribution, %				
conditions[a]	potential, V	*n* value	pentylidene-cyclopentane	5-decyne	1-decen-5-yne	5-decyn-1-ol	unreduced starting material
RI, TMAP	−1.35	0.75	46	11	19		13
RI, TMAP	−1.45	0.92	42	15	27	<1	1
RI, TMAP	−1.70	0.99	27	30	30	1	
RI, TMAP	−1.85	1.00	17	33	32	2	
RI, TBAP	−1.35	0.51	38	6	12		29
RI, TBAP	−1.45	0.85	40	11	21	1	12
RI, TBAP	−1.60	0.90	41	19	27	2	2
RI, TBAP	−1.70	0.98	34	24	29	1	<1
RBr, TMAP	−1.85	0.93	5	41	33	2	1

[a] RI = 1-iodo-5-decyne, RBr = 1-bromo-5-decyne, TMAP = 0.1 M tetramethylammonium perchlorate, TBAP = 0.1 M tetra-*n*-butylammonium perchlorate.

the possibility that vitreous carbon might be useful as a cathode material for electrosyntheses based on the intramolecular cyclization of electrogenerated radicals.

Experimental Section

Reagents and Electrodes. Dimethylformamide employed as solvent, tetramethylammonium perchlorate and tetra-*n*-butylammonium perchlorate used as supporting electrolytes, and nitrogen utilized to deaerate solutions were handled as described previously.[1] Outlined elsewhere[1] are the synthesis, purification, and characterization of 1-iodo-5-decyne and 1-bromo-5-decyne.

Vitreous carbon microelectrodes used for cyclic voltammetric experiments were prepared from rods purchased from the Tokai Electrode Manufacturing Co. (Tokyo, Japan), and disks of reticulated vitreous carbon used as cathodes for large-scale controlled-potential electrolyses were cut from blocks of material (RVC 2X1-45S) obtained from The Fluorocarbon Co. (Anaheim, CA). Details about fabrication, polishing, and cleaning of these electrodes are presented in an earlier publication.[2]

Cells, Instrumentation, and Procedures. A three-electrode, single-compartment cell similar to that described previously[3,4] was employed for cyclic voltammetry, and a complete account of the two-compartment cell for large-scale electrolyses with reticulated vitreous carbon cathodes appears in a recent publication.[2] 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;[5,6] this electrode has a potential of −0.75 V vs. the aqueous saturated calomel electrode at 25 °C.

At the conclusion of a large-scale controlled-potential electrolysis, the solution containing the reduction products was partitioned between diethyl ether and water; then the ether phase was washed with water, dried over anhydrous magnesium sulfate, concentrated with the aid of a rotatory evaporator, and analyzed by means of gas chromatography or gas chromatography–mass spectrometry according to procedures described in our previous paper.[1] All product yields reported in this paper are absolute and are expressed as the percentage of starting material incorporated into a particular species.

Product Identification. Pentylidenecyclopentane, 5-decyne, 1-decen-5-yne, 5-decyn-1-ol, 5,15-eicosadiyne, and diethyl 5-decyn-1-ylmalonate were identified as electrolysis products by comparison of their gas chromatographic retention data and mass spectra with those of authentic compounds synthesized in our earlier investigation.[1]

For electrolyses done in the presence of deuterium-labeled trapping agents, the extent of deuterium incorporation into pentylidenecyclopentane and 5-decyne was determined by means of gas chromatography–mass spectrometry with selected-ion monitoring and by comparison of ratios of intensities of peaks having m/e values of 138, 139, and 140.

Results and Discussion

Cyclic Voltammetric Behavior of 1-Iodo-5-decyne and 1-Bromo-5-decyne. In dimethylformamide that contains 0.1 M tetramethylammonium perchlorate, a cyclic voltammogram obtained with a vitreous carbon electrode for a 2.5 mM solution of 1-iodo-5-decyne or 1-bromo-5-decyne exhibits a single cathodic wave corresponding to irreversible reductive cleavage of the carbon–halogen bond. At a scan rate of 100 mV s^{-1}, the peak potentials for reductions of 1-iodo-5-decyne and 1-bromo-5-decyne are −1.42 and −1.90 V, respectively. These values are in excellent agreement with peak potentials for the reduction of 1-iododecane (−1.41 V) and 1-bromodecane (−1.85 V) at a vitreous carbon electrode, at the same scan rate, and in the same solvent-supporting electrolyte system.[2] Except for the small differences in peak potentials, the cyclic voltammograms for 1-iodo-5-decyne and 1-bromo-5-decyne are virtually indistinguishable from those for 1-iododecane and 1-bromodecane pictured in an earlier paper.[2]

In a recent investigation[2] the reduction of 1-iododecane at a vitreous carbon electrode in dimethylformamide containing 0.1 M tetramethylammonium perchlorate was examined by means of chronoamperometry. We found that reduction of 1-iododecane, which gives just one voltammetric wave, is a net two-electron process. If the reasonable assumption is made that the diffusion coefficients of 1-iodo-5-decyne and 1-bromo-5-decyne are both similar to the diffusion coefficient of 1-iododecane, we conclude that the voltammetric waves for the two acetylenic halides are attributable to overall two-electron reduction of the carbon–halogen sites, because peak currents for identical concentrations of all three organic halides are nearly equal for the same scan rate and electrode area.

When 0.1 M tetra-*n*-butylammonium perchlorate is used as supporting electrolyte, the peak potential for cyclic voltammetric reduction of 1-iodo-5-decyne at vitreous carbon in dimethylformamide is −1.57 V at a scan rate of 100 mV s^{-1}. This negative shift of 150 mV in the peak potential for the acetylenic iodide as one switches the electrolyte cation from tetramethylammonium to tetra-*n*-butylammonium is comparable to the electrolyte-caused changes in peak potentials and half-wave potentials for alkyl halides that have been observed in other studies.[1,7-10]

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Table II. Coulometric Data and Product Distributions for Electrolytic Reduction of 2.5 mM Solutions of 1-Iodo-5-decyne and 1-Bromo-5-decyne at Reticulated Vitreous Carbon in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate and Various Proton Donors

			product distribution, %					
conditions[a]	potential, V	*n* value	pentylidenecyclopentane	5-decyne	1-decen-5-yne	5-decyn-1-ol	diethyl 5-decyn-1-ylmalonate	unreduced starting material
RI	−1.45	0.92	42	15	27	<1		1
RI, H_2O	−1.40	0.94	42	16	26	5		1
RI, DEM	−1.45	1.16	48	23			16	1
RI, HFIP	−1.45	1.40	60	31	1			
RI	−1.70	0.99	27	30	30	1		
RI, H_2O	−1.60	1.20	30	39	16	7		
RI, DEM	−1.70	1.49	34	40			18	
RI, HFIP	−1.70	1.77	40	51	2			
RBr	−1.85	0.93	5	41	33	2		1
RBr, DEM	−1.85	1.69	6	74	1		3	2

[a] RI = 1-iodo-5-decyne, RBr = 1-bromo-5-decyne, H_2O = 1 M water, DEM = 5 mM diethyl malonate, HFIP = 5 mM 1,1,1,3,3,3-hexafluoroisopropyl alcohol.

Controlled-Potential Electrolyses of 1-Iodo-5-decyne and 1-Bromo-5-decyne. Compiled in Table I are coulometric data and product distributions for controlled-potential electrolyses of 1-iodo-5-decyne and 1-bromo-5-decyne at reticulated vitreous carbon cathodes in dimethylformamide containing either 0.1 M tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate. Pentylidenecyclopentane, 5-decyne, 1-decen-5-yne, and 5-decyn-1-ol have been identified as the principal electrolysis products. Except for electrolyses of 1-iodo-5-decyne carried out at a potential (−1.35 V) corresponding to the rising portion of the voltammetric wave, the *apparent* coulometric *n* value for reduction of either acetylenic halide is essentially unity regardless of potential.

When the electrolytic reduction of 1-iodo-5-decyne at a reticulated vitreous carbon cathode is compared to that at a mercury pool electrode, some notable differences are seen. At the least negative potential (−1.35 V) employed with a carbon electrode, pentylidenecyclopentane is the predominant product. On the other hand, when 1-iodo-5-decyne is electrolyzed at a mercury pool cathode held at a potential corresponding to the first polarographic wave for the acetylenic iodide, di-5-decynylmercury is the major product and only very small amounts of pentylidenecyclopentane are formed.[1] As indicated in Table I, when the potential of a reticulated vitreous carbon electrode is made more negative, the yield of pentylidenecyclopentane declines as the quantities of 5-decyne and 1-decen-5-yne increase.

Because 1-bromo-5-decyne is more difficult to reduce than its iodo analogue, only a narrow range of potentials is available for a large-scale electrolysis. At a potential of −1.85 V (Table I), the major products derived from reduction of 1-bromo-5-decyne are 5-decyne and 1-decen-5-yne, and just a small amount (5%) of pentylidenecyclopentane is obtained.

For all electrolyses performed in this work, the percentages of various products (together with any unreduced starting material) do not add up to the theoretical value of 100%. In a previous investigation of the electrochemistry of 1-iododecane and 1-bromodecane in dimethylformamide containing tetraalkylammonium salts,[8] we accounted for a similar trend by showing that a family of telomeric products is formed, apparently from the reaction between 1-decene and a radical or anionic fragment of the solvent. Formation of telomers has been implicated in our earlier studies of the reduction of 1-iodo-5-decyne, 1-bromo-5-decyne, 6-iodo-1-phenyl-1-hexyne, and 6-bromo-1-phenyl-1-hexyne at mercury cathodes.[1,10] We suspect, though we have not proved, that in the present system there may be production of small quantities of telomeric species arising from interaction of 5-decyne or 1-decen-5-yne with fragments of dimethylformamide.

Electrolyses of 1-Halo-5-decynes in the Presence of Proton Donors. A series of experiments was carried out to determine the effect of added proton donors on the course of electrolysis of both 1-iodo-5-decyne and 1-bromo-5-decyne in dimethylformamide containing tetramethylammonium perchlorate. Listed in Table II are results obtained with three different proton donors—water, diethyl malonate, and 1,1,1,3,3,3-hexafluoroisopropyl alcohol—at a potential (−1.40 to −1.45 V) close to the peak and at a potential (−1.60 to −1.70 V) beyond the peak of the voltammetric wave for 1-iodo-5-decyne; also included in the compilation is a pair of entries pertaining to the reduction of 1-bromo-5-decyne at −1.85 V in the presence and absence of diethyl malonate.

For the electrolysis of 1-iodo-5-decyne at −1.40 V, the presence of 1 M water has little influence on the coulometric *n* value or on the yield of any product except 5-decyn-1-ol; on the other hand, reduction at −1.60 V in the presence of 1 M water leads to a noticeably larger coulometric *n* value and to the formation of more pentylidenecyclopentane, more 5-decyne, and less 1-decen-5-yne. Regardless of potential, low concentrations of diethyl malonate and hexafluoroisopropyl alcohol cause the *n* value to increase, the yields of pentylidenecyclopentane and 5-decyne to rise, and the quantity of 1-decen-5-yne to fall. In addition, when diethyl malonate serves as a proton donor, a significant amount of diethyl 5-decyn-1-ylmalonate is produced, presumably via attack of deprotonated diethyl malonate on unreduced 1-iodo-5-decyne; a similar reaction between 1-iododecane and the conjugate base of diethyl malonate has been observed previously.[2,11] Note that changes caused by the presence of a proton donor are most pronounced with hexafluoroisopropyl alcohol, the strongest acid among the three species employed in our experiments and the conjugate base of which is poorest in its nucleophilic attack on the carbon–halogen bond of unreduced 1-iodo-5-decyne.[2]

Electrolysis of 1-bromo-5-decyne in the presence of diethyl malonate leads to a large increase in the *n* value, a

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Table III. Coulometric Data and Product Distributions for Electrolytic Reduction of 2.5 mM Solutions of 1-Iodo-5-decyne at Reticulated Vitreous Carbon in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate and Either 1 M H_2O or D_2O

			product distribution,[a] %				
conditions	potential, V	*n* value	pentylidene-cyclopentane	5-decyne	1-decen-5-yne	5-decyn-1-ol	unreduced starting material
H_2O	-1.40	0.94	42	16	26	5	1
D_2O	-1.40	1.06	39 + 3 (*d*)	11 + 10 (*d*)	19	7 (*d*)	1
H_2O	-1.60	1.20	30	39	16	7	
D_2O	-1.60	1.16	29 + 3 (*d*)	17 + 19 (*d*)	18	7 (*d*)	
H_2O	-1.80	0.90	17	41	21	10	
D_2O	-1.80	1.04	16 + 2 (*d*)	21 + 23 (*d*)	21	8 (*d*)	

[a] *d* = deuteriated.

Table IV. Coulometric Data and Product Distributions for Electrolytic Reduction of 1-Iodo-5-decyne at Reticulated Vitreous Carbon in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate at -1.70 V

		product distribution, %					
[RI], mM[a]	*n* value	pentylidene-cyclopentane	5-decyne	1-decen-5-yne	5-decyn-1-ol	5,15-eicosadiyne	unreduced starting material
1.0	1.00	17	35	28	7		
2.5	0.99	25	32	30	2		
5.0	1.00	27	29	31	1		
10.0	0.72	35	13	16	1	1	27[b]

[a] RI = 1-iodo-5-decyne. [b] This entry actually indicates 17% unreduced starting material and 10% 1-iododecadiene (see text for explanation).

dramatic rise in the yield of 5-decyne, a modest increase in the amount of pentylidenecyclopentane, a small quantity of diethyl 5-decyn-1-ylmalonate, and almost complete disappearance of 1-decen-5-yne (Table II).

To ascertain the importance of carbanion intermediates in the formation of products from electrolyses of 1-iodo-5-decyne, three pairs of experiments were performed in dimethylformamide containing 0.1 M tetramethylammonium perchlorate and either 1 M H_2O or 1 M D_2O. As revealed in Table III, when deuterium oxide is present, approximately 6–10% of the total quantity of pentylidenecyclopentane formed is monodeuteriated at the vinyl position, whereas 50% of the resulting 5-decyne is $C_4H_9C{\equiv}CC_4H_8D$; as expected, the product of dehydrohalogenation (1-decen-5-yne) is not deuteriated, and the alcoholic side product is $C_4H_9C{\equiv}CC_4H_8OD$ exclusively. In a study of the reduction of iodobenzene at mercury in dimethylformamide containing tetraethylammonium bromide, de la Torre and Sease[12] determined that the kinetic isotope ratio (k_H/k_D) for protonation (deuteriation) of the electrogenerated phenyl carbanion in the presence of equal concentrations of H_2O and D_2O is 1.25. If we assume that the foregoing result is applicable to our electrolyses of 1-iodo-5-decyne and if the yield of each deuteriated product in Table III is increased by 25% to account for this kinetic isotope effect and to permit a strict comparison of experiments involving the use of H_2O and D_2O, there is no change in the essential conclusions about the role of carbanion intermediates: (i) the major pathway to formation of pentylidenecyclopentane does not involve carbanions, (ii) production of 5-decyne probably involves a carbanion precursor exclusively (for additional reasons discussed later), and (iii) 5-decyn-1-ol is obviously derived from attack of hydroxide (deuterioxide) on the starting material.

Effect of Changing the Concentration of Starting Material. Table IV shows the results of electrolyses of different concentrations of 1-iodo-5-decyne ranging from 1 to 10 mM that were performed at -1.70 V in dimethylformamide containing 0.1 M tetramethylammonium perchlorate. For the first three entries in Table IV, it is obvious that an increase in the concentration of 1-iodo-5-decyne causes no change in the *n* value; however, there are a significant rise in the yield of pentylidenecyclopentane, a small growth in the quantity of 1-decen-5-yne, and drops in the amounts of 5-decyne and 5-decyn-1-ol. These trends parallel those seen previously in our study of the electrochemical reduction of 6-iodo-1-phenyl-1-hexyne at mercury in dimethylformamide.[10]

When the concentration of 1-iodo-5-decyne reaches 10 mM, more complicated behavior is observed. Although yields of 5,15-eicosadiyne, 5-decyne, and 1-decen-5-yne continue to follow the established trends, two new compounds appear. One of these, 5,15-eicosdiyne, is a minor product formed in a yield of only 1–2%. More importantly, gas chromatographic analysis of an electrolyzed solution with the aid of an 18 ft × $^1/_8$ in. stainless-steel column packed with 3% OV-101 on 100–120 mesh Chromosorb WHP revealed a peak just barely resolved from that of unreduced starting material. Gas chromatography–mass spectrometry indicated that the new species has a mass spectrum [(70 eV) *m*/*e* (relative intensity) 264, M^+ (11.5); 137, $M^+ - I$ (3.4); 95, $M^+ - C_3H_6I$ (100)] very similar to the one reported earlier[1] for 1-iodo-5-decyne. On the basis of the preceding information, as well as knowledge about isomerizations of 1-phenyl-1-hexyne to 1-phenyl-1,2-hexadiene[13] and of 6-chloro-1-phenyl-1-hexyne to 6-chloro-1-phenyl-1,2-hexadiene[14] which occur during electrolyses of relatively high concentrations of these alkynes, we suspect that the new compound is 1-iododecadiene, though the positions of the carbon–carbon double bonds are not known. Base-catalyzed interconversions of alkynes, allenes, and dienes have been well documented.[15] If a

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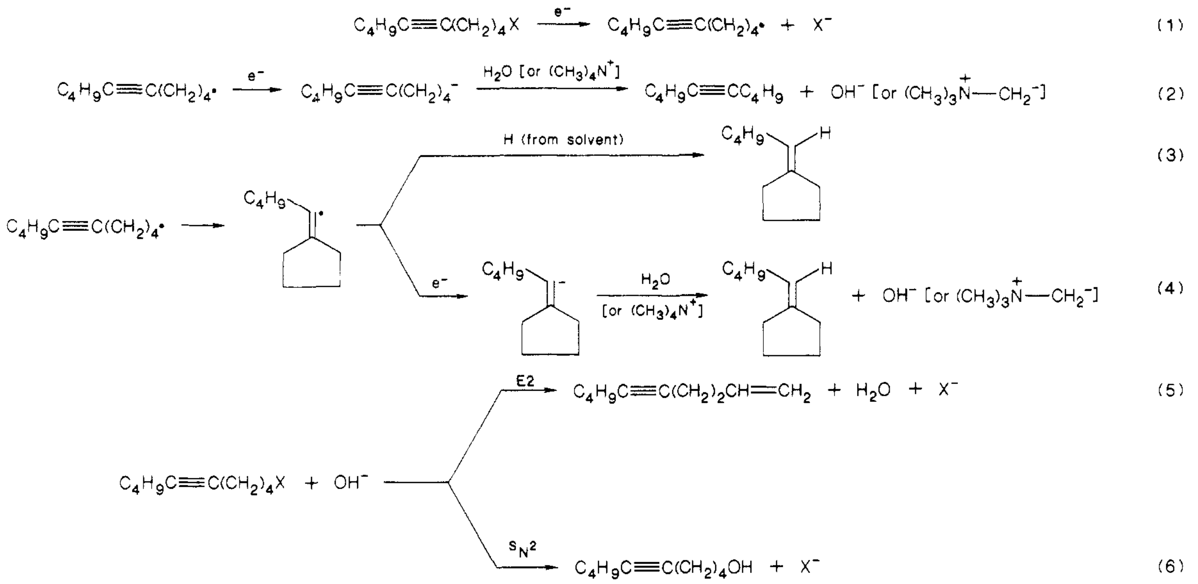
Scheme I



previously electrolyzed dimethylformamide–tetramethylammonium perchlorate solution containing residual 1-iodo-5-decyne, the postulated 1-iodododecadiene, and all the other products is electrolyzed a second time at a fresh reticulated vitreous carbon cathode held at −1.70 V, neither 1-iodo-5-decyne nor 1-iodododecadiene remains.

Mechanistic Aspects of the Reduction of 1-Halo-5-decynes at Reticulated Vitreous Carbon. Even though 1-iodo-5-decyne and 1-bromo-5-decyne both exhibit single voltammetric waves corresponding to overall two-electron scission of a carbon–halogen bond, it is reasonable to believe that the pathway for reduction proceeds via a radical intermediate which is generated transiently and reduced quickly to the carbanion. Moreover, because the potential required to reduce a carbon–iodine bond is not so negative as that needed to cleave a carbon–bromine bond, 5-decyn-1-yl radicals derived from 1-iodo-5-decyne should persist, before uptake of a second electron, for a longer (but still very short) time than the same radicals formed from 1-bromo-5-decyne.

Scheme I presents the reaction pathways that we believe account for the production of 5-decyne, pentylidenecyclopentane, 1-decen-5-yne, and 5-decyn-1-ol. As the first step in the mechanistic scheme, a one-electron reduction of the 1-halo-5-decyne gives the 5-decyn-1-yl radical (reaction 1).

Formation of 5-decyne undoubtedly occurs by protonation of the carbanion generated upon one-electron reduction of the 5-decyn-1-yl radical (or overall two-electron reduction of the starting material). It is not likely that 5-decyne arises via reaction of the 5-decyn-1-yl radical with a hydrogen atom donor (e.g., dimethylformamide) because intramolecular cyclization of the radical is much preferred. Evidence in support of the carbanion pathway (reaction 2) rests on the observations that (i) the voltammetric characteristics of 1-iodo-5-decyne and 1-bromo-5-decyne are identical with those of 1-iodododecane which does undergo a two-electron reduction at a vitreous carbon electrode[2] and (ii) approximately one-half of the 5-decyne obtained from electrolysis of 1-iodo-5-decyne in the presence of 1 M D_2O is monodeuteriated (Table III). Previous findings suggest that, even under conditions for which electrolysis of an alkyl halide leads with high efficiency to alkyl carbanions, these anions are not protonated exclusively by water when it is present in large excess. First, upon reduction of 1-iodododecane at a reticulated vitreous carbon cathode in dimethylformamide containing 0.1 M tetramethylammonium perchlorate, 5 mM H_2O, and 50 mM D_2O, only 15% of the decane formed is monodeuteriated.[3] Second, we have shown in a recent investigation[16] that, when *tert*-butyl bromide is reduced at a mercury pool electrode in dimethylformamide containing 0.1 M tetramethylammonium perchlorate-d_{12} and 15 mM H_2O, 34% of the resulting 2-methylpropane is monodeuteriated. Third, in electrolyses performed at mercury pool cathodes in dimethylformamide containing 0.1 M tetramethylammonium perchlorate and 1 M D_2O, 82% of the decane obtained from 1-iodododecane[11] and 66% of the octane produced from 2-iodooctane[17] are monodeuteriated. Taken together, these results indicate that the tetramethylammonium cation competes with water for protonation of alkyl carbanions, even in dimethylformamide containing 1 M H_2O and 0.1 M tetramethylammonium perchlorate.

Intramolecular cyclization of the 5-decyn-1-yl radical, followed by abstraction of a hydrogen atom from dimethylformamide, appears to be the predominant process responsible for the formation of pentylidenecyclopentane (reaction 3). An alternate mechanism (reaction 4) involving reduction of the cyclized radical and uptake of a proton from either water or tetramethylammonium ion must be of minor importance; as shown in Table III, when 1-iodo-5-decyne is electrolyzed in the presence of D_2O, no more than 10% of the resulting pentylidenecyclopentane is deuteriated. Moreover, there is even less reason to think that pentylidenecyclopentane might be formed via cyclization and protonation of the 5-decyn-1-yl *carbanion*; protonation of the primary carbanion, as soon as it is generated, to give 5-decyne is a far more favorable process than intramolecular cyclization of the primary carbanion. Electrolysis of 1-bromo-5-decyne (which is reduced at a potential nearly 500 mV more negative than that required for 1-iodo-5-decyne) almost assuredly leads mainly to a carbanion instead of a radical intermediate, so it is not surprising that the quantity of pentylidenecyclopentane derived from 1-bromo-5-decyne is comparatively small (Table I); in a number of previous studies,[1,7,17] we have seen a greater tendency for carbanions to be formed electro-

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[16] Vieira, K. L.; Mubarak, M. S.; Peters, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 5372–5373.

[17] Mbarak, M. S.; Peters, D. G. *J. Org. Chem.* **1982**, *47*, 3397–3403.

lytically from alkyl bromides than from alkyl iodides.

Reactions leading to the production of 1-decen-5-yne and 5-decyn-1-ol are analogous to processes reported in our previous paper.[1] When water (usually present residually at a concentration of 20–25 mM in the solvent-supporting electrolyte) acts as a proton donor for carbanions, the resulting hydroxide ion can dehydrohalogenate a molecule of unreduced starting material to yield 1-decen-5-yne (reaction 5) or can attack a molecule of unreduced starting material to afford 5-decyn-1-ol (reaction 6). Both of these reactions, the former being more facile, account for the fact that the coulometric *n* value is essentially unity (Table I) in the absence of a good proton donor. In a preparative-scale electrolysis, approximately one-half of the original 1-halo-5-decyne is reduced in a two-electron process, whereas the remainder of the starting material is consumed chemically via the E2 and S_N2 reactions; however, on the short time scale of a cyclic voltammetric or chronoamperometric measurement, these follow-up chemical reactions do not occur to a significant extent. When a proton donor (diethyl malonate or hexafluoroisopropyl alcohol) is introduced into the system, the occurrence of these strictly chemical processes is minimized because the hydroxide ion is reprotonated before it can attack the starting material. In turn, when chemical consumption of the 1-halo-5-decyne is less, the *n* value rises because more of the starting material is available for electrolysis, the yields of pentylidenecyclopentane and 5-decyne increase, and the amounts of 1-decen-5-yne and 5-decyn-1-ol decrease.

Implications of Our Results for Purposes of Electrosynthesis. A number of previous studies[18-24] have been concerned with the intramolecular reductive cyclization of acetylenic halides. Crandall and his co-workers[20,22-24] have reported that a variety of organometallic reductants can induce cyclizations of acetylenic halides via a predominantly free-radical pathway. For example, treatment of 6-bromo-1-phenyl-1-hexyne with tri-*n*-butyltin hydride in benzene[20] or with lithium biphenyl in tetrahydrofuran[20] or with chromium(II) in aqueous dimethylformamide containing ethylenediamine[24] affords benzylidenecyclopentane in a yield of at least 92%; reduction of 1-bromo-5-undecyne with either tri-*n*-butyltin hydride or lithium biphenyl produces hexylidenecyclopentane in a yield of 99%.[20] Thus, under favorable conditions, carbocyclic species can be formed almost exclusively from certain acetylenic halides, though the time required for complete reaction may be many hours.

In our earlier efforts to effect intramolecular cyclizations of 6-halo-1-phenyl-1-hexynes and 1-halo-5-decynes by electrolytic reduction of these species at mercury cathodes in dimethylformamide containing tetraalkylammonium perchlorates,[1,10] we found that both radical and carbanion intermediates can be generated but that the radical (6-phenyl-5-hexyn-1-yl or 5-decyn-1-yl), instead of preferentially undergoing intramolecular cyclization, interacts strongly with mercury ultimately to yield stable diorganomercury compounds. Accordingly, we were led to the present investigation in which an electrode material (vitreous carbon) was employed that was not anticipated to react chemically with 5-decyn-1-yl radicals electrogenerated via reduction of 1-halo-5-decynes.

Our expectations have been justified by the fact that use of a vitreous carbon cathode for the electrolysis of 1-iodo-5-decyne does afford pentylidenecyclopentane in substantial yield. In the absence of an added proton donor, reduction of the acetylenic iodide in dimethylformamide containing tetramethylammonium perchlorate leads to formation of the carbocycle in yields exceeding 40–45% (Table I). However, if electrolysis of 1-iodo-5-decyne is performed in the presence of a slight excess of hexafluoroisopropyl alcohol—a proton donor which blocks extraneous chemical consumption of the acetylenic iodide via E2 and S_N2 reactions involving the hydroxide ion—the yield of pentylidenecyclopentane can rise to 60% (Table II). In terms of a laboratory-scale synthesis of pentylidenecyclopentane, the latter result means that electrolysis for 1 h of 50 mL of a 2.5 mM solution of 1-iodo-5-decyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate and 5 mM hexafluoroisopropyl alcohol at a vitreous carbon cathode having an area[2] of 200 cm^2 and held at −1.45 V will afford approximately 10 mg of the carbocycle (which must be separated from about 5 mg of 5-decyne). However, by increasing the solution volume to 500 mL and by raising the concentrations of starting material and hexafluoroisopropyl alcohol to 10 and 20 mM, respectively, one should be able to obtain up to 400 mg of pentylidenecyclopentane from a single electrolysis and there is no reason to believe that the scale of the electrosynthesis cannot be increased considerably more if desired.

Crandall and Michaely[22] have demonstrated that phenyl-conjugated acetylenic halides such as 6-iodo-1-phenyl-1-hexyne undergo intramolecular cyclization approximately 40 times faster than analogous alkyl-substituted acetylenic halides such as 1-iodo-5-decyne. Those observations are consistent with our previous findings that, under otherwise identical conditions, electrolysis of 6-iodo-1-phenyl-1-hexyne at mercury[10] leads to benzylidenecyclopentane (24%) more efficiently than reduction of 1-iodo-5-decyne at mercury[1] gives pentylidenecyclopentane (9%). On the basis of this comparison, we have begun to examine the electrochemical reduction of 6-iodo-1-phenyl-1-hexyne at vitreous carbon in dimethylformamide containing tetraalkylammonium salts to ascertain if benzylidenecyclopentane can be obtained in attractively high (if not virtually quantitative) yield.

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