concentrated to give an oily yellow solid. The solid was chromatographed on 25 g of activity I neutral alumina (3:2 ether/hexane) to afford 0.06 g (0.3 mmol, 61%) of a white solid: mp 92–93 °C (lit.[2] mp 93–95 °C); IR ($CHCl_3$) 3000, 1740, 1435, 1285, 1265, 1210, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.53 (t, 1, J = 3.3 Hz), 2.83 (m, 2), 3.17 (m, 2), 3.30 (m, 2), 3.48 (s, 3), 3.50 (m, 2); ^{13}C NMR ($CDCl_3$) δ 35.6 (2), 42.7 (2), 44.6 (2), 46.2 (2), 51.4, 52.1, 170.7, 219.1. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.84; H, 5.99.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-810-2938.

Registry No. 1, 4572-17-2; **5a**, 86496-36-8; **7b**, 66824-74-6; **8b**, 86471-09-2; **10b**, 935-50-2; 11, 86480-31-1; **13a**, 86471-10-5; 18, 86471-11-6.

Electrochemical Reductive Carboxylation: Reduction of Unsaturated Compounds in the Presence of Methyl Chloroformate

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Received October 8, 1982

Mono- and dicarboxylated derivatives have been obtained by electroreduction of various unsaturated compounds in acetonitrile at a mercury-pool cathode in the presence of methyl chloroformate. Unsaturated compounds included activated olefins, ketones, aromatic Schiff bases, nitro compounds, and nitrogen heterocycles. The distribution of the products and their yields depend on the nature of the supporting electrolyte (Et_4NClO_4 or $LiClO_4$). Reduction mechanisms accounting for the nature of the reduction products are proposed on the basis of voltammetric and coulometric data. In some cases it is possible to obtain the kinetic parameters.

The electrochemical reductive carboxylation with CO_2 in aprotic solvents has been described for a number of substrates: polycyclic aromatic hydrocarbons,[1] olefins,[2-10] acetylenes,[3] ketones,[3,11] alkyl halides,[8] azomethine compounds,[12-14] and N-heterocyclic compounds.[15-18]

The standard potential for the reduction of CO_2 in dry DMF is −2.21 V vs. SCE,[19] and its value should not be very different in acetonitrile. This negative value explains that few carboxylations have been carried out by reduction of CO_2 to its radical anion $CO_2^{-}\cdot$, which would further react with the substrate. Besides the formation of oxalic acid by reaction of $CO_2^{-}\cdot$ with CO_2,[20] only ethylene[9] and butadiene[10] have been carboxylated in this way. In all the other experiments, the substrate is reduced to a radical anion that reacts with CO_2 to give a carboxylated radical. This radical is reduced in turn to a dianion that undergoes a second carboxylation or a protonation by the residual water (Scheme I). Most often these carboxylic acids are then transformed into esters.

Scheme I

$$A + e \rightleftharpoons A^{-}\cdot \xrightarrow{CO_2} ACOO^{-}\cdot$$

$$ACOO^{-}\cdot + e \rightarrow ACOO^{2-} \xrightarrow{CO_2} A(COO^{-})_2$$

$$ACOO^{2-} \xrightarrow{H^+} HACOO^{-}$$

We report herein the direct formation of esters through the reduction of unsaturated compounds in acetonitrile in the presence of methyl chloroformate.

As concerns the mechanism of this reaction, several possibilities must be taken into account as in the case of the reduction of unsaturated derivatives in the presence of halogenated derivatives as electrophiles:[21-24]

(i) A reaction between the substrate and $ClCOOCH_3$ may occur to give a cation.[25] This positively charged species will be more easily reduced than the substrate—for example, an immonium cation is more easily reduced than an imine—and a new more positive reduction wave will appear on the cyclic voltammogram.[24]

(ii) In other cases an ECEC mechanism as in Scheme I may take place, and the different possible reactions are summarized in Scheme II. The substrate is first reduced to a radical anion, which can either react with $ClCOOCH_3$

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(1) Wazwonec, S., Wearring, D. *J. Am. Chem. Soc.* **1959**, *81*, 2067.
(2) Wazwoneck, S.; Blaha, E. W.; Berkey, R.; Runner, M. E. *J. Electrochem. Soc.* **1955**, *102*, 235.
(3) Wazwoneck, S.; Guderson, A. *J. Electrochem. Soc.* **1960**, *107*, 537.
(4) Wazwoneck, S.; Duty, R. C.; Wagenknecht, J. H. *J. Electrochem. Soc.* **1964**, *111*, 74.
(5) Dietz, R.; Peover, M. *Discuss. Faraday Soc.* **1968**, *45*, 154.
(6) Tyssee, D. A.; Baizer, M. M. *J. Org. Chem.* **1974**, *39*, 2819.
(7) Tyssee, D. A.; Baizer, M. M. *J. Org. Chem.* **1974**, *39*, 2823.
(8) Lamy, E.; Nadjo, L.; Saveant, J. M. *Nouv. J. Chim.* **1979**, *3*, 21.
(9) Gambino, S.; Silvestri, G. *Tetrahedron Lett.* **1973**, 3025.
(10) Van Tiblorg, W. J. H.; Smit, C. J. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 437.
(11) Wazwoneck, S.; Gunderson, A. J. *Electrochem. Soc.* **1964**, *107*, 324.
(12) Weinberg, N. L.; Hoffman, A. K.; Reddy, T. B. *Tetrahedron Lett.* **1971**, 2271.
(13) Kato, S.; Mizutani, Y. "Abstracts of Papers", First, Meeting on Electroorganic Chemistry, Kyoto, Japan, April 1980; 9.
(14) Hess, U. Z. *Chem.* **1980**, *20*, 148.
(15) Lund, H. *Denki Kagaku* **1977**, *45*, 2.
(16) Michelet, D. Fr. Demande Pat. 2 444 030; *Chem. Abstr.* **1981**, *94*, 164821*k*.
(17) Hess, U.; Fuchs, P.; Jacob, E.; Lund, H. *Z. Chem.* **1980**, *20*, 64.
(18) Fuchs, P.; Hess, U.; Holst, H. H.; Lund, H. *Acta Chem. Scand., Ser. B* **1981**, *B35*, 185.
(19) Lamy, E.; Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *78*, 403.
(20) Gressin, J. C.; Michelet, D.; Nadjo, L.; Saveant, J. M. *Nouv. J. Chim.* **1979**, *3*, 545 and references therein.
(21) Lund, H.; Simonet, J. *Bull. Soc. Chim. Fr.* **1973**, 1843.
(22) Simonet, J.; Lund, H. *Bull. Soc. Chim. Fr.* **1975**, 2547.
(23) Degrand, C.; Compagnon, P. L.; Belot, G.; Jacquin, D. *J. Org. Chem.* **1980**, *45*, 1189.
(24) Belot, G.; Degrand, C. *J. Org. Chem.* **1982**, *47*, 325.
(25) "The Chemistry of Acyl Halides"; Pataĭ, S., Ed.; Interscience: New York, 1972; p 381.

0022-3263/83/1948-2847$01.50/0

Table I. Electrochemical Reduction of Unsaturated Compounds in the Presence of Methyl Chloroformate

unsaturated compd	expt[a]	applied potential, V	isolated compd	yield,[b] %
methyl cinnamate (1)	1	−1.95	methyl 3-phenylpropanoate (2)	39
			dimethyl 2-phenylbutanedioate (3)	41
benzophenone (4)	1	−1.65	methyl diphenylmethyl carbonate (5)	71
fluorenone (6)	1	−1.35	9-(methoxycarbonyl)fluoren-9-yl methyl carbonate (7)	73
fluorenone anil (9)	1	−1.40	*N*-(methoxycarbonyl)-*N*-phenylfluoren-9-amine (10)	36
	2	−1.20	*N*-phenylfluorenyl-9-amine (11)	57
p-isopropylnitrobenzene (12)	1	−1.15	*N,O*-bis(methoxycarbonyl)-1-(hydroxylamino)-4-isopropylbenzene (13)	44
			O-(methoxycarbonyl)-1-(hydroxylamino)-4-isopropylbenzene (14)	36
phenazine (15)	1	−1.30	5,10-dihydro-5-(methoxycarbonyl)phenazine (16)	48
			5,10-dihydro-5,10-bis(methoxycarbonyl)phenazine (17)	32
	2	−1.05	5,10-dihydro-5-(methoxycarbonyl)phenazine (16)	82
2,3-diphenylquinoxaline (18)	1	−1.60	1,4-dihydro-1,4-bis(methoxycarbonyl)-2,3-diphenylquinoxaline (19)	64
2-phenylquinoxaline (20)	1	−1.70	1,4-dihydro-1,4-bis(methoxycarbonyl)-2-phenylquinoxaline (21)	15
			1,4-dihydro-1-(methoxycarbonyl)-2-phenylquinoxaline (22)	25
			1,4-dihydro-4-(methoxycarbonyl)-2-phenylquinoxaline (23)	20
5,12-diacetyl-5,12-dihydroquinoxalino-[2,3-*b*]quinoxaline (24)	1	−1.50	5,12-dihydro-5,12-diacetyl-6,11-bis(methoxycarbonyl)-quinoxalino[2,3-*b*]quinoxaline (25)	66
[1]-benzopyrano[2,3-*b*]quinoxalin-12-one (26)	1	−1.00	6,11-dihydro-6,11-bis(methoxycarbonyl)-[1]-benzopyrano[2,3-*b*]quinoxalin-12-one (27)	55
2,3-diphenylpyrazine (28)	1	−1.90	1,4-dihydro-1,4-bis(methoxycarbonyl)-2,3-diphenylpyrazine (29)	15
benzo[*c*]cinnoline (30)	1	−1.30	1,2-dihydro-1,2-bis(methoxycarbonyl)benzo[*c*]-cinnoline (31)	72
phthalazine (32)	1	−0.60	1,1′,2,2′-tetrahydro-2,2′-bis(methoxycarbonyl)-1,1′-biphthalazyl (33)	74
	1	−1.80	1,1′,2,2′,3,3′,4,4′-octahydro-2,2′,3,3′-tetrakis-(methoxycarbonyl)-1,1′-biphthalazyl (34)	58

[a] (1) Supporting electrolyte: Et_4NClO_4 (0.15 M). (2) Supporting electrolyte: $LiClO_4$ (0.15 M). [b] Yields of isolated products except for phenazine in experiment 1 where the ratio of **16** and **17** was determined by NMR.

or be protonated by residual water. The obtained neutral radical can be further reduced either at the electrode (ECE mechanism) or in solution (DISP mechanism)[26] to give an anion that will react with $ClCOOCH_3$ or with residual water.

Scheme II

$$A + e \rightleftharpoons A^{-}\cdot \quad (1)$$

$$A^{-}\cdot + ClCOOCH_3 \xrightarrow{k_2} ACOOCH_3\cdot + Cl^- \quad (2)$$

$$A^{-}\cdot + H^+ \xrightarrow{k_3} AH\cdot \quad (3)$$

$$ACOOCH_3\cdot + e \rightleftharpoons ACOOCH_3^- \quad (4)$$

$$ACOOCH_3\cdot + A^{-}\cdot \rightleftharpoons ACOOCH_3^- + A \quad (5)$$

$$AH\cdot + A^{-}\cdot \rightleftharpoons AH^- + A \quad (6)$$

$$ACOOCH_3^- + ClCOOCH_3 \xrightarrow{k_7} A(COOCH_3)_2 + Cl^- \quad (7)$$

$$ACOOCH_3^- + H^+ \xrightarrow{k_8} HACOOCH_3 \quad (8)$$

$$AH^- + H^+ \xrightarrow{k_9} AH_2 \quad (9)$$

In this case the one-electron reduction wave of the substrate will increase to two electrons while shifting to more positive potentials upon addition of $ClCOOCH_3$.

(26) Amatore, C.; Saveant, J. M. (a) *J. Electoanal. Chem. Interfacial Electrochem.* **1977**, *85*, 27; (b) *Ibid.* **1978**, *86*, 227; (c) *Ibid.* **1979**, *102*, 21; (d) *Ibid.* **1980**, *107*, 353.

(iii) A catalytic mechanism can also be brought into play either at the level of the radical anion (Scheme III followed by eq 7 or 8) or at the level of the dianion (Scheme IV).[21-22]

Scheme III

$$A + e \rightleftharpoons A^{-}\cdot \quad (1)$$

$$A^{-}\cdot + ClCOOCH_3 \underset{}{\overset{k_{10}}{\rightleftharpoons}} A + ClCOOCH_3^{-}\cdot \quad (10)$$

$$ClCOOCH_3^{-}\cdot \rightarrow COOCH_3\cdot + Cl^- \quad (11)$$

$$A^{-}\cdot + COOCH_3\cdot \rightarrow ACOOCH_3^- \quad (12)$$

In this case the first wave will also increase to two electrons. The dianion can be formed at the potential of the second wave or through a disproportionation reaction (Scheme IV followed by eq 7 or 8). In this case also two electrons will be consumed.

Scheme IV

$$A^{-}\cdot + e \rightleftharpoons A^{2-} \quad (13)$$

$$A^{-}\cdot + A^{-}\cdot \rightleftharpoons A + A^{2-} \quad (14)$$

$$A^{2-} + ClCOOCH_3 \rightleftharpoons A^{-}\cdot + ClCOOCH_3^{-}\cdot \quad (15)$$

$$ClCOOCH_3^{-}\cdot \rightarrow ClCOOCH_3\cdot + Cl^- \quad (11)$$

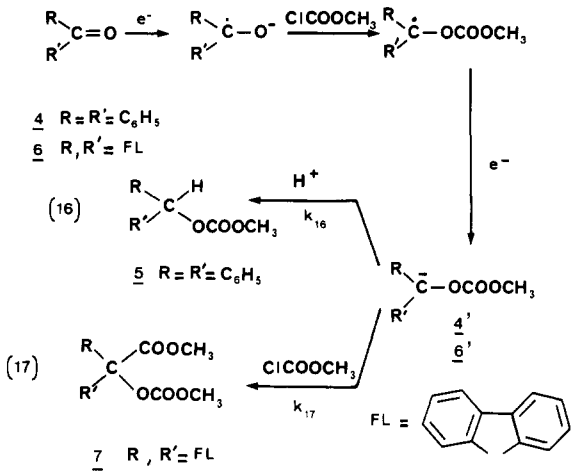
$$A^{-}\cdot + COOCH_3\cdot \rightarrow ACOOCH_3^- \quad (12)$$

Preparative Results

The results of the preparative electrolysis are given in Table I, and the coulometric values are reported in the Experimental Section.

Methyl Cinnamate (1). The reduction only gives a mixture of methyl 3-phenylpropanoate (**2**,

Scheme V



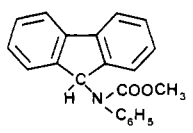
$C_6H_5CH_2CH_2COOCH_3$) and dimethyl 2-phenylbutanedioate (**3**, $C_6H_5CH(COOCH_3)CH_2COOCH_3$). Clearly, the carboxylated anion is formed in both cases and reacts competitively according to reaction 7 to give **3** and according to reaction 8 to give **2**.

Ketones. Reduction of benzophenone (**4**) leads to the methyl diphenylmethyl carbonate (**5**) while fluorenone **6** gives the 9-(methoxycarbonyl)fluoren-9-yl methyl carbonate (**7**). These reactions are summarized in Scheme V, which is written for the case of an ECEC mechanism but which could be written alternatively as a catalytic mechanism (see iii above). Mechanism i can be ruled out as cations formations between ketones and methyl chloroformate are unknown. It should be remarked that **4** leads only to a monocarboxylated derivative while **6** only gives a dicarboxylated compound. There is a competition at the level of the anions **4'** and **6'** between a protonation by residual water and a second carboxylation, i.e., between the basicity and the nucleophilicity of the carbanion. Anion **6'** is cyclopentadienyl-like and the charge is delocalized; it should therefore be less basic.

When benzophenone is reduced in DMF in the presence of CO_2, benzilic acid ($(C_6H_5)_2C(OH)COOH$) is the only product that is obtained. The radical anion thus appears in the carboxylation reactions as an ambident nucleophile.

Anils. Preparative electrolysis of benzaldehyde anil (**8**) in the presence of methyl chloroformate gives polymeric products. The complex mixture that is obtained contains only a small amount of carboxylated compounds.

In the case of fluorenone anil (**9**) the final mixture contained 45% of *N*-(methoxycarbonyl)-*N*-phenylfluoren-9-amine (**10**). The NMR spectrum of the raw



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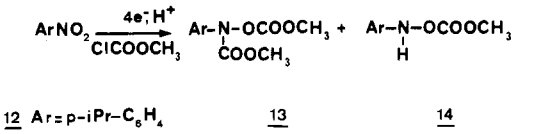
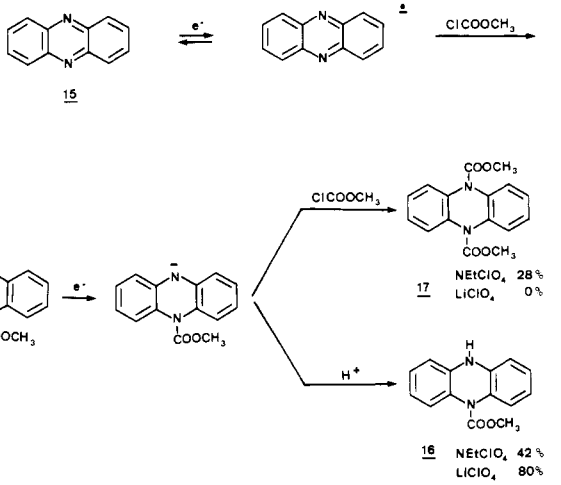
material obtained after electrolysis show that no C-9 carboxylated products are obtained. Interestingly, the reduction of imines in DMF in the presence of CO_2 does not give N-monocarboxylated products but only gives C-monocarboxylated products.[15]

If the electrolysis of **9** is performed in the presence of $LiClO_4$ instead of NEt_4ClO_4 as supporting electrolyte, the protonation increases: no carboxylated derivative **10** is obtained and only *N*-phenylfluorenyl-9-amine (**11**) is obtained. The influence of the supporting electrolyte will be discussed later.

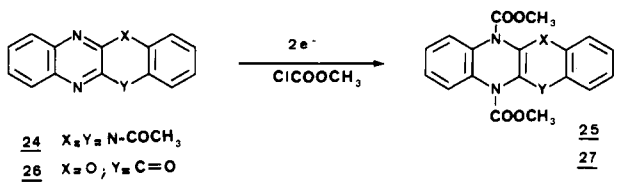
Scheme VI



Scheme VII



Scheme VIII



Nitro Compounds. The *p*-nitrocumene (**12**), which is a representative example of aromatic nitro compounds, gives a mixture of mono- and dimethoxycarboxylated hydroxylamines (**13** and **14**, Scheme VI).

N-Heterocycles. The behavior of N-heterocycles with a single nitrogen atom has not been investigated as these compounds give unstable cations with chloroformate.[27]

Pyrazine-Derived Heterocycles. Phenazine (15). Upon reduction **15** gives a mixture of monocarboxylated (**16**) and dicarboxylated (**17**) compounds. If this mixture is dissolved in $ClCOOCH_3$ for 2 days, it gives quantitatively the dicarboxylic compound **17**. In the presence of $LiClO_4$ as supporting electrolyte, only the monocarboxylated compound **16** is obtained (Scheme VII). These results (increased monocarboxylation at the expense of dicarboxylation) should be compared with those observed during the reduction of ketones $R_2C{=}O$ in the presence of alkyl halides: the yield of monoalkylated product is higher when the quaternary ammonium supporting electrolyte is replaced by $LiClO_4$.[21]

Quinoxalines. The 2,3-diphenylquinoxaline (**18**) only gives 1,4-bis(methoxycarbonyl)-1,4-dihydro-2,3-diphenylquinoxaline (**19**). The 2-phenylquinoxaline (**20**) leads to a mixture of 1,4-bis(methoxycarbonyl)-1,4-dihydro-2-phenylquinoxaline (**21**), 1-(methoxycarbonyl)-1,4-dihydro-2-phenylquinoxaline (**22**), and 4-(methoxycarbonyl)-1,4-dihydro-2-phenylquinoxaline (**23**). Reduction of quinoxaline itself leads to polymeric products.

The 5,12-diacetyl-5,12-dihydroquinoxalino[2,3-*b*]-quinoxaline (**24**) is reduced to 5,12-diacetyl-5,12-dihydro-6,11-bis(methoxycarbonyl)quinoxalino[2,3-*b*]quinoxaline

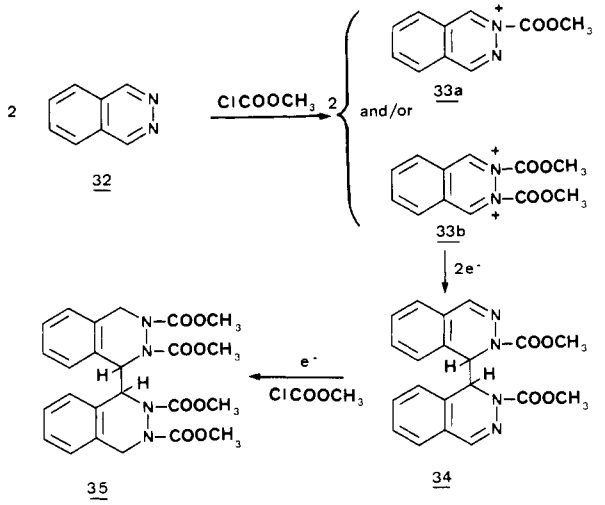
(27) "The Chemistry of Acyl Halides", Patai, S., Ed.; Interscience: New York, 1972; p 388.

Table II. Cyclic Voltammetry of Substrates[a]

substrate	E_{p_1}	E_{p_2}	E_{p_3}
benzophenone (4)	−1.78 1e[b] R[c]	−2.03 1e IRR	
fluorenone (6)	−1.32 1e R	−1.82 1e IRR	
phenazine (15)	−1.18 1e R	−1.52 1e IRR	
2,3-diphenylquinoxaline (18)	−1.64 1e R	−2.05 1e IRR	−2.46 2e IRR
benzo[c]cinnoline (30)	−1.52 1e R	−2.41 1e IRR	
phthalazine (32)	−1.99 1e IRR[c]	−2.39 1e IRR[d]	

[a] Scan rate 0.2 V s^{-1}. Reference saturated calomel electrode. [b] 1e = monoelectronic peak. [c] R = reversible peak, IRR = irreversible peak. [d] Irreversible peak, becomes reversible at v = 2 V s^{-1}.

Scheme IX



(25). In the same way, [1]-benzopyrano-[2,3-*b*]-quinoxalin-12-one (26) furnishes 27 (Scheme VIII).

2,3-Diphenylpyrazine (28). The result is similar to that obtained in the case of 2-phenylquinoxaline (mixture of mono- and dicarboxylated (29) compounds), but the monocarboxylated derivative is reoxidized during the HPLC separation into the starting diphenylpyrazine.

Pyridazine-Derived Heterocycles. Benzo[*c*]-cinnoline (30). It is reduced into 1,2-bis(methoxycarbonyl)-1,2-dihydrobenzo[*c*]cinnoline (31).

Phthalazine. In the presence of methyl chloroformate (5-fold excess), phthalazine (32) can be reduced at E = −0.6 V, i.e., at a potential more than 1.4 V positive to the reduction potential of phthalazine itself, indicating the formation of a cation.[24]

The reduction of **33a** or **33b** (vide infra) leads to a dimer **34**, which can be reduced to **35** (Scheme IX). The behavior of **33** is similar to that of 2-methylphthalazinium iodide in aqueous medium;[28] in both cases the same type of dimer is obtained.

Electroanalytical Results

Methyl chloroformate exhibits in cyclic voltammetry at 0.2 V s^{-1} a single irreversible peak at E_p = −2.60 V in acetonitrile. When the sweep rate is raised, the peak shifts to more negative potentials and merges with the background discharge. The voltammetric characteristics of the substrates investigated are summarized in Table II. Let us describe first the typical behavior of phenazine (15). Upon addition of increasing amounts of methyl chloroformate to a 10^{-3} M solution of phenazine, the first reversible system (I_c, I_a) of phenazine becomes irreversible, the height of Ic increases and Ia disappears. This behavior is shown in Figure 1 for a 10^{-1} M concentration of methyl

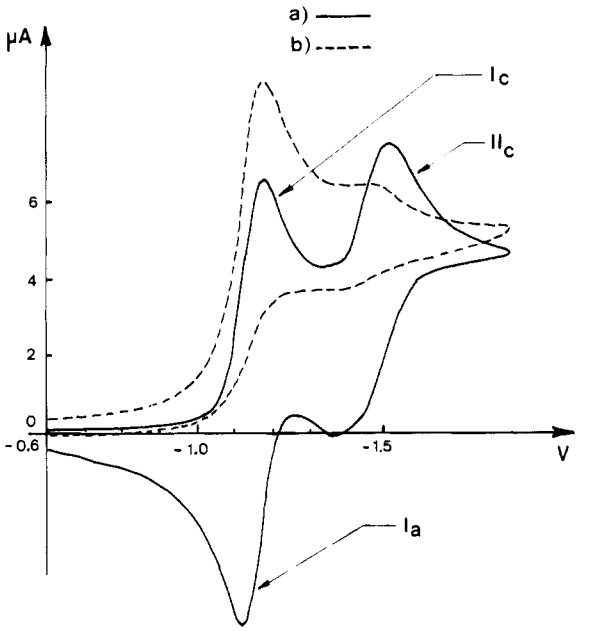


Figure 1. Cyclic voltammogram of **15** (10^{-3} M) in CH_3CN on a hanging mercury drop electrode. Et_4NClO_4 10^{-1} M; scan rate 0.2 v s^{-1}: (a) **15** alone, (b) with 10^{-1} M $ClCOOCH_3$.

chloroformate. At the same time the second peak of phenazine (II_c) progressively disappears upon addition of methyl chloroformate. An anodic peak appears at −0.1 V if and only if the first peak of phenazine has been scanned beforehand. This peak is identical with the oxidation peak of chlorine anions. If, in the presence of an excess of methyl chloroformate, Ep, the peak potential of the first peak (I_c) of **15**, is plotted against log v (v being the scan rate in V s^{-1}), a straight line is obtained with a 30 mV/decade slope followed by a horizontal straight line at higher scan rates. If, under the same conditions, the peak current is plotted as a function of log c (c being the concentration of methyl chloroformate), a curve is obtained that can be nicely fitted to the theoretical curve for an ECE or a DISP process.[29] The same behavior is observed in the cases of benzophenone and benzo[c]cinnoline (10^{-3} M), but in these cases, a 1.29 × 10^{-2} M concentration of methyl chloroformate is sufficient to transform the one-electron reversible first peak of benzophenone into a two-electron irreversible peak. In the case of fluorenone, a 2 × 10^{-1} M concentration of methyl chloroformate must be added in order to observe a two-electron behavior. In the case of benzo[c]cinnoline (30) we also checked by addition of Cl^- that the reaction of methyl chloroformate is irreversible (no change is observed on the cyclic voltammogram).

The behavior of phthalazine (32) is completely different. First of all the anodic wave of chloride ions is observed in a solution containing phthalazine (10^{-3} M) and methyl

(28) Lund, H.; Jensen, E. T. *Acta Chem. Scand.* **1970**, *24*, 1867.

(29) Mastragostino, H.; Nadjo, L.; Saveant, J. M. *Electrochim. Acta* **1968**, *13*, 721.

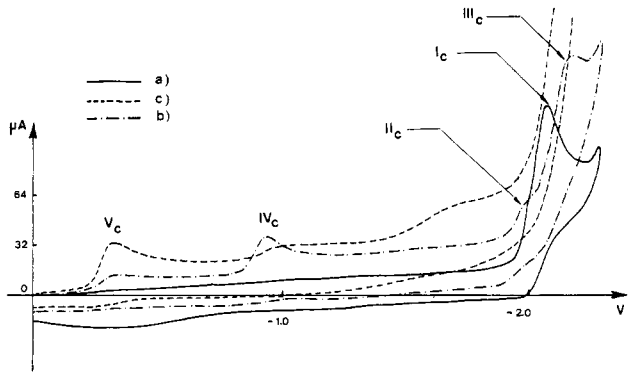


Figure 2. Cyclic voltammogram of **32** (10^{-3} M) in CH_3CN on a vitreous carbon electrode. Et_4NClO_4 10^{-1} M; scan rate 0.2 V s^{-1}: (a) **32** alone, (b) with 2.58×10^{-2} M of $ClCOOCH_3$, (c) with 1 M $ClCOOCH_3$.

chloroformate ($2.58\ 10^{-2}$ M) even if the potential scan does not encompass the peak of phthalazine. Upon addition of 2.58×10^{-3} M concentration of methyl chloroformate to a solution of phthalazine, the first peak of phthalazine (I_c) is replaced by a small more positive peak (II_c) (E_p = −1.92 V) while a new peak (III_c) appears at E_p = −2.13 V. At more positive potentials another new small cathodic peak (IV_c) appears at −0.88 V (Figure 2). If the chloroformate concentration is increased, peak IV_c develops and reaches about one-fourth of the initial height of peak I_c. At the same time a new peak (V_c) appears at −0.33 V. Upon continuous addition of methyl chloroformate, the height of peak IV_c decreases while that of V_c increases. For both peaks IV_c and V_c, the E_p − log v plot shows an initial straight line with a 20-mV slope.

Diphenylquinoxaline presents a behavior which is intermediate between that of phenazine and that of phthalazine: upon addition of methyl chloroformate the first peak increases and shifts to more positive potentials, but for a 2.5×10^{-1} M concentration of methyl chloroformate, a new peak appears at E_p = −0.95 V and for a 7.75×10^{-1} M concentration, another peak is evidenced at E_p = −0.45 V. At this concentration, the anodic peak of chloride ions can be evidenced even if the voltage scan does not encompass the first peak of quinoxaline.

Discussion

In the case of phthalazine (**32**), cations are formed on addition of methyl chloroformate as is indicated by the decrease of the height of the phthalazine peak and the appearance of two new peaks at more positive potentials as well as by formation of chloride ions in the bulk of the solution. Peak IV_c, which increases and then decreases at the expense of peak V_c, can be assigned to a monocation **33a** where a single nitrogen atom is quaternized while peak V_c can be assigned to a dication **33b** with the two nitrogens being quaternized. As only one electron per molecule is consumed during the reduction at −0.6 V, the final product must be the dication of the dimer, which upon work up gives **34**. At the level of both the monocation (**33a**) and the dication (**33b**), the dimerization must take place by coupling of two neutral radicals as indicated by the 20 mV/decade slope of the E_p − log v plot.[30] From this plot it is possible[30] to measure the rate constant for the dimerization of the monocation **33a** ($k = 4 \times 10^7$ M^{-1} s^{-1}) and for the dication **33b** ($k = 4.8 \times 10^5$ M^{-1} s^{-1}), the lower value of the dimerization rate constant of **33b** being most likely related to the coulombic repulsion between the two positively charged radicals.

Table III. Maximal Rate Constants for a Catalytic Mechanism (See Text)

substrate	E°_1 + 2.60	k_{10} calcd, M^{-1} s^{-1}
benzophenone (**4**)	0.82	4.0×10^{-5}
fluorenone (**6**)	1.28	4.9×10^{-13}
phenazine (**15**)	1.42	1.9×10^{-15}
2,3-diphenylquinoxaline (**18**)	0.96	1.6×10^{-7}
benzo[*c*]cinnoline (**30**)	1.08	1.4×10^{-9}

Let us now examine the case of benzophenone (**4**), fluorenone (**6**), phenazine (**15**), and benzo[*c*]cinnoline (**30**), where no cation formation is observed. First it is possible to rule out mechanism iii at the level of the dianion; indeed, this mechanism implies the consumption of two electrons at the level of the second wave, and we have seen that the second wave of all the compounds listed above disappear upon addition of methyl chloroformate.

It is also possible to eliminate a catalytic mechanism at the level of the first wave as follows. The equilibrium constant of reaction 10 can be estimated from the standard

$$A^{-\cdot} + ClCOOCH_3 \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} A + ClCOOCH_3^{-\cdot} \qquad (10)$$

potentials E°_1 and E°_2 of the $A/A^{-\cdot}$ and $ClCOOCH_3/ClCOOCH_3^{-\cdot}$ couples from $RT \ln K = -nF(E^\circ_1 - E^\circ_2)$. The standard potential of the $A/A^{-\cdot}$ couple is known from cyclic voltammetry (Table II) and that of $ClCOOCH_3/ClCOOCH_3^{-\cdot}$ cannot be obtained as the peak of methyl chloroformate is irreversible; however, it is certainly more negative than −2.60 V as shown by the fact that this peak shifts toward negative potentials when the sweep rate is increased. Thus, $\ln K < -(F/RT)(E^\circ_1 + 2.60)$. The values of the second term are listed in Table III. Moreover, $K = k_{10}/k_{-10}$, and k_{-10} can be taken at the diffusion limit in order to estimate an upper value of k_{10}. Thus, the values of k_{10} calculated in this way[31] with $k_{diff} = 5 \times 10^9$ M^{-1} s^{-1} are the maximum conceivable rate constants of the carboxylation reaction under a catalytic mechanism. With such small values of the rate constants, addition of methyl chloroformate to a stable solution of the radical anion would lead to a very slow disappearance of the color of this latter species. An experiment carried out under these conditions with benzophenone shows an immediate disappearance of the blue color.

Let us now show that mechanism ii is followed for the compounds that do not give rise to the formation of cations. For all these compounds in the presence of an excess of methyl chloroformate, one observes a straight line with a 30-mV slope on the E_p − log v diagram, indicating an ECE or DISP mechanism[29] where a first-order rate-determining chemical reaction follows the first electronic transfer. Moreover, in the case where the reaction is slow enough (i.e., in the cases of **6** and **15**), it is possible to obtain a peak current − log c plot that can be fitted to the theoretical curve for an irreversible ECE or DISP process.[29] From the E_p − log v or from the peak current − log c plot, it is possible to obtain the rate constant k_2 of the rate-determining reaction 2 of the radical anion with methyl chloroformate. These values are summarized in Table IV. A DISP process should be operative for the slower reactions of **4**, **6**, and **15** and an ECE mechanism for **30**.[26]

In the case of diphenylquinoxaline, both an ECEC mechanism (ii) and a cation formation mechanism (i) seem

(30) (a) Andrieux, C. P.; Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1970**, *26*, 147. (b) Andrieux, C. P.; Saveant, J. M. *Ibid.* **1970**, *26*, 223.

(31) Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *30*, 41.

Table IV. Rate Constants of the Reaction of Methyl Chloroformate with Radical Anions

substrate	k_2, M^{-1} s^{-1}
benzophenone (4)	8×10^4 [a]
fluorenone (6)	10^3 [a]
phenazine (15)	11 [a,b]
benzo[c]cinnoline (30)	3×10^5 [a]

[a] From peak potential measurement. [b] From peak current measurement.

to be operative: An increase and a positive shift of the first wave is observed upon addition of methyl chloroformate; at more positive potentials two positive waves appear that are indicative of the formation of a cation.

The effect of Li^+ as supporting electrolyte, which decreases the dicarboxylation at the profit of the monocarboxylation in the case of phenazine (**15**) and which suppresses the carboxylation in the case of fluorenone anil (**9**), can be related to the formation of a tight ion pair between the carboxylated anion and Li^+ in the case of **15** and between the radical anion and Li^+ in the case of **9**. This ion pair would be less nucleophilic than the free anion, and protonation would be favored at the expense of a second carboxylation.

Experimental Section

Melting points are uncorrected. ^1H NMR spectrum were recorded on a Varian A 60 or a Bruker WH 80 spectrometer using tetramethylsilane (Me_4Si) as internal standard. The apparatus and techniques used for the electrochemical studies have been described previously.[32] All the potentials were referred to the saturated calomel electrode (SCE); the temperature of the solutions was 20 °C. The cyclic voltammetry equipment was composed of a signal generator (Tacussel GSTP 3), a fast-rise wide-band potensiostat,[33] a memory oscilloscope (Tektronix 7313), and an X–Y recorder. The preparative electrolyses were carried out with the help of a high-output potentiostat (Tacussel ASA 100-1) and a coulometer (Tacussel IG5-N). Preparative HPLC was performed on Lichioprep RP 8 in the case of 2,3-diphenylpyrazine (25-cm length, 0.25 in. i.d., eluent 60:40 methanol/H_2O at 60 mL/h) and on Spherosil X04 400 in the case of 2-phenylquinoxaline (25-cm length, 0.25 in. i.d., eluent CH_2Cl_2 with a 700-ppm water content). The microanalyses were performed by the Service de Microanalyse, Université Pierre et Marie Curie. The following abbreviations are used in reporting NMR results: s = singlet, d = doublet, t = triplet, q = quartet. Compounds **1**, **4**, **6**, **12**, **15**, **30**, and **32** are commercially available (Aldrich). Other compounds have been prepared according to literature procedures: **9**,[34] **18**,[35] **20**,[36] **24**,[37] **26**,[38] and **28**.[39]

General Electrolysis Procedure. The three compartments of the H-type cell[32] were filled with acetonitrile of analytical grade. Et_4NClO_4 or $LiClO_4$ (0.15 M) was the supporting electrolyte. The catholyte (55 mL) contained the substrate and 2 mL of methyl chloroformate (Aldrich). The cathode was a mercury pool and the anode a Pt grid. The potentials were measured vs. a saturated calomel electrode (SCE) and maintained constant during the electrolysis. The catholyte was dearated with argon. The electrolyses were stopped when the current had diminished to a negligible value. The catholyte was diluted with 300 mL of water. Pyridine (1 mL) and sodium bicarbonate (1 g) were then added to destroy excess methyl chloroformate. After 10 min, the solution was extracted with diethyl ether. Etheral extracts were dried with Na_2SO_4, and the solvent was evaporated to give a residue that was recrystallized or from which different products were separated by HPLC.

Electroreduction of Methyl Cinnamate (1). Substrate **1** (730 mg, 4.5 mmol) was reduced in the presence of $ClCOOCH_3$ (3 mL, 39 mmol) and 10 g of activated alumina[40] (to eliminate traces of water) at −1.9 V (n = 2.15); the crude product was separated by preparative HPLC. Isolated were methyl 3-phenylpropanoate (**2**, 288 mg, 39%) and dimethyl 2-phenylbutanedioate (**3**, 410 mg, 41%), which were identified by comparison with authentic samples of **2**[41] and **3**.[42]

Electroreduction of Benzophenone (4). Substrate **4** (600 mg, 3.3 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.65 V (n = 2.10); the residue was recrystallized from methanol/water to give methyl diphenylmethyl carbonate (**5**, 566 mg, 71%): mp 57 °C; ^1H NMR ($CDCl_3$) δ 3.75 (s, 3, $COOCH_3$), 6.73 (s, 1, $(Ph)_2CH$), 7.37 (s, 10, aromatic protons). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.25; H, 5.90.

Electroreduction of Fluorenone (6). Substrate **6** (540 mg, 3 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.35 V (n = 2.25); the residue was recrystallized from methanol/water to give 9-(methoxycarbonyl)fluoren-9-yl methyl carbonate (**7**, 653 mg, 73%): mp 147–148 °C; ^1H NMR ($CDCl_3$) δ 3.70, 3.80 (s, 6, $COOCH_3$), 7.2–8.0 (m, 8, aromatic protons). Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.57; H, 4.77.

Electroreduction of Fluorenone Anil (9). Experiment 1 (Et_4NClO_4 as supporting electrolyte): Substrate **9** (635 mg, 2.5 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.4 V (n = 1.90); the solid residue was a complex mixture from which *N*-(methoxycarbonyl)-*N*-phenylfluoren-9-amine (**10**, 282 mg, 36%) was isolated by preparative HPLC: mp 132–133 °C; ^1H NMR ($CDCl_3$) δ 3.78 (s, 3, $COOCH_3$) 6.6–7.8 (m, 14, H-9 and aromatic protons). Anal. Calcd for $C_{21}H_{17}O_2N$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.12; H, 5.35; N, 4.51.

Experiment 2 ($LiClO_4$ as supporting electrolyte): Substrate **9** (940 mg, 3.75 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.2 V (n = 1.95); the residue was recrystallized from methanol/water to give *N*-phenylfluoren-9-amine (**11**, 540 mg, 57%): mp 122 °C (lit.[43] mp 121 °C).

Electroreduction of *p*-Isopropylnitrobenzene (12). Substrate **12** (495 mg, 3 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.15 V (n = 4.20). From the oily residue, two products were isolated by preparative HPLC: *N*,*O*-bis(methoxycarbonyl)-1-(hydroxylamino)-4-isopropylbenzene (**13**, (352 mg, 44%) [mp 52 °C; ^1H NMR ($CDCl_3$) δ 1.28 (s, 6, CH_3 of *i*-Pr) 2.6–3.3 (m, 1, H of *i*-Pr), 3.78, 3.83 (s, 2 × 3, $OCOOCH_3$ + $NCOOCH_3$), 6.9–7.6 (m, 4, aromatic protons). Anal. Calcd for $C_{13}H_{17}NO_5$: C, 58.43; H, 6.37; N, 5.25. Found: C, 58.36; H, 6.42; N, 5.34] and *O*-(methoxycarbonyl)-1-(hydroxylamino)-4-isopropylbenzene (**14**, 226 mg, 36%) [oil; ^1H NMR ($CDCl_3$) δ 1.17 (s, 6, CH_3 of *i*-Pr), 2.6–3.3 (m, 1, H of *i*-Pr), 3.70 (s, 3, $OCOOCH_3$), 6.35 (br s, 1, NH), 6.9–7.6 (m, 4, aromatic protons). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70. Found: C, 63.27; H, 7.28; N, 6.81].

Electroreduction of Phenazine (15). Experiment 1 ($LiClO_4$ as supporting electrolyte): Substrate **15** (540 mg, 3 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.05 V (n = 1.90); the residue was recrystallized from methanol/water to give 5,10-dihydro-5-(methoxycarbonyl)phenazine (**16**, 576 mg, 80%): mp 171–172 °C; ^1H NMR ($CDCl_3$) δ 3.78 (s, 3, 5-$COOCH_3$), 5.87 (br s, 1, H-10, exchanged with D_2O), 6.6–7.6 (m, 8, aromatic protons). Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.12; H, 5.12; N, 11.50.

Experiment 2 (Et_4NClO_4 as supporting electrolyte): Substrate **15** (540 mg, 3 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.30 V (n = 2.20). The solid obtained (635 mg, 80%) was shown by NMR to be a mixture of 60% **16** and 40% **17**.

(32) Armand, J.; Chekir, K.; Pinson, J. *Can. J. Chem.* **1978**, *56*, 1804.
(33) Garreau, D.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *35*, 309.
(34) Reddelien, G. *Chem. Ber.* **1910**, *43*, 2479.
(35) Hinsberg, O.; Konig, F. *Chem. Ber.* **1894**, *27*, 2181.
(36) Hinsberg, O. *Ann. Chem.* **1887**, *237*, 327; **1896**, *292*, 245.
(37) Armand, J.; Boulares, L.; Bellec, Ch.; Pinson, J. *Can. J. Chem.* **1982**, *60*, 2797.
(38) Vinot, N.; Maitte, P. *J. Heterocycl. Chem.* **1982**, *19*, 349.
(39) Mason, A. T.; Dryfoos, L. A. *J. Chem. Soc.* **1893**, *63*, 1297.
(40) Lines, P.; Jensen, B. S.; Parker, V. D. *Acta Chem. Scand., Ser B* **1978**, *B32*, 510.
(41) Vogel, A. I. *J. Chem. Soc.* **1948**, 654.
(42) Ramart-Lucas, P.; Papadakis, M. Z. *Ann. Chim. (Rome)* **1932**, *18*, 32.
(43) Staudiger, H.; Gaule, A. *Chem. Ber.* **1916**, *49*, 1956.

Preparation of 5,10-Dihydro-5,10-bis(methoxycarbonyl)-phenazine (17). A suspension of 200 mg of **16** in 2 mL of methyl chloroformate was stirred for 48 h at room temperature. The mixture was then poured into 150 mL of water containing 1 mL of pyridine and 1 g of $NaHCO_3$. The solid that precipitated was filtered, dried, and recrystallized from methanol to give **17** (223 mg, 90%); mp 161–162 °C; ^1H NMR ($CDCl_3$) δ 3.82 (s, 6, 5-$COOCH_3$ + 10-$COOCH_3$), 7.05–7.65 (AA'BB' pattern, 8, aromatic protons). Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.33; H, 4.90; N, 9.34.

Electroreduction of 2,3-Diphenylquinoxaline (18). Substrate **18** (600 mg, 2.13 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.60 V (n = 2.15). The residue was recrystallized from methanol/water to give 1,4-dihydro-1,4-bis(methoxycarbonyl)-2,3-diphenylquinoxaline (**19**, 545 mg, 64%): mp 173–174 °C; ^1H NMR ($CDCl_3$) δ 3.62 (s, 6, 1-$COOCH_3$ + 4-$COOCH_3$), 7.0–7.90 (m, 14, aromatic protons). Anal. Calcd for $C_{24}H_{20}N_2O_4$: C, 71.98; H, 5.03; N, 7.00. Found: C, 72.09; H, 5.13; N, 6.91.

Electroreduction of 2-Phenylquinoxaline (20). Substrate **20** (500 mg, 2.4 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.70 V (n = 2.2); the solid residue was a complex mixture from which were isolated by preparative HPLC **21** (118 mg, 15%), **22** (160 mg, 25%), and **23** (128 mg, 20%).

1,4-Dihydro-1,4-bis(methoxycarbonyl)-2-phenylquinoxaline (21): mp 145 °C; ^1H NMR ($CDCl_3$) δ 3.50, 3.92 (s, 2 × 3, 1-$COOCH_3$ + 4-$COOCH_3$), 6.80 (s, 1, H-3), 7.1–8.2 (m, 9, aromatic protons). Anal. Calcd for $C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.80; H, 4.96; N, 8.70.

1,4-Dihydro-1-(methoxycarbonyl)-2-phenylquinoxaline (22): mp 137 °C; ^1H NMR ($CDCl_3$) δ 3.67 (s, 3, 1-$COOCH_3$), 5.80 (s, 1, H-3), 7.1–8.0 (m, 9, aromatic protons). Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.01; H, 5.38; N, 10.62.

1,4-Dihydro-4-(methoxycarbonyl)-2-phenylquinoxaline (23): mp 142 °C; ^1H NMR ($CDCl_3$) δ 3.95 (s, 3, 4-$COOCH_3$), 6.65 (s, 1, H-3), 7.1–8.0 (m, 9, aromatic protons). Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.99; H, 5.38; N, 10.39.

Electroreduction of 5,12-Dihydro-5,12-Diacetylquinoxalino[2,3-*b*]quinoxaline (24). Substrate **24** (800 mg, 2.5 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.5 V (n = 2.15). The solid obtained was filtered, dried, and recrystallized from $CHCl_3$/Ligroin (30:70 v/v) to give 5,12-dihydro-5,12-diacetyl-6,11-bis(methoxycarbonyl)quinoxalino[2,3-*b*]quinoxaline (**25**, 724 mg, 66%): mp 294 °C; ^1H NMR (TFA) δ 2.48 (s, 6,5-$COCH_3$ + 12-$COCH_3$), 3.98 (s, 6, 6-$COOCH_3$ + 11-$COOCH_3$), 7.3–8.0 (m, 8, aromatic protons). Anal. Calcd for $C_{22}H_{20}N_4O_6$: C, 60.54; H, 4.62; N, 12.84. Found: C, 60.60; H, 4.57; N, 12.76.

Electroreduction of [1]-Benzopyrano[2,3-*b*]quinoxalin-12-one (26). Substrate **26** (485 mg, 2 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.00 V (n = 2.1). The crude product was recrystallized from methanol to give 6,11-dihydro-6,11-bis(methoxycarbonyl)-[1]-benzopyrano[2,3-*b*]-quinoxalin-12-one (**27**, 402 mg, 55%): mp 205–206 °C; ^1H NMR ($CDCl_3$ + TFA) δ 3.87, 4.00 (s, 2 × 3, 6-$COOCH_3$ + 11-$COOCH_3$), 7.0–8.3 (m, 8, aromatic protons). Anal. Calcd for $C_{19}H_{14}N_2O_6$: C, 62.29; H, 3.85; N, 7.65. Found: C, 62.13; H, 3.88; N, 7.77.

Electroreduction of 2,3-Diphenylpyrazine (28). Substrate **28** (700 mg, 3 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.90 V (n = 2.20). The solid residue was a complex mixture from which were isolated by preparative HPLC 1,4-dihydro-1,4-bis(methoxycarbonyl)-2,3-diphenylpyrazine (**29**, 158 mg, 15%) and **28** (70 mg, 10%). ^1H NMR of **29**: ($CDCl_3$) δ 3.60 (s, 6, 1-$COOCH_3$ + 4-$COOCH_3$), 6.67 (s, 2, H-4 + H-5), 7.1–7.8 (m, 10, aromatic protons). Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.71; H, 5.25; N, 7.87.

Electroreduction of Benzo[*c*]cinnoline (30). Substrate **30** (500 mg, 2.8 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −1.30 V (n = 1.95). The solid obtained was filtered, dried, and recrystallized from methanol to give 1,2-dihydro-1,2-bis(methoxycarbonyl)benzo[*c*]cinnoline (**31**), 596 mg, 72%): mp 179–180 °C; ^1H NMR ($CDCl_3$) δ 3.72 (s, 6, 1-$COOCH_3$ + 2-$COOCH_3$), 7.0–7.85 (m, 8, aromatic protons). Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.56; H, 4.67; N, 9.51.

Electroreduction of Phthalazine (32). Experiment 1. Substrate **32** (650 mg, 5 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −0.60 V (n = 0.93). The crude product was recrystallized from methanol to give 1,1',2,2'-tetrahydro-2,2'-bis(methoxycarbonyl)-1,1'-biphthalazyl (**34**, 699 mg, 74%): mp 237–238 °C; ^1H NMR ($CDCl_3$, temperature 10 °C) δ 3.21, 3.35, 3.63, 3.75 (s, 6, 2-$COOCH_3$ + 2'-$COOCH_3$), 5.57, 5.72 (s, 2 × 1, H-1 + H-1'), 6.75–7.90 (m, 10, H-4 + H-4' + aromatic protons). At probe temperature (38 °C) the NMR spectrum was ill-defined, probably due to a slow rotation around the C(1)–C(1') bond. Anal. Calcd for $C_{20}H_{18}N_4O_4$: C, 63.48; H, 4.80; N, 14.81. Found: C, 63.61; H, 4.92; N, 14.69.

Experiment 2. Substrate **32** (650 mg, 5 mmol) was reduced in the presence of $ClCOOCH_3$ (2 mL, 26 mmol) at −0.60 V until the current decreased to 5 mA. The potential was then put at −1.80 V (n = 2.15). The solid residue was recrystallized from methanol to give 1,1',2,2',3,3',4,4'-octahydro-2,2',3,3'-tetrakis-(methoxycarbonyl)-1,1'-biphthalazyl (**35**, 722 mg, 58%): mp 210–211 °C; ^1H NMR ($CDCl_3$) δ 3.75, 3.90 (s, 2 × 6, 2-$COOCH_3$ + 2'-$COOCH_3$ + 3-$COOCH_3$ + 3'-$COOCH_3$), 4.5–5.5 (m, 4, CH_2-4 + CH_2-4'), 6.05–6.25 (m, 2, H-1 + H-1'), 6.8–7.4 (m, 8, aromatic protons). Anal. Calcd for $C_{24}H_{26}N_4O_8$: C, 57.82; H, 5.26; N, 11.24. Found: C, 57.72; H, 5.33; N, 11.10.

Registry No. **1**, 103-26-4; **2**, 103-25-3; **3**, 15463-92-0; **4**, 119-61-9; **5**, 85926-25-6; **6**, 486-25-9; **7**, 85926-26-7; **9**, 10183-82-1; **10**, 85926-27-8; **11**, 31859-87-7; **12**, 1817-47-6; **13**, 85926-28-9; **14**, 85926-29-0; **15**, 92-82-0; **16**, 85926-30-3; **17**, 85926-31-4; **18**, 1684-14-6; **19**, 85926-32-5; **20**, 5021-43-2; **21**, 85926-33-6; **22**, 85926-34-7; **23**, 85926-35-8; **24**, 65182-17-4; **25**, 83769-65-7; **26**, 82501-03-9; **27**, 85926-36-9; **28**, 1588-89-2; **29**, 85926-37-0; **30**, 230-17-1; **31**, 85926-38-1; **32**, 253-52-1; **34**, 85926-39-2; **35**, 85926-40-5; Et_4NClO_4, 2567-83-1; $LiClO_4$, 7791-03-9; $ClCOOCH_3$, 79-22-1.