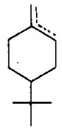
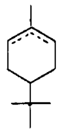
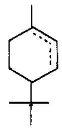

11


12


13

hydrogenated at essentially the same rate as would be expected if very similar adsorbed species were involved. That these rates were not diffusion limited can be seen by the fact that these same olefins could be hydrogenated under the same conditions over other catalysts at considerably faster rates. The involvement of a π-allyl species also explains the facile isomerization noted with palladium-catalyzed hydrogenations. Since these π-allyl species are formed by the extraction of an allylic hydrogen, this can also account for the marked dilution of the deuterium pool on the catalyst when palladium is used to deuterate double bonds. Thus, deuterations of **6**, **7**, and **9** over palladium give methylcyclohexanes with the d_0 species predominating and little polydeuterated material (Table IV). Recovered olefins show more deuterium exchange than observed with either platinum or rhodium (Table V), as would be expected if a π-allyl intermediate were involved.

One exception to the general absence of much polydeuterated material from these reactions is the presence of a considerable amount of a d_5 species in the methylcyclohexane formed on deuteration of **7** (Table IV). Since this entity was formed only when **7** was deuterated, it was suspected that the excess exchange was taking place on the methyl group through the intermediacy of a 7,1,2-π-allyl similar to **11**. The absence of any appreciable polydeuterated material in the $M-CH_3$ region of the mass spectrum of this product established that these extra deuteria were indeed located on the methyl group. It seems, then, that both the 7,1,2-π-allyl **11** and 6,1,2-π-allyl species **12** are involved in the palladium-catalyzed hydrogenation of 1-methylcyclohexenes.

Ruthenium and Iridium. Because olefin hydrogenations over these catalysts were extremely slow, they were only used in the pressure–stereochemistry studies. The results obtained, while not conclusive, indicate that while it is between 50 and 150 times less reactive than platinum depending on substrate and pressure, iridium is probably mechanistically similar to platinum. Ruthenium, though, is anomalous as shown particularly from the data depicted in Figure 2. Why this behavior occurred is not readily apparent. The fact that the other metals have an *fcc* crystalline arrangement while ruthenium has an *hcp* arrangement could be of some importance. More work is needed before any definitive answer can be given.

Registry No. **2**, 13294-73-0; **3**, 3419-74-7; **6**, 1192-37-6; **7**, 591-49-1; **8**, 591-48-0; **9**, 591-47-9; Pt, 7440-06-4; Rh, 7440-16-6; Pd, 7440-05-3; C, 7440-44-0.

Anodic Oxidation Potentials of Substituted Pyrroles: Derivation and Analysis of Substituent Partial Potentials

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With cyclic voltammetry, anodic oxidation potentials for a series of 117 substituted pyrroles have been measured and analyzed. The pyrroles studied are useful intermediates for the synthesis of polypyrrole pigments, and the information gained is related to reactivity in pyrrole systems and should be applicable to synthetic endeavors. Substituent partial potentials for the various common peripheral groups are derived by using a least-squares analysis and are interpreted. With a few exceptions, on the basis of the derived substituent contributions it is possible to deduce accurate calculated oxidation potentials for virtually any common substituted pyrrole. Calculated and measured oxidation potentials differ in two major circumstances: (a) when two strongly electron-withdrawing substituents are located at the 2- and 5-positions and (b) when an unsubstituted 2-position occurs concomitantly with a strongly electron-withdrawing 5-position substituent. Though correlations between electrochemical substituent partial potentials and standard σ_p and σ_m coefficients are not apparent, a good correlation was obtained between pK_a and oxidation potential for a series of pyrrole-5-carboxylic acids.

Introduction

Pyrroles are "π-excessive" heterocycles[1,2] that are readily oxidized. Several studies of anodic oxidation of pyrroles[3] have been described, and the major thrust in these investigations has been directed toward the formation of "pyrrole black", a stable, flexible "metallic polymer" with p-type conductivity.[4-10] One-electron anodic oxidation of simple pyrroles is irreversible,[3,10] the resulting π-cation radical reacting further either with pyrrole in situ (to give polymers) or with added or adventitious nucleophiles (to give substitution products). For example, anodic oxidation in the presence of methoxide[11] or cyanide[12] affords regioselectively substituted products.[13] Anodic oxidation of polyarylpyrroles has been extensively investigated,[14-20]

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but limited attention appears to have been devoted to simple substituted pyrroles, which are key intermediates in the synthesis of porphyrin systems.[21] Since oxidation potential can be related to reactivity and nucleophilicity in pyrroles (a key parameter in regiospecific pyrrole coupling chemistry), it is surprising that a systematic study of substituent partial potentials in standard pyrroles has not heretofore been reported; so far as we are aware, the only attempt to assess comparative pyrrole reactivity in, for example, pyrromethane synthesis was carried out by the Liverpool group, wherein pK_a values of a few selected pyrrole-5-carboxylic acids were determined and then related to reaction conditions required for coupling, as the corresponding lithium salts, to pyridinium salts of 2-(halomethyl)pyrroles.[22] In this paper we describe a study of anodic oxidation potentials, measured by means of cyclic voltammetry, in a series of 117 pyrroles, and we derive electrochemical substituent partial potentials for common peripheral groups.

Results and Discussion

The observed oxidation potentials for pyrroles **1–117** are given in Table I. On the basis of variations within the series of pyrroles studied and the contribution of 920 mV by the unsubstituted pyrrole nucleus, substituent contributions were computed, and these are given in Table II. Thus, Table I also includes a column of calculated oxidation potentials that are derived from Table II; the right-hand column in Table I shows the difference between the observed and calculated oxidation potentials, in millivolts.

Voltammograms were typical of those expected for an irreversible first electron abstraction. Use of a higher scan rate causes the oxidation to occur at a more positive potential, adding further proof of irreversibility,[23] presumably owing to the highly reactive nature of the resulting pyrrole π-cation radical.

Substituent partial potentials were derived as follows. The observed potential data for the 117 pyrroles were fitted to the 40 substituent parameters using a least-squares computation. This afforded substituent partial potentials and calculated oxidation potentials with standard deviation (55.8 mV) and root-mean-square deviation (45.2 mV) that were unacceptably high. In order to identify anomalous behavior of certain substituents that might be causing the large errors, a crude manipulation of the observed data was carried out. A value of −400 mV for the partial potential of the 2-methyl group was derived by subtraction of the observed potential of compound **2** from compound **1**. Likewise, the partial potential of a 3-methyl substitient was derived to be −140 mV by subtraction of the observed potential of compound **3** from compound **1**. In this way partial potentials for all 40 substituents were roughly calculated, and these values were used to derive calculated oxidation potentials for the 117 pyrroles studied. In the above calculations and in the subsequent least-squares procedure, no attempt was made to differentiate between identical substituents at the 3- and 4-positions, or at the 2- and 5-positions. The substituent contributions at the 3- and 4-positions are clearly variable depending upon the nature of the 2 and 5 groups, but we believe that detailing of these minor variations would not contribute significantly to our overall conclusions. Thus, for example, the E_p values for pyrroles **13** and **18** vary by 50 mV, even though they have the same substituents, but in the case of **18** the methyl is "conjugated" with the 5 ester. There is, therefore, clearly a difference that depends upon whether or not the 3/4 substituent is conjugated with the 2/5 electron-withdrawing group, and this will lead to small errors in the determination of substituent partial potentials. We regard these effects to be too minor to warrant provision of two sets of 3/4 substituent effects, which would only add confusion to the more simple picture we wish to present here.

After the crude hand calculations of oxidation potentials for the 117 pyrroles were completed, it was apparent that in all cases where the 2- *and* 5-positions were substituted with electron-withdrawing groups, or when an unsubstituted 2-position occurred with a 5-position electron-withdrawing group, observed oxidation potentials were significantly lower than calculated. Thus, those pyrroles (**4**, **19–26**, **71**, **72**, **85**, **87–108**, **115**, **116**) were excluded from the least-squares analysis (unfortunately, along with the partial potentials for EtOAc, 2-COMe, and 2-CN), and a least-squares fit of the remaining 81 pyrrole oxidation potential data with the 37 partial potential parameters was performed. On this occasion, the standard deviation was 18.9 mV and the root-mean-square deviation was 13.9 mV, and the resulting partial potentials are given in Table II. The EtOAc, 2-COMe, and 2-CN values were calculated as indicated in the footnotes to Table II. With use of the partial potentials in Table II, calculated oxidation potentials for the complete series of 117 pyrroles were derived, and these are given in Table I, along with a value for the observed minus calculated potentials.

With the exception of anomalies outlined above, most observed and calculated oxidation potentials are within at least 30 mV of each other. However, as mentioned earlier on the basis of the crude initial calculations, some significant anomalies are notable. For example, 2-unsubstituted pyrroles bearing an electron-withdrawing group at position 5 (e.g., pyrroles **4**, **19–26**, **87**, **88**) invariably possessed oxidation potentials that were usually between 100 and 200 mV lower than calculated from the values in Table II. The origin of this anomalously low oxidation potential for such 2-unsubstituted pyrroles is nuclear.

A larger variation between observed and calculated potentials was noted for pyrroles, e.g., **71**, **72**, **85**, **90–108**, **115**, and **116** that bear electron-withdrawing groups at both the 2- and 5-positions. The result is that these pyrroles, in which the two electron-withdrawing groups are conjugated, have a lower oxidation potential than predicted, usually by about 300–500 mV. It appears that the presence of two electron-withdrawing groups does not double the π-electron depletion in the system, and only between 60 and 80% of the double substituent effect is felt. When three strongly electron-withdrawing groups are on the pyrrole nucleus (e.g., pyrroles **104** and **106**), the difference between observed and calculated E_p is even greater. These

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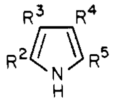
Table I. Structures and Oxidation Potentials (E_p; vs. Ag/AgNO$_3$) of Substituted Pyrroles[a]



					E_p, mV		
compd	R^2	R^3	R^4	R^5	obsd	calcd	obsd − calcd
1	H	H	H	H	920	(920)	
2	H	H	H	Me	520	522	−2
3	H	H	Me	H	780	795	−15
4	H	H	H	CO_2H	1380	1501	−121
5	Me	H	H	CO_2H	1110	1103	7
6	Me	H	H	CO_2Et	1065	1070	−5
7	Me	H	H	CO_2Bz	1085	1090	−5
8	Me	Br	H	CO_2Bz	1155	1158	−3
9	H	Me	CO_2H	H	1060	1060	0
10	H	Me	CO_2Et	H	1020	1036	−16
11	H	Me	CO_2Bz	H	1020	1052	−32
12	H	H	CO_2Et	CO_2H	1765	1741	24
13	Me	Me	H	CO_2Bz	930	965	−35
14	Me	P(Me)	Me	H	370	333	37
15	Me	P(Me)	Me	CO_2H	890	914	−24
16	Me	H	Me	CO_2H	980	978	2
17	Me	H	Me	CO_2Et	960	945	15
18	Me	H	Me	CO_2Bz	980	965	15
19	H	Me	Me	CO_2Bz	1095	1239	−144
20	H	Me	P(Me)	CO_2-*t*-Bu	1085	1265	−180
21	H	Et	Me	CO_2Bz	1100	1269	−169
22	H	P(Me)	Me	CO_2Bz	1135	1301	−166
23	H	Me	P(Me)	CO_2Bz	1085	1301	−216
24	H	Me	EtCl	CO_2-*t*-Bu	1120	1274	−154
25	H	Me	EtOAc	CO_2-*t*-Bu	1090	1244	−154
26	H	Br	Me	CO_2Et	1320	1396	−76
27	Me	Me	Me	CO_2Et	810	820	−10
28	Me	Me	Me	CO_2-*t*-Bu	810	805	5
29	Me	Me	Et	CO_2Bz	875	870	5
30	Me	Me	P(Me)	CO_2Bz	915	902	13
31	Me	Et	Me	H	290	301	−11
32	Me	Et	Me	CO_2Me	860	862	−2
33	Me	Et	Me	CO_2Et	870	850	20
34	Me	Et	Me	CO_2Bz	865	870	−5
35	Me	Et	Me	CO_2-*t*-Bu	825	835	−10
36	Me	Pr	Me	CO_2Et	840	858	−18
37	I	Pr	Me	CO_2Bz	1040	1017	23
38	I	Me	Et	$CONMe_2$	800	783	17
39	Me	*i*-Bu	Me	CO_2Bz	870	870	0
40	Me	*i*-Bu	Me	CO_2Et	850	850	0
41	Me	Et	Me	$CONMe_2$	625	642	−17
42	Me	Me	H	$CONMe_2$	730	737	−7
43	Me	P(Me)	Me	$CONMe_2$	680	674	6
44	Me	P(Me)	Me	CO_2Bz	915	902	13
45	Me	P(Et)	Me	CO_2Et	880	873	7
46	Me	A(Me)	Me	CO_2Bz	970	953	17
47	Me	B(Me)	Me	CO_2Bz	890	890	0
48	Me	EtCl	Me	CO_2Bz	960	960	0
49	Me	H	P(Me)	CO_2Bz	1015	1027	−12
50	Me	P(Me)	H	CO_2Bz	985	1027	−42
51	Me	A(Me)	H	CO_2Bz	1065	1078	−13
52	CH_2OAc	Me	Et	CO_2Bz	1100	1099	1
53	CH_2OAc	Et	Me	CO_2Bz	1100	1199	1
54	CH_2OAc	Pr	Me	CO_2Bz	1100	1106	−6
55	CH_2OAc	P(Me)	Me	CO_2Bz	1140	1131	9
56	CH_2OAc	A(Me)	P(Me)	CO_2Bz	1240	1244	−4
57	Me	*i*-Bue	Me	CO_2Et	750	750	0
58	Me	Pente	Me	CO_2Bz	710	710	0
59	Me	Me	CN	CO_2Bz	1330	1330	0
60	Me	COMe	Me	CO_2Et	1180	1186	−6
61	Me	COMe	Me	CO_2H	1220	1219	1
62	Me	COMe	Me	CO_2Me	1200	1198	2
63	Me	CO_2Bz	Me	CO_2Bz	1250	1222	28
64	Me	CO_2Bz	Me	CO_2-*t*-Bu	1200	1187	3
65	Me	COMe	Et	CO_2Et	1220	1216	4
66	Me	CO_2-*t*-Bu	P(Et)	CO_2Et	1260	1250	10

Table I (Continued)

					E_p, mV		
compd	R^2	R^3	R^4	R^5	obsd	calcd	obsd − calcd
67	Me	COMe	P(Et)	CO$_2$Et	1225	1239	−14
68	Me	CHO	A(Et)	CO$_2$Et	1410	1408	2
69	Me	CO$_2$Me	Me	CONMe$_2$	1020	1010	10
70	Me	CO$_2$-*t*-Bu	Me	CONMe$_2$	980	990	−10
71	CO$_2$Bz	P(Me)	Me	CONMe$_2$	1190	1642	−452
72	CO$_2$Bz	Me	EtOAc	CONMe$_2$	1200	1621	−421
73	Me	CO$_2$Me	Me	CO$_2$H	1240	1250	−10
74	Me	P(Et)	A(Et)	CO$_2$Et	985	987	−2
75	Me	Br	A(Et)	CO$_2$Et	1150	1128	22
76	Me	CHO	H	CO$_2$-*t*-Bu	1395	1403	−8
77	Me	CHO	H	CO$_2$Bz	1445	1439	6
78	Me	Acr(Et)	A(Et)	CO$_2$Et	1100	1122	−22
79	Me	Acr(Et)	Me	CO$_2$Et	1030	1008	22
80	Me	Acr(H)	Me	CO$_2$Et	1015	1015	0
81	Me	H	Me	CHO	1040	1048	−8
82	Me	Br	Me	CHO	1120	1116	4
83	Me	Et	Me	CHO	950	952	2
84	Me	P(Me)	Me	CHO	990	984	6
85	CO$_2$Et	P(Et)	Me	CO$_2$Bz	1480	1841	−361
86	Me	COMe	H	CO$_2$Bz	1345	1331	14
87	H	CO$_2$Et	Me	CHO	1520	1686	−166
88	H	CO$_2$Bz	Me	CHO	1560	1703	−143
89	CHO	CO$_2$Me	Me	H	1340	1719	−379
90	CHO	Et	Me	CO$_2$Bz	1500	1920	−420
91	CO$_2$Me	Et	Me	CO$_2$Bz	1495	1829	−334
92	CO$_2$H	Et	Me	CO$_2$-*t*-Bu	1415	1814	−399
93	CO$_2$H	Me	Et	CONMe$_2$	1230	1622	−392
94	CO$_2$H	P(Me)	Me	CO$_2$Bz	1485	1882	−397
95	CO$_2$H	P(Me)	Me	CO$_2$Me	1465	1873	−408
96	CO$_2$H	P(Me)	Me	CO$_2$-*t*-Bu	1435	1846	−409
97	CN	Et	Me	CO$_2$Bz	1630	2050	−420
98	CN	Et	Me	CO$_2$H	1520	2062	−542
99	CO$_2$H	EtCl	Me	CO$_2$Bz	1550	1891	−341
100	CO$_2$Bz	Me	EtCl	CO$_2$Bz	1550	1879	−329
101	CO$_2$-*t*-Bu	Me	EtCl	CO$_2$Bz	1510	1843	−333
102	CO$_2$Bz	Me	EtCl	CO$_2$-*t*-Bu	1500	1843	−343
103	CO$_2$-*t*-Bu	P(Me)	Me	CO$_2$Bz	1465	1834	−369
104	CHO	CO$_2$Et	Me	CO$_2$Et	1790	2235	−445
105	CO$_2$H	Et	Me	CO$_2$H	1470	1862	−398
106	CHO	CO$_2$Bz	Me	CO$_2$Et	1700	2252	−552
107	COMe	Me	Et	CO$_2$H	1420	1812	−392
108	CO$_2$Bz	Me	Me	CONMe$_2$	1240	1580	−340
109	CH$_2$Cl	CO$_2$Et	Me	CO$_2$Et	1430	1422	8
110	CH$_2$Cl	CO$_2$Bz	Me	CO$_2$Et	1430	1438	−8
111	CH$_2$Br	CO$_2$Et	Me	CO$_2$Et	1380	1380	0
112	I	CO$_2$Et	Me	CO$_2$Bz	1330	1346	−16
113	I	Cl	Me	CO$_2$Bz	1230	1230	0
114	I	Br	Me	CO$_2$Et	1130	1154	−14
115	CHO	P(Me)	Cl	CO$_2$-*t*-Bu	1760	2165	−405
116	CO$_2$H	P(Me)	Cl	CO$_2$-*t*-Bu	1660	2095	−435
117	Me	I	Me	CO$_2$Bz	1100	1101	1

[a] Abbreviations: A(Et) = CH$_2$CO$_2$Et; A(Me) = CH$_2$CO$_2$Me; Acr(Et) = CH═CHCO$_2$Et; Acr(H) = CH═CHCO$_2$H; Bz = CH$_2$C$_6$H$_5$; B(Me) = CH$_2$CH$_2$CH$_2$CO$_2$Me; *i*-Bu = CH$_2$CH(Me)$_2$; *i*-Bue = CH═C(Me)$_2$; *t*-Bu = C(Me)$_3$; EtCl = CH$_2$CH$_2$Cl; EtOAc = CH$_2$CH$_2$OCOMe; P(Et) = CH$_2$CH$_2$CO$_2$Et; P(Me) = CH$_2$CH$_2$CO$_2$Me; Pente = CH═CHCH$_2$CH$_2$Me; Pr = CH$_2$CH$_2$Me. Calculated values for the oxidation potentials were derived from the partial potentials given in Table II. Values were derived by least-squares analysis, in which the standard and root-mean-square deviations were 18.9 and 13.9 mV, respectively.

conclusions are not novel; in studies of porphyrin reduction potentials it was noted[24] that addition of a second acetyl group to an acetylporphyrin does not double the effect of the first one but rather the second contributes about 75% of the effect of the first one. The fact that, in the pyrrole series, the second electron-withdrawing substituent contributes even less an effect than in porphyrins is probably a consequence of the smaller aromatic system and the fact that the two groups are directly conjugated in pyrroles. This type of nonadditive phenomenon, indeed, has ample precedent in organic systems.[25] Pyrroles that have conjugated electron-withdrawing substituents at the 4- and 5-positions (e.g., pyrrole **59**) appear to give observed potentials very close to those calculated.

When the two electron-withdrawing substituents are sited, for example, at the 2- and 4-positions [i.e., unconjugated (e.g., pyrroles **60–70**, **73**, **76–80**, **86**, **109–111**)] the

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Table II. Substituent Contributions to Observed Oxidation Potentials (E_p) of Substituted Pyrroles[a,b]

substit	$R^{2,5}$ mV	$R^{3,4}$ mV
Me	−398	
		−125
Et		−95
Pr		−89
i-Bu		−95
CH_2OAc	−169	
CH_2Cl	−163	
CH_2Br	−204	
EtCl		−54
EtOAc		−84[c,d]
i-Bue		−195
Pente		−255
CO_2Bz	569	
		257
CO_2Et	549	
		240
CO_2-*t*-Bu	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[c,e]	
		241
CHO	651	
		348
CN	781[c,f]	
		365
Br		68
Cl		124
I	−257	
		135

[a] Contribution of the unsubstituted pyrrole ring is 920 mV. Values were derived by least-squares analysis (see text) that afforded standard and root-mean-square deviations of 18.9 and 13.9 mV, respectively. [b] Abbreviations are as given in Table I. [c] This value not derived by least squares. [d] From **25** − **24** − 54 mV. [e] From **107** − **105** + 581 mV. [f] From **97** − **90** + 651 mV.

effect of both substituents does appear to be additive.

Some trends are apparent in the substituent partial potentials given in Table II. For example, the strongly electron-withdrawing effect of the 3/4 carboxylate, e.g., CO_2Me (+273 mV), drops to −12 mV when a methylene is inserted to give CH_2CO_2Me [A(Me)] and when further separated from the nucleus, as in $CH_2CH_2CO_2Me$ [P(Me)] and $CH_2CH_2CH_2CO_2Me$ [B(Me)], it drops further to −63 and −75 mV, respectively. Thus, the P(Me) and B(Me) contributions approach that for ethyl (−95 mV). When the 2-methyl group (partial potential −398 mV) is transformed into CH_2Br, CH_2OAc, or CH_2Cl, the values change, as expected, to −204, −169, and −163 mV, respectively. Similarly, attachment of an OAc group to the β-carbon of ethyl (i.e., in EtOAc) causes an increase in the partial potential from −95 to −84 mV, and attachment of a chlorine has an even larger effect from the −95 mV of ethyl to the −54 mV of chloroethyl; this is exactly as would be anticipated from electronegativity considerations.

It might have been expected that acrylates, being the vinyl analogues of simple esters, would be strongly electron withdrawing and therefore would have a large positive partial potential approaching that of the 3/4 carboxylate (240–280 mV). As can be seen from Table II, the acrylic acid [Acr(H)] and the corresponding ethyl ester [Acr(Et)] have positive partial potentials only in the 60–70 mV region, presumably because the positive charge in the cation radical can be delocalized into them. Delocalization of the positive charge into the conjugated alkene substituents is more favorable than for the acrylates, and partial potentials of −195 and −255 mV are observed for the isobutenyl and 1-pentenyl substituents, respectively.

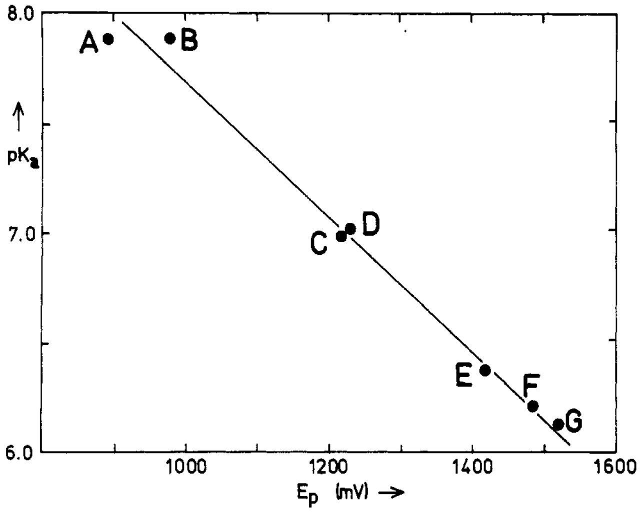

Figure 1. Plot of oxidation potential (E_p) vs. apparent dissociation constant (pK_a) in 2-methoxyethanol–water:[22,31] A, pyrrole **15**; B, **16**; C, **61**; D, **93**; E, **92**; F, **94**; G, **98**.

The partial potentials for 3/4 halo substituents are in the region 70–135 mV; the only 2-halopyrroles available were 2-iodo substituted, and here the iodo substituent moves from being electron withdrawing (135 mV) at the 3-position to being strongly electron releasing (−257 mV) at the 2-position. This effect is presumably due to the fact that the positive charge in the cation–radical is greater at C-2, and so more demand is put on the ability of the halogen at that position to donate electrons. This observation is in accord with the hypothesis that oxidation of aryl chlorides and bromides involves removal of an electron from the π-system,[26] but that one-electron abstraction from aryl iodides affords the corresponding iodonium salt via the π-cation radical.[27] Again, this effect is not unexpected since toluene (E_p = 1.93 V),[28] when substituted at the 4-position with bromine, shows an E_p of 1.95 V, but *p*-iodotoluene has an E_p of 1.26 V.[29] A similar trend with benzene (E_p = 1.94 V),[28] chlorobenzene (E_p = 2.07 V),[26] bromobenzene (E_p = 1.98 V),[30] and iodobenzene (E_p = 1.77 V)[28] has also been observed.

Attempts to demonstrate a correlation between the partial potentials given in Table II and σ_m and σ_p coefficients were unsuccessful. However, Figure 1 shows a plot of E_p vs. pK_a[31] for a limited series of pyrrole-2-carboxylic acids. The correlation is good, and this is satisfying in that several of the pyrrole carboxylic acids used given anomalously low E_p values (vide infra). It seems clear that the electronic basis for the partial multiple contributions by

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electron-withdrawing groups on the observed E_p values (Table I) is also manifest in the corresponding experimental pK_a values.

As observed by other workers, oxidation of pyrrole (**1**) results in the deposition of "pyrrole black" at the working electrode. Similarly, the 2,5-diunsubstituted pyrroles **3**, **10**, and **11** deposit "metallic" conducting polymers at the working electrode, but 3-methylpyrrole-4-carboxylic acid (**9**) forms a soluble yellow polymer that fails to adhere to the electrode surface. No other pyrroles gave evidence of polymer formation, indicating that unsubstituted 2- *and* 5-positions are required for manifestation of this phenomenon.

Experimental Section

Pyrroles 1–117 used in this study were available from synthetic work carred out over the past 20 years in Liverpool and Davis. Synthetic origins of the majority of the pyrroles are obvious and are published; specific details in particular examples are available by writing to K.M.S. Acetonitrile was dried by refluxing over calcium hydride, then distilled, and stored over 3-Å molecular sieves. The supporting electrolyte tetra-*n*-butylammonium perchlorate (Kodak) was vacuum dried at 60 °C before use.

A three-compartment electrochemical cell was used, with a main compartment of 20–mL capacity; the cell included a reference electrode (Ag/$AgNO_3$, a silver wire in 0.1 M $AgNO_3$ in acetonitrile; potential 0.337 V vs. the aqueous saturated calomel electrode), a platinum counterelectrode, and a platinum wire working electrode. The last was cleaned in 10 M nitric acid and then heated four times in a flame to incandescence prior to each run. Voltammetric measurements were made with a PAR Model 175 programmer and a PAR Model 173 potentiostat/galvanostat attached to a PAR Model RE0074 XY recorder. Sample solutions consisted of 2 mM pyrrole in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate, and measurements were performed with a scan rate of 100 mV/s.

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Registry No. **1**, 109-97-7; **2**, 636-41-9; **3**, 616-43-3; **4**, 634-97-9; **5**, 3757-53-7; **6**, 3284-51-3; **7**, 87462-15-5; **8**, 89909-39-7; **9**, 64276-66-0; **10**, 2199-49-7; **11**, 89909-40-0; **12**, 89909-41-1; **13**, 4868-30-8; **14**, 54474-51-0; **15**, 13219-76-6; **16**, 4513-93-3; **17**, 2199-44-2; **18**, 40236-19-9; **19**, 954-92-7; **20**, 42419-19-2; **21**, 51089-83-9; **22**, 31896-88-5; **23**, 51671-83-1; **24**, 51089-80-6; **25**, 51644-01-0; **26**, 89909-42-2; **27**, 2199-46-4; **28**, 50634-31-6; **29**, 61538-85-0; **30**, 33317-06-5; **31**, 517-22-6; **32**, 42781-37-3; **33**, 2199-47-5; **34**, 1925-61-7; **35**, 31896-92-1; **36**, 4758-64-9; **37**, 32900-45-1; **38**, 13219-71-1; **39**, 89909-43-3; **40**, 4989-24-6; **41**, 13219-74-4; **42**, 4868-32-0; **43**, 37531-54-7; **44**, 20303-31-5; **45**, 54278-10-3; **46**, 31837-62-4; **47**, 69366-55-8; **48**, 51089-69-1; **49**, 53365-82-5; **50**, 89909-44-4; **51**, 89909-45-5; **52**, 56015-18-0; **53**, 3750-36-5; **54**, 5866-63-7; **55**, 859-38-1; **56**, 50622-67-8; **57**, 4989-24-6; **58**, 69912-10-3; **59**, 89909-46-6; **60**, 2386-26-7; **61**, 2386-28-9; **62**, 89909-47-7; **63**, 52459-55-9; **64**, 89909-48-8; **65**, 37013-86-8; **66**, 31695-39-3; **67**, 40515-73-9; **68**, 6122-77-6; **69**, 40593-29-1; **70**, 40593-48-4; **71**, 37538-31-1; **72**, 31837-66-8; **73**, 50296-60-1; **74**, 53700-91-7; **75**, 89909-49-9; **76**, 32900-47-3; **77**, 89909-50-2; **78**, 6122-78-7; **79**, 52648-98-3; **80**, 52649-02-2; **81**, 2199-58-8; **82**, 89909-51-3; **83**, 6250-80-2; **84**, 18818-25-2; **85**, 89909-52-4; **86**, 87462-14-4; **87**, 6339-66-8; **88**, 89909-53-5; **89**, 52459-25-3; **90**, 965-20-8; **91**, 5866-53-5; **92**, 31897-11-7; **93**, 951-64-4; **94**, 978-24-5; **95**, 89909-54-6; **96**, 89909-55-7; **97**, 965-19-5; **98**, 942-74-5; **99**, 51089-73-7; **100**, 89909-56-8; **101**, 89909-57-9; **102**, 51089-77-1; **103**, 31837-46-4; **104**, 2199-60-2; **105**, 89909-58-0; **106**, 52649-06-6; **107**, 32900-44-0; **108**, 16132-27-7; **109**, 5408-12-8; **110**, 89909-59-1; **111**, 57745-26-3; **112**, 81972-01-2; **113**, 89909-60-4; **114**, 89909-61-5; **115**, 89909-62-6; **116**, 89909-63-7; **117**, 89909-64-8.

Addition Reactions to *syn*- and *anti*-Sesquinorbornenes Involving Ionic Mechanisms. The Role of Tetracyanoethylene

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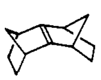
Addition of bromine or of acids to *anti*-sesquinorbornene is more rapid and less readily reversible than that to the syn isomer, whereas other addition reactions proceeding by concerted or free-radical mechanisms show a small rate advantage for *syn*-sesquinorbornene and no reversibility. Tetracyanoethylene (TCNE) does not undergo cycloaddition with *syn*- or *anti*-sesquinorbornene, nor can any dipolar ion from TCNE and sesquinorbornene be trapped by methanol, as in the case of TCNE and vinyl ethers.[18] However, under the conditions of such experiments TCNE catalyzes the addition of methanol to yield sesquinorbornyl methyl ether, or of water to yield sesquinorbornanol, the TCNE undergoing no apparent chemical change. From a comparative study of TCNE and *p*-toluenesulfonic acid it is concluded that the TCNE reaction is an example of acid catalysis, probably by the complex between TCNE and the alcohol or water. *syn*-Sesquinorbornene adds methanol in CD_3CN, reaching an equilibrium constant of about 2.04 ± 0.14 L/mol at ~30 °C, and adds water in CD_3CN with the lower equilibrium constant of about 0.54 ± 0.05 L/mol at ~30 °C. *anti*-Sesquinorbornene in similar additions shows an equilibrium more favorable to addition by about 3 orders of magnitude. These reactions are discussed in light of the general character and behavior of the sesquinorbornenes. A new route to *anti*-sesquinorbornene is described that gives better yields than the former electrolytic preparation.

The sesquinorbornenes, syn (**1**)[1] (SSNB) and anti (**2**)[2] (ASNB), have some special properties that make them useful in the study of reaction mechanisms at the double bond. These properties include very low reactivity toward singlet oxygen as compared to the related olefin biadamantylidene; exclusive cis addition; exclusive exo attack



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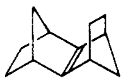

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