time at lower potentials and/or at low temperature. These materials showed on GLC t_R = 149 and 140 s, respectively. Their identity was confirmed by the comparison to the authentic samples. Products obtained in the electrolysis of **2a** and **2b** were examined analytically on GLC and were assigned by the comparison to the products obtained in electroreduction of 1. The 1-deuterio-1-phenylethane was isolated from GLC, t_R = 680 s (105 °C column, 150 °C injector, 200° C detector, He, 75 mL/min, filament current 100 mA, chart speed 90 s/in.), and was a subject of polarimetric analyses. Reinjection of the sample of the isolated 1-deuterio-1-phenylethane did not show any impurities and its NMR signals δ 1.24 (d, 3, $-CH_3$), 2.67 (m, 1, $-CHD-$), and 7.23 (s, 5, $-C_6H_5$) were consistent with the structural assignment. From the mass spectrum the deuterium content was calculated as 0.97 atom of D per molecule.

The catholyte in the electroreduction of 1 carried out at 0 °C and at red light was examined by TLC performed at 6 °C and in the absence of light. The spot having R_f value 0.20 was observed by characteristic mercury vapor development under UV light on a fluorescence silica gel plate.[36] The lifetime of the compound was no longer than 30 min under the reported conditions. The catholyte containing 1 in an open circuit cell (at ambient temperature and on visible light) was examined by TLC. It showed a spot with R_f 0.02 exhibiting mercury vapor development by irradiation with UV light.[37] The thermal decomposition of that compound (in dark) on a silica gel plate was complete in 5 h.

Polarographic Measurements. Polarographic analyses were carried out using 10^{-2} mol of tetraethylammonium fluoroborate in DMF. The concentration of 1 was 10^{-4} M. Half-wave potentials are reported vs. the saturated calomel electrode at room temperature. A dropping mercury electrode and a Tokai glassy carbon cathode[14] were used in this work. The half-wave potentials were determined on a mercury electrode as $E_{1/2}^1 = -0.86$, $E_{1/2}^2 = -1.32$, and $E_{1/2}^3 = -1.36$ V. Measurements on a carbon cathode gave one wave, $E_{1/2} = -1.485$ V. The reported data are the average values of five independent runs.

Polarimetric Analysis. The purities of all solvents used in polarimetric measurements were checked by GLC, NMR, and IR. The racemic 1-phenylethane was fractionally distilled. The fraction boiling at 136 °C was used as a solvent in optical rotation analysis on 1-deuterio-1-phenylethane obtained as the reduction product in electrolysis of **2a** and **2b**. Optical rotation was calculated by a previously reported method[38] and employed Mosher's value[39] for the rotation of enantiomerically pure 1-deuterio-1-phenylethane.

A water-jacketed polarimetric cell was allowed to thermostat at the desired temperature at least 1 h prior to analysis. The mercury and sodium lamps were warmed up through the same period of time.

The background readings (using solvent in both sample and reference cell) were recorded from a digital display in sequences of 5 s during 8 min (96 readings). Polarimetric measurements on **2a**, **2b** and electroreduction products were performed in the same manner. The magnitude of the background rotation was in all experiments less than ±0.0006° and was subtracted from the optical rotation obtained in measurement of reduction products.

The possible racemization of **2a** and **2b** during preparative electrolysis was examined polarimetrically. Temperature in the polarimetric cell was held constant at 0 °C as it was in electroreductions of optically active 1-phenyl-1-bromoethanes. A gentle stream of dry nitrogen (precooled to 0 °C) was passed through the polarimetric cave with cells to prevent any cloudiness on cell windows. Optical rotations were recorded on solutions having the same qualitative and molar composition as that of catholyte in the electrochemical cell. Polarimetric data in these experiments were obtained from the same period of time as required for the electrolysis completion and no racemization of **2a** or **2b** was observed.

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Registry No. 1, 38661-81-3; **2a**, 69150-79-4; **2b**, 71927-77-0; **3**, 100-41-4; **3-*d***, 65805-35-8; **3a**, 71886-64-1; **3b**, 71886-65-2; **4**, 2726-21-8; **5**, 4613-11-0; **6**, 71886-66-3; **7**, 71886-67-4; acetophenone, 98-86-2; 1-phenyl-1-ethanol, 13323-81-4; 1-deuterio-1-phenyl-1-ethanol, 71886-68-5; (±)-1-deuterio-1-phenyl-1-ethyl hydrogen phthalate, 71886-69-6; (–)-1-deuterio-1-phenyl-1-ethyl hydrogen phthalate brucine salt, 71886-71-0; (+)-1-deuterio-1-phenyl-1-ethyl hydrogen phthalate brucine salt, 71886-73-2; (–)-1-deuterio-1-phenylethyl hydrogen phthalate, 71886-70-9; (+)-1-deuterio-1-phenylethyl hydrogen phthalate, 71886-72-1.

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[36] Numerous dialkylmercurials synthesized in our laboratory are of identical R_f value and show mercury vapor development under ultraviolet light.

[37] Benzylmercuric bromide and 1-(mercuribromo)-3-bromo-1-phenylethane were synthesized electrochemically in our laboratory and gave identical R_f behavior on thin layer chromatography.

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Electroreduction of α,β-Unsaturated Esters and Amides. 3. Polarographic Comparison of Compounds from Saturated and Unsaturated Alcohols and Amines[1a]

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Polarographic reduction data for a variety of esters and N-substituted amides of cinnamic and phenylpropiolic acids in anhydrous and aqueous acetonitrile are reported. In general, it was found that unsaturation in the alcohol or amine moiety facilitates electroreduction (i.e., decreases the value of $-E_{1/2}$) of the compound as compared to the case for the corresponding methyl and ethyl esters and *N*-methylamides, respectively.

In previous papers[2-10] we described the syntheses of a number of α,β-unsaturated esters of general formula Ar$(C_2)'CO_2CH_2(C_2)Y$ and α,β-unsaturated amides of general formula $Ph(C_2)'CONHCH_2(C_2)Ph$, where the (C_2) and $(C_2)'$

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[1] (a) This investigation was supported by Grant No. GM 12730 from the National Institute of General Medical Sciences, U.S. Public Health Service. For paper 2 in this series see ref 13. (b) Research Assistant, 1968–1971; NDEA Fellow, 1971–1972.

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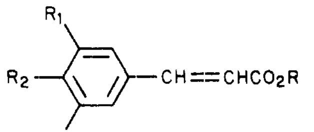
Table I. Polarographic Reduction Data for Some Cinnamate Esters (1)

					$-E_{1/2}$[b] (first wave)		$-E_{1/2}'$ [b] (second wave)	
compd[a]	R_1	R_2	R_3	R	anhyd MeCN	aq MeCN[c]	anhyd MeCN	aq MeCN[c]
1a	H	H	H	Et	1.86 (4.2)	*d*	2.23 (3.4)	*d*
1b	H	H	H	HC≡CCH$_2$	1.77 (2.9)	1.71 (3.3)	2.16 (2.2)	1.91 (3.3)
1c	H	H	H	PhC≡CCH$_2$	1.76 (4.0)	1.67 (5.0)	poor wave	1.89 (4.0)
1d[e]	OCH$_2$O		H	Et	1.91	1.80	2.25	2.00
1e	OCH$_2$O		H	*trans*-3,4-methylenedioxycinnamyl	1.84[f] (4.7)	1.77 (5.1)	2.27[f] (5.1)	2.24 (5.4)
1f	MeO	MeO	H	Et	1.94 (2.4)[g]	1.83 (2.6)	2.26 (2.1)	1.99 (2.6)
1g	MeO	MeO	H	*trans*-3,4-dimethoxycinnamyl	1.87 (5.5)	1.79 (6.5)	2.31 (5.0)	2.29 (5.6)
1h	MeO	MeO	MeO	Et	1.87 (2.3)	1.78 (4.0)	2.23 (2.8)	1.94 (3.4)
1i	MeO	MeO	MeO	*trans*-3,4-methylenedioxycinnamyl	1.82 (4.1)	1.73 (5.0)	2.24 (5.5)	2.23 (5.0)
1j[h]	MeO	MeO	MeO	*trans*-3,4-methylenedioxycinnamyl	1.82 (4.2)	1.73 (4.4)	2.24 (5.6)	2.23 (4.3)
3[i]	*trans*-3,4-methylenedioxycinnamyl alcohol				none	none	2.54 (3.8)	2.45 (4.0)

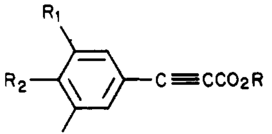
[a] Compounds 1a–i are *trans*-cinnamates. [b] In volts vs. the saturated calomel electrode. Some of these reduction potentials have been reported in earlier papers.[12,13] Numbers in parentheses are wave heights (*w*) in microamperes for a 1 mM solution. [c] From dilution of the anhydrous MeCN solution with 3.85 vol % of H_2O. [d] Not measured. [e] Gives an irregular polarogram; *w* can not be determined accurately. [f] This wave was shown to be diffusion controlled by conformance to the equation $I_d = k'P^{1/2}$, where I_d is the diffusion current, *P* is the pressure of the mercury column, and *k'* is a constant.[14] [g] Coulometry gives $n = 1.07 \pm 0.05$ for the uptake of electrons per molecule in this wave. [h] Compound 1j is the *cis*-cinnamate. [i] A reference compound for the cinnamyl esters.

units are variously *cis*-CH=CH, *trans*-CH=CH, and C≡C groupings, and Y is either H or an aryl group. It was found that some of these diunsaturated esters and amides undergo facile intramolecular Diels–Alder reaction in refluxing Ac_2O, while others give limited or no cyclization under the same conditions.[11] In continuation of studies on these substances we now report polarographic reduction data for them, as well as for some reference monounsaturated compounds.

Polarograms were obtained both in anhydrous MeCN containing Et_4NBr (0.05 M) as supporting electrolyte and in the same solvent diluted with 3.85 vol % of water. Data for cinnamate esters **1**, phenylpropiolate esters **2**, phenylpropiolamides **4**, and cinnamamides **7** are presented in Tables I–IV, respectively.



1



2

PhC≡CCONHR

4

PhCH=CHCONHR

7

Discussion

Reduction of Cinnamate Esters. As we have noted previously[12,13] and as is apparent from Table I (see **1a–i**), *trans*-cinnamate esters with or without alkoxy substituents on the phenyl ring and with either saturated or unsaturated R groups in the alcoholic moiety show two reduction waves in anhydrous MeCN. The first half-wave reduction potential, $E_{1/2}$, is shifted to a less negative value ($-\Delta E_{1/2}$ = 0.06–0.11 V) for these substrates upon the addition of water. However, the substrates are clearly divisible into two different categories on the basis of the effect of added water on the second half-wave reduction potential, $E_{1/2}'$. Thus, three substrates (**1e**, **1g**, and **1i**) of similar alkoxy-substituted structure show almost no change in $E_{1/2}'$, while four others (the three ethyl esters **1d**, **1f**, and **1h** and a propargyl ester **1b**) show large similar changes (0.27 ± 0.02 V) in this potential. Only one *cis*-cinnamate ester, **1j**, an isomer of **1i**, was investigated. Except for small differences in wave heights, these stereoisomers are polarographically indistinguishable.

By coulometry, the first wave of ethyl ester **1f** in anhydrous MeCN was found to involve the uptake of one electron. The second wave (of approximately the same height) must result from the uptake of a second electron. This relationship is corroborated by the isolation of a good yield of β,β-coupled cyclic hydro dimer on macroscale electroreduction of **1f** at a cathode potential maintained midway between $E_{1/2}$ and $E_{1/2}'$.[13] In aqueous MeCN, water must be involved in both reduction steps in order to cause the observed shifts in reduction potentials. Macroscale reduction of **1f** in aqueous MeCN at a potential more negative than $E_{1/2}'$ should lead to simple hydrogenation of the carbon–carbon double bond, consistent with observations made on similar substrates.[12] It is likely that electroreductions of the other ethyl esters **1a**, **1d**, and **1h** also involve two one-electron waves in aqueous MeCN.

While careful study in an effort to correlate electron uptake with isolated products for alkenyl and alkynyl cinnamates has not yet been made, it is remarkable that in every case (cf. **1b** and **1c** with **1a**, **1e** with **1d**, **1g** with **1f**, and **1i** with **1h**) the diunsaturated ester is more readily reduced (by 0.05–0.10 V for $E_{1/2}$) than is its reference ethyl ester in anhydrous MeCN. The same effect, but less

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(11) Only five of the nine possible types of esters where Y = aryl have yet been synthesized. For Y = H, cis and trans (C_2) units are identical and only three of the six possible types have been synthesized. All of the nine types of amides have been prepared, but cyclization studies have been conducted on only seven of them.

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Table II. Polarographic Reduction Data for Some Phenylpropiolate Esters (2)

compd	R_1	R_2	R_3	R[a]	$-E_{1/2}$[b] (1st wave) anhyd MeCN	$-E_{1/2}$[b] (1st wave) aq MeCN[c]	$-E_{1/2}'$[b] (2nd wave) anhyd MeCN	$-E_{1/2}'$[b] (2nd wave) aq MeCN[c]	$-E_{1/2}''$[b] (3rd wave), anhyd MeCN
2a	H	H	H	Et	1.94 (4.0)	1.81 (12.0)	2.21 (3.3)	none	2.55 (2.9)
2b	H	H	H	$HC{\equiv}CCH_2$ (0.5 H_2O)	2.12 (7.2)	2.03 (8.1)	none	none	
2c	H	H	H	$CH_2{=}CHCH_2$	1.87 (4.4)	1.79 (14.0)	2.22 (1.6)	none	2.56 (4.0)
2d	MeO	H	MeO	Et	1.91 (3.0)	1.78 (10.0)	2.15 (2.9)	none	2.54 (2.2)
2e	MeO	H	MeO	$HC{\equiv}CCH_2$ (0.75 H_2O)	2.08 (5.2)	1.99 (6.3)	none	none	
2f	OCH_2O		H	Me	1.97 (4.6)	1.82 (13.0)	2.23 (2.8)	none	2.62 (3.2)
2g	OCH_2O		H	$HC{\equiv}CCH_2$ (0.5 H_2O, 0.25 EtOH)	1.82 (2.8)	1.74 (5.9)	2.22 (3.8)	1.96 (4.3)	none
2h	OCH_2O		H	*trans*-3,4-methylenedioxycinnamyl	1.80 (4.5)	1.75 (6.9)	2.25 (?)	2.23 (12.0)	none
2i	MeO	MeO	MeO	Me	1.93 (4.6)	1.80 (13.0)	2.20 (3.6)	none	2.57 (4.1)
2j	MeO	MeO	MeO	$HC{\equiv}CCH_2$ (0.25 H_2O)	1.82 (5.4)	1.75 (17.0)	2.57 (7.0)	none	none
2k	MeO	MeO	MeO	*trans*-3,4-methylenedioxycinnamyl	1.80 (3.5)	1.74 (5.3)	2.29 (2.5)	2.19 (8.8)	2.58 (5.9)
2l	MeO	MeO	H	Et	2.02 (5.3)	1.87 (13.0)	2.26 (3.2)	none	2.64 (2.2)
2m	MeO	MeO	H	*trans*-3,4-methylenedioxycinnamyl	1.85 (4.4)	1.79 (5.3)	2.44 (4.7)	2.24 (8.8)	none

[a] The propargyl esters used contained water (plus, in the case of **2g**, ethanol) of solvation, which is very tightly bound.[7] The molar ratios present are shown in parentheses. [b] See footnote *b*, Table I. [c] See footnote *c*, Table I.

pronounced, is noticeable in aqueous MeCN. Thus, the presence of the unsaturated alcoholic moiety in the diunsaturated cinnamate esters facilitates electroreduction of the cinnamoyl moiety. We ascribe this effect to electronic interaction between the two centers of unsaturation in the molecule, but the mechanism by which such interaction occurs is uncertain at this time.

Each cinnamyl cinnamate undergoes a second reduction wave at a potential ($E_{1/2}'$) which is nearly the same or slightly more negative than that of the corresponding ethyl reference compound. However, the value of $E_{1/2}'$ for the former molecule is not significantly altered by the presence of water, in marked contrast to the situation for the ethyl ester and for the reference alcohol **3**. In fact, the considerably lower (ca. 0.3 V) values of $E_{1/2}'$ for **1e** and **1i**, as compared to that of **3**, in anhydrous solvent again implies the presence of electronic interaction between the cinnamoyl and cinnamyl moieties. Propargyl cinnamate (**1b**), on the other hand, reduces more readily than **1a** for both waves in anhydrous solvent and involves reaction with water in both steps under aqueous conditions.

Reduction of Phenylpropiolate Esters. The methyl and ethyl phenylpropiolates (**2a**, **2d**, **2f**, and **2i**; Table II) show three waves in anhydrous solvent. Comparison with corresponding alkyl cinnamates (**1a**, **1d**, and **1h**) from Table I shows that cinnamates reduce more readily than phenylpropiolates (by 0.06–0.08 V in $E_{1/2}$) in anhydrous MeCN.[12] In aqueous MeCN, however, there is no significant difference in $E_{1/2}$ (cf. **1d** with **2f** and **1h** with **2i**). The propargyl phenylpropiolates (**2b**, **2e**, **2g**, and **2j**) show smaller values for $-\Delta E_{1/2}$ than their corresponding alkyl reference compounds, but this is expected on the basis that the propargyl substrates are already hydrated (probably covalently)[7] themselves.

Comparative Reductions of Amides and Esters. From Tables I–IV it is apparent that *N*-methylcinnamamides and *N*-phenylpropiolamides give simpler polarograms than do the corresponding ethyl cinnamates and phenylpropiolates.[15] Thus, in anhydrous MeCN, phenylpropiolamide **4a** shows only two reduction waves (instead of three), and cinnamamide **7a** shows only one (instead of two). In contrast to the esters the triple-bonded amide reduces slightly more readily (0.07 V) than the double-bonded amide, but (consistent with the fact that oxygen is more electronegative than nitrogen) the esters reduce more readily than the amides. For R = phenylpropargyl, the cinnamate ester (**1c**) also reduces more readily than do the amides **4b** and **7c**. Again, for the diunsaturated amides enhanced electroreducibility is observed (cf. **4b**–**d** with **4a**, **7c** with **7a**) in several cases, but not for the *N*-cinnamyl-*trans*-cinnamamides (cf. **7f** and **7g** with **7a**). In contrast to the esters, the *cis*- and *trans*-cinnamamides are polarographically distinguishable in anhydrous solvent. There is a marked consistency in values of $-E_{1/2}$ (1.90 ± 0.03 V) and $-E_{1/2}'$ (2.43 ± 0.02 V) for the various amides in aqueous MeCN. Apparently the latter wave (absent in **4a** and **7a**, of similar wave height in **4c**, **4d**, and **7d**–**g**, but of approximately double height in **7b** and **7c**) is associated with reduction of the R group, while the first wave corresponds to reduction of the carbon–carbon multiple bond in the acid moiety (uptake of four electrons per molecule in **4b** and **4c** but of only two electrons in **7c**). This regularity was not observed for the esters.

The two esters **1b** (R = propargyl) and **1c** (R = phenylpropargyl) as well as the three amides **4b**, **7b**, and **7c**

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(15) It is presumed that methyl and ethyl groups can be interchanged without significant alteration in the polarograms observed.

Table III. Polarographic Reduction Data for Some N-Substituted Phenylpropiolamides (4) and Compounds 5 and 6

		$-E_{1/2}$[a] (1st wave)		$-E_{1/2}'$[a] (2nd wave)	
compd	R	anhyd MeCN	aq MeCN[b]	anhyd MeCN	aq MeCN[b]
4a	Me	2.07 (2.4)	1.93 (10.8)	2.47 (6.3)	none
4b	$PhC{\equiv}CCH_2$	1.96 (2.2)[d]	1.90 (12.2)[e]	2.50	*c*
4c	*cis*-$PhCH{=}CHCH_2$	2.01 (1.5)[f]	1.92 (11.6)[g]	2.51 (10.4)	2.43 (3.6)
4d	*trans*-$PhCH{=}CHCH_2$	2.02 (2.2)	1.91 (11.5)	2.50 (10.5)	2.43 (3.2)
5[h]	$PhC{\equiv}CCH_2NHAc$	none	none	2.58 (10.6)	2.42
6[h]	*cis*-$PhCH{=}CHCH_2NHAc$	none	none	2.57	2.44

[a] See footnote *b*, Table I. [b] See footnote *c*, Table I. [c] Not measured. [d] $n = 0.45$ electron/molecule, measured by coulometry. [e] $n = 3.82 \pm 0.02$. [f] $n = 0.46 \pm 0.04$. [g] $n = 3.86 \pm 0.15$. [h] Model compound for comparison.

Table IV. Polarographic Reduction Data for Some N-Substituted Cinnamamides (7)

			$-E_{1/2}$[a] (1st wave)		$-E_{1/2}'$[a] (2nd wave)	
compd	CH=CH geometry	R	anhyd MeCN	aq MeCN[b]	anhyd MeCN	aq MeCN[b]
7a	trans	Me	2.14 (5.8)	1.92 (6.2)	none	none
7b	cis	$PhC{\equiv}CCH_2$	1.98[c] 2.19 (3.5)[d]	1.88 (5.7)	poor wave	2.43 (10.2)
7c	trans	$PhC{\equiv}CCH_2$	1.99[c] 2.28 (4.6)[e,d]	1.88 (5.7)[f]	poor wave	2.45 (10.2)
7d	cis	*cis*-$PhCH{=}CHCH_2$	2.08 (4.9)	1.90 (6.3)	2.55 (4.0)	2.44 (5.0)
7e	cis	*trans*-$PhCH{=}CHCH_2$	2.09 (5.9)	1.90 (6.4)	2.54 (4.5)	2.42 (4.5)
7f	trans	*cis*-$PhCH{=}CHCH_2$	2.14 (4.2)	1.90 (5.2)	2.58 (3.2)	2.44 (4.1)
7g	trans	*trans*-$PhCH{=}CHCH_2$	2.14 (4.6)	1.91 (5.2)	2.56 (3.5)	2.42 (4.3)

[a] See footnote *b*, Table I. [b] See footnote *c*, Table I. [c] Consists of two overlapping subwaves of approximately equal height. [d] For sum of two overlapping waves. [e] $n = 1.78 \pm 0.12$ electrons/molecuie, measured by coulometry. [f] $n = 1.85 \pm 0.15$.

(R = phenylpropargyl) are of special interest because they are the most readily reducible compounds in anhydrous MeCN in their respective tables. This implies either that the carbon–carbon triple bond of the R group takes up electrons per se or that it interacts strongly with the unsaturated π system of the acid moiety. In anhydrous MeCN the first waves for **4b** and **4c** involve the uptake of only half an electron per molecule, i.e., correspond to the formation of a dimer radical anion. Comparison of the wave heights of **4a–c** and consideration of the high values of the first half-wave reduction potentials of reference compounds **5** and **6** indicate that all of the electrons involved in the first wave of **4b**, whether in anhydrous or aqueous solvent, may actually enter the lowest unoccupied molecular orbital (LUMO) of the phenylpropiolyl moiety (as modified by the presence of the R group). Phenylpropargyl cinnamates **7b** and **7c** clearly exhibit the division of the first reduction wave involving two electrons into two subwaves of approximately equal height. The average values for $-E_{1/2}$ for these subwaves are 2.08 and 2.13 V, respectively, i.e., values experimentally identical with the reduction potentials of the other N-substituted *cis*- and *trans*-cinnamamides in Table IV. Again, these two electrons apparently enter unoccupied molecular orbitals of the cinnamoyl moiety. A macroscale electroreduction of **7b** at a cathode potential of −2.32 V gave two crystalline products, one of which was the expected *N*-phenylpropargyl-3-phenylpropionamide. The other product has not yet been identified.

For di-α,β-unsaturated esters of the general formula $EtO_2CCH{=}CH(CH_2)_nCH{=}CHCO_2Et$, Anderson et al.[16] found that molecules wherein $n = 1$–4 showed both enhanced polarographic reducibility and facile intramolecular cyclization through β,β-coupling. For molecules with $n > 4$, however, electroreducibility was normal and cyclization failed. With our diunsaturated esters and amides, on the other hand, no correlation between electroreducibility and the facility of undergoing cyclization (in an intramolecular Diels–Alder fashion) was apparent.

Experimental Section

General Methods. In general, compounds in Tables I–IV were available from previous research projects.[2-10] Compounds **5** and **6** resulted from acetylation of the corresponding amines,[9] while **4a** and **7a** were prepared by reactions between methylamine and the corresponding esters.[17] The apparatuses and general procedures for polarography and coulometry were described previously.[12,13] Polarograms were run at three different concentrations [(2.2–5.8) × 10^{-4} M] of substrate in 0.05 M Et_4NBr in anhydrous MeCN and at one concentration (5.6 × 10^{-4} M) after dilution of the solvent–electrolyte with 3.85 vol % of water. Reproducibility in $E_{1/2}$ values was ±0.01 V.

Macroscale Electroreduction of *N*-Phenylpropargyl-*cis*-cinnamamide (7b). In the manner previously described[13] a solution of 206 mg of **7b** in anhydrous MeCN was added dropwise to the catholyte of an electrochemical cell wherein the cathode was maintained at a constant potential of −2.32 V. Processing of the mixture gave 175 mg of crude product. Crystallization from acetone–hexane yielded 120 mg of unidentified white crystals, mp 54–58 °C, and 30 mg (15%, mp 102–104 °C) of *N*-phenylpropargyl-3-phenylpropionamide: needles from ether–hexane, mp 111–111.5 °C; IR ($CHCl_3$) 3450 (NH), 1675 (C=O), 1505 cm^{-1} (amide II);[18] ^1H NMR ($CDCl_3$) δ 7.45 and 7.33 (2 overlapping s, 10 H, phenyl groups), 6.17 (br, 1 H, NH), 4.28 (d, $J = 5.5$ Hz, 2 H, $CH_2C{\equiv}C$), 2.3–3.2 (m, 4 H, CH_2CH_2). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.00; H, 6.43; N, 5.21.

Registry No. 1a, 4192-77-2; **1b**, 29584-63-2; **1c**, 40918-86-3; **1d**, 24393-66-6; **1e**, 6941-33-9; **1f**, 24393-65-5; **1g**, 40918-88-5; **1h**, 31892-98-5; **1i**, 7460-41-5; **1j**, 71616-31-4; **2a**, 2216-94-6; **2b**, 29577-30-8; **2c**, 29577-34-2; **2d**, 29577-38-6; **2e**, 29577-32-0; **2f**, 31893-02-4; **2g**, 29577-31-9; **2h**, 71616-32-5; **2i**, 71616-33-6; **2j**, 29577-33-1; **2k**, 6259-84-3; **2l**, 71616-34-7; **2m**, 6259-86-5; **3**, 58095-76-4; **4a**, 26218-49-5; **4b**, 59015-33-7; **4c**, 59015-31-5; **4d**, 59015-32-6; **5**, 71616-35-8; **6**, 71616-36-9; **7a**, 25695-84-5; **7b**, 59015-39-3; **7c**, 59015-36-0; **7d**, 59015-37-1; **7e**, 59015-38-2; **7f**, 59015-34-8; **7g**, 59015-35-9.

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