(Z)-1-(Lithiooxy)prop-1-ene (4Z): ^{1}H NMR (270 MHz, THF-d_8) δ 6.69 (d, 1 H, $J = 3.0$, LiOCH=), 3.6 (vinyl H, obscured by solvent), 1.47 (d, 3 H, $J = 6.0$ Hz, vinyl Me).

(E)-1-(Lithiooxy)prop-1-ene (4E): ^{1}H NMR (270 MHz, THF-d_8) δ 6.72 (d, $J = 11.0$ Hz, LiOCH=), 4.08 (m, 1 H, MeCH=), 1.40 (d, 3 H, $J = 5.9$ Hz, vinyl Me).

(Z)-3,3-Dimethyl-1-(lithiooxy)but-1-ene (5Z): ^{1}H NMR (270 MHz, THF-d_8) δ 6.46 (d, 1 H, $J = 6.5$ Hz, LiOCH=CH), 3.37 (d, 1 H, $J = 6.5$ Hz, LiOCH=CH), 1.08 (s, 9 H, $(CH_3)_3$C); ^{13}C NMR (70 MHz, THF-d_8) δ 150.3 (LiOC=C), 108.6 (LiOC=C), 33.9 ($(CH_3)_3$C), 32.9 ($(CH_3)_3C$).

(E)-3,3-Dimethyl-1-(lithiooxy)but-1-ene (5E): ^{1}H NMR (300 MHz, THF-d_8) δ 6.75 (d, 1 H, $J = 11.5$ Hz, LiOCH=CH), 4.29 (d, 1 H, $J = 11.5$ Hz, LiOCH=CH), 0.96 (s, 9 H, $(CH_3)_3$C); ^{13}C NMR (70 MHz, THF-d_8) δ 150.5 (LiOC=C), 111.7 (LiOC=C), 33.0 ($(CH_3)_3$C), 31.7 ($(CH_3)_3C$).

Electrochemical Reduction of Phenylpropadiene at Mercury Cathodes in Dimethylformamide: Isomerization of the Allene to 1-Phenyl-1-propyne

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Received August 28, 1986

Polarograms and cyclic voltammograms exhibit two waves for reduction of phenylpropadiene at a mercury electrode in dimethylformamide containing tetra-n-butylammonium perchlorate; the first wave signals reduction of phenylpropadiene to 1-phenyl-1-propene and the second wave is attributable to reduction of 1-phenyl-1-propene to 1-phenylpropane. However, the first wave is abnormally small because phenylpropadiene undergoes substantial rearrangement to 1-phenyl-1-propyne, which is reducible to 1-phenylpropane at nearly the same potential as 1-phenyl-1-propene. Controlled-potential electrolyses of phenylpropadiene, 1-phenyl-1-propene, and 1-phenyl-1-propyne at mercury pool cathodes have verified the processes elucidated by means of polarography and cyclic voltammetry. In the presence of diethyl malonate (a proton donor), base-catalyzed isomerization of phenylpropadiene to 1-phenyl-1-propyne is blocked totally; at a potential corresponding to the first wave for reduction of phenylpropadiene, electrolysis products are *trans*-1-phenyl-1-propene, *cis*-1-phenyl-1-propene, and 1-phenyl-2-propene, whereas 1-phenylpropane and 1-phenyl-2-propene are obtained at a potential on the second reduction wave for phenylpropadiene.

Two recent reviews[1,2] have dealt extensively with the electrochemical reduction and oxidation of allenes. In general, the allene moiety is not electroreducible unless it is conjugated to one or more phenyl groups or unless it is bonded to another activating substituent.

Our interest in the electrochemistry of phenylpropadiene stems from a paper by Doupeux, Martinet, and Simonet[3] concerning the cathodic behavior of several haloallenes, among which was 1-phenyl-3-bromopropadiene. These authors observed that, in dimethylformamide containing 0.1 M tetraethylammonium bromide, reduction of 1-phenyl-3-bromopropadiene gives rise to four polarographic waves, the third and fourth being attributed to stepwise reduction of phenylpropadiene to 1-phenyl-1-propene and to 1-phenylpropane. As part of the same work, the polarographic and coulometric characteristics of 3-chloro-3-phenyl-1-propyne in dimethylformamide containing 0.1 M tetraethylammonium perchlorate were examined, and the starting material was postulated to undergo a sequence of electron-transfer and proton-transfer reactions having phenylpropadiene as an intermediate. In a brief survey of the electrochemistry of 1-phenyl-1-hydroxy-2-propyne in dimethylformamide containing 0.1 M tetra-n-butylammonium iodide, Lund and co-workers[4] implied that, in the presence of a proton donor, phenylpropadiene might be involved in the overall course of the reduction. In none of these investigations, however, was the existence of phenylpropadiene actually demonstrated. Moreover, there has been no publication pertaining to the electrochemistry of phenylpropadiene itself.

Accordingly, we report the results of the first study of the electrochemical reduction of phenylpropadiene at mercury in dimethylformamide containing 0.1 M tetra-n-butylammonium perchlorate and of the electrolytically induced isomerization of phenylpropadiene to 1-phenyl-1-propyne.

Experimental Section

Reagents. Dimethylformamide used as solvent and tetra-n-butylammonium perchlorate employed as supporting electrolyte were handled as described in a previous paper.[5] Triply distilled mercury (Troy Chemical Corp., Wood Ridge Chemical Division) was utilized as electrode material. All deaeration and drying operations were carried out with either Matheson PP or Air Products UHP nitrogen.

Instrumentation and Procedures. Cells for polarography, cyclic voltammetry, and controlled-potential electrolyses were similar to those described in earlier publications.[5-7] 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;[8,9] this electrode has a potential of −0.75 V vs. the aqueous saturated calomel electrode at 25 °C.

Controlled-potential electrolyses were performed with the aid of a Princeton Applied Research Corporation (PARC) Model 173

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potentiostat–galvanostat equipped with a PARC Model 176 current-to-voltage converter capable of providing *iR* compensation. Polarograms and cyclic voltammograms were obtained by use of a PARC Model 175 Universal Programmer coupled to the potentiostat–galvanostat and were recorded with a Houston Instruments Model 2000-5-5 X–Y plotter.

Details about the procedures for polarography, cyclic voltammetry, and controlled-potential electrolysis are contained in previous reports from this laboratory.[6,10,11] In carrying out a large-scale electrolysis, we deaerated the solvent-supporting electrolyte solution and then performed a pre-electrolysis at −2.10 V; a known amount of starting material was introduced into the cell and was electrolyzed at the desired potential until the current decayed to the background level. At the end of the electrolysis, an accurately weighed quantity of an internal standard (ethylbenzene or 1-decene) was added to the catholyte; the solution was partitioned between water and diethyl ether, and the ether phase was washed with ice-cold water and then concentrated with the aid of a rotatory evaporator. Analysis of the ether extract containing electrolysis products was accomplished with a Hewlett-Packard Model 5712A gas chromatograph equipped with a thermal conductivity detector and coupled to a Hewlett-Packard Model 3380S integrator. Products were separated on either a 2 ft × $^1/_8$ in. stainless-steel column packed with 10% OV-101 on 80–100-mesh Supelcoport or a 20 ft × $^1/_8$ in. stainless-steel column packed with 15% Carbowax 20M on 80–100-mesh Chromosorb W. An absolute yield for each product was determined by comparison of its peak area with that of the internal standard; experimentally measured gas chromatographic response factors were established for the internal standard and the various products.

Product Identification. We confirmed the identity of each electrolysis product (1-phenyl-1-propyne, *trans*-1-phenyl-1-propene, *cis*-1-phenyl-1-propene, 1-phenylpropane, 1-phenyl-2-propene, and tri-*n*-butylamine) by comparing its gas chromatographic retention time and spectroscopic data with those of an authentic sample of the compound. Mass spectra were acquired with a Hewlett-Packard Model 5992 gas chromatograph–mass spectrometer system. Infrared spectra were obtained with a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were recorded with either a Varian Model T60-A or XL-100 spectrometer; all chemical shifts are reported in ppm downfield from tetramethylsilane.

Synthesis of Phenylpropadiene. Modifications of published methods were devised for the preparation of 1,1-dibromo-2-phenylcyclopropane[12] and of phenylpropadiene.[13]

In a flask fitted with a condenser and a drying tube, 2.49 g (63.7 mmol) of potassium and 50 mL of freshly distilled *tert*-butyl alcohol were refluxed until all the potassium was consumed; potassium *tert*-butoxide was isolated by evaporation of the excess alcohol. Immediately after being obtained, the potassium *tert*-butoxide was dissolved by transfer of 16 mL of *n*-pentane into the flask, and 3.03 g (29.1 mmol) of freshly distilled styrene was added. A dropping funnel equipped with a nitrogen line was used to deliver bromoform (14.9 g, 58.9 mmol) at the rate of one drop per minute into the solution (which was kept in an ice–salt bath); after addition of bromoform was completed, the reaction mixture was stirred at room temperature for 10 h. Then the reaction mixture was extracted with diethyl ether, the ether extract was washed with water and was dried over anhydrous magnesium sulfate, and ether and pentane were removed with the aid of a rotatory evaporator. Finally, pure 1,1-dibromo-2-phenylcyclopropane was obtained by vacuum distillation: bp 90–91 °C (0.1 torr); yield 5.21 g (65%); ^{1}H NMR ($CDCl_3$) δ 7.22 (s, 5, C_6H_5), 2.90 (t, 1, CH, J = 9.5 Hz), 1.98 (dd, 2, CH_2, J = 9.5 Hz, J' = 3 Hz); mass spectrum (70 eV), *m/e* (relative intensity) 197 (9), 195 (10), 117 (6), 116 (50), 115 (100).

In a nitrogen atmosphere, 10 mL of diethyl ether (freshly distilled from a sodium–benzophenone mixture) was transferred into a flask kept in a dry ice–acetone bath. Next, 1,1-dibromo-2-phenylcyclopropane (10.6 g, 38.4 mmol) was dissolved in the ether, methyllithium (30 mL of 1.5 M solution in ether) was quickly injected with a syringe through a septum into the flask, and the solution was stirred vigorously for 1 min. Immediately, 30 mL of 10% hydrochloric acid was added to quench the reaction. Then the mixture was extracted with diethyl ether, the ether phase was washed with water and was dried over anhydrous magnesium sulfate, and the ether was evaporated. Phenylpropadiene was distilled as a colorless liquid: bp 29 °C (0.8 torr); yield 3.12 g (70%); ^{1}H NMR ($CDCl_3$) δ 7.22 (s, 5, C_6H_5), 6.10 (t, 1, CH, J = 7 Hz), 5.07 (d, 2, CH_2, J = 7 Hz); IR 3100, 1940, 860 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 117 (6), 116 (68), 115 (100), 89 (28). After being prepared, phenylpropadiene was stored in the dark under nitrogen at −10 °C.

Synthesis of 1-Phenyl-1-deuteriopropadiene. Alternative Synthesis of Phenylpropadiene. We followed a general procedure suggested by Zweifel, Horng, and Snow[14] for the preparation of 1-phenyl-1-deuteriopropadiene.

Over a period of 45 min, 130 mL of 1.5 M methyllithium in diethyl ether was transferred via a cannula into a flask containing 18.6 g (182 mmol) of phenylacetylene and equipped with a magnetic stirring bar; then the mixture was stirred at room temperature for 1 h. Paraformaldehyde (10 g) in a second flask was decomposed thermally into formaldehyde, the formaldehyde was swept by a stream of nitrogen into the lithium phenylacetylide solution, and the mixture stood overnight. Next, the reaction mixture was extracted with diethyl ether, the ether extract was washed with water and dried over anhydrous magnesium sulfate, and the ether was evaporated. Phenyl propargyl alcohol was recovered as a colorless, viscous liquid by means of vacuum distillation: bp 83 °C (0.8 torr); yield 16.9 g (70%); ^{1}H NMR ($CDCl_3$) δ 7.30 (s, 5, C_6H_5), 4.50 (d, 2, CH_2, J = 5 Hz), 2.40 (t, 1, OH, J = 5 Hz); IR 3600–3200, 2250 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 132 (54), 131 (76), 115 (24), 77 (94), 31 (100).

Phenyl propargyl alcohol (2.59 g, 19.6 mmol) and tri-*n*-butylamine (3.63 g, 19.6 mmol) were dissolved in 10 mL of carbon tetrachloride contained in a flask at 0 °C. Thionyl chloride (2.33 g, 19.6 mmol) was added slowly to the solution through a dropping funnel during a 10-min period; the solution was allowed to warm to room temperature and was stirred for 1 h. Then the solution was extracted with diethyl ether, the ether was washed with 10% hydrochloric acid and dried over anhydrous magnesium sulfate, and the ether was evaporated. Phenyl propargyl chloride was vacuum distilled as a colorless liquid: bp 63 °C (0.8 torr); yield 2.32 g (79%); ^{1}H NMR ($CDCl_3$) δ 7.33 (s, 5, C_6H_5), 4.37 (s, 2, CH_2); mass spectrum (70 eV), *m/e* (relative intensity) 152 (4), 151 (2), 150 (13), 115 (100).

A three-necked flask was equipped with a nitrogen inlet and two dropping funnels. In the flask were placed 1.06 mL (8.62 mmol) of boron trifluoride etherate (redistilled at 50 °C and kept under nitrogen prior to its use), 1.83 mL (17.2 mmol) of 2-methyl-2-butene, and 5 mL of dry tetrahydrofuran (distilled from a sodium–benzophenone mixture); in one dropping funnel was a solution of 0.385 g (9.2 mmol) of $NaBD_4$ in 10 mL of tetrahydrofuran and the other funnel contained a solution of 1.29 g (8.56 mmol) of phenyl propargyl chloride in 10 mL of tetrahydrofuran. Under a nitrogen atmosphere and at −4 °C, the $NaBD_4$ solution was added slowly to the flask and the resulting mixture was stirred for 1 h. Then the phenyl propargyl chloride was added at −20 °C, and the mixture was stirred at 0 °C for 30 min. At −20 °C the reaction mixture was treated with 2 mL of 6 M sodium hydroxide solution, was stirred for 30 min, and was oxidized with 2 mL of 30% hydrogen peroxide. Next, the solution was extracted with diethyl ether, and the ether phase was washed with water and was dried over anhydrous magnesium sulfate. Finally, the ether solution was loaded onto a short glass column packed with alumina, and hexane was employed as eluent to separate the side product (3-methyl-2-butanol) from the desired 1-phenyl-1-deuteriopropadiene: ^{1}H NMR ($CDCl_3$) δ 7.30 (s, 5, C_6H_5), 5.13 (s, 2, CH_2); mass spectrum (70 eV), *m/e* (relative intensity) 118 (6), 117 (68), 116 (100), 89 (68).

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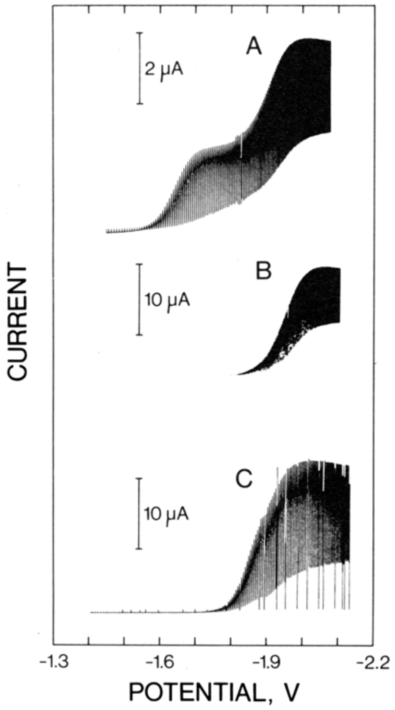


Figure 1. Polarograms for starting material and two electrolysis products in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate: curve A, 0.50 mM phenylpropadiene; curve B, 3.60 mM *trans*-1-phenyl-1-propene; curve C, 2.06 mM 1-phenyl-1-propyne.

If sodium borohydride is substituted for sodium borodeuteride, the preceding procedure can be utilized for the preparation of phenylpropadiene.

Synthesis of *cis*-1-Phenyl-1-propene. Into a two-necked flask was placed 50 mg of Lindlar catalyst (5% palladium on calcium carbonate), 90 μL (0.72 mmol) of 1-phenyl-1-propyne, and 25 mL of spectrograde hexanes; the system was deaerated and hydrogen gas (0.73 mmol) was passed into the system at room temperature. After a reaction time of 5 min, the Lindlar catalyst was removed by means of filtration and the hexanes were evaporated; the gas chromatographic retention time of authentic *cis*-1-phenyl-1-propene matched that of one of the minor electrolysis products.

Results and Discussion

Polarographic and Cyclic Voltammetric Behavior of Phenylpropadiene. As shown in Figure 1A, a polarogram for the reduction of phenylpropadiene in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate exhibits two waves with half-wave potentials of −1.63 and −1.90 V; however, the relative heights of the waves depend on the initial concentration of starting material. At a concentration of 0.50 mM, the ratio of the limiting current for the second wave to that for the first wave is 1.33, whereas this ratio is 2.34 when the concentration of phenylpropadiene is 2.30 mM. If, as proposed by Doupeux, Martinet, and Simonet,[3] phenylpropadiene did undergo straightforward stepwise reduction, first to 1-phenyl-1-propene and then to 1-phenylpropane, the ratio of heights of the two waves would be unity, regardless of the concentration of starting material.

At a scan rate of 200 mV s^{-1}, a cyclic voltammogram for the reduction of a 2 mM solution of phenylpropadiene at a hanging mercury drop electrode shows a pair of irreversible waves with peak potentials of −1.74 and −1.96 V. For the first negative-going scan from −1.4 to −2.1 V, the peak currents are nearly identical; on the second cathodic scan the peak current for the first wave is only 21% of its original value, and the first wave is absent altogether for the third cathodic scan. On the other hand, the peak current for the second wave exhibits a growth of 20% from the first to the third cathodic scan. For an electron-transfer process controlled only by diffusional mass transport, normal depletion of an electroactive species at the surface of an electrode causes the peak current to decrease after five or six voltage scans to a steady-state value approximately 80% of the initial peak current; we have verified this result experimentally for the reversible one-electron reduction of benzophenone and for the irreversible two-electron reduction of 1-iododecane in dimethylformamide containing tetraalkylammonium salts.

If, during a cyclic voltammetric experiment, the potential is scanned forward and backward between −1.4 and −1.85 V (a range of potentials which encompasses just the first step for the reduction of phenylpropadiene), one observes the same rapid decrease in cathodic peak current that is seen when the potential is scanned between −1.4 and −2.1 V.

Our explanation for the polarographic and cyclic voltammetric behavior of phenylpropadiene is that reduction of the starting material produces an intermediate that promotes efficient isomerization of the allene to 1-phenyl-1-propyne. As a consequence of this chemical rearrangement, phenylpropadiene disappears quickly, and there is an accompanying rapid decrease in current for both stages of its reduction; 1-phenyl-1-propyne (which undergoes one-step, four-electron reduction at a potential close to that for the second stage of reduction of phenylpropadiene) is the species that actually contributes to most of the observed current. Preparative-scale electrolyses confirm the correctness of this picture.

Controlled-Potential Electrolyses of Phenylpropadiene. Using mercury pool cathodes we performed preparative-scale electrolyses of phenylpropadiene in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate to determine the effect of potential on the products formed.

When a solution containing 2 mM phenylpropadiene is electrolyzed at a potential (−1.73 V) on the plateau of the first polarographic wave, the decay of the current is unusually rapid, in agreement with the disappearance of the first voltammetric wave for the allene after just a few complete cathodic–anodic voltage sweeps. Coulometry indicated that only 0.23 electron per molecule of the starting material was transferred, and our analysis of the electrolysis products revealed the presence of 1-phenyl-1-propyne (85%) and *trans*-1-phenyl-1-propene (9%). Because *trans*-1-phenyl-1-propene is the only true reduction product—1-phenyl-1-propyne arises via the non-electron-consuming isomerization of phenylpropadiene—and because formation of *trans*-1-phenyl-1-propene requires the uptake of two electrons per molecule of starting material, we calculate from the yield of *trans*-1-phenyl-1-propene that the *n* value should be 0.18, which agrees satisfactorily with the coulometric *n* value of 0.23.

For the electrolysis of 0.5 mM phenylpropadiene at −1.73 V, the experimental coulometric *n* value was 0.46 and the products were 1-phenyl-1-propyne (77%) and *trans*-1-phenyl-1-propene (23%). Though these results for an electrolysis of a relatively dilute solution of phenylpropadiene show that 1-phenyl-1-propyne is still the major product, the larger *n* value and the higher yield of *trans*-1-phenyl-1-propene demonstrate that the allene-to-alkyne rearrangement proceeds to a smaller extent during the electrolysis of a lower concentration of phenylpropadiene.

Large-scale electrolyses of phenylpropadiene at concentrations ranging from 2 to 2.5 mM were carried out at

Table I. Distribution of Products during Reduction of 1-Phenyl-1-propyne (16.7 mM) at Mercury Pool Cathode in Dimethylformamide Containing 0.1 M Tetra-*n*-butylammonium Perchlorate at -2.00 V

electrolysis time	product distribution, %			
	1-phenyl-1-propyne	*cis*-1-phenyl-1-propene	*trans*-1-phenyl-1-propene	1-phenylpropane
0	100			
8 min	64	36		
38 min	42	53	4	
2.50 h	18	49	26	7
3.25 h	14	21	51	14
4.00 h	3	16	61	21
4.50 h		10	57	32
5.50 h		10	44	45
7.00 h		10	23	64
10.00 h				95

Table II. Distribution of Products during Reduction of Phenylpropadiene (16.7 mM) at Mercury Pool Cathode in Dimethylformamide Containing 0.1 M Tetra-*n*-butylammonium Perchlorate at -1.73 V

electrolysis time, min	product distribution, %			
	phenylpropadiene	*cis*-1-phenyl-1-propene	*trans*-1-phenyl-1-propene	1-phenyl-1-propyne
0	100			
0.5	96	4		
2	56	4		40
4		6	2	91
20		1	6	92

a potential (-2.00 V) corresponding to the plateau of the second polarographic wave. A coulometric *n* value of 4.01 was measured; the sole product, 1-phenylpropane, was formed in a yield of at least 97% and tri-*n*-butylamine was detected as a byproduct in a yield three to four times that of 1-phenylpropane. We did not attempt to detect and determine 1-butene (the other species arising from the Hofmann elimination reaction of the tetra-*n*-butylammonium cation); however, 1-butene was identified in an earlier investigation[6] of the reduction of 1-phenyl-1-hexyne at mercury in dimethylformamide containing tetra-*n*-butylammonium perchlorate.

Electrochemistry of *trans*-1-Phenyl-1-propene and 1-Phenyl-1-propyne. Both *trans*-1-phenyl-1-propene and 1-phenyl-1-propyne are expected to be electroactive. Therefore, we examined the voltammetric and coulometric behavior of each compound in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate.

A polarogram for *trans*-1-phenyl-1-propene consists of a single wave with a half-wave potential of -1.94 V (Figure 1B) and a cyclic voltammogram recorded at a scan rate of 200 mV s^{-1} exhibits one irreversible cathodic peak at -1.97 V. Electrolysis of *trans*-1-phenyl-1-propene at -2.10 V involves the uptake of two electrons per molecule of starting material, and the products are 1-phenylpropane (94%) and tri-*n*-butylamine (obtained in a yield twice that of 1-phenylpropane).

Polarograms for 1-phenyl-1-propyne show only one reduction wave with a half-wave potential of -1.88 V (Figure 1C); electrolysis of 1-phenyl-1-propyne at -2.00 V is a four-electron process and results in the formation of 1-phenylpropane in a yield of 97% as well as tri-*n*-butylamine in a yield 3.2 times that of 1-phenylpropane.

In a previous investigation[6] it was discovered that, during the electrolysis of 1-phenyl-1-hexyne at a mercury pool cathode, the alkyne undergoes substantial isomerization to 1-phenyl-1,2-hexadiene; the mixture of these compounds is reduced to *trans*-1-phenyl-1-hexene, *cis*-1-phenyl-1-hexene, and *trans*-1-phenyl-2-hexene and, in turn, these olefins are eventually converted into 1-phenylhexane. Therefore, we were interested in determining whether electrolysis of 1-phenyl-1-propyne leads to any phenylpropadiene. An experiment was performed in which a 16.7 mM solution of 1-phenyl-1-propyne in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate was electrolyzed at a mercury pool held at -2.00 V. Over a period of 10 h, samples of the solution were withdrawn and analyzed for starting material and products. As shown in Table I, *cis*-1-phenyl-1-propene appeared at the start of the electrolysis and, as time passed, isomerized to *trans*-1-phenyl-1-propene; later, the 1-phenyl-1-propenes were reduced to 1-phenylpropane. No electrochemical or spectroscopic evidence was obtained to indicate the occurrence of any isomerization of 1-phenyl-1-propyne to phenylpropadiene during the experiment.

Electrolytically Induced Isomerization of Phenylpropadiene to 1-Phenyl-1-propyne. As stated earlier, electrolysis of phenylpropadiene at a potential corresponding to its first stage of reduction leads mainly to formation of its isomer, 1-phenyl-1-propyne. Starting with a 16.7 mM solution of phenylpropadiene in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate, we monitored the appearance of products during an electrolysis at a mercury pool cathode held at -1.73 V. As data in Table II reveal, within 30 s after the beginning of the electrolysis, *cis*-1-phenyl-1-propene was formed in 4% yield and no 1-phenyl-1-propyne had appeared. After the electrolysis had proceeded for 4 min, the starting material had been converted to a mixture of *cis*-1-phenyl-1-propene (6%), *trans*-1-phenyl-1-propene (2%), and 1-phenyl-1-propyne (91%). When the electrolysis was terminated after only 20 min, most of the *cis*-1-phenyl-1-propene formed earlier had isomerized to *trans*-1-phenyl-1-propene and the yield of 1-phenyl-1-propyne was virtually unchanged.

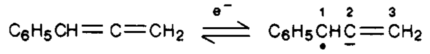
Another experiment was performed in which a solution of phenylpropadiene was subjected to electrolysis for just 1 min (during which time the equivalent of 0.12 electron per molecule was transferred) and then was allowed to stand for 20 min without passage of additional current. At the end of the 20-min period, the products were 1-phenyl-1-propyne (92%) and *trans*-1-phenyl-1-propene (8%). It is evident that the isomerization of phenylpropadiene to 1-phenyl-1-propyne is a rapid, self-propagating process.

Electrochemical Reduction of Phenylpropadiene in the Presence of a Proton Donor (Diethyl Malonate). Isomerization of phenylpropadiene to 1-phenyl-1-propyne involves a base-catalyzed 1,3-proton transfer. Conceivably, the radical-anion, $[C_6H_5CH{=}C{=}CH_2]^{\bullet-}$, generated by one-electron reduction of phenylpropadiene is the catalytic species responsible for the prototropic rearrangement. Alternatively, the radical-anion might be protonated by unreduced allene to yield a neutral radical and the conjugate base of the starting material; then the latter anion, $[C_6H_5\bar{C}{=}C{=}CH_2 \leftrightarrow C_6H_5C{\equiv}C\bar{C}H_2]$, could promote a self-propagating allene-to-alkyne isomerization. These considerations prompted us to investigate the electrochemical reduction of phenylpropadiene in the presence of an excess of diethyl malonate, a proton donor capable of intercepting an electrogenerated base and of blocking the allene-to-alkyne rearrangement.

A polarogram for a 2 mM solution of phenylpropadiene in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate and 24 mM diethyl malonate exhibits two reduction waves with half-wave potentials of

−1.66 and −1.87 V. Interestingly, the height of the first wave is greater than that of the second wave. A preparative-scale electrolysis of this solution at −1.73 V required the transfer of precisely two electrons to each molecule of starting material to yield *trans*-1-phenyl-1-propene (68%), *cis*-1-phenyl-1-propene (22%), and 1-phenyl-2-propene (7%); the absence of 1-phenyl-1-propyne among the products is notable. At a potential of −2.00 V, reduction of phenylpropadiene in the presence of diethyl malonate leads to an *n* value of 3.53 and to the production of 1-phenylpropane (89%) and 1-phenyl-2-propene (9%); assuming that 1-phenylpropane and 1-phenyl-2-propene are formed by processes that involve four and two electrons, respectively, we calculate an *n* value of 3.74 on the basis of the measured product yields. Because 1-phenyl-2-propene is not electroactive, the current for the second polarographic wave is contributed only by 1-phenyl-1-propene; therefore, the current for the second polarographic wave is lower than that for the first wave.

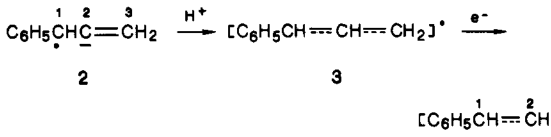
Mechanistic Aspects of the Reduction and Isomerization of Phenylpropadiene. At a potential (−1.73 V) on the first voltammetric wave for phenylpropadiene (**1**), the initial step in the reduction is proposed to be addition of one electron to the phenyl-conjugated double bond; the resulting radical-anion (**2**) is written with the negative charge localized on C_2 because formation of a trigonal carbanion is favored:



$$C_6H_5CH{=}C{=}CH_2 \overset{e^-}{\rightleftharpoons} C_6H_5\underset{\bullet}{\overset{1}{C}}H\underset{-}{\overset{2}{C}}{=}\overset{3}{C}H_2$$

1 2

This electron-transfer reaction should be reversible; however, we did not observe a cyclic voltammetric wave for the oxidation of **2** even at scan rates as high as 100 V s^{-1}, undoubtedly because of a rapid follow-up chemical reaction. Protonation of **2** produces an allyl radical (**3**) that can be further reduced at the mercury cathode to yield an allylic anion (**4**):



$$C_6H_5\underset{\bullet}{\overset{1}{C}}H\underset{-}{\overset{2}{C}}{=}\overset{3}{C}H_2 \xrightarrow{H^+} [C_6H_5CH{\dots}CH{\dots}CH_2]^{\bullet} \xrightarrow{e^-} [C_6H_5\overset{1}{C}H{\dots}\overset{2}{C}H{\dots}\overset{3}{C}H_2]^-$$

2 3 4

If the allylic anion (**4**) is protonated at C_3, the product is 1-phenyl-1-propene, the thermodynamically more stable trans olefin being preferred; formation of *cis*-1-phenyl-1-propene seems to be kinetically more facile, but the cis isomer apparently rearranges to *trans*-1-phenyl-1-propene (Table II). When phenylpropadiene is electrolyzed at −1.73 V in the presence of excess diethyl malonate, protonation of **4** occurs predominantly at C_3 to yield *trans*- and *cis*-1-phenyl-1-propene; however, the appearance of a small amount of 1-phenyl-2-propene implies that some protonation of the allylic anion (**4**) does take place at C_1. These mechanistic pathways are analogous to those suggested in a previous publication[6] dealing with the reduction of 1-phenyl-1,2-hexadiene at mercury in dimethylformamide containing 0.1 M tetra-*n*-butylammonium perchlorate.

An electrolysis performed at a potential on the second wave for the reduction of phenylpropadiene leads exclusively to 1-phenylpropane (as well as tri-*n*-butylamine) in the absence of a potent proton donor; when diethyl malonate is added to the system, 1-phenyl-2-propene is formed in low yield along with 1-phenylpropane but no tri-*n*-butylamine. It is evident, from our observations of the time-dependent changes in product distributions during electrolyses of 1-phenyl-1-propyne and phenylpropadiene (Tables I and II, respectively), that *cis*- and *trans*-1-phenyl-1-propene are intermediates in the electrochemical formation of 1-phenylpropane from reduction of the allene at −2.00 V. Both *cis*- and *trans*-1-phenyl-1-propene can accept one electron to yield a radical-anion, $[C_6H_5CH{\dots}CHCH_3]^{\bullet-}$, which is protonated, reduced, and protonated again to afford 1-phenylpropane. Similarly, any 1-phenyl-1-propyne formed during the electrolysis of phenylpropadiene will undergo an overall reduction (which obviously includes 1-phenyl-1-propene as intermediate) involving four electrons and four protons to give 1-phenylpropane. Because tri-*n*-butylamine is obtained as a byproduct in amounts commensurate with the total quantity of protons required to convert phenylpropadiene into 1-phenylpropane—and, in addition, to transform both 1-phenyl-1-propyne and 1-phenyl-1-propene into 1-phenylpropane—there is little doubt that the tetra-*n*-butylammonium cation (which undergoes a Hofmann elimination to yield the amine and 1-butene) is the ultimate source of protons for carbanions electrogenerated at −2.00 V.

Rearrangement of phenylpropadiene to 1-phenyl-1-propyne is the principal process that occurs when the allene is electrolyzed at −1.73 V in dimethylformamide containing tetra-*n*-butylammonium perchlorate and when no proton donor is present (except for the supporting-electrolyte cation and adventitious water). Klein and Brenner[15] have reported that in dimethyl sulfoxide-d_6 the isomerization of phenylpropadiene to 1-phenyl-1-propyne is catalyzed by the dimsyl-d_5 anion and that there is less than 5% incorporation of deuterium into the alkyne; thus, under the experimental conditions used by those investigators, the rearrangement *appears* to follow the "conducted tour" mechanism invoked by Cram and his co-workers[16] to account for the high degree of intramolecularity observed in the isomerization of 1,3,3-triphenyl-3-deuteriopropyne to deuteriotriphenylpropadiene in dimethyl sulfoxide–methanol containing 1,4-diazabicyclo[2.2.2]octane as a base. In addition, Klein and Brenner observed that, soon after 1-phenyl-1-propyne had been produced, its methyl protons began to exchange with deuterons from the solvent. A relatively recent monograph[17] and a review chapter[18] include thorough discussions of prototropic alkyne–allene isomerizations.

In the present study we found that, in dimethylformamide (whose solvent properties resemble those of dimethyl sulfoxide), the polarographic characteristics of 1-phenyl-1-deuteriopropadiene and phenylpropadiene are indistinguishable. Large-scale electrolysis of 1-phenyl-1-deuteriopropadiene at −1.73 V afforded a mixture of both deuterated and undeuterated 1-phenyl-1-propyne and 1-phenyl-1-propene. A ^1H NMR spectrum for the alkyne exhibited signals for aromatic (δ 7.27) and propargylic (δ 2.03) protons, and a ^2H NMR spectrum revealed deuterium at the propargyl position by the appearance of a triplet (δ 2.19, J = 2.4 Hz); integration of the peaks of the ^1H NMR spectrum indicated that the 1-phenyl-1-propyne consisted of $C_6H_5C{\equiv}CCH_2D$ (90%) and $C_6H_5C{\equiv}CCH_3$ (10%). Unfortunately, the mass spectrum of the alkyne

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failed to show the presence of $C_6H_5C{\equiv}CCH_2D$. On the other hand, when compared to mass spectra for authentic undeuterated *cis*- and *trans*-1-phenyl-1-propene [*m/e* (70 eV) (relative intensity) 119 (7), 118 (71), 117 (100), 115 (40), and 91 (27)], the observed mass spectral data for the minor electrolysis products, *cis*-1-phenyl-1-propene [*m/e* (70 eV) (relative intensity) 120 (78), 119 (100), 118 (69), 117 (54), 116 (56), and 115 (52)] and *trans*-1-phenyl-1-propene [*m/e* (70 eV) (relative intensity) 120 (40), 119 (83), 118 (100), 117 (70), 116 (57), and 115 (76)], suggest that these olefins possessed at least one if not two deuterium atoms per molecule. In fact, the *cis*-1-phenyl-1-propene, a product which is formed early in an electrolysis of 1-phenyl-1-deuteriopropadiene (Table II), did appear, on the basis of its mass spectrum, to contain two deuterium atoms per molecule; however, the *trans*-1-phenyl-1-propene, formed later during an electrolysis, seems to be a mixture of monodeuterated and dideuterated species.

Ostensibly, the preceding results show that unreduced phenylpropadiene acts as a proton donor for the anionic precursors of *cis*- and *trans*-1-phenyl-1-propene, although our findings do not exclude the possibility that another source of protons is involved as well; evidence exists that certain carbon acids (fluorene and 9-methylfluorene)[19,20] function well as proton donors for their own or related conjugate bases in dimethyl sulfoxide and, presumably, other similar solvents. If radical-anion **2** is protonated by unreduced starting material (**1**) to yield allyl radical **3** and the conjugate base, $C_6H_5\bar{C}{=}C{=}CH_2$ (**5**), of phenylpropadiene, the latter anion (**5**) could simply be protonated to regenerate **1**. However, **5** could rearrange and then accept a proton (conceivably from another molecule of phenylpropadiene) to give 1-phenyl-1-propyne via what becomes essentially a self-propagating *intermolecular* allene-to-alkyne isomerization. An alternative process is that once **5** is formed it could act catalytically to promote the *intramolecular* "conducted tour" rearrangement of phenylpropadiene to 1-phenyl-1-propyne. More investigations are underway in our laboratory to characterize further the electrolytically induced, base-catalyzed alkyne–allene transformations that 1-phenyl-1-hexyne and phenylpropadiene both undergo in dimethylformamide.

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Thermal and Catalyzed Intramolecular Diels–Alder Cyclizations of 2,8,10-Undecatrienals

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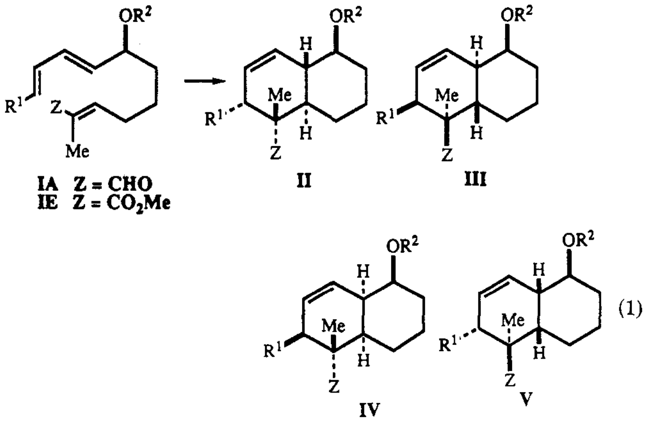
Received September 25, 1986

A comparative study of thermal and Lewis acid catalyzed intramolecular Diels–Alder cyclizations of substituted 2,8,10-undecatrienals was undertaken to determine the effect of substituents on the stereochemistry of the reaction. Substituents examined included 11-methyl, 4-methyl, 9-Me_3Si, 7-OMOM, 7-OTBS, and anti-4,6-dimethyl in various combinations. In all cases, the catalyzed reactions were highly endo selective (90:10 or greater). In thermal cyclizations the 9-Me_3Si, the 4-methyl, and the anti-4,6-dimethyl derivatives showed complete endo selectivity and the 11-methyl derivative was moderately endo selective.

We have previously shown that 2,8,10-undecatrienals IA undergo facile intramolecular Diels–Alder cyclizations upon treatment with alkylaluminum halides at −78 to −10 °C.[1] These reactions proceed with high endo selectivity affording the trans-fused diastereoisomers IIA and IIIA as major products. The corresponding esters, IE, on the other hand, give no reaction when treated similarly and decompose when warmed to 0 °C or above in the presence of Lewis acids.[2] Thermal cyclizations of IE lead to a mixture of all four stereoisomeric hydronaphthalenes with the exo products IVE and VE predominating.[2] The endo product II is of special interest as a substructural unit of the macrocyclic antibiotic chlorothricolide.[3]



IA Z = CHO
IE Z = CO_2Me

II

III

IV

V

(1)

In view of the enhanced reactivity shown by the conjugated aldehyde dienophile we thought it worthwhile to extend our studies to thermal Diels–Alder cyclizations of various 2,8,10-undecatrienals. Conjugated aldehydes have only rarely been employed for intramolecular Diels–Alder reactions so the results of such a study would provide useful semiquantitative information on the directing ability of this dienophile.[4] In addition, we were interested in the

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