layer was dried ($MgSO_4$), filtered, and concentrated to yield an oil. The oil was purified by silica gel chromatography (40% EtOAc/hexanes), concentrated to an oil, and triturated with Et_2O to give 2.42 g (63%) of **9** as a white solid: mp 118–119 °C; ^{1}H NMR ($CDCl_3$) 2.22 (d, *J* = 4 Hz, 1 H), 2.44 (s, 3 H), 2.49 (s, 3 H), 2.55 (d, *J* = 7 Hz, 1 H), 2.91 (m, 1 H), 3.06 (m, 1 H), 3.18 (m, 1 H), 4.98 (t, 1 H), 7.31 (d, *J* = 8 Hz, 2 H), 7.36 (m, *J* = 8 Hz, 2 H), 7.71 (d, *J* = 8 Hz, 2 H), 7.79 (d, *J* = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 22.3 (q), 32.5 (t), 38.6 (d), 43.8 (t), 127.5 (d), 128.5 (d), 130.3 (d), 134.5 (s), 137.1 (s), 144.1 (s), 145.5 (s); mass spectrum (CI), *m/z* (intensity) 381 (100), 155 (95). Anal. Calcd for $C_{17}H_{20}N_2O_4S_2$: C, 53.66; H, 5.30; N, 7.36; S, 16.85. Found: C, 53.78; H, 5.39; N, 7.41, S, 16.73.

***N*,*N*′-Bis(*p*-tolylsulfonyl)-1,2-diaminobutane (10). Addition of Methylmagnesium Bromide to 9.** To a solution of 380 mg (1 mmol) of **9** in 5 mL of anhydrous THF under an N_2 atmosphere was added 1 mL (3 mmol) of 3 M MeMgBr solution in diethyl ether, and the mixture was refluxed for 15 h. When cool, the mixture was partitioned between 20 mL of pH 7 buffer and 2 × 20 mL of EtOAc. The combined EtOAc layers were dried ($MgSO_4$), filtered, and concentrated to give 399 mg of an oil, which was purified by chromatography on silica gel (30% EtOAc/hexanes) to give an oil, which solidified on trituration with Et_2O/hexanes. The solid was collected by vacuum filtration to give 116 mg (29%) of **10**: ^{1}H NMR ($CDCl_3$) 0.68 (t, 3 H), 1.30 (m, 2 H), 2.35 (s, 6 H), 2.96 (m, 2 H), 3.44 (m, 1 H), 5.10 (m, 2 H), 7.09–7.45 (m, 4 H), 7.49–7.96 (m, 4 H); mass spectrum (CI), *m/z* (intensity) 397 (100); HRMS (CI), calcd for $C_{18}H_{24}N_2O_4S_2$ 397.1268, found 397.1239.

***N*,*N*′-Bis(*p*-tolylsulfonyl)-4,5-diaminopentanoic Acid (12).** To 380 mg (1 mmol) of **9** and 454 μL of diethyl malonate was added 10 mL of 0.3 M NaOEt made by treating 100 mL of EtOH with 690 mg (30 mmol) of Na. The resulting solution was refluxed for 1.25 h and partitioned between 50 mL of H_2O and 50 mL of EtOAc. The EtOAc layer was washed with saturated NaCl, dried ($MgSO_4$), filtered, and concentrated to give 450 mg of viscous oil. To the oil was added 50 mL of 6 N HCl, and the mixture was refluxed for 1.5 h. When cool, the mixture was extracted with 50 mL of EtOAc. The EtOAc layer was washed with saturated NaCl, dried ($MgSO_4$), filtered, and concentrated to give an oil, which was crystallized from EtOAc/hexanes to give 208 mg (73%) of a white solid: mp 165–166 °C; ^{1}H NMR (CD_3OD) 2.08 (m, 2 H), 2.70 (m, 2 H), 3.26 (m, 2 H) 3.65–4.25 (br m, 1 H), 7.34 (d, *J* = 8 Hz, 4 H), 7.60 (d, *J* = 8 Hz, 2 H), 7.70 (d, *J* = 8 Hz, 2 H); IR (KBr) 3660–2770, 1710, 1320, 1160, cm^{-1}; mass spectrum (CI), *m/z* (intensity) 423 (72), 269 (100). Anal. Calcd for $C_{19}H_{24}N_2O_6S_2$: C, 51.70; H, 5.49; N, 6.36; S, 14.56. Found: C, 52.10; H, 5.62; N, 6.30; S, 14.33.

Registry No. 1, 119244-91-6; **2**, 119244-92-7; **3**, 119244-93-8; **4**, 105655-80-9; **5**, 119244-94-9; **6**, 54798-70-8; **7**, 119244-95-0; **8**, 119244-96-1; **9**, 119244-97-2; **10**, 119244-99-4; *trans*-**11**, 119244-99-4; *cis*-**11**, 119245-01-1; **12**, 119245-00-0; 1,3-diamino-2-hydroxypropane, 616-29-5; benzyl chloroformate, 501-53-1.

Electrochemical Study of the Nonaqueous Oxidation of Dipyrrolic Compounds

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With use of cyclic voltammetry, electrochemical oxidation potentials vs Ag/AgCl in acetonitrile of 26 pyrromethanes, 10 pyrromethenes, and 2 pyrroketones are measured. Compounds of these types are valuable intermediates in the organic synthesis of porphyrins. Analysis of the measured potentials shows that substituent partial potentials previously established for monopyrroles (Tabba and Smith, *J. Org. Chem.* 1984, *49*, 1870) can usually be used to accurately predict the experimental data, except under circumstances where pyrromethanes possess a terminal α-methyl group. An ECE mechanism is proposed for the electrochemical oxidation of pyrromethanes **1**, which are shown to afford pyrromethene salts **2** by way of a two-electron oxidation at a potential approximating the corresponding monopyrrole calculated value. An additional wave at higher potential probably corresponds to oxidation of the pyrromethene **2**, and this potential is pH sensitive. A pyrromethane (**42**) bearing a *gem*-dimethyl function at the interpyrrole carbon and acetonepyrrole (**43**) fail to afford pyrromethene upon oxidation, and their insulated dipyrrole or polypyrrole systems behave as simple monopyrroles.

Introduction

In a recent paper[4] we reported the anodic oxidation potentials of 117 pyrroles comprising a diverse variety of substitution patterns and derived substituent partial potentials for most pyrrolic substituents found in intermediates for porphyrin synthesis. Other authors have shown that oxidation of pyrroles in the presence of various nucleophiles affords regioselectively substituted products.[5] Electrochemical oxidations of open-chain tetrapyrroles[6] and porphyrins[7] have also been reported. More recently, Falk[8] reported electrochemical oxidations of a pyrromethene and several pyrromethenones. So far as we are aware, no in depth study of the anodic oxidation, or cyclic voltammetry, of the common dipyrroles, pyrromethanes **1**, pyrromethenes **2**, or pyrroketones **3**, has been reported. In this paper we describe a detailed investigation of the cyclic voltammetry of a large variety of dipyrroles that are in-

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(1) Yarmouk University.

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(3) University of California.

(4) Tabba, H. D.; Smith, K. M. *J. Org. Chem.* 1984, *49*, 1870–1875.

(5) For a review, see: Bobbitt, J. M.; Kulkarna, C. L.; Willis, J. P. *Heterocycles* 1981, *15*, 495–513.

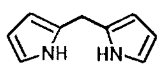
(6) Eivazi, F.; Lewis, W. M.; Smith, K. M. *Tetrahedron Lett.* 1977, 3083–3086.

(7) Fuhrhop, J.-H. in *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam; 1975; pp 593–623.

(8) Falk, H.; Leodolter, A. *Monatsh. Chem.* 1978, *109*, 183–192.

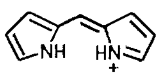
0022-3263/89/1954-1943$01.50/0

termediates in porphyrin syntheses.



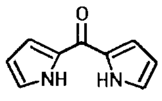
Pyrromethane

1



Pyrromethene Salt

2



Pyrroketone

3

Results and Discussion

Pyrromethanes, pyrromethenes, and pyrroketones are key intermediates in the total syntheses of porphyrins.[9] It is therefore of paramount importance, as was the case with simple monopyrroles[4] from which they were derived, to be able to evaluate electron availability and chemical reactivity in a comparative sense. Thus, in the case of the monopyrroles, we were able to measure oxidation potentials of 117 pyrroles bearing various combinations of common substituents and thereby to derive a series of substituent partial potentials from which the potential of virtually any pyrrole could be subsequently calculated. For completeness, Table I displays these pyrrole partial potentials.[10] It was one of our aims to determine whether or not these data could be applied to the more complex dipyrrolic systems and, if not, to attempt to evaluate any anomalies from a mechanistic standpoint. Thus, we wished to determine whether cyclic voltammograms would show oxidation potentials that could be correlated with the calculated potentials for each of the individual rings or whether some interaction between the rings would introduce unexpected effects.

The measured oxidation potentials of 26 pyrromethanes (**4–29**), 10 pyrromethenes (**30–39**), and 2 pyrroketones (**40**, **41**) are presented in Tables II, III, and IV, respectively. Conditions for their measurement are given in the Experimental Section.

Pyrromethanes. In most pyrromethane cases two oxidation potentials were clearly observed and, as with monopyrroles, both of these waves are irreversible.[11] A representative cyclic voltammogram is presented in Figure 1, and the shape of the curve indicates two irreversible electron transfers, except in the case of pyrromethanes **21–24**, where only one wave was apparent and this occurred at a potential approximating the average of the two calculated potentials.

In Table II the first two columns of potentials represent calculated values based on substituent partial potentials of the composite pyrroles (Table I) derived earlier; in all cases the dipyrrole ring with the highest calculated potential is given first (column A). In these calculations, a pyrrolylmethylene substituent is considered empirically to contribute a partial potential of −70 mV. This action obviously oversimplifies the situation (owing to the variable potential of the pyrrole connected to the methylene in question) but this is clearly not a major problem. With the exceptions of pyrroles **21–24** (all of which bear an R^6-methyl substituent), the agreement between the lowest calculated potential (column B) and the first observed oxidation potential (obsd E^1) is usually strikingly close; the deviation column indicates the difference between these two data. For example, the oxidation potentials of pyrromethanes **8** and **9** differ by 70 mV, which is approximately the increment expected (Table I) for transformation of two β-methyls into ethyls.

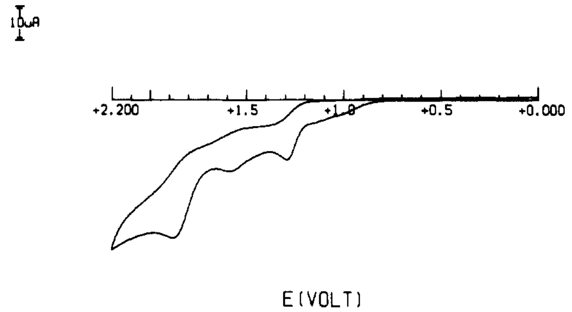


Figure 1. Cyclic voltammogram (BAS 100A electrochemical workstation) of pyrromethane **9** in acetonitrile. Conditions are as outlined in the Experimental Section.

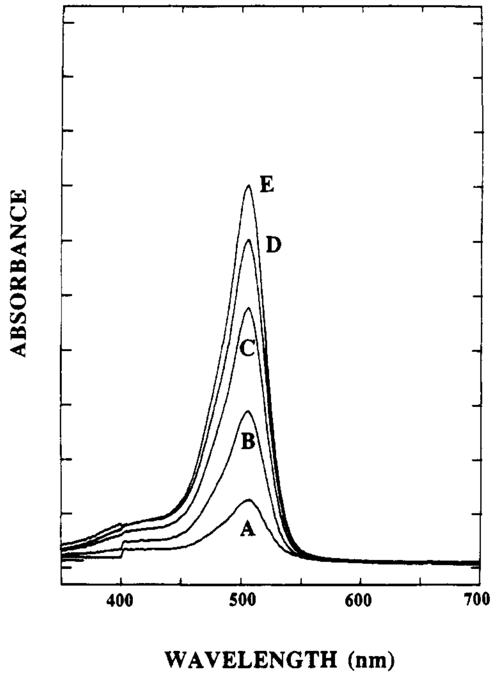
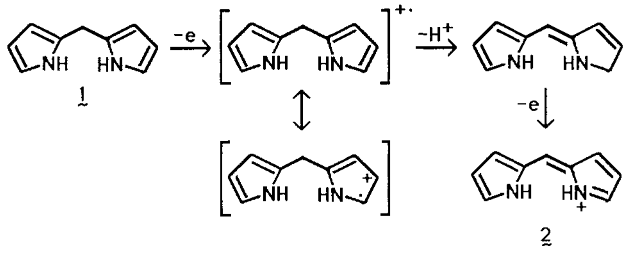


Figure 2. Spectroelectrochemical study of pyrromethane **9** in acetonitrile, showing formation of the corresponding pyrromethene at different applied potentials. A, 1.00 V; B, 1.10 V; C, 1.20 V; D, 1.25 V; E, 1.35 V. Conditions are as outlined in the Experimental Section.

Scheme I. Electrochemical ECE Oxidation of Pyrromethane 1 to Pyrromethene Salt 2



It was assumed initially that both observed waves (Figure 1) corresponded to two consecutive one-electron oxidations, and thus the difference between the calculated second potentials (column A) and the observed potential (obsd E^2) was a source of confusion. However, the number of electrons involved in the first anodic oxidation was determined (specifically for compound **9**) to be approximately *two* by use of thin-layer spectroelectrochemistry.[12]

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(9) Smith, K. M. in *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam; 1975; Chapter 2.

(10) The pyrrole potential (1060 mV) in Table I is referenced to Ag/AgCl, whereas that in the original paper[4] (900 mV) was referenced to Ag/AgNO$_3$.

(11) Cauquis, G.; Parker, V. D. in *Organic Electrochemistry*; Baizer, M. M., Ed.; Marcel Dekker Inc.; New York; 1973; p 118.

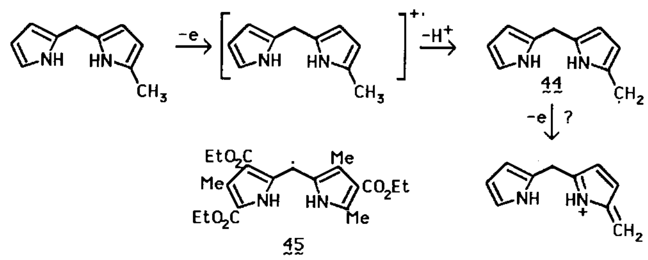
Table I. Substituent Contributions to Observed Oxidation Potentials of Substituted Pyrroles[a,b]

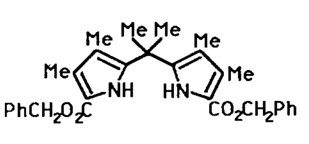
substit	contribtn at $R^{2,5}$	contribtn at $R^{3,4}$
Me	−398	−125
Et		−95
Pr		−89
i-Bu		−95
CH_2OAc	−169	
CH_2Cl	−163	
CH_2Br	−204	
EtCl		−54
EtOAc		−84
i-Bue		−195
Pente		−255
CO_2Bz	569	257
CO_2Et	549	240
CO_2Bu^t	533	252
CO_2Me	560	273
CO_2H	581	265
A^{Et}		−11
A^{Me}		−12
P^{Et}		−72
P^{Me}		−63
B^{Me}		−75
Acr^{Et}		63
Acr^{H}		70
$CONMe_2$	341	
COMe	531	241
CHO	651	348
Br		68
Cl		124
I	−257	135

[a] Contribution from the unsubstituted pyrrole ring is 1060 mV. [b] Abbreviations are A^{Et} = CH_2CO_2Et; A^{Me} = CH_2CO_2Me; Acr^{Et} = $CH{=}CHCO_2Et$; Acr^{H} = $CH{=}CHCO_2H$; Bz = CH_2Ph; B^{Me} = $CH_2CH_2CH_2CO_2Me$; i-Bu = $CH_2CH(Me)_2$; i-Bue = $CH{=}C(Me)_2$; Bu^t = $C(Me)_3$; EtCl = CH_2CH_2Cl; EtOAc = CH_2CH_2OAc; P^{Et} = $CH_2CH_2CO_2Et$; P^{Me} = $CH_2CH_2CO_2Me$; Pente = $CH{=}CHCH_2CH_3$; Pr = $CH_2CH_2CH_3$.

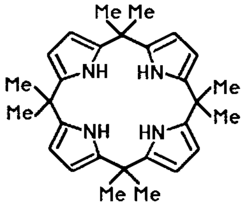
Indeed, observation of the electrode surface during cyclic voltammetry revealed the production of a red product at potentials associated with the first oxidation wave, which could be monitored spectroelectrochemically (Figure 2). Chemical synthesis of an authentic sample of the pyrromethene **30** derived from **9** showed that the product from the electrochemical oxidation at the lower potential was indeed the pyrromethene salt **30**, probably obtained through a typical ECE process (Scheme I). The pyrromethene salt **30** then suffers further anodic oxidation at a higher potential (obsd E^2), which is not a property of the original pyrromethane but rather of the resulting pyrromethene. This observation, implicating the involvement of pyrromethenes, was the reason for extension of our studies to consider anodic oxidation of pyrromethenes (vide infra). In one case it is possible to directly compare oxidation potentials of a pyrromethane (**9**) and the corresponding pyrromethene hydrobromide **30** and pyrromethene free base **38**; for the pyrromethane, the second oxidation wave (obsd E^2) peaks at 1510 mV, whereas the first oxidation wave of the pyrromethene free base (**38**) occurs at 1380 mV (Table III). This pyrromethene potential was pH dependent; in presence of added trifluoroacetic acid (0.25 mL added to a total cell volume of 10.0 mL) it occurred at 1470 mV, with added 70% perchloric acid (0.25 mL) at 1870 mV, and with 33% hydrobromic acid (0.25 mL) the peak was moved to 1900 mV (cf. Table II, compound **30**). We therefore suggest that the second wave in the pyrromethane oxidations (Table II, obsd E^2) correlates with oxidation of pyrromethene salts obtained from the corresponding pyrromethane as indicated in Scheme I. After a single one-electron abstraction, the two pyrrole rings interact to facilitate a spontaneous second-electron abstration and pyrromethene salt formation (Scheme I). In order to confirm this hypothesis, the hexamethylpyrromethane **42** was synthesized (from acetone and benzyl 3,4-dimethylpyrrole-2-carboxylate).[13] Anodic oxidation of this compound failed, as expected, to yield a pyrromethene, and cyclic voltammetry revealed a single anodic wave at 1300 mV, a potential very close to that calculated (1310 mV;[14] Table I) for a monopyrrole without any interaction between the two pyrromethane rings. Similarly, acetonepyrrole (**43**)[15] afforded two potentials, at 920 and 1180 mV; the first of these can be accounted for by the base-line pyrrole oxidation value (1060 mV; Table I) plus two α-pyrrolylalkylated substituents (contributing −70 mV each) to yield a calculated value of 920 mV.

Scheme II. Electrochemical ECE Oxidation of R^6-Methylpyrromethanes (e.g., 21–24) To Give Unconjugated Oxidation Product 44





42



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Pyrromethanes **21–24** are the only ones in Table II with significant deviations between the calculated and observed potentials. In all cases, these pyrromethanes possess R^6 = methyl substituents and are always >400 mV more difficult to oxidize than is calculated on the basis of the Table I values. Here we suggest that an ECE process causes formation (Scheme II) of the primary benzylic radical, **44**. Stabilization of the intermediate radical on the terminal benzylic methylene rather than on the usual interpyrrolic methine (e.g. structure **45**) is presumably a consequence of the electron deficiency of the A ring with its conjugated electron-withdrawing substituents (R^1 or $R^{1,3}$; Table I, calcd A) compared with the relative electron richness of the B ring (calc B). In confirmation of this

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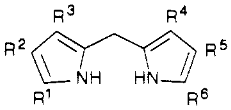
[12] Rohrback, D. F.; Heineman, W. R.; Deutsh, E. *Inorg. Chem.* **1979**, *18*, 2536–2542.

[13] J. A. S. Cavaleiro, H. Xie, K. M. Smith, unpublished results.

[14] Here we again use a partial potential of −70 mV for the pyrrolylisopropyl moiety.

[15] Fischer, H.; Orth, H. *Die Chemie des Pyrrols*; Akademische Verlag: Leipzig; 1934; Vol. I, p 393.

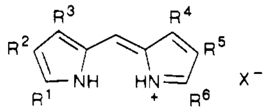
Table II. Oxidation Potentials (E_p) of Substituted Pyrromethanes (vs Ag/AgCl) in Acetonitrile, Measured by Cyclic Voltammetry[a]



							E_p, mV				
compd	R^1	R^2	R^3	R^4	R^5	R^6	calcd, A[b]	calcd B[b]	obsd E^1	obsd E^2	devn
4	CO_2Bz	Me	Et	Et	Me	CO_2Bz	1340	1340	1350	1690	10
5	CO_2Bz	Me	P^{Me}	P^{Me}	Me	CO_2Bz	1370	1370	1400	1550	30
6	CO_2Et	Me	Et	Et	Me	CO_2Et	1320	1320	1300	1650	−20
7	CHO	Me	Et	Et	Me	CHO	1420	1420	1420	1650	0
8	CO_2Bz	Et	Et	Et	Et	CO_2Bz	1370	1370	1370	1690	0
9	CO_2Bz	Me	Me	Me	Me	CO_2Bz	1310	1310	1300	1610	−10
10	CO_2Bz	Me	Et	Et	Me	CO_2Et	1340	1320	1300	1650	−20
11	CO_2Bz	Me	Et	Me	Et	$CONMe_2$	1340	1110	1150	1650	40
12	CO_2Bz	Me	P^{Me}	Et	Me	CO_2Bz	1370	1340	1380	1690	40
13	CO_2Bz	Me	EtCl	Me	Me	CO_2Bz	1380	1310	1350	1730	40
14	CO_2Bz	Me	EtCl	Me	Me	CO_2Bu^t	1380	1270	1310	1730	40
15	CO_2Bz	Me	EtCl	Me	Me	CO_2Et	1380	1290	1340	1730	50
16	CHO	Me	A^{Me}	Me	Me	CO_2Bu^t	1500	1270	1400	1750	130
17	CO_2Bz	Me	A^{Me}	Me	Me	CO_2Bz	1420	1310	1340	1750	30
18	CO_2Bz	Me	A^{Me}	Me	Me	CO_2Bu^t	1420	1270	1310	1750	40
19	CO_2Bz	Me	A^{Et}	Me	A^{Et}	CO_2Bu^t	1420	1380	1390	1640	10
20	CO_2Bz	Me	A^{Et}	Me	A^{Et}	H	1420	855	880	1500	25
21	CO_2Et	Me	CO_2Et	Me	CO_2Et	Me	1555	705	1120		415
22	CO_2Et	Me	Et	Me	CO_2Et	Me	1320	705	1140		435
23	CO_2Bz	Me	Et	Me	CO_2Et	Me	1340	705	1120		415
24	CO_2Bz	Me	CO_2Et	Me	CO_2Et	Me	1680	705	1160		455
25	CO_2Bu^t	Me	CO_2Bz	Me	Et	CO_2Bz	1660	1340	1400	1840	60
26	$CONMe_2$	Me	CO_2Me	P^{Me}	Me	CO_2Bz	1475	1370	1410	1500	40
27	CO_2Bz	Me	CO_2Me	Me	Et	$CONMe_2$	1710	1110	1160	1530	50
28	CO_2Bu^t	H	Et	P^{Me}	Me	CO_2Bz	1420	1345	1340	1540	−5
29	CO_2Bu^t	Me	Me	A^{Me}	Me	Acr^{Me}	1275	1075	1080	1600	5

[a] Conditions as in Experimental Section; abbreviations as in Table I. [b] A and B refer to individual pyrrole rings in the dipyrrole.

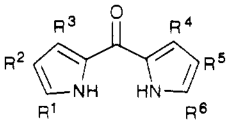
Table III. Oxidation Potentials (E_p) of Substituted Pyrromethenes (vs Ag/AgCl) in Acetonitrile, Measured by Cyclic Voltammetry[a]



								E_p, mV		
compd	X	R^1	R^2	R^3	R^4	R^5	R^6	obsd 1	obsd 2	obsd 3
30	Br	CO_2Bz	Me	Me	Me	Me	CO_2Bz	800	1100	1900
31	Br	CO_2Bz	Me	Et	Me	Et	Me	800	1100	1650
32	Br	CO_2Bz	Me	Et	Me	P^{Me}	Me	830	1130	1750
33	Br	Br	Me	Et	Et	Me	Br	800	1100	1700
34	Br	Br	Me	Br	Me	Br	Me	850	1100	1630
35	Cl	Me	Me	H	Me	H	Me	1230	1400	1610
36	Cl	Me	Et	Me	Me	H	Me	1200	1420	1700
37	FB	Me	Et	Me	Me	Et	Me	720	1340	1550
38[b]	FB	CO_2Bz	Me	Me	Me	Me	CO_2Bz	1380	1900	
39	FB	Br	Me	Br	Me	Br	Me	1200	1630	1780

[a] Conditions as in Experimental Section; FB = free base; other abbreviations as in Table I. [b] Potential dependent upon pH, see text.

Table IV. Oxidation Potentials (E_p) of Substituted Pyrroketones (vs Ag/AgCl) in Acetonitrile, Measured by Cyclic Voltammetry[a]



							E_p, mV			
compd	R^1	R^2	R^3	R^4	R^5	R^6	obsd	calcd A[b]	calcd B[b]	devn
40	CO_2Bz	Me	Et	Me	P^{Me}	Me	1400	1940	1000	400
41	CO_2Bz	Me	P^{Me}	Me	P^{Me}	Me	1390	1970	1000	390

[a] Conditions as in Experimental Section; abbreviations as in Table I. [b] A and B refer to individual pyrrole rings in the dipyrrole.

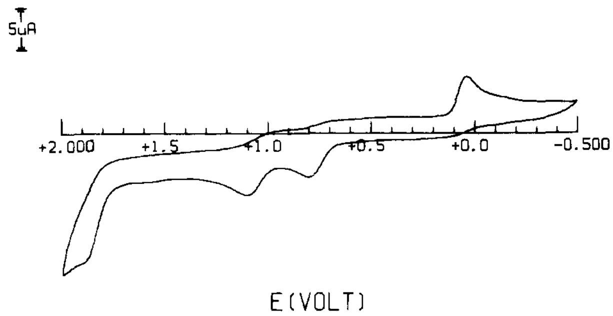
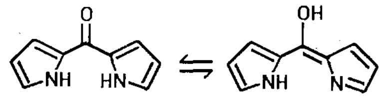


Figure 3. Cyclic voltammogram (BAS 100A electrochemical workstation) of pyrromethene **30** in acetonitrile. Conditions are as outlined in the Experimental Section.

hypothesis, no red pyrromethene color was observed at the anode during voltammetry, and spectroelectrochemistry failed to reveal formation of pyrromethene over extended periods of time (cf. Figure 2).

Pyrromethenes. Anodic oxidation potentials derived from cyclic voltammetry of the series of pyrromethenes **30**–**39** are presented in Table III. In almost every case three separate waves were observed (see typical cyclic voltammogram in Figure 3). For the hydrobromide salts **30**–**34**, the first two of these were shown to correlate with the oxidation of bromide to bromine (ca. 800, 1100 mV), while for the hydrochlorides **35** and **36** the first wave could be ascribed to oxidation of chloride (ca. 1200 mV).[16] Thus, for the pyrromethene hydrobromides (Table III) we assign the first two peaks (ca. 800 and 1100 mV) to interfering bromide and the pyrromethene hydrochlorides likewise show chloride interference in the peak around 1200 mV. In general, throughout the pyrromethene series, oxidations were accomplished at potentials that were significantly higher than those of the corresponding pyrromethane species. The pyrromethene free bases **38** and **39** show oxidation peaks at potentials somewhat lower than the corresponding hydrobromides or hydrochlorides (ignoring the halogen waves), and this observation is in line with expectation when one considers the reduced electron availability introduced by protonation of the pyrromethene system and the observed pH dependence (vide supra) of the potentials.

Pyrroketones. Cyclic voltammograms of the two pyrroketones (**40**, **41**) studied (Table IV) showed only one oxidation wave. These potentials are somewhat higher than those observed for pyrromethenes, even though a tautomeric form (**46**) can be written for pyrroketones that involves a pyrromethene. Clearly, the higher oxidation potentials are related to the electron-withdrawing nature of the (amide-like) central carbonyl function. Our previous work[4] characterized the partial potential (530 mV) for an α-acetyl function, and it is possible to calculate potentials for the two halves of the pyrroketones assuming the existence of the corresponding α-acetylpyrroles. Table IV shows the calculated potentials for each of the two halves of the pyrroketones on this basis, and our results indicate a 400-mV difference between calculated and observed first potentials. This difference is close to what would have been expected from our earlier work[4] where we noted that the presence of two strongly electron withdrawing groups on a monopyrrole results in less than twice the expected partial potential increment in the calculation.



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Experimental Section

Cyclic voltammetric measurements were carried out with a BAS 100A electrochemical workstation. A three-compartment cell with platinum wire working and counter electrodes, and an Ag/AgCl reference electrode, was employed. A sweep rate of 0.1 $V \cdot s^{-1}$ was used and pure argon was bubbled through solutions for 10 min before each run. Approximately 2 mM solutions of the dipyrroles were prepared in chromatography grade acetonitrile containing 0.2 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The peak potential for oxidation of internal ferrocene using these conditions was 445 mV (vs Ag/AgCl) or 495 mV (vs aqueous SCE). Preparative electrochemical oxidations were carried out on a BAS synthetic potentiostat (Model SP2) in an H-type cell separated by a Celanese potential membrane, platinum gauze working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode.

Typically, the pyrromethane (e.g., **9**) (100 mg) in acetonitrile (20 mL) and 0.2 M tetraethylammonium perchlorate were oxidized at a potential of 1.5 V for 6 h, during which time a red color developed. The solvent was removed by evaporation in vacuo and the residue was taken up in chloroform, washed with water, dried (anhydrous Na_2SO_4), and evaporated under vacuum to give the pyrromethene salt. Addition of HBr in acetic acid, followed by addition of ether, caused precipitation of the required pyrromethene hydrobromide **30**. This material was identical with an authentic sample prepared as follows: The pyrromethane **9** (220 mg) in glacial acetic acid (0.5 mL) was treated with bromine (90 μL) in acetic acid (1 mL). The mixture was stirred for 15 min after which time the pyrromethene hydrobromide salt **30** crystallized. It was collected and recrystallized from chloroform/hexane to give 230 mg (90%). [Proton NMR GE QE300, in $CDCl_3$, 13.34 (br, 2 H, NH), 7.72 (s, 1 H, —CH═), 7.3–7.6 (m, 10 H, Ph), 5.50 (s, 4 H, CH_2Ph), 2.32, 2.20 (each s, 6 H, Me); UV/vis λ_{max} 508 nm (ϵ 60 500); MS, EI mode, *m/e* (rel intensity) 468 (45), 91 (100). Anal. Calcd for $C_{29}H_{29}BrN_2O_4$: C, 63.39; H, 5.32; N, 5.10. Found: C, 62.99; H, 5.37; N, 5.12.] The corresponding pyrromethene free base **38** was prepared by washing a chloroform solution of the hydrobromide salt **30** with dilute aqueous ammonium hydroxide and then with water. After drying over anhydrous sodium sulfate and evaporation to dryness, the free base **38** was obtained in quantitative yield. [UV/vis λ_{max} 458 nm (ϵ 19 800).]

Thin layer spectroelectrochemistry was performed by using a gold minigrid (100 lines/cm^2 80% transmission; obtained from Buckbee-Mears Co.) working electrode sandwiched between quartz plates. Potentials in the order of 1.0–1.5 V (vs Ag/AgCl) were applied. Electrolysis at any given potential was continued until a steady state was achieved (15 min), at which time the optical spectrum was recorded on a Hewlett-Packard HP8450A diode array spectrophotometer. Changes in optical density were thereby measured as a function of applied potential (Figure 2), and this correlation was used, together with the Nernst equation, to calculate the number of electrons associated with the electrochemical oxidation in the pyrromethane series; the logarithmic plot of the change in optical density vs applied potential (not shown) gave a slope proportional to the number of electrons and the intercept $E_{1/2}$ value associated with the process.[12] In the case of the pyrromethane used (Figure 2) the derived value was 1.7, which correlates with a two-electron process.

Pyrromethanes,[17] pyrromethenes,[18] and pyrroketones[19] were prepared by using standard procedures and were drawn from

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(16) For confirmation of the interference of halide the cyclic voltammograms of tetrabutylammonium bromide and the chloride were measured in acetonitrile with the Ag/AgCl reference electrode. The bromide showed two oxidation peaks at 770 and 1070 mV, while the chloride showed only a single wave at 1120 mV.

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stocks accumulated in the course of our work on the synthesis of porphyrins. Precise details of the synthesis of any examples are available from K.M.S.

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Synthesis of ω-Unsaturated Acids

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A short, high-yield method for the synthesis of ω-unsaturated acids has been developed that precludes any double-bond migration or hydrogenation. Key is the coupling reaction between Grignards of ω-unsaturated alkyl halides and the bromomagnesium salt of ω-bromo fatty acids. The reaction has been successfully extended to ω-bromo nitriles. The use of ω-chloro acids or α-bromo acids gives lower yields of heterocoupling products and substantial homocoupling. A catalyst study shows Li_2CuCl_4 to yield the most heterocoupling of several catalysts tried for the chloro acids, and Ni(II) or Cu(I) are best for the α-bromo acids.

ω-Unsaturated acids are of interest for use as ultra thin-layer photoresists[1] and for the synthesis of ω-radioiodinated fatty acids for use as myocardial imaging agents.[2] The syntheses in the literature involve many steps.[1a,3] The products are not adequately pure for photoresists because of the small amounts of double-bond migration and hydrogenation that occur in the final synthesis step. This is the Wolff–Kishner reduction (or the Huang–Minlon modification) of the intermediate ω-unsaturated keto acids. These side reactions have been noted before.[4a] Even the milder reduction conditions used by Hunig[4b] or the sodium borohydride reduction of the tosyl hydrazone of the keto group are reported[4c] to give small amounts of these side reactions.

The long-chain ω-unsaturated fatty acid molecules align on a solid surface as a Langmuir–Blodgett film or monolayer oriented so that the polar carboxylic acid groups are at the solid surface. The double-bond end groups are exposed unhindered for polymerization by high-energy radiation. Traces of byproducts with internal double bonds, no double bonds, or shorter or longer chain lengths will terminate polymer chain propagation by the X-ray or electron-beam polymerization of the terminal double bonds. Thus, high purity is necessary for high resolution in the photoresist by electron-beam microlithography.[1c]

A shorter route than those reported and especially one that precludes double-bond migration and/or hydrogenation was successfully used for the synthesis of ω-tricosenoic acid (22-tricosenoic acid) V, a particularly suitable ω-unsaturated fatty acid.[1] The ω-bromododecanoic acid I was prepared by the reaction of cyclododecanone with peroxytrifluoroacetic acid to form the lactone,[5] lactone hydrolysis with dilute sodium hydroxide to produce 12-hydroxydodecanoic acid,[6] and then conversion of the hydroxy acid to 12-bromododecanoic acid with 48% hydrobromic acid in the presence of sulfuric acid.[7] The product after recrystallization showed no evidence of 11-bromododecanoic acid (NMR, GC) and had properties identical with the literature.

$$\underset{\text{I}}{\mathrm{Br(CH_2)_{11}CO_2H}} + \mathrm{C_2H_5MgBr} \xrightarrow{\text{THF}} \underset{\text{II}}{\mathrm{Br(CH_2)_{11}CO_2MgBr}} + \mathrm{C_2H_6} \tag{1}$$

$$\mathrm{CH_2{=}CH(CH_2)_9OH} + \mathrm{SOCl_2} \xrightarrow{\mathrm{C_5H_5N}} \underset{\text{III}}{\mathrm{CH_2{=}CH(CH_2)_9Cl}} \tag{2}$$

$$\text{III} + \mathrm{Mg} \xrightarrow{\text{THF}} \underset{\text{IV}}{\mathrm{CH_2{=}CH(CH_2)_9MgCl}} \tag{3}$$

$$\text{II} + \text{IV} \xrightarrow[\text{THF}]{\mathrm{Li_2CuCl_4}} \underset{\text{V}}{\mathrm{CH_2{=}CH(CH_2)_{20}CO_2H}} \tag{4}$$

Compound III was prepared in 91% yield from 10-undecenyl alcohol and thionyl chloride with properties identical with those reported for III made by another route.[8] The method of Baer and Carney[9] was used for the coupling reaction. The reaction of the Grignard IV (made from III) with II (the bromomagnesium salt of I) in the presence of dilithium tetrachlorocuprate in tetrahydrofuran gave V, after hydrolysis of the reaction product. The

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