Attempted distillation of **9** led to clean reversal!

2-Nitrospiro[cyclopropane-1,9′-fluorene] (10). A solution of nitroethylene (2.85 g, 0.04 mol) in sodium-dried benzene (25 mL) was added over 0.75 h to a stirred solution of 9-diazofluorene[23] (7.5 g, 0.04 mol) in dry benzene (75 mL). After a 2-min induction period, nitrogen evolution started, and the expected volume of nitrogen was collected rapidly. Solvents were removed under reduced pressure at 45–50 °C, and the resulting cake powdered and was dried under vacuum. Crystallization from benzene gave 9.0 g (97%) of **10**: mp 110–111 °C; IR (KBr) ν_{max} 1531, 1351 cm^{-1} (nitro); NMR ($CDCl_3$) δ 7.3 (m, aromatic), 4.82 (dd, $HCNO_2$), 2.85 (dd, syn proton), 2.2 (t, anti proton).

Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 76.02; H, 4.65; N, 5.82.

3-(β-Nitroethyl)indole (11) and 3-(β,δ-Dinitrobutyl)indole (12). A stirred benzene solution of indole (1.2 g, 0.010 mol, 20 mL) at 0 °C was treated, in drops, with a dry benzene solution of nitroethylene (1.5 g, 0.02 mol, 10 mL). The reaction mixture was stirred for 20 h at room temperature, and the solvents were evaporated. The residue on preparative TLC (silica gel, 100% benzene) gave two pure compounds. The compound with higher R_f was **11**: yield 1.5 g (80%); mp 50–51 °C (recrystallized from benzene–hexane); IR (KBr) ν_{max} 1538, 1370 cm^{-1} (nitro); NMR ($CDCl_3$) δ 7.9 (br, NH), 7.2 (m, aromatic), 4.63 (t, CH_2NO_2), 3.43 (t, $CH_2CH_2NO_2$).

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.26. Found: C, 62.78; H, 5.56.

The compound with lower R_f was identified as **12**: yield 0.4 g (15%); mp 100–101 °C (crystallized from benzene–hexane); IR (KBr) ν_{max} 1563, 1370 (nitro), 1538, 1351 cm^{-1} (nitro); NMR ($CDCl_3$) δ 8.0 (br, NH), 7.2 (m, aromatic), 4.9 (m, $HCNO_2$), 4.4 (t, CH_2NO_2), 3.4 (dd, indolyl CH_2), 2.55 (q, $CH_2CH_2NO_2$).

Anal. Calcd for $C_{12}H_{13}O_4N_3$: C, 54.75; H, 4.94. Found: C, 54.44; H, 5.21.

2,6-Bis(β-nitroethyl)cyclohexanone (15). Under N_2, a stirred and cooled (~10 °C) solution of 1-morpholinocyclohexene[24] (2 g, 0.012 mol, in 20 mL of dry benzene) was treated dropwise with a solution of nitroethylene (1.83 g, 0.025 mol, in 10 mL of dry benzene) over a period of 0.5 h. The reaction mixture was stirred for an additional 20 h, treated with cold 2 N H_2SO_4 (50 mL) dropwise, and extracted with ether, and the organic layer was washed with bicarbonate and saturated sodium chloride and dried ($MgSO_4$). The residue on preparative TLC (silica gel, benzene–EtOAC, 80:20) gave pure product which on crystallization from benzene–petroleum ether gave colorless crystals of **15**: mp 64° C; yield 1.75 g (60%); IR (KBr) ν_{max} 1701 (carbonyl), 1536, 1370 cm^{-1} (nitro); NMR ($CDCl_3$) δ 4.45 (t, CH_2NO_2).

Anal. Calcd for $C_{10}H_{16}N_2O_5$: C, 49.18; H, 6.54; N, 11.4. Found: C, 48.95; H, 6.5; N, 11.3.

Reaction of Nitroethylene with β-Pinene: Isolation of Ene Product 16. A stirred dry benzene solution of β-pinene (1.36 g, 0.01 mol, 10 mL) was treated with nitroethylene (0.73 g, 0.01 mol, in 10 mL of benzene), the reaction mixture was refluxed for 16 h, the solvents were evaporated, and the residue on chromatography on silica gel gave on elution with a mixture of benzene–hexane (60:40) the ene product **16**: yield 0.33 g [90% based on recovered β-pinene (1.2 g)]; IR (neat) ν_{max} 1555, 1383 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 5.18 (br, olefinic), 4.27 (t, CH_2NO_2), 0.76 (shielded methyl).

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.89; H, 9.09. Found: C, 68.90; H, 8.51.

Acknowledgment. We thank Dr. M. M. Dhar and Dr. Nityanand of CDRI, Lucknow, and Dr. S. Rajappa of CIBA, Bombay, for NMR facilities. Financial assistance from CSIR and UGC, New Delhi, is gratefully acknowledged.

Registry No. 1, 874-44-2; 2, 72776-94-4; 2a, 72726-24-0; 3, 60262-57-9; 3a, 60247-74-7; 4, 72726-25-1; 5, 72726-26-2; 6, 72726-27-3; 7, 72726-28-4; 8, 5462-90-8; 9, 72726-29-5; 10, 34163-56-9; 11, 31731-23-4; 12, 72726-30-8; 15, 72726-31-9; 16, 72726-32-0; nitroethylene, 3638-64-0; 5-(methoxymethyl)cyclopentadiene, 39872-54-3; 5-(2,6-dithiacyclohexyl)cyclopentadiene, 72726-33-1; 5-(trimethylsilyl)cyclopentadiene, 3559-74-8; spirocycloheptadiene, 765-46-8; tetraphenylcyclopentadienone, 479-33-4; furan, 110-00-9; acetoxyfulvene, 699-15-0; 9-diazofluorene, 832-80-4; indole, 120-72-9; 1-morpholinocyclohexene, 670-80-4; β-pinene, 127-91-3.

Supplementary Material Available: NMR spectra of nitroethylene and products described in this paper (14 pages). Ordering information is given on any current masthead page.

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One-Step Synthesis of Cyclic Compounds by Electrochemical Reduction of Unsaturated Compounds in the Presence of Dielectrophiles

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Received April 24, 1979

The one-step synthesis of cyclic compounds is achieved in a few cases by electroreduction of unsaturated compounds in DMF, at a mercury pool cathode, in the presence of a more difficultly reducible dielectrophile. Unsaturated compounds include activated olefins, aromatic Schiff bases, ketones, and azo, nitroso, and nitro compounds. Four dielectrophiles are used; they are tri- or tetramethylene bromide, succinyl chloride, and 4-bromobutyryl chloride. The electrochemical synthesis of derivatives of cyclohexane, piperidine, pyrrolidine, hexahydropyridazine, tetrahydropyridazinone, tetrahydropyridazinedione, tetrahydrooxazine, isoxazolidine, and spirolactone can be successfully performed. Their yields range from 8 to 78% depending on competitive reactions. Results of chemical reduction by alkali metals and electrochemical reduction are compared.

Electrochemical reductive alkylation of unsaturated compounds may occur if a stable radical anion is produced in the first reduction step. Nucleophilic attack of the radical anion on the alkyl halide is usually observed in a second step and a radical is formed (EC mechanism). Such an S_N2 reaction has been suggested or proved in the case

0022-3263/80/1945-1189$01.00/0

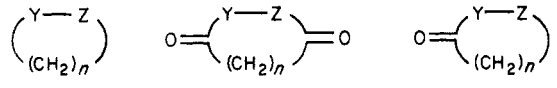
Table I. Electrochemical Reduction of Unsaturated Compounds in the Presence of Tri- or Tetramethylene Bromide

unsaturated compounds (mmol)	dielectrophiles (mmol)	applied potential, V	F consumed	isolated compounds	yield, %
1,2-bis(2-pyridyl)ethylene (11)	4b (13)	−1.8	2.15	7a	25
				7b	7
				8	12
				9	2
N-benzalaniline (3.3)	4a (7)	−1.8	3.45	11a	13
(3.4)	4b (3.5)	−1.8	2.1	11b	38[a]
(3.4)	4b (35)	−1.8	3.1	11b	59[a]
N-(2-pyridylmethylene)aniline (11)	4a (110)	−1.56	8.3	12	23[a]
				13a	6
benzo[*c*]cinnoline (2.8)	4b (5.6)	−1.5	2.1	14	78
azobenzene (2.8)	4b (22.4)	−1.3	2.0	15	64
(2.8)	4b (22.4)	−1.25-1.30	1.95	15	81[b]
nitrobenzene (4.9)	4a (49)	−1.14	4.1	16a	48
(4.1)	4b (17)	−1.3	4.7	16b	42
				17	28
				azobenzene	6

[a] See ref 13. [b] See ref 11.

of activated olefins,[1,2] Schiff bases,[3] ketones,[3] and azo,[4] nitroso, and nitro compounds.[5] The same mechanism holds for the acylation by acetic anhydride of some activated olefins,[6] ketones,[7] and azo,[8] nitro, and nitroso compounds.[9,10] The radicals formed may dimerize[7] or disproportionate,[3] but in most of the cases, the EC reaction is followed by a further reduction to an anion (ECE mechanism). The last step is a competition between protonation and alkylation (or acylation) of the monosubstituted anion.

In the present work, the one-step electrochemical syntheses of some compounds of the type **1**, **2**, and **3** are described. These compounds are obtained by electro-



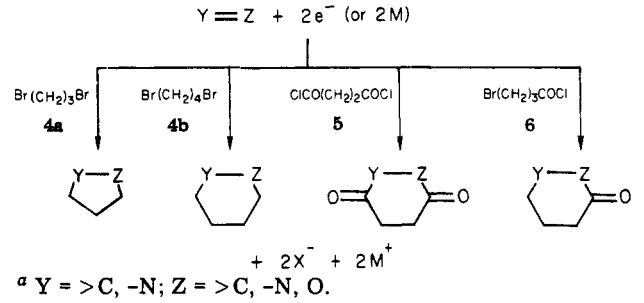
1 **2** **3**

Y = >C, -N; Z = C<, N-, O; n = 2, 3, . . .

chemical reduction in aprotic medium of unsaturated compounds Y=Z in the presence of dielectrophiles such as α,ω-alkyl dihalides, aliphatic α,ω-diacid chlorides, and ω-halogeno acid chlorides. The results we present include the use of four electrophiles, 1,3-dibromopropane **4a**, 1,4-dibromobutane **4b**, succinyl chloride **5**, and 4-bromobutyryl chloride **6**.

Electrochemical results are compared, in many cases, with the results obtained by chemical reduction with alkali metals (M). In both methods, the overall scheme of reductive cyclization, if observed, is given in Scheme I. However, the successive steps which lead to cyclic compounds are usually different. When chemical reduction of unsaturated compounds is performed by alkali metals in diethyl ether or liquid ammonia, dianions are usually the reductive species during alkylation or acylation (EECC mechanism). The last step in both chemical and electrochemical methods is a competition between protonation and alkylation (or acylation) of the monosubstituted anion. Protonation is unfavorable in diethyl ether and liquid ammonia. When the electrochemical method is used, great care must be taken to avoid water.[4] When a dielectrophile such as **4a**, **4b**, **5**, or **6** is used, the intramolecular cyclization competes, during the last step, with intermolecular alkylation or acylation by a second molecule. In order to favor the formation of cyclic compounds, our experiments are performed on a mercury pool cathode, in dry DMF, in the presence of 1 equiv of **4a**, **4b**, **5**, or **6**. The yields of the isolated compounds are calculated after purification by column chromatography. If we consider the amount of depolarizer which is reduced in each electrolysis (from 0.8 to 13 mmol) and the large number of compounds isolated in most of the experiments, the purification of compounds having closed R_f values decreases the yields. Hence, optimal yields may not be expected with our experimental conditions. On the other hand, we have not tried to isolate carboxylic acids which may be formed in the presence of **5** or **6**. The material balance in part B may therefore be lowered. The unsaturated compounds chosen give a stable radical anion in DMF during their first reduction step. They are activated olefins (Y = Z = C), aromatic Schiff bases (Y = C, Z = N), ketones (Y = C, Z = O), and azo (Y = Z = N), nitroso (Y = N, Z = O), and nitro (Y = N→O, Z = O) compounds.

Scheme I[a]



[a] Y = >C, -N; Z = >C, -N, O.

Electrochemical synthesis according to Scheme I of hexahydropyridazine and pyrazolidine derivatives has been

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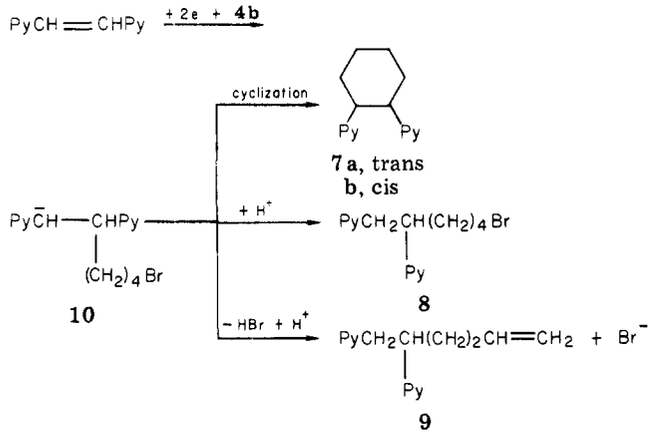
performed in hexamethylphosphoric triamide (HMPT).[11] The electrochemical syntheses in DMF of *N*-phenylperhydro-1,2-oxazepine[5] and of cyclopentanodihydroanthracene[12] have been described. We have reported elsewhere the electrochemical syntheses in DMF of pyrrolidine and piperidine derivatives[13] and of tetrahydropyridazinones and -diones.[14]

Results and Discussion

A. Electrochemical Reduction in the Presence of α,ω-Dibromoalkanes. Table I gives the structures of the isolated products and their yields after purification by column chromatography. Radical anions are formed during the first reduction step of the unsaturated compounds chosen. However, radical anions of Schiff bases are susceptible to protonation[16] and are the least stable ones. All the unsaturated compounds chosen are reduced at potentials corresponding to the first reduction step. These potentials are more positive than the half-wave potentials of 1,3-dibromopropane (−2.0 V) and 1,4-dibromobutane. Little or no increase in the height of the polarographic wave of the unsaturated compounds is observed when the alkyl dihalide is added, indicating that nucleophilic attack of the radical anion (EC mechanism) is rather slow.

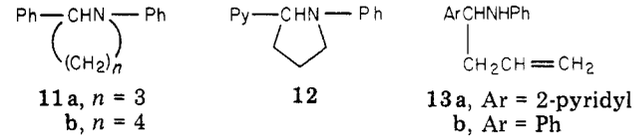
1,2-Bis(2-pyridyl)ethylene. Mono- or dialkylated saturated compounds are isolated when activated olefins are reductively alkylated.[1,2] Reduction of 1,2-bis(2-pyridyl)ethylene in the presence of **4b** leads to the cyclic compound **7a** as major product. **7a** is proposed to be the trans isomer from chemical and NMR data (see the Experimental Section). The electron-withdrawing property of both pyridinic nuclei decreases the basicity of the anion **10**; its intramolecular alkylation may compete with its protonation.



Py = 2-pyridyl

Only the trans isomer of 1,2-diphenylcyclohexane is isolated when chemical reduction of stilbene by sodium is followed by addition of 1,4-dichlorobutane.[15]

Schiff Bases. Electrochemical reductive alkylation of aromatic Schiff bases by alkyl halides leads to mono-C- or N-alkylated amines as well as dialkylated saturated compounds.[3] As already mentioned, radical anions of Schiff bases are susceptible to protonation.[16] We have

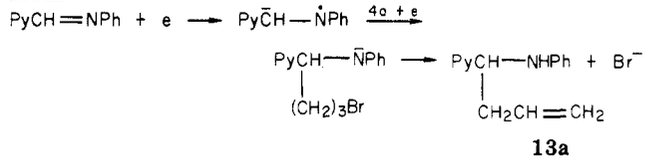


Py = 2-pyridyl

observed[13] that when *N*-benzalaniline and *N*-(2-pyridylmethylene)aniline are reduced in the presence of an excess of alkyl dihalide, better yields of cyclic compounds **11b** and **12** are achieved.

Electrochemical reduction of *N*-benzalaniline in the presence of 1,3-dibromopropane (**4a**) leads to 1,2-diphenylpyrrolidine (**11a**) in low yield. In this experiment, the electrolysis was stopped before total depletion of the faradaic current (i.e., after 3.45 F were consumed). Since the reduction potentials of *N*-benzalaniline and **4a** differ by about 0.2 V, an indirect reduction of dibromopropane is observed, the radical anion of the Schiff base being the mediator.[17]

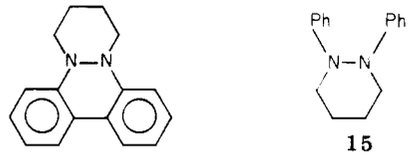
When *N*-(2-pyridylmethylene)aniline is reduced in the presence of **4a**, a minor compound (**13a**) is isolated in addition to the pyrrolidine derivative **12**. The formation of **13a** probably results from an alkylation at the carbon atom.



Py = 2-pyridyl

Aromatic imines first undergo chemical alkylation at carbon.[19-21] Substituted pyrrolidine and piperidine derivatives are produced when the disodium adduct of benzophenone anil is treated with tri- and tetramethylene bromide.[20] However, it has been shown that attempts to utilize the dianion of *N*-benzalaniline in order to prepare the pyrrolidine derivative **11a** failed.[21] **13b** is the major compound obtained by chemical reduction of *N*-benzalaniline with potassium in the presence of crown ether and **4a**.[21] The dianion formed reacts with **4a** and gives **13b** through a carbon anionic site attack. The electrochemical synthesis of pyrrolidine derivatives has been performed recently by electroreductive addition of alkyl halide to immonium salts.[18]

Azo Compounds. An excess of **4b** is present during the electroreduction in DMF of benzo[*c*]cinnoline and azobenzene. The excess (8 equiv) is the same when azobenzene is reduced either in HMPT[11] or in DMF. Since only the cyclic derivatives **14** and **15** are isolated, we may



conclude that intramolecular alkylation is faster than in-

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Table II. Electrochemical Reduction of Unsaturated Compounds in the Presence of Succinyl Chloride (5) or 4-Bromobutyryl Chloride (6)

unsaturated compounds (mmol)	acid chloride (mmol)	applied potential, V	F consumed	isolated compounds	yield, %
fluorenone (2.8)	5 (3.1)	−1.2	2.0	**26**	22
				27	33
azobenzene (11)	5 (89)	−1.2	3.6	**28**	49[a]
cinnoline (3.8)	5 (22)	−1.3	2.8	**29**	26[a]
benzo[*c*]cinnoline (2.8)	5 (2.8)	−1.2	2.3	**30**	49[a]
(11)	5 (89)	−1.2	4.3	**30**	54[a]
azobenzene (2.75)	6 (2.75)	−0.6	1.3	azobenzene	30[a]
				31	30[a]
(2.75)	6 (2.75)	−1.3	2.0	azobenzene	21[a]
				hydrazobenzene	12[a]
				33	8[a]
benzo[*c*]cinnoline (2.8)	6 (5.6)	−0.5	2.1	benzo[*c*]cinnoline	30[a]
				32	40[a]
(2.8)	6 (2.8)	−1.5	2.2	benzo[*c*]cinnoline	20[a]
				32	10[a]
				34	16[a]
(2.8)	6 (2.8)	−1.5	2.8	**34**	62[a,b]
N-benzalaniline (13)	6 (14)	−1.0	1.3	**36**	14
				37a	12
				37b	17
				38	19
nitrobenzene (4.9)	6 (14.5)	−0.8	4.5	**39**	72

[a] See ref 14. [b] 6 is added after generation of radical anions of benzo[*c*]cinnoline.

Table III. Polarographic Reduction (Volts) of Unsaturated Compounds (10^{-3} M) in the Presence of 1 Equiv of Acid Chloride or Anhydride

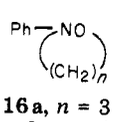
unsaturated compounds	$E_{1/2}$, wave A	acid chloride or acid anhydride	$E_{1/2}$, wave C	$E_{1/2}$, wave D
azobenzene	−1.30	5 or acetyl chloride	−0.20[a]	−1.10[a]
		acetic anhydride		−1.15
benzo[*c*]cinnoline	−1.40	5	−0.28[a]	−1.30[a]
cinnoline	−1.49	5	−0.32[a]	−1.30[a]
N-benzalaniline	−1.83	5	−0.70	
		6	−0.70	
Nitrosobenzene	−0.90[b]	5	−0.16[c]	−0.64[c]
		6	−0.30[c]	−0.64[c]
Nitrobenzene	−1.15[d]	5	−0.96[c]	−1.10
		6	−0.90[c]	−1.05[c]
Fluorenone	−1.35[e]	5	−0.66	−1.07[c]
		6	−0.66	−1.08[c]

[a] See ref 14. [b] M. R. Asirvatham and M. D. Hawley, *J. Electroanal. Chem.*, 57, 179 (1974); M. Lipsztajn, T. M. Krygowski, E. Laren, and Z. Galus, *J. Electroanal. Chem.*, 57, 339 (1974). [c] Ill-defined wave (polarographic maxima). [d] W. H. Smith and A. J. Bard, *J. Am. Chem. Soc.*, 97, 5203 (1975). [e] M. K. Kalinowski, *Chem. Phys. Lett.*, 7, 55 (1970).

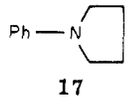
termolecular alkylation. **15** (85%) was previously obtained by chemical reduction.[22]

Nitroso- and Nitrobenzenes. Electrogenerated nitrosobenzene and nitrobenzene radical anions react with alkyl halides to give, in both cases, *N*,*O*-dialkylphenylhydroxylamines.[5] Better yields are obtained when nitrobenzene is reduced since the formation of azoxybenzene from nitrobenzene radical anion is not favored. When nitrobenzene is reduced, dihalogenoalkanes must be present in excess (3 equiv) since alkoxides or ether derivatives are formed;[5] 4 F is consumed in this case.

Reduction of nitrobenzene in the presence of **4a** leads to a reasonable yield of the isoxazolidine derivative **16a**. As shown in the experimental part, this compound is unstable even in the absence of air. When nitrobenzene is reduced in the presence of **4b**, two main compounds (**16b** and **17**) are obtained, besides a small amount of azobenzene. The formation of *N*-phenylpyrrolidine (**17**) and of a small amount of azobenzene is unexpected. The presence of azobenzene cannot be explained through the intermediate formation of further reduced azoxybenzene, since the reduction potential of azoxybenzene (−1.4 V[34]) is more negative than the potential applied during the electrolysis (−1.3 V). The intermediate formation of a nitrene should be considered. Formation of azobenzene during reductive acylation of nitro- or nitrosobenzene has been reported and is due to an intermediate nitrene.[10] This problem will be considered further in a future publication.



16a, $n = 3$
b, $n = 4$
c, $n = 5$



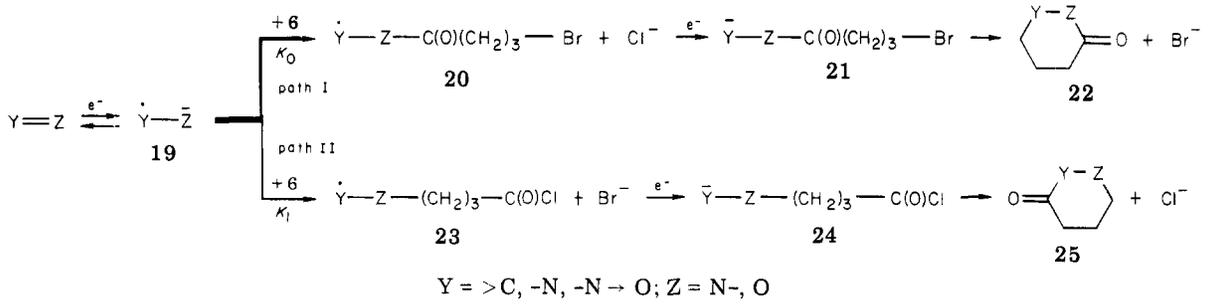
17

The derivative **16b** is easily formed by addition of 1,3-butadiene to nitrosobenzene and catalytic hydrogenation of the resulting unsaturated heterocycle.[23] On the other hand, syntheses of isoxazolidine derivatives are scarce. As already stressed by Wagenknecht,[5] who obtained **16c** electrochemically, the formation of **16a** in a reasonable yield shows the synthetic utility of this method.

B. Electrochemical Reduction in the Presence of Succinyl Chloride and 4-Bromobutyryl Chloride. The structures and yields of the compounds obtained when the unsaturated compounds described below are reduced in the presence of **5** or **6** are listed in Table II.

(23) Yu. A. Arbuzov, *Dokl. Akad. Nauk SSSR*, 76, 681 (1951). *Chem. Abstr.*, 45, 8535f.

Scheme II. Waves A and D



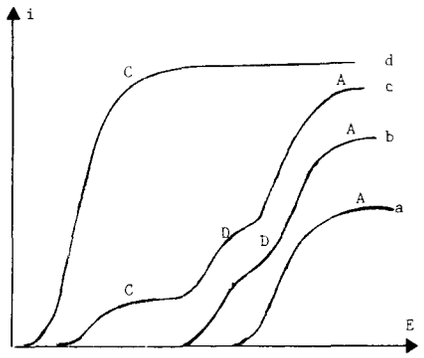


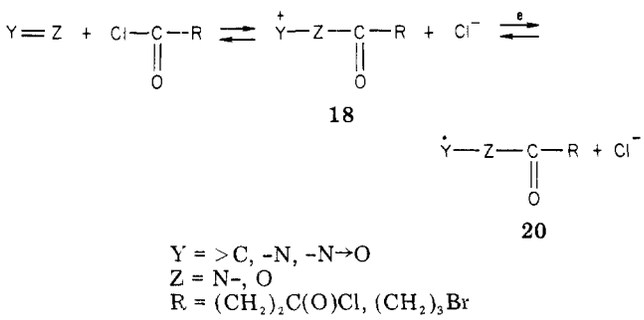
Figure 1. Polarographic behavior of an unsaturated compound Y=Z: (a) alone; (b) acetic anhydride added; (c) acid chloride added; (d) large excess of acid chloride added.

Electroreductive acetylation of unsaturated compounds has been performed in the presence of acetic anhydride[6-10,24] or acetyl chloride.[8]

When acetic anhydride is present ($E_{1/2}$ = -2.6 V), an acetylation of the radical anion takes place (EC mechanism) and the overall reaction corresponds, in most of the cases, to an ECEC mechanism.[6-10] The changes in the polarogram of Y=Z by the occurrence of such a mechanism are known.[25] A new wave, D, precedes the first reversible wave A of Y=Z (Figure 1b and Table III).

In the presence of acetyl chloride ($E_{1/2}$ = -1.4 V), a more positive wave, C, is observed in addition to waves A and

wave C



D (Figure 1c and Table III) when the double bond of the unsaturated compound Y=Z contains a heteroatom (N, O). The same polarographic modifications are observed in the presence of acid chlorides **5** and **6**. When a large excess of acid chloride is present, waves D and A merge and it may even happen that C is the only wave observed (Figure 1d). C is a kinetic wave which corresponds to the reduction of the acylated cation **18**.

In Table III are given the half-wave potentials ($E_{1/2}$) of waves A, C, and D of the compounds which have been reduced in the presence of **5** or **6**.

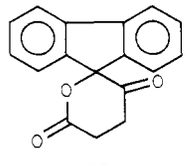
When electrolyses are performed at potentials of wave C, the radical **20** is first generated and then further reduced. When they are performed at potentials of waves A and D, direct reduction of Y=Z to the radical anion **19** competes with reduction of the kinetically generated cationic species **18** to **20**.

In the presence of **5**, an acid may be formed if the radical **20** (R = $(CH_2)_3C(O)Cl$) does not lead to a cyclic compound. In our experiments, no compound with a carboxylic acid function is isolated after electrolysis, since extraction of the electrolysis products by diethyl ether is performed in aqueous alkaline solutions where carboxylate anions are present. When 4-bromobutyryl chloride (**6**) is present, the radical anion **19** may react in two different ways which are shown in Scheme II.

Since acid chlorides are much more easily reduced than bromoalkanes, the acylation rate (K_0) of the radical anion **19** seems a priori higher than its alkylation rate (K_1). Thus, path I with formation of the radical **20** should be favored. In our previous work about the reduction of aromatic azo compounds,[14] the cyclic products **22** and **25** were indistinguishable, since in the substrate Y and Z were identical; thus the intermediate **23** is only hypothetical. We have not tried to isolate carboxylic acids which might be formed from **24** (path II, vide supra).

Cyclic compound **22** may be obtained if intramolecular alkylation or acylation of anion **21** is fast enough to compete with intramolecular protonation, alkylation or acylation. Protonation is favored when an acid chloride is present, due to its hydrolysis by residual water and the formation of carboxylic acid. Several byproducts may be expected from these competitive reactions.

Fluorenone. The spirolactone **26** is obtained by reduction of fluorenone in the presence of **5**. Due to the small intensity of the kinetic current at potentials of wave C, the electrolysis is performed at the potentials of wave D. The formation of a high yield of pinacol **27** shows that protonation of the radical anion of the ketone is difficult to avoid and competes with acylation.



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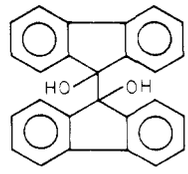
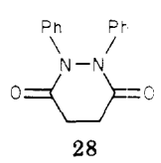


27

Azo compounds. We have described elsewhere[14] the electrochemical reduction of azobenzene, cinnoline, and benzo[*c*]cinnoline in the presence of **5** and the formation of **28-30**. These results are reported in Table II in order to compare them with the following results obtained by chemical means.

When 2 equiv of lithium and then 1 equiv of succinyl chloride are added to an ethereal solution of benzo[*c*]-cinnoline, only 10% of **30** is isolated. Reduction of the

(24) H. Lund, *Acta Chem. Scand., Ser. B*, 31, 424 (1977).
(25) B. S. Jensen and V. D. Parker, *Electrochim. Acta*, 18, 665 (1973).



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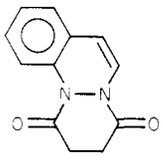

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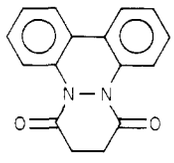
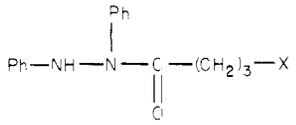


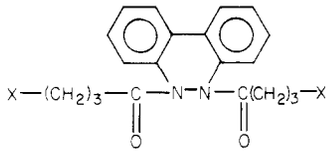
30

carbon rings by lithium is partially observed. A better yield is obtained in the presence of crown ether (32%) or in the presence of an excess of lithium (28% in the presence of 5 equiv).

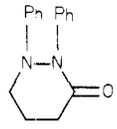
In Table II are reported the results we have previously obtained by reduction of azobenzene and benzo[*c*]cinnoline in the presence of **6**.[14] The formation of the cyclic compounds **33** and **34** was suggested to take place through path



31 a, X = Br
b, X = Cl



32 a, X = Br
b, X = Cl



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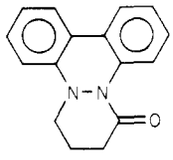
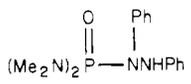


34

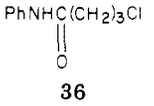
II (Scheme II).[14] However, a different explanation which was proposed by one of the reviewers and which seems more reasonable is that the observed products **33** and **34** are formed through path I and are the result of a concentration effect. Let us consider the reduction of benzo[*c*]cinnoline in the presence of **6**. When the concentration of **6** is in large excess compared to the concentration of the intermediate anion **21**, formation of the diacylated compounds **32a** and **32b** is favored. This condition is fulfilled when the electrolysis is carried out at −0.5 V (wave C) where the current density is less, and thus the concentration of **21** is low relative to that of **6**. On the opposite side, when the concentration of **21** is high relative to that of **6**, the formation of the cyclic compound **34** is favored. This condition is fulfilled when first **21** is generated in a large amount and then **6** is added. The chloro derivatives **31b** and **32b** result from a nucleophilic substitution of the intermediate bromo derivative or of 4-bromobutyryl chloride by the chloride anions which appear during the electrolysis. It is known that in DMF the order of nucleophilicity is $Cl^- > Br^- > I^-$ and promotes this exchange.

Attempts to prepare **33** and **34** by chemical means fail, no matter what solvent (diethyl ether, liquid ammonia, or HMPT), alkali metal (Li with or without crown ether, Na or K), or molar ratio is used. In HMPT with K as the reducing agent, the anion of azobenzene attacks the solvent and leads to the phosphoramide **35**.

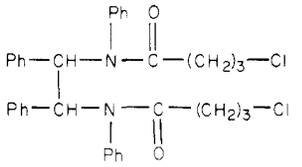


35

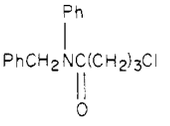
***N*-Benzalaniline.** Reduction of *N*-benzalaniline in the presence of **6** can be performed only at a potential corresponding to wave C since waves A and D are beyond the discharge of **6**. Hence, the reduced species is the acylated cation **18**. Benzaldehyde, **36**, **37**, and **38** are isolated. In the presence of acid chloride **6**, *N*-benzalaniline is unstable and decomposes to benzaldehyde and amide **36**. A complete decomposition is obtained within 5 h. The formation of the dimeric amides **37a** and **37b** shows that the dimerization of the radical **20** is very fast since it competes with further reduction to **38**.



36



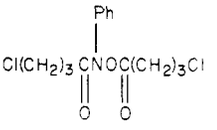
37a,b (diastereoisomers)



38

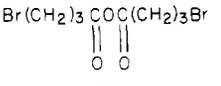
Nitro- and Nitrosobenzenes. Several attempts at electrochemical synthesis of tetrahydrooxazinedione by reduction of nitro- or nitrosobenzene in the presence of succinyl chloride (**5**) failed. Some polymeric materials are isolated no matter what potential is applied. In one experiment, we first generated radical anions of nitrosobenzene and then added **5**. In this case, azobenzene (9%) is isolated in addition to azoxybenzene (36%). Formation of azobenzene during reductive acylation of nitro- or nitrosobenzene has been reported and is due to the intermediate formation of nitrene.[10]

Electrolysis of nitrobenzene in the presence of **6** provides the diacylated derivative **39** and a trace of azoxybenzene.



39

The results described in this section show that intermolecular reactions are, in most cases, faster than intramolecular cyclization when 4-bromobutyryl chloride (**6**) is present. Indeed, as already mentioned, **6** is transformed into its chloro derivative in DMF, if chloride anions appear during electrolysis. On the other hand, acylation and protonation reactions are promoted since acylation by acid chlorides is much faster than alkylations by bromo- and chloroalkanes and since formation of carboxylic acid from residual water is difficult to avoid. Better results may be expected in different solvents or in the presence of the acid anhydride **40**. Synthesis and purification of **40** are actually



40

on study. First results seem promising since some cyclic compound **34** could be isolated by reducing benzo[*c*]cinnoline in the presence of **40**, the purification of which was not achieved.

Experimental Section

All compounds are commercially available.

An Amel-552 poteniostat, a Tacussel coulometer, and a 3-electrode Tacussel polarograph are used. NMR spectra are recorded on a Hitachi R24 spectrometer with $CDCl_3$ as the solvent (internal standard Me_4Si). IR spectra are recorded on a Beckman IR-8 and a Perkin-Elmer 577 spectrometer. Mass spectra are recorded on a Finnigan 3002 spectrometer.

General Electrolysis Procedure. The three compartments of the H-type cell are filled with dry *N*,*N*-dimethylformamide (4-Å

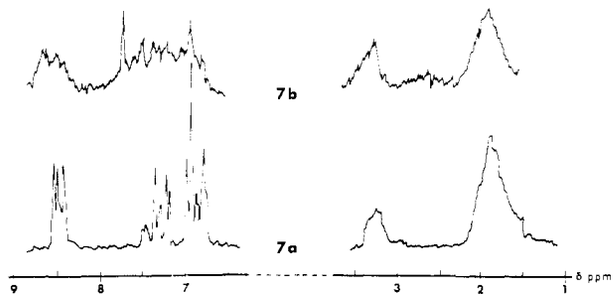


Figure 2. NMR spectra of compounds **7a** and **7b**.

molecular sieves and neutral alumina). Bu_4NI or Bu_4NPF_6 (0.1 M) is the supporting electrolyte. The cathode is a mercury pool and the anode a Pt grid. The potentials are measured vs. a saturated calomel electrode (SCE) and maintained constant during the electrolysis. The catholyte is deaerated with argon. If not specified, the electrolyses are stopped when the current has diminished to a negligible value. The catholyte is diluted with water and adjusted to pH 9–10 by sodium carbonate, and the products are extracted with diethyl ether. After the solution is dried, the ether is evaporated and the residue separated by column chromatography on silica gel.

Electroreduction of 1,2-Bis(2-pyridyl)ethylene in the Presence of 1,4-Dibromobutane (4b). Substrate (2 g, 11 mmol) is reduced in the presence of **4b** (1.6 mL, 13 mmol) at −1.8 V ($E_{1/2}$ = −1.92 V vs. Ag/AgCl or −1.36 V vs. SCE), n = 2.15; crude product 2.2 g; column chromatography eluant diethyl ether. The compounds are isolated in the order **7a** (25% yield), **7b** (7%), **9** (2%), and **8** (12%).

***trans*-1,2-Bis(2-pyridyl)cyclohexane (7a)**: mp 77–8 °C (petroleum ether); NMR ($CDCl_3$) (see Figure 2) δ 1.88 (m, 8, alicyclic H), 3.23 (m, 2, picolic H), 6.70–7.00 (m, 4, pyridine β-H), 7.15–7.50 (m, 2, pyridine γ-H), 8.50 (dd, 2, pyridine α-H); IR (KBr) 3080, 3010, 2930, 2920, 2850, 1590, 1567, 1473, 1433, 1150, 1000, 795, 785, 780, 755, 550, 408 cm^{-1}; mass spectrum, m/e (relative intensity) 238 (9, $M^{+\cdot}$), 183 (21, M − C_4H_7), 160 (46, M − C_5H_4N), 159 (71, M − C_5H_5N), 146 (100, 160 − CH_2), 132 (41, 146 − CH_2), 130 (27), 118 (33, 132 − CH_2), 117 (46), 106 (70), 104 (21), 93 (56, $C_6H_7N^+$), 80 (60), 79 (36, pyridinium), 78 (51). Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.55; H, 7.51; N, 11.59.

***cis*-1,2-Bis(2-pyridyl)cyclohexane (7b)**: NMR ($CDCl_3$) δ 1.88 (m, 6, alicyclic H), 3.2 (m, 2, picolic H), 6.7–7.9 (m, 6, β- and γ-pyridine H), 8.2–8.8 (m, 2, α-pyridine H). See Figure 2 for comparison. The equivalence of the two equatorial pyridinic nuclei is observed in the case of **7a**. In the case of **7b**, a broadening of the aromatic multiplet is observed, due to the superposition of the signals of two nonequivalent nuclei since one is axial and one equatorial. Mass spectrum, m/e (relative intensity) 238 (9, $M^{+\cdot}$), 183 (27, M − C_4H_7), 182 (41, M − C_4H_8), 181 (100, M − C_4H_9), 160 (25, M − C_5H_4N), 159 (40, M − C_5H_5N), 146 (62, 160 − CH_2), 132 (22, 146 − CH_2), 118 (18, 132 − CH_2), 117 (21), 106 (40), 104 (39), 93 (44, $C_6H_7N^+$), 80 (23), 79 (19, pyridinium), 78 (42).

Assay of Isomerization of 7a. If the isolated isomer **7a** was the cis form, an isomerization of the 2-picolyl anion leading, after protonation, to the more stable trans form should be observed. The following experiment rejects this hypothesis. Bis(2-pyridyl)cyclohexane (**7a**) (0.093 g, 0.39 mmol) is added to a solution of potassium amide (from potassium 0.019 g, 0.49 mmol, and traces of ferric nitrate) in 100 mL of liquid ammonia. The mixture is stirred during 3 h and then hydrolyzed by an excess of NH_4Cl and H_2O. The diethyl ether extract is dried (Na_2SO_4) and concentrated. The white crystals (0.060 g) are dissolved in $CDCl_3$ for NMR spectrum recording. The spectrum obtained is the same as that for **7a**.

6-Bromo-1,2-bis(2-pyridyl)hexane (8): liquid; NMR ($CDCl_3$) δ 1–1.5 (m, 2, CH_2), 1.5–2.0 (m, 4, CH_2), 3.0–3.4 (m, 5, CH_2Br and picolinic H), 6.7–7.1 (m, 4, pyridine β-H), 7.2–7.6 (m, 2, pyridine δ-H), 8.4–8.6 (m, 2, pyridine α-H); IR (neat) 3050–2850, 1580, 1560, 1470, 1430, 1250, 1140, 1070, 990, 780, 745 cm^{-1}; mass spectrum, m/e (relative intensity) 320 (2, $M^{+\cdot}$), 318 (2, $M^{+\cdot}$), 239 (18, M − Br), 228 (28, M − C_6H_6N), 226 (27, M − C_6H_6N), 197 (57), 184 (83), 183 (79, M − C_4H_7Br), 119 (17), 118 (31), 117 (31), 106 (75), 93 (100, $C_6H_7N^+$), 78 (39, $C_5H_4N^+$). Anal. Calcd for $C_{16}H_{19}BrN_2$: C, 60.19; H, 6.00; Br, 25.03; N, 8.77. Found: C, 59.30; H, 6.44; Br, 26.00; N, 8.20.

1,2-Bis(2-pyridyl)-5-hexene(9). This compound cannot be isolated pure. It is identified by its vinylic proton position in the NMR spectrum δ ($CDCl_3$) 4.6–5.0 (CH_2=CH), 5.4–6.0 (CH=CH_2).

Electroreduction of *N*-Benzalaniline in the Presence of 1,3-Dibromopropane (4a). Substrate (0.6 g, 3.3 mmol) is reduced in the presence of **4a** (0.8 mL, 7 mmol) at −1.8 V. The electrolysis is stopped after consumption of 3.45 F. The faradaic current drops from 80 to 20 mA; crude product 0.69 g. Its NMR spectrum shows the presence of unreduced substrate and some benzaldehyde. 1,2-Diphenylpyrrolidine [**11a**; 13%, mp 63 °C (EtOH) (lit.[26] mp 63 °C)] is purified by column chromatography with 10:90 hexane–petroleum ether eluant.

Electroreduction of *N*-(2-Pyridylmethylene)aniline in the Presence of 1,3-Dibromopropane (4a). The experimental conditions of electrolysis are described in ref 13. Substrate (2 g, 11 mmol) is reduced in the presence of **4a** (15 mL, 110 mmol). The electrolysis products are separated from the excess of **4a** by aqueous acid extraction; crude product 1.7 g; column chromatography eluant 50:50 diethyl ether–petroleum ether. The compounds are isolated in the order **12** [23%, mp 90 °C (petroleum ether) (lit.[13] mp 90 °C)], **13a** (6%).

1-Anilino-1-(2-pyridyl)-3-butene (13a): white solid, mp 65 °C (petroleum ether); NMR ($CDCl_3$) δ 2.5–2.8 (m, 2, CH_2), 4.6 (t, J = 6 Hz, 2, 1 H exchangeable by D_2O, CH and NH), 4.9–5.3 (m, 2, CH_2=CH), 5.5–6.2 (m, 1, CH=CH_2), 6.5–6.85 (m, 2, pyridine β,γ-H), 7.0–7.8 (m, 5, benzene H), 8.05–8.2 (m, 1, pyridine α-H); IR (KBr) 3210–3150 (NH), 3050, 2850, 1640, 1600 cm^{-1}; mass spectrum m/e (relative intensity) 224 (3), 184 (15), 183 (100, M − C_3H_5), 182 (13), 181 (8), 177 (7), 130 (5), 117 (5), 100 (10). Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.15; H, 7.21; N, 12.51.

Electroreduction of Benzo[*c*]cinnoline in the Presence of 1,4-Dibromobutane (4b). Substrate (0.5 g, 2.8 mmol) is reduced in the presence of **4b** (0.66 mL, 5.6 mmol) at −1.5 V, n = 2.1; crude product 1.3 g; column chromatography eluant 5:95 diethyl ether–petroleum ether.

1,2,3,4-Tetrahydro-4a,12b-diazatriphenylene (14): 78% yield; mp 62 °C (petroleum ether); NMR ($CDCl_3$) δ 1.6–1.9 (m, 4, CH_2–CH_2), 3.2–3.5 (m, 4, CH_2–N), 6.7–7.2 (m, 6, aromatic H), 7.5–7.7 (m, 2, aromatic H); IR (KBr) 2800–3050, 1600, 1500, 1480, 1440, 1250, 1200, 1100, 935, 910, 895, 780, 770, 755, 725, 722, 695 cm^{-1}; mass spectrum, m/e (relative intensity) 237 (18, M + 1), 236 (100, $M^{+\cdot}$), 207 (44), 182 (12), 181 (96), 180 (75, benzo[*c*]-cinnolinium), 152 (60, 180–N_2), 151 (20). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.83; N, 11.85. Found: C, 81.71; H, 6.73; N, 11.55.

Electroreduction of Nitrobenzene in the Presence of 1,3-Dibromopropane (4a). Substrate (0.6 g, 4.9 mmol) and **4a** (6.5 mL, 49 mmol) are reduced at −1.14 V, n = 4.1; crude product 5.1 g; column chromatography eluant 30:70 diethyl ether–petroleum ether. After elution of **4a** in excess, **16a** (48%) is isolated.

***N*-Phenylisoxazolidine (16a)**: liquid, bp 51–2 °C (3 mmHg) dec; NMR ($CDCl_3$) δ 2.02 (q, J = 7 Hz, 2, CH_2–C), 3.3 (t, J = 7 Hz, 2, CH_2–N), 3.8 (t, J = 7 Hz, 2, CH_2–O), 6.7–7.3 (m, 5, aromatic H); IR (neat) 3050–2850, 1590, 1490, 1280, 1125, 1080, 1030, 930–880, 755, 695 cm^{-1}; mass spectrum, m/e (relative intensity) 150 (10, M + 1), 149 (100, $M^{+\cdot}$), 148 (10), 132 (18), 131 (10), 130 (16), 118 (10), 106 (17), 105 (14), 104 (26), 93 (15), 92 (77), 91 (10), 90 (50), 77 (15), 76 (84). The compound is unstable even at −18 °C under argon. Within a few hours, the uncolored oil turns brown. Hence a microanalysis could not be performed.

Electroreduction of Nitrobenzene in the Presence of 1,4-Dibromobutane (4b). Substrate (0.5 g, 4.1 mmol) and **4b** (2 mL, 17 mmol) are reduced at −1.3 V, n = 4.7; crude product 2.0 g; column chromatography eluant 5:95 diethyl ether–petroleum ether. The compounds are separated in the order azobenzene (6%), **17** (28%), **16b** (42%).

***N*-Phenyltetrahydrooxazine (16b)**: liquid, synthesis previously reported in ref 23; NMR ($CDCl_3$) δ 1.4–1.9 (m, 2, CH_2–CH_2), 3.15 (t, J = 5 Hz, 2, CH_2–N), 3.93 (t, J = 5 Hz, 2, CH_2–O), 6.7–7.4 (m, 5, aromatic H); IR (neat) 3050–2850, 1590, 1490, 1250,

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1180, 1075, 1020, 755, 692 cm^{-1}; mass spectrum, *m/e* (relative intensity) 164 (12, M + 1), 163 (100, $M^{+\cdot}$), 137 (12), 135 (14), 122 (40), 118 (14), 106 (20), 105 (48), 104 (36), 94 (17), 92 (24), 78 (80).

***N*-Phenylpyrrolidine (17)**: liquid, synthesis reported in ref 33; NMR ($CDCl_3$) δ 1.75–2.05 (m, 4, CH_2–CH_2), 3.05–3.35 (m, 4, CH_2–N), 6.37–6.80 (m, 3, aromatic H-2, -4, -6), 7.00–7.43 (m, 2, aromatic H-3, -5). Anal. Calcd for $C_{10}H_{13}N$: C, 81.63; H, 8.84; N, 9.52. Found: C, 81.68; H, 9.16; N, 9.17.

Electroreduction of Fluorenone in the Presence of Succinyl Chloride (5). Substrate (0.5 g, 2.8 mmol) and **5** (0.35 mL, 3.1 mmol) are reduced at –1.2 V, n = 2; crude product 0.46 g; column chromatography eluant 35:65 acetone–petroleum ether. The compounds are isolated in the order **27** [33%, mp 190 °C (chloroform) (lit.[27] mp 190–192 °C)], **26** (22%).

Fluorene-9-spiro-5′-(γ-oxo-δ-valerolactone) (26): mp 192 °C (chloroform–petroleum ether); NMR ($CDCl_3$) δ 2.8–3.4 (m, 4, $COCH_2CH_2CO$), 7.2–7.75 (m, 8, aromatic H); IR (KBr) 3050–2850, 1730 (O—C=O), 1710 (C=O), 1590 cm^{-1}; mass spectrum, *m/e* (relative intensity) 264 (19), 236 (17, M – CO), 192 (17, 236 – CO_2), 182 (32), 181 (100, fluorenone cation), 180 (62), 164 (44), 163 (60), 153 (35), 152 (69, fluorenone – CO), 151 (22), 78 (82). Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.57; O, 18.16. Found: C, 77.26; H, 4.54; O, 18.00.

Chemical Reduction by Alkali Metals of Y=Z Compounds in the Presence of Acylating Agent. Under nitrogen, alkali metal (1 mequiv of Li, 1 to 5 mequiv of Na or K, 1 mequiv of Li with 12-crown-4) is stirred under reflux of the chosen solvent (diethyl ether, liquid ammonia, or HMPT, 30 mL mequiv), then the Y=Z compound (azobenzene or benzo[*c*]cinnoline, 1 mequiv) is added; the reflux is maintained during 1 or 3 h. To the cold solution is added the acylating agent (**5** or **6**, 1 or 2 mequiv), dissolved in the same solvent (30 mL, but Et_2O in the case of liquid NH_3). The colored mixture is stirred during an additional hour and then hydrolyzed with a large excess of water, neutralized, and extracted with diethyl ether. The composition of the extract is determined by NMR and TLC; substrates and products obtained by electrosynthesis are used as references. With the molar ratio 2:1:2 potassium–azobenzene–4-bromobutyryl chloride in HMPT, azo- and hydrazobenzenes are isolated in addition to **35**.

***N*,*N*,*N*′*N*′-Tetramethyl-*N*″-phenyl-*N*″-anilinophosphorus Triamide (35)**: white crystals, mp 230 °C (ethyl acetate–acetone); IR (KBr) 3235 (N-H), 3105, 3030, 2935, 1600, 1490, 1305 (P=O), 1275, 1237, 1195–1180 (P=O··H), 995 (P-N), 945, 770, 753–745 (P-N), 692, 667; NMR ($CDCl_3$) δ 2.50 (s, 6, NMe_2), 2.67 (s, 6, NMe_2), 5.90 (br s, 1, NH), 6.6–7.6 (m, 10, aromatic H). Anal. Calcd for $C_{16}H_{23}N_4OP$: C, 60.36; H, 7.22; N, 17.60; O, 5.02; P, 9.72. Found: C, 60.52; H, 7.00; N, 17.42; P, 9.50.

Electroreduction of *N*-Benzalaniline in the Presence of 4-Bromobutyryl Chloride (6). Substrate (2.4 g, 13 mmol) and **6** (1.8 mL, 14 mmol) are reduced at –1.0 V, n = 1.3; crude product 4.1 g; column chromatography eluant 50:50 diethyl ether–petroleum ether. Crude product (0.45 g) is insoluble in the eluant; this corresponds to **37a** (12%). The compounds are separated in the order benzaldehyde (12%), **37b** (12%), **38** (19%), and **36** (14%).

4-Chlorobutananilide (36): mp 70 °C (diethyl ether) (lit.[28] mp 69–70 °C); NMR ($CDCl_3$) δ 1.95–2.6 (m, 4, CH_2CH_2CO), 3.6 (t, J = 6 Hz, 2, CH_2Cl), 7.0–7.6 (m, 5, aromatic H), 7.8–8.1 (br s, 1, N-H, exchangeable by D_2O); IR (KBr) 3310 (N-H), 1650 (N—C=O), 1590, 1530 cm^{-1}.

1,12-Dichloro-5,6,7,8-tetraphenyl-5,8-diazadodecane-4,9-dione (37a): mp 195 °C (diethyl ether–chloroform); NMR ($CDCl_3$) δ 1.6–2.1 (m, 8, CH_2CH_2CO), 3.1–3.4 (t, J = 6 Hz, 4, CH_2Cl), 5.7–6.1 (m, 2), 6.2–6.5 (m, 2), 6.70 (s, 2, *CH–*CH), 6.8–7.6 (m, 6), 7.36 (s, 10, aromatic H), no exchange with D_2O; IR (KBr) 3060, 2960, 1640 (N—C=O), 1590, 1490, 1388, 1302, 1262, 1248, 785, 715, and 700 (C-Cl) cm^{-1}; mass spectrum, *m/e* (relative intensity) 378 (<1), 377 (1), 376 (1.4), 375 (3, M – $PhNCOC_3H_6Cl$), 288 (15), 286 (40, M/2:$PhN(CHPh^+)COC_3H_6Cl$), 250 (1, 286 – HCl), 183 (20), 182 (100, $PhNHCHPh^+$), 181 (10), 180 (15), 119 (6, $PhNCO^+$), 105 (8), 104 (10), 91 (8, tropylium), 77 (26, Ph^+). Anal. Calcd for $C_{34}H_{34}Cl_2N_2O_2$: C, 71.19; H, 5.97; Cl, 12.36; N, 4.88; O, 5.58. Found: C, 70.41; H, 5.89; Cl, 12.58; N, 4.85; O, 5.49.

1,12-Dichloro-5,6,7,8-tetraphenyl-5,8-diazadodecane-4,9-dione (37b), diastereoisomer from **37a**: mp 149 °C (diethyl ether–petroleum ether); NMR ($CDCl_3$) δ 1.8–2.4 (m, 8, CH_2CH_2CO), 3.3–3.8 (t, J = 5 Hz, 4, CH_2Cl), 5.7–6.3 (m, 2), 6.62 (s, 2, *CH*CH), 6.75–8.2 (m, 8), 6.90 (s, 10, aromatic H), no exchange with D_2O; IR (KBr) 3060, 2920, 1640 (N—C=O), 1590, 1490, 1390, 1300, 1262, 1268, 785, 713, 709, and 700 (C-Cl) cm^{-1}; mass spectrum, *m/e* (relative intensity) 378 (<1), 377 (<1), 376 (<1), 375 (2, M – $PhNCOC_3H_6Cl$), 288 (15), 286 (42, M/2), 250 (1, 286–HCl), 183 (19), 182 (100, $PhNHCHPh^+$), 181 (10), 180 (12), 119 (3, $PhNCO^+$), 105 (10), 104 (10), 91 (3, tropylium), 77 (21, Ph^+). Anal. Calcd for $C_{34}H_{34}Cl_2N_2O_2$: Cl, 12.36; N, 4.88. Found: Cl, 12.30; N, 4.80.

***N*-Benzyl-4-chlorobutananilide (38)**: liquid; NMR ($CDCl_3$) δ 1.9–2.3 (m, 4, CH_2CH_2CO), 3.45–3.6 (t, J = 6 Hz, 2, CH_2Cl), 4.83 (s, 2, $PhCH_2N$), 6.85–7.35 (m, 10, aromatic H); IR (neat) 3100–2900, 1645 (N—C=O), 1590, 1480, 1390, 1250, 1210, 1070, 1030, 775, 725, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{18}ClNO$: C, 70.94; H, 6.30; Cl, 12.32; N, 4.87; O, 5.56. Found: C, 70.75; H, 6.54; Cl, 12.26; N, 4.73; O, 5.74.

Electroreduction of Nitrobenzene in the Presence of 4-Bromobutyryl Chloride (6). Substrate (0.6 g, 4.9 mmol) and **6** (2 mL, 14.5 mmol) are reduced at –0.80 V, n = 4.5; crude product 1.5 g; column chromatography eluant 30:70 acetone–petroleum ether. Azoxybenzene (traces) and **39** (72%) are isolated.

***N*,*O*-Bis(4-chlorobutyroyl)phenylhydroxylamine (39)**: liquid; NMR ($CDCl_3$) δ 1.95–2.8 (m, 8, CH_2CH_2CO), 3.45–3.75 (m, 4, CH_2Cl), 7.45 (s, 5, aromatic H); IR (neat) 3060, 2980–2900, 1785 (N—O—C=O), 1685 (N—C=O), 1590, 1490, 1380, 1100, 695 cm^{-1}; mass spectrum, *m/e* (relative intensity) 321 (M + 4), 319 (M + 2), 317 (<1, M), 215, 213 (37, M – C_4H_5OCl), 199, 197 (213 – oxygen), 161 (197 – HCl), 133, 129, 119 (10, $PhNCO^+$), 109 (65), 107 (31, $ClC_3H_6CO^+$), 105 (100, $ClC_3H_6CO^+$), 93 (84), 91 (47, 119 – CO:$C_6H_5N^+$), 77 (60, $C_6H_5^+$), 65 (19), 64 (10, 119 – [HCN + CO]). Anal. Calcd for $C_{14}H_{17}Cl_2NO_3$: C, 52.84; H, 5.38; Cl, 22.28; N, 4.40; O, 15.08. Found: C, 52.91; H, 5.52; Cl, 21.81; N, 4.38; O, 15.26.

Acknowledgment. We thank M. Rigaud, Engineer, Station de Technologie des Produits Végétaux, INRA, Dijon, for recording the mass spectra.

Registry No. 4a, 109-64-8; **4b**, 110-52-1; **5**, 543-20-4; **6**, 927-58-2; **7a**, 72709-25-2; **7b**, 72709-26-3; **8**, 72709-27-4; **9**, 72709-28-5; **11a**, 72709-29-6; **11b**, 72709-30-9; **12**, 72709-31-0; **13a**, 72709-32-1; **14**, 66489-79-0; **15**, 63378-87-0; **16a**, 72709-33-2; **16b**, 53780-77-1; **17**, 4096-21-3; **26**, 72709-34-3; **27**, 3073-51-6; **28**, 22264-17-1; **29**, 70526-00-0; **30**, 70526-01-1; **31**, 70525-98-3; **31b**, 72709-35-4; **32a**, 70526-02-2; **32b**, 72709-36-5; **33**, 70525-99-4; **34**, 70573-12-5; **35**, 20805-85-0; **36**, 7578-45-2; **37a**, 72709-37-6; **37b**, 72709-38-7; **38**, 72709-39-8; **39**, 72709-40-1; quinoline, 91-22-5; hydrazobenzene, 122-66-7; nitrosobenzene, 586-96-9; 1,2-bis(2-pyridyl)ethylene, 1437-15-6; *N*-benzalaniline, 538-51-2; *N*-(2-pyridylmethylene)aniline, 7032-25-9; benzo[*c*]quinoline, 260-94-6; nitrobenzene, 98-95-3; azobenzene, 103-33-3; fluorenone, 486-25-9.

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