Electrochemical Reduction of 1-Iodo-5-decyne and 1-Bromo-5-decyne at Mercury Cathodes in Dimethylformamide

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Pulse polarograms for 1-iodo-5-decyne in dimethylformamide containing tetramethylammonium perchlorate exhibit two waves. At potentials corresponding to the first wave, electrolysis of 1-iodo-5-decyne at mercury results in 5-decynyl radicals that (i) adsorb onto and interact with the mercury electrode to give 5-decynylmercury radicals which disproportionate into di-5-decynylmercury or (ii) cyclize and then accept a hydrogen atom to yield pentylidenecyclopentane. At potentials on the second wave, reduction of 1-iodo-5-decyne is largely a two-electron process leading to the 5-decynyl carbanion which is protonated by water in the solvent-supporting electrolyte to yield 5-decyne and hydroxide ion; hydroxide ion then attacks unreduced starting material to give 1-decen-5-yne and 5-decyn-1-ol. In the presence of excess proton donor (diethyl malonate), neither 1-decen-5-yne nor 5-decyn-1-ol is obtained, but diethyl 5-decynylmalonate is produced, the quantity of 5-decyne is increased, and the coulometric n value is raised. Pulse polarograms for 1-bromo-5-decyne show a single wave. For reduction of 1-bromo-5-decyne, the yields of 5-decyne and 1-decen-5-yne are comparable to those derived from 1-iodo-5-decyne; some di-5-decynylmercury is produced, but no pentylidenecyclopentane is formed.

In previous research^{1,2} we examined the electrochemical behavior of the family of 6-halo-1-phenyl-1-hexynes at mercury cathodes in dimethylformamide containing tetraalkylammonium perchlorates. Our interest in the electrochemistry of these species stemmed from earlier reports³⁻⁸ that certain acetylenic halides undergo intramolecular cyclization when treated homogeneously with organometallic reducing agents.

A study of the electrochemical reduction of 6-chloro-1phenyl-1-hexyne¹ revealed that the primary process is transfer of one electron to the phenyl-conjugated carboncarbon triple bond, after which intramolecular cyclization of the radical anion (with displacement of chloride) can occur; alternatively, the electrogenerated radical anion of 6-chloro-1-phenyl-1-hexyne can promote isomerization of the starting material to 6-chloro-1-phenyl-1,2-hexadiene. Most significantly, from either the parent compound or the allene, a mixture of electrolysis products, including both alicyclic and acyclic materials, is obtained.

In contrast to the behavior of 6-chloro-1-phenyl-1-hexyne, the first step in the electrolytic reduction of 6-iodo-1-phenyl-1-hexyne² is one-electron cleavage of the carbon-halogen bond; the two dominant reactions of the resulting primary radical are (i) intramolecular cyclization to yield (after hydrogen atom abstraction) benzylidenecyclopentane and (ii) interaction with the mercury electrode to give (via disproportionation of adsorbed organomercury radicals) an acyclic diorganomercury compound. At potentials more negative than those needed to cause just one-electron scission of the carbon-iodine bond, the carbon-halogen site can accept two electrons to form an alkyl carbanion and, in addition, the phenyl-conjugated carbon-carbon triple bond becomes electroactive; consequently, at these potentials the electrochemistry of 6iodo-1-phenyl-1-hexyne (as well as that of its bromo analogue) is complicated by processes involving reduction of acetylenic and allenic moieties along with the carbonhalogen bond.

In the present work, we have investigated the electrochemical reduction of 1-iodo-5-decyne and 1-bromo-5-decyne at mercury electrodes in dimethylformamide containing tetramethylammonium perchlorate. These acetylenic halides do not possess electroactive carbon-carbon triple bonds, so that electrolytic cleavage of the carbonhalogen bonds can be studied exclusively over a relatively wide range of potentials. Yet, the acetylenic moieties of these compounds are appropriately positioned to allow intramolecular attack (leading to the formation of pentylidenecyclopentane) of the reduced carbon-halogen site on the triple bond.

Experimental Section

Reagents. Tetramethylammonium perchlorate, tetra-*n*-butylammonium perchlorate, and tetra-*n*-hexylammonium perchlorate, all obtained from the G. Frederick Smith Chemical Co., were used without further purification as supporting electrolytes. Dimethylformamide utilized as solvent was purchased from Burdick and Jackson Laboratories, Inc.; it was distilled through a 40-cm Vigreux column at a pressure of 15-20 torr. Matheson prepurified nitrogen (99.998%) was employed to deaerate solutions.

Starting materials (1-bromo-5-decyne and 1-iodo-5-decyne) were prepared by addition of the appropriate 1,4-dihalobutane to a solution of lithium butylacetylide (obtained from reaction of *n*-butyllithium with 1-hexyne in tetrahydrofuran).^{5,7} Distillation of 1-bromo-5-decyne gave a clear liquid: bp 62 °C (0.4 torr); NMR (CCl₄) δ 3.40 (t, 2, CH₂Br), 2.25–1.15 (m, 12, CH₂), and 0.93 (t, 3, CH₃). Mass spectra at 70 eV yielded the following results, relative abundances being reported in parentheses: m/e 218, M⁺ (0.4%); 216, M⁺ (0.5%); 137, M⁺ – Br (4.3%); and 95, M⁺ – C₃H₆Br (100%). For 1-iodo-5-decyne, the following data were obtained: bp 72 °C (0.4 torr); NMR (CCl₄) δ 3.18 (t, 2, CH₂I), 2.26–1.16 (m, 12, CH₂), and 0.92 (t, 3, CH₃); mass spectrum (70 eV), m/e 264, M⁺ (1.2%); 137, M⁺ – I (1.6%); and 95, M⁺ – C₃H₆I (100%).

Instrumentation and Procedures. Electrochemical cells and instrumentation for conventional and pulse polarography and for cyclic voltammetry as well as procedures for controlled-potential electrolyses have been described previously.⁹ All potentials are quoted with respect to a reference electrode consisting of a sat-

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urated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.75 V vs. the aqueous saturated calomel electrode.^{10,11}

After a controlled-potential electrolysis was finished, the solution was subjected to the same procedure for extraction of products that is outlined in earlier papers;^{2,9} the ether extract obtained from the electrolyzed solution was concentrated and analyzed by means of gas chromatography. Gas chromatographic measurements were performed with the aid of a Hewlett-Packard Model 5712A dual-column instrument equipped with a thermal conductivity detector; columns used were a 20 in. \times $^{1}/_{8}$ in. stainless-steel column packed with 10% OV-101 on 80–100 mesh Gas Chrom P, a 14 ft $\times 1/8$ in. stainless-steel column packed with 15% Carbowax 20M-TPA on 80-100 mesh Chromosorb WHP, and a 12 ft \times ¹/₈ in. stainless-steel column packed with 3% Carbowax 20M-TPA on 80–100 mesh Chromosorb WHP.

A Varian EM-360 spectrometer was used to record ¹H NMR spectra; chemical shifts are reported in ppm downfield from tetramethylsilane. Gas chromatographic-mass spectrometric data for individual electrolysis products were obtained from a Hewlett-Packard Model 5710A gas chromatograph coupled to a Hewlett-Packard Model 5980A mass spectrometer.

A known quantity of an electroinactive internal standard (ndodecane) was added to each solution prior to electrolysis. An experimentally measured gas chromatographic response factor for each major electrolysis product permitted the absolute yield of that product to be determined; however, it proved necessary to obtain the amount of di-5-decynylmercury from a calibration curve. Accordingly, all product yields reported in this paper are absolute and are expressed in terms of the percentage of starting material incorporated into a particular species.

Product Identification. We identified 5-decyne as the major hydrocarbon electrolysis product by matching its properties to those of commercially available material: bp 36 °C (2 torr); NMR (CCl₄) δ 2.12 (m, 4, C=CCH₂), 1.43 (m, 8, CH₂), and 0.91 (m, 6, (CH_3) ; mass spectrum (70 eV), m/e 138, M^+ (17.7%); 123, M^+ – CH_3 (3.1%); 109, $M^+ - C_2H_5$ (14.1%); 95, $M^+ - C_3H_7$ (43.3%); and 81, $M^+ - C_4 H_9$ (100%).

By adding 4-bromo-1-butene to a solution of lithium butylacetylide, we synthesized an authentic sample of 1-decen-5-yne: bp 45-46 °C (4 torr); NMR (CCl₄) δ 6.0-5.54 (m, 1, CH₂=CH), 5.07-4.85 (t, 2, CH_2 =CH), 2.13 (m, 6, CH_2C =CCH₂CH₂C=C), 1.41 (m, 4, CH_2), and 0.91 (m, 3, CH_3); the gas chromatographic retention time of this 1-decen-5-yne was in good agreement with that of one of the electrolysis products. In addition, gas chromatography-mass spectrometry of the electrolysis product gave the following results: m/e (70 eV) 136, M^+ (0.3%); 135, $M^+ - 1$ (1.6%); 121, $M^+ - CH_3$ (56.3%); 107, $M^+ - C_2H_5$ (34.5%); and 93, $M^+ - C_3 H_7$ (100%).

Preparation of pentylidenecyclopentane involved mixing equivalent quantities of a 10% solution of tri-n-butyltin hydride in benzene and a 0.07 M solution of 1-bromo-5-decyne in benzene (containing 1.8 mol % of azobis(isobutyronitrile) as an initiator) followed by refluxing for 36 h;⁵ the product of interest was purified by means of distillation: bp 50–51 °C (4 torr); NMR (CCl₄) δ 5.13 (m, 1, C=CH), 2.13 (m, 6, CH₂C=C), 1.6–1.3 (m, 8, CH₂), and 0.88 (t, 3, CH₃). We found that the gas chromatographic retention time of this product is identical with that of the suspected product. Gas chromatography-mass spectrometry of the electrolysis product revealed the expected spectrum: m/e (70 eV) 138, M⁺ (23.9%); 123, M⁺ – CH₃(0.7%); 109, M⁺ – C₂H₅(6.5%); and 95, $M^+ - C_3 H_7 (100\%).$

We isolated di-5-decynylmercury from electrolyzed solutions by means of gel-permeation chromatography with a 100-cm \times 1.5-cm glass column containing Bio-Beads S-X12 (200-400 mesh, Bio-Rad Laboratories); toluene was employed as the mobile phase. Mass spectra at 70 eV provided the following data: m/e 137, M⁺ $-C_{10}H_{17}Hg$ (8.6%); 95, M⁺ $-C_{10}H_{17}Hg(CH_2)_3$ (100%); and the characteristic isotope pattern of elemental mercury [198 (5.7%), 199 (11.4%), 200 (11.4%), 201 (8.6%), 202 (17.1%), and 204 (2.9%)]. To verify that the diorganomercury electrolysis product contains no carbocyclic moiety, ¹³C NMR spectra were recorded at 90.8 MHz with a Nicolet 360-MHz spectrometer. Peak assignments were made with respect to several reference compounds (3-hexyne, 3-heptyne, 4-octyne, methylenecyclopentane, and methylenecyclobutane); spectra for the diorganomercury species revealed the presence of the sp carbon atoms of an alkynyl group which absorb at 80.3 and 80.2 ppm (downfield from tetramethylsilane), but no signal appeared in the region from 110 to 150 ppm where sp^2 carbon atoms of an alkene absorb. Consequently, the product isolated from electrolyses is exclusively di-5-decynylmercury.

Another compound found in electrolyzed solutions was 5-decyn-1-ol; this product was identified by comparison of its gas chromatographic retention time and mass spectrum with those of a synthesized sample. We prepared this compound by stirring 1-iodo-5-decyne and tetramethylammonium hydroxide in dimethylformamide for 1-2 h. Mass spectra obtained at 70 eV for 5-decyn-1-ol yielded the following results: m/e 126, $M^+ - C_2H_4$ (6.4%); 111, $M^+ - C_3H_7$ (21%); 97, $M^+ - C_4H_9$ (33%); 79, $M^+ - C_4H_9$ $C_4H_{11}O(100\%)$; 73, $M^+ - C = CC_4H_0(69\%)$; 57, $C_4H_0^+(24\%)$; and 31, CH₂=OH⁺ (59%).

Identification of diethyl 5-decynylmalonate was accomplished by means of gas chromatography-mass spectrometry: m/e (70 eV) 296, M⁺ (0.3%); 251, M⁺ - C₂H₅O (4.8%); 223, M⁺ - COOC₂H₅ (59%); 173, M⁺ – C₉H₁₅ (20%); 159, M⁺ – C₁₀H₁₇ (7.8%); and 137, $M^+ - CH(COOC_2H_5)_2$ (8.6%).

An authentic sample of 5,15-eicosdiyne (the dimer derived from the 1-halo-5-decynes) was prepared by addition of the Grignard reagent of 1-bromo-5-decyne to a suspension of silver bromide in anhydrous diethyl ether;² the desired dimeric product exhibited the following mass spectrum at 70 eV: m/e 274, M⁺ (0.1%); 245, $\begin{array}{l} \mathbf{M}^{+} - \mathbf{C}_{2}\mathbf{H}_{5} \ (0.8\%); \ 217, \ \mathbf{M}^{+} - \mathbf{C}_{4}\mathbf{H}_{9} \ (9.6\%); \ 161, \ \mathbf{M}^{+} - \mathbf{C}_{8}\mathbf{H}_{17} \ (11\%); \\ 95, \ \mathbf{M}^{+} - \mathbf{C}_{13}\mathbf{H}_{23} \ (42\%); \ 81, \ \mathbf{M}^{+} - \mathbf{C}_{14}\mathbf{H}_{25} \ (73\%); \ \text{and} \ 67, \ \mathbf{M}^{+} - \mathbf{M}_{13}\mathbf{H}_{17} \ (11\%); \\ \mathbf{M}^{+} - \mathbf{M}_{13}\mathbf{H}_{23} \ (42\%); \ 81, \ \mathbf{M}^{+} - \mathbf{M}_{14}\mathbf{H}_{25} \ (73\%); \ \mathbf{M}_{15}^{+} - \mathbf{M}_{15}\mathbf{H}_{17} \ \mathbf{M}_{17}^{+} - \mathbf{M}_{17} \ \mathbf{M}_{17}^{+} - \mathbf{M}_{18}\mathbf{H}_{17} \ \mathbf{M}_{18}^{+} - \mathbf{M}_{18}\mathbf{H}_{18}^{+} - \mathbf{M}_{18}\mathbf{H}_{18}^{+}$ $C_{15}H_{27}$ (100%). Gas chromatographic and mass spectrometric data for 5,15-eicosdiyne indicated that this species is not among the products obtained from controlled-potential electrolyses of 1-bromo-5-decyne and 1-iodo-5-decyne.

Results and Discussion

Polarographic Behavior of 1-Iodo-5-decyne and 1-Bromo-5-decyne. Conventional dc polarograms for 1-iodo-5-decyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate are similar in appearance to those published previously for 1-iododecane under comparable experimental conditions.⁹ Changing the identity of the supporting electrolyte to tetra-n-butylammonium perchlorate or tetra-n-hexylammonium perchlorate has the same effects on the half-wave potentials of the polarographic waves and on the position and size of the polarographic maximum that have been observed in earlier work.^{2,12-14} A dc pulse polarogram for 1-iodo-5-decyne provides the best proof that the carbon-iodine bond undergoes stepwise reductive cleavage, first to the radical and then to the carbanion; for a 1 mM solution of the acetylenic iodide in dimethylformamide containing 0.1 M tetramethylammonium perchlorate, the two pulse polarographic waves are well resolved (having half-wave potentials of -0.93 and -1.36 V) and the heights of the two waves are equal. Pulse polarograms for 1-iodo-5-decyne are virtually identical with those for 1-iododecane.9

Polarograms for 1-bromo-5-decyne differ from those for 1-bromodecane. An ordinary dc polarogram for 1bromo-5-decyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate exhibits a single wave, but there is a pronounced current maximum on the rising portion of the wave. Although 1-bromodecane exhibits one polarographic wave with a half-wave potential (-1.40 V)

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 Table I. Coulometric Data and Product Distributions for Electrolytic Reduction of 0.0025 M 1-Iodo-5-decyne in Dimethylformamide Containing 0.1 M Tetraalkylammonium Perchlorates

	product distribution, %						
potential, V	n value	5-decyne	1-decen- 5-yne	pentylidene- cyclopentane	5-decyn- 1-ol	di-5-decynyl- mercury	total recovery, %
-1.0 ^{<i>a</i>}	0.97	, a - 1 - 1 - 1 - 1		4		89	93
-1.2^{a}	0.99	4		3	1	85	93
-1.3^{a}	1.00	12	2	3	1	72	90
-1.4^{a}	1.01	27	11	2	<1	48	88
-1.5^{a}	1.00	38	16	1	1	23	79
-1.7^{a}	0.99	42	21	1	2	13	79
-1.2^{b}	0.93	1		9		81	91
-1.3^{c}	0.93	2		9		80	91

 a Supporting electrolyte was tetramethylammonium perchlorate. b Supporting electrolyte was tetra-*n*-butylammonium perchlorate.

 Table II.
 Coulometric Data and Product Distributions for Electrolytic Reduction of 0.0025 M 1-Bromo-5-decyne in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate

potential, V	n value	5-decyne	1-decen- 5-yne	pentylidene- cyclopentane	5-decyn- 1-ol	di-5-decynyl- mercury	total recovery, %
-1.25	0.93	17	2	1	<1	65	91 <i>ª</i>
-1.4	1.08	41	16		1	21	79
-1.55	1.07	47	23		1	7	78
-1.7	1.10	50	24		1	2	77

^a Included in this total recovery is 6% unreduced 1-bromo-5-decyne.

approximately equal to that for 1-bromo-5-decyne, the simple alkyl bromide shows no polarographic maximum. For 1-bromo-5-decyne a single pulse polarographic wave is observed with a half-wave potential of -1.41 V and with a height equal to the sum of the two steps of the pulse polarogram for 1-iodo-5-decyne; such behavior indicates that 1-bromo-5-decyne undergoes essentially direct two-electron reduction to form an alkyl carbanion.

Controlled-Potential Electrolyses of 1-Iodo-5-decyne and 1-Bromo-5-decyne. Summarized in Tables I and II are results of controlled-potential electrolyses of 1-iodo-5-decyne and 1-bromo-5-decyne at mercury pool cathodes in dimethylformamide containing a tetraalkylammonium perchlorate as supporting electrolyte; for all of the experiments, the solvent-supporting electrolyte contained water.¹⁵ Over the range of potentials explored, the coulometric *n* value is essentially unity for both starting materials, although it is slightly higher for the bromo compound; thus, each acetylenic halide undergoes *net* one-electron reduction. Five species—di-5-decynylmercury, 5-decyne, pentylidenecyclopentane, 1-decen-5yne, and 5-decyn-1-ol—have been identified as electrolysis products.

For the reduction of 1-iodo-5-decyne, the distribution of products as a function of potential follows a pattern similar to that for 6-iodo-1-phenyl-1-hexyne.² At potentials (-1.0 and -1.2 V) corresponding to the first pulse polarographic wave for 1-iodo-5-decyne, di-5-decynylmercury is the predominant product, and small quantities of pentylidenecyclopentane and 5-decyne are formed. As the potential is shifted to more negative values on the rising portion (-1.3 and -1.4 V) and on the plateau (-1.5 and -1.7 V) of the second pulse polarographic wave, the yields of di-5-decynylmercury and pentylidenecyclopentane decrease, while the amounts of 5-decyne and 1-decen-5-yne increase; the quantity of 5-decyn-1-ol is variable and small.

(15) We have found that the concentration of water is approximately 0.05 M in solvent-supporting electrolyte that is not subjected to any special drying procedure; this water concentration is at least 20 times that of the starting material.

A notable difference between the electrochemical behavior of 1-bromodecane¹² and that of 1-bromo-5-decyne is the formation of substantial amounts of a diorganomercury product, namely di-5-decynylmercury, from the latter starting material. When 1-bromo-5-decyne is electrolyzed at -1.25 V (Table II), we contend (in part, as discussed later, from the absence of any sizable effect due to an added proton donor) that the starting material undergoes predominantly one-electron reduction to yield an adsorbed organomercury radical that disproportionates to produce di-5-decynylmercury in 65% yield. A potential of -1.25 V corresponds to the foot of the pulse polarographic wave for 1-bromo-5-decyne; more significantly, this potential is positive with respect to the current maximum seen on a conventional dc polarogram. In earlier investigations,^{2,9,12,13,16,17} we concluded that the appearance of a polarographic current maximum for an alkyl halide is related to the reduction of adsorbed organomercury radicals and that this phenomenon serves as a diagnostic criterion for predicting the formation of diorganomercury compounds from the electrolytic reduction of alkyl halides. Because 1-bromodecane exhibits no polarographic maximum, didecylmercury is not an expected electrolysis product and, indeed, none is formed at any potential. Electrolyses of 1-bromo-5-decyne at potentials increasingly more negative than the polarographic maximum (or at potentials near the top or on the plateau of the pulse polarographic wave) result in less di-5-decynylmercury plus increased yields of 5-decyne and 1-decen-5-yne; little, if any, pentylidenecyclopentane and 5-decyn-1-ol are obtained.

As the potential is made more negative, the total recovery of products listed in Tables I and II decreases. We suspect that some 1-decen-5-yne is converted into telomers analogous to those found¹² for the reduction of 1-iododecane and 1-bromodecane and to those proposed² to form

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 Table III. Comparison of Coulometric Data and Product Distributions for Electrolytic Reductions of 0.0025 M

 1-Iodo-5-decyne and 1-Bromo-5-decyne in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate

 in the Absence and Presence of Diethyl Malonate

	product distribution, %						
potential, V	l, <i>n</i> value	5-decyne	1-decen- 5-yne	pentylidene- cyclopentane	5-decyn- 1-ol	di-5-decynyl- mercury	total recovery, %
		· · · · · · · · · · · · · · · · · · ·	(1) 1-Iodo	-5-decyne			
-1.0	0.97		× /	4		89	93
-1.0^{a}	0.96			4		89	94 ^b
-1.7	0.99	42	21	1	2	13	79
-1.7^{a}	1.50	64		-	-	10	88 <i>°</i>
			(2) 1-Brom	o-5-decyne			
-1.95	0.93	17	2	1	<1	65	91 d
-1.25^{a}	0.94	19	24	-		66	94 e
-1.7	1.10	50	24		1	2	77
-1.74	2.00	81	<i>~</i> -		-	-	81

^a In each of these experiments, the concentration of diethyl malonate was 0.005 M. ^b A 1% yield of diethyl 5-decynylmalonate is included. ^c A 14% yield of diethyl 5-decynylmalonate is included. ^d A 6% yield of unreduced 1-bromo-5decyne is included. ^e A 2% yield of diethyl 5-decynylmalonate and a 7% yield of unreduced 1-bromo-5-decyne are included.



during electrolyses of 6-iodo-1-phenyl-1-hexyne and 6bromo-1-phenyl-1-hexyne; however, we have not attempted to identify or quantitate such telomers in the present work. If we assume that the unrecovered products (telomers) are derived from 1-decen-5-yne, the corrected yield of 1-decen-5-yne is nearly the same as the observed percentage of 5-decyne.

Controlled-Potential Electrolyses of 1-Iodo-5-decyne and 1-Bromo-5-decyne in the Presence of a Proton Donor (Diethyl Malonate). Compiled in Table III are coulometric data and product distributions for controlled-potential electrolyses of 1-iodo-5-decyne and 1-bromo-5-decyne in dimethylformamide containing 0.1 M tetramethylammonium perchlorate and 5 mM diethyl malonate. For purposes of comparison, results are listed for electrolyses conducted in the presence and absence of diethyl malonate at -1.0 and -1.7 V for 1-iodo-5-decyne (potentials corresponding, respectively, to the rising portion of the first pulse polarographic wave and to the plateau of the second pulse polarographic wave) and at -1.25 and -1.7 V for 1-bromo-5-decyne (potentials corresponding, respectively, to the foot and to the plateau of the single pulse polarographic wave); the chosen potentials are, respectively, more positive and more negative than the polarographic maximum for each compound.

At potentials positive with respect to the polarographic maximum, the product distributions and coulometric data show little, if any, dependence on whether or not diethyl malonate is introduced into the system. On the other hand diethyl malonate has a profound effect at potentials negative of the polarographic maximum. Comparing results obtained for reduction of the acetylenic halides at -1.7 V, we observed a substantial increase in the coulometric nvalue for each compound with added diethyl malonate. In addition, at -1.7 V with the proton source present, the yield of 5-decyne is greater, no 1-decen-5-yne or 5-decyn-1-ol is found, and there is a small decrease in the quantity of di-5-decynylmercury. A new species, diethyl 5-decynylmalonate, is produced; this compound is presumably formed by attack of the diethyl malonate anion on unreduced starting material.

Mechanism for Reduction of 1-Halo-5-decynes. Reactions 1 through 4 in Scheme I characterize the electrochemistry of 1-iodo-5-decyne at potentials on the first pulse polarographic wave. All evidence is consistent with the conclusion that di-5-decynylmercury and pentylidenecyclopentane arise from processes involving the 5decynyl radical. First, as revealed by the first pair of entries in Table III, the coulometric n value and product distribution are not affected by addition of a proton donor—an observation indicating the absence of a carbanionic intermediate. Second, the production of diorganomercury compounds does appear to proceed via adsorbed alkyl radicals, 2,9,12,16-18 and intramolecular cyclization of 1-iodo-5-decyne in the presence of a reducing agent such as tri-n-butyltin hydride is well established as a radical reaction.⁵ Relative yields of the diorganomercury and carbocyclic species depend on the rates of competitive processes involving 5-decynyl radicals: (i) generation and disproportionation of adsorbed organomercury radicals to yield di-5-decynylmercury and (ii) intramolecular cyclization of 5-decynyl radicals, followed by hydrogen atom abstraction from the solvent,¹⁹ to form pentylidenecyclopentane. It is not possible to distinguish whether pentylidenecyclopentane originates from cyclization of adsorbed or solution-soluble 5-decynyl radicals.

We believe that the small amount (4%) of 5-decyne, obtained at a potential (-1.2 V) corresponding to the first pulse polarographic wave for 1-iodo-5-decyne, is formed by one-electron reduction of 5-decynyl radicals, followed by transfer of a proton (probably from water present in the solvent-supporting electrolyte) to 5-decynyl carbanions. This pathway (steps 5 and 6 in Scheme I) is preferred over transfer of a hydrogen atom to a 5-decynyl radical because no 5-decyne appears until the potential on the plateau of the first pulse polarographic wave is sufficiently negative to be actually on the foot of the second pulse polarographic wave.

At potentials corresponding to the first pulse polarographic wave and in dimethylformamide containing 0.1 M tetra-n-butylammonium perchlorate, electrolytic reduction of 6-iodo-1-phenyl-1-hexyne gives benzylidenecyclopentane (24%),² whereas electrolysis of 1-iodo-5-decyne affords pentylidenecyclopentane (9%). These observations are consistent with those of Crandall and Michaely,⁷ who proposed that, in the presence of organometallic reducing agents, phenyl-conjugated acetylenic halides undergo intramolecular cyclization approximately 40 times faster than analogous alkyl-substituted acetylenic halides because the phenyl moiety confers extra stability on the cyclic vinyl radical intermediate. However, the amounts of carbocycles produced electrolytically are considerably smaller than the nearly quantitative yields of carbocyclic species obtained with homogeneous-phase reductants.

On the basis of ¹³C NMR spectra, none of the diorganomercury compound derived from 1-iodo-5-decyne possesses a carbocyclic moiety. For the electrolysis of 6-iodo-1-phenyl-1-hexyne,² we found that only a small fraction of the diorganomercury compound contained the benzylidenecyclopentane group. Thus, there is little, if any, incorporation of carbocyclic radicals into dialkylmercury species, despite the fact that electrolytic reduction of acetylenic halides does yield alicyclic hydrocarbons.

At potentials on the second pulse polarographic wave, the major intermediate derived from reduction of 1-iodo-5-decyne is the 5-decynyl carbanion, which reacts as shown in Scheme I. However, the appearance of di-5-decynylmercury at these potentials (Table I), as well as the absence of a significant change in the yield of the diorganomercury compound with added proton donor (Table III), confirms that the 5-decynyl radical is formed along the pathway from starting material to carbanion. Except for the radical-cyclization process leading to formation of pentylidenecyclopentane, the various steps in Scheme I are analogous to those for the reduction of 1-iododecane at the most negative potentials attainable.⁹ We propose that the 5-decynyl carbanion is protonated by water in the solvent-supporting electrolyte to yield 5-decyne and hydroxide ion. Hydroxide subsequently attacks unreduced 1-iodo-5-decyne in an E2 elimination to give 1-decen-5-yne; a small quantity of 5-decyn-1-ol results from the $S_N 2$ reaction between hydroxide and 1-iodo-5-decyne. Because consumption of one molecule of starting material via a chemical (E2 or S_N 2) pathway is coupled with two-electron electrolytic cleavage of the carbon-halogen bond of another molecule of starting material, the apparent coulometric nvalue is close to unity. Diethyl malonate blocks the E2 and $S_N 2$ reactions; presumably, hydroxide ions are protonated by diethyl malonate and are not available to attack the unreduced starting material, and the coulometric n value increases to 1.5.

A key to comprehending the electrochemistry of 1bromo-5-decyne is the current maximum (peaking at -1.39V) which appears on the rising portion of the conventional dc polarographic wave and which divides the potential region of interest into two parts. For the narrow range of potentials more positive than the maximum (i.e., from approximately -1.15 to -1.35 V), the predominant intermediate is the 5-decynyl radical. Supporting this conclusion is the production of di-5-decynylmercury in 65% yield at -1.25 V (Table II) as well as our observation that the coulometric n value and product distribution for electrolysis of 1-bromo-5-decyne at -1.25 V are relatively insensitive to the presence or absence of diethyl malonate (Table III). Nevertheless, notice in Table III that electrolysis of 1-bromo-5-decyne at -1.25 V leads to the formation of 5-decyne and 1-decen-5-yne in yields of 17% and 2%, respectively, in the absence of diethyl malonate, whereas 5-decyne is produced in 19% yield and 1-decen-5-yne is not obtained in the presence of diethyl malonate. These results suggest that, even at potentials positive with respect to the polarographic maximum for 1-bromo-5-decyne, 5decyne arises via two-electron reduction of the acetylenic bromide to form the 5-decynyl carbanion, which accepts a proton from water.

For the reduction of 1-bromo-5-decyne at potentials more negative than the polarographic maximum (i.e., from approximately -1.35 to -1.90 V, the latter being the cathodic limit in dimethylformamide containing 0.1 M tetramethylammonium perchlorate), the principal process appears to be two-electron cleavage of the carbon-bromide bond to yield the 5-decynyl carbanion. A comparison of data in Tables I and II indicates that, at the most negative potentials, the acetylenic bromide displays a greater tendency than the acetylenic iodide to undergo two-electron reduction. At a potential of -1.7 V, very little di-5decynylmercury is produced from 1-bromo-5-decyne, whereas electrolysis of 1-iodo-5-decyne affords the diorganomercury compound in 13% yield. In the presence of diethyl malonate at -1.7 V (Table III), 5-decyne is the only electrolysis product obtained from 1-bromo-5-decyne and the coulometric n value is essentially two.

No pentylidenecyclopentane is produced from 1bromo-5-decyne at potentials negative of the polarographic maximum. This implies that the 5-decynyl carbanion is more likely to gain a proton from the solvent-supporting electrolyte system to give 5-decyne than it is to undergo intramolecular cyclization to the anionic precursor of pentylidenecyclopentane. Such behavior is consistent with

⁽¹⁸⁾ Mbarak, M. S.; Peters, D. G. J. Org. Chem. 1982, 47, 3397-3403.
(19) We do not know, nor have we investigated, the fate of the radical derived by removal of a hydrogen atom from a solvent molecule.

observations previously reported by Crandall and Keyton⁵ concerning the reaction of 6-bromo-1-phenyl-1-hexyne with lithium biphenyl.

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Registry No. Hg, 7439-97-6; C₄H₉C=C(CH₂)₄, 40215-73-4; $C_4H_9C \equiv C(CH_2)_4Hg$, 86669-18-3; $C_4H_9C \equiv C(CH_2)_4I$, 42049-41-2; $C_4H_9C \equiv C(CH_2)_4Br$, 35843-78-8; $C_4H_9C \equiv CC_4H_9$, 1942-46-7; $C_4H_9C \equiv C(CH_2CH = CH_2, 82511-32-8; C_4H_9C \equiv C(CH_2)_4OH$, 68274-97-5; $[C_4H_9C \equiv C(CH_2)_4]_2Hg$, 86669-20-7; diethyl 5-decynylmalonate, 86669-19-4.

Solvent Isotope Effects on the Kinetics of Nucleophilic Addition of Water to a β -Nitrostyrene

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The hydrolysis rate of 3,4-(methylenedioxy)- β -nitrostyrene (S) has been measured in H₂O and in 99% D₂O buffer solutions from pH -0.9 to 10.6. The kinetic solvent isotope effect (KSIE), $k(H_2O)/k(D_2O)$, is 6.2 at pH 2.5, where k is independent of pH in both solvents and attains a higher value, approximately 22, at about pH 6.2. The isotope effects $k_i(H_2O)/k_i(D_2O)$ on the rate constants for the individual steps of the mechanism have been determined and their contributions to the overall KSIE evaluated. Accordingly, the KSIE on the pH-rate plateau at pH 1-4 can be separated into two factors: 5.0 for K_{12} , the ionization constant of S as a pseudo-base in water; and 1.4 for $k_3^{\rm H}$, the rate constant for rate-controlling protonation of the resulting anion by H₃O⁺. At pH 6.2, the higher KSIE (7.6) on $k_3^{\rm H_2O}$ becomes important while the uncatalyzed addition of water to the double bond is partly rate controlling. The rate at the midpoint of a proton–inventory plot (49.5% D_2O) shows a negative deviation from linearity of 18%.

When β -nitrostyrenes act as substrates in nucleophilic addition reactions in aqueous solutions, the retro-Knoevenagel process, hydrolytic cleavage, takes place.¹⁻⁵ In our last paper,⁴ we reported the rate of hydrolysis of 3,4-(methylenedioxy)- β -nitrostyrene (S), at pH 1-11, to the products P_1 and P_2 .

The anion⁶ T_{OH}- (Scheme I), readily formed by addition of hydroxide ion to S, was identified by its reversion to S after a pH jump. The nitro alcohol T_{OH} was prepared and used for direct observation of some of the intermediate reactions. The rate of condensation of the products P to form T_{0^-} was determined.⁴

In D_2O , the hydrolysis of S shows a rather large kinetic solvent isotope effect (KSIE). The object of this research was to measure the KSIE over a wide pH range and to separate the overall effect into KSIE's for the successive steps in the mechanism. The results support the previously proposed mechanism in which hydration of S occurs prior to the steps involving acid-base catalysis.

Results

In all experiments except one at pH 12, noted below, the rate of disappearance of the olefin S was followed by the decrease in its UV absorption. We define the initial rate coefficient⁷ k by dS/dt = -kS. Above pH 6, k is easily obtained since the reaction is first order. At lower pH, the cleavage of the intermediate T_{OH} is no longer fast compared with its reversion to S and the kinetics are characteristic of first-order consecutive reactions (eq 1).

$$S \xrightarrow[k_{-123}]{k_{-123}} T_{OH} \xrightarrow{k_{45}} P$$
 (1)

The uppermost set of points in Figure 1, for example, shows the decrease in nitrostyrene concentration with time, plotted as $\ln (S_0/S)$, in 0.0032 M HCl. The value of k can be obtained by estimating the initial slope of the curve, by approximation methods⁸ or by programming and fitting the exact solution⁹ to the rate equations for eq 1. Since the last procedure is necessary for D₂O solutions, which cause an earlier decrease in slope than H_2O , it was used in all three parallel runs at $[L^+] = 0.0032$, pL 2.5,¹⁰ shown in Figure 1. The same value of k_{45} , 1.5×10^{-7} s⁻¹, sufficed to fit all three, suggesting that the KSIE on the rate of cleavage of T_{OH} is small, though this could be more reliably determined by using the nitro alcohol T_{OH} itself as the substrate.⁴ The equilibrium constant k_{123}/k_{-123} for the best fit was approximately 0.46 in H_2O and 0.15 in D_2O ;¹¹ the mean value 0.30 was chosen for HDO. The rate constants k_{123} for these three particular runs were then computed: $1.64 \times 10^{-7} \text{ s}^{-1}$ in H₂O, $7.5 \times 10^{-8} \text{ s}^{-1}$ in HDO, and $2.5 \times 10^{-8} \text{ s}^{-1}$

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our previous notation (ref 4): T_{OH^-} for A_{1^-} , T_{OH} for 2, $T_{OH}^{O^-}$ for A_{2^-} and T^{\pm} for A^{\pm} .

⁽⁷⁾ k is the same as k_{ψ} in ref 4; k_{123} is the rate constant encompassing steps 1-3 in Scheme I, etc.
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⁽¹⁰⁾ L represents hydrogen, whether H or D.

^{(11) &}quot;D₂O" used as solvent throughout this work was 99.0% D₂O, 1.0% CH₂OH; "HDO" was 49.5% D₂O, 49.5% H₂O, 1.0% CH₃OH.