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Electrochemistry of Electron Transfer Probes. α-Aryloxyacetoveratrones and Implications for the Mechanism of Photo-yellowing of Pulp[1]

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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Standard potentials (E°) of a series of substituted α-aryloxyacetoveratrone derivatives have been determined from a correlation of the ^{13}C NMR chemical shifts of the carbonyl group and a similar correlation (E° vs. ^{13}C NMR shifts) within a series of α-anilinoacetoveratrones. Using these potentials the rate constants for fragmentation of the radical anions were determined by digital simulation of the voltammetric waves. The rate contants for C–O cleavage in the radical anions correlate with the pK_a of the corresponding phenols. The fragmentations are all in the activated region of a general free energy relationship for this class of compound ($\alpha = 0.5$). The standard potential and rate constant for fragmention of the α-guaiacoxyacetoveratrone radical anion also were determined. This species is a model compound for one of the lignin substructures. The implication of these results on the currently accepted mechanism for photo-yellowing of lignin rich paper is discussed.

The chemistry and photochemistry of α-(aryloxy)-acetophenones have been of considerable interest as models of one of the substructures of lignins. Much of the work has focused on understanding photo-yellowing of lignin-rich paper which is believed to involve oxdation of phenoxy radicals. Photochemical studies have shown that both the singlet and triplet states of α-(aryloxy)-acetophenones undergo β-cleavage to produce phenacyl and phenoxy radicals[2–4] with the triplet channel being enhanced in protic solvents.[5] This photocleavage process is believed to be a significant, but not the major, source of phenoxyl radicals leading to the photoyellowing of lignin-rich paper.

α-Guaiacoxyacetoveratrone (2-methoxyphenoxy-3′,4′-dimethoxyacetophenone) is one of the most simple lignin model compounds (i.e. having the essential substitution pattern) to have been thoroughly studied. Photochemical cleavage of this compound has been suggested to involve the photoreduction of the triplet state by a hydrogen atom donor to form a ketyl radical, which rapidly undergoes a β-cleavage.[6] In basic solution the formation of radical anions was observed, and the cleavage appeared to be suppressed. However, Huang *et al.* suggested that the cleavage of the β-phenoxyketyl radical was too slow to be mechanistically feasible.[7] In that study it was shown that the unsubstituted β-phenoxy-acetophenone ketyl fragments with a rate constant $\leqslant 10\ s^{-1}$. One route to the formation of phenoxyl radicals that has not been seriously considered is photoinduced electron transfer reduction of the α-aryloxyacetophenone moieties of the lignin structure to the corresponding radical anions. These are viable routes to a number of reactive radical anions.[8,9] Alternatively, the α-aryloxy-acetophenone radical anions can also be formed by deprotonation of ketyl radicals. At this time the relative cleavage rates of the ketyl radical and the radical anion are not known.

In principle, many of these questions can be answered using electrochemical approaches. The use of electrochemistry in connection with studies of lignins has mainly focused on the anodic cleavage of α-aryloxy-acetophenones which leads to oxidative degradation of

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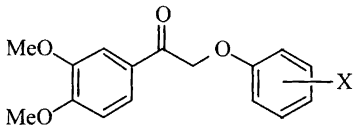


1a: X = H
1b: X = *o*-MeO
1c: X = *m*-MeO
1d: X = *p*-MeO
1e: X = *m*-CF_3
1f: X = *m*-CN
1g: X = *p*-CN

lignins into low molecular weight aromatic compounds.[10–12] Only a few reports of the electrochemical reduction of these compounds have appeared.[10,13–16] Recently, we reported the determination of rate constants for cleavage of a wide range of substituted phenoxyacetophenones using a combination of electrochemical and laser flash techniques.[14–16] Depending on the substituent, the lifetime of the corresponding radical anions may be as short as nanoseconds or as long as seconds. The purpose of this paper is to extend this study to include substituted α-aryloxyacetoveratrones (**1a–g**) in order to assess the importance of radical anion cleavage relative to the ketyl radical cleavage in more structurally relevant systems.

Results and discussion

Cyclic voltammetry and coulometry. Reductions of α-substituted acetophenones in aprotic solvents were first studied by Lund[17] and Savéant.[18] Reduction of the α-aryloxyacetoveratrones, **1a–g**, at a hanging mercury drop electrode (HMDE) in DMF containing 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte gave an irreversible cathodic peak followed by a reversible redox couple. The potential of the first peak (E_p) depended on the substituent, and changed from −2.179 V (**1g**) to −2.293 V (**1d**) versus the ferrocene/ferrocenium couple (Fc/Fc^+) at a scan rate (ν) of 1 V s^{-1}. The reversible couple at more negative potentials, however, was independent of the substituent on the phenoxy ring, and is attributed to the reduction of acetoveratrone ($E^\circ = -2.605$ V vs. Fc/Fc^+). Reduction of **1a–g** in the presence of 2,6-di-*tert*-butylphenol (DBP) changed the appearance of the cyclic voltammograms. Typical cyclic voltammograms of **1g**, **1b** and **1d** in the presence of 8 mM DBP are shown in Fig. 1. The voltammograms now consisted of two irreversible peaks. The height of the first cathodic peaks increased by a factor of almost two upon addition of DBP, but the peak potentials were unaffected. The second peak became irreversible and the peak current increased to almost the same value as that observed for the first peak. The peak potential of the second peak was, again, independent of the substituent on the phenoxy ring. Thus, the cathodic

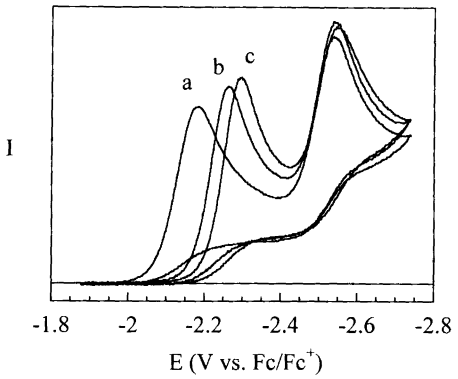


Fig. 1. Cyclic voltammogram of 2 mM (a) **1g** (b) **1b** and (c) **1d** in the presence of 8 mM DBP in DMF, 0.1 M TEAP, HMDE, $T = 25$ °C.

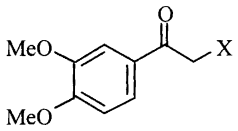
behavior of these α-aryloxyacetoveratrones is, as expected, identical with the corresponding α-aryloxyacetophenones.[14] In all cases the oxidation of the product phenoxide ion was observed at higher potentials. This was especially prevalent in the constant current coulometric experiments (see below).

Constant current coulometry was carried out using a current of 30 mA. This low current ensured that the applied potential was always more positive than the peak potential of the first reduction wave.[14] The reduction of **1b**, **1d** and **1g** in the presence of 3 equivalents of DBP consumed 2.1, 2.0 and 2.0 F mol^{-1}, respectively. Analysis of the catholytes by HPLC after 60–70% conversion, showed that acetoveratrone and the corresponding phenol were the only reduction products.

Estimating E° *values.* We have previously shown that the standard potentials, E°, of *para* and *meta* substituted α-methoxyacetophenones correlate linearly with the standard potentials of the corresponding acetophenones.[14] The α-methoxyacetophenones form stable radical anions on the timescale of the electrochemistry experiments so it is possible to determine their E° values accurately. The correlation is described by eqn. (1), where the potentials are given versus the ferrocene/ferrocenium couple, Fc/Fc^+.

$$E^\circ[ArC(O)CH_2OMe] = -0.098\ V + 0.910E^\circ[ArC(O)CH_3] \quad (1)$$

The standard potential of acetoveratrone (**2**) is −2.605 V vs. Fc/Fc^+ in DMF, 0.1 M TEAP. From eqn. (1) a value of $E^\circ = -2.469$ V vs. Fc/Fc^+ for α-methoxyacetoveratrone (**3**) is estimated which is in good agreement



2: X = H, **3**: X = MeO

with the experimental value of −2.475 V. The very close agreement between these two values confirms that the electronic structure is very similar in the acetophenones and the acetoveratrones even though the latter series of compounds have disubstituted acetophenone rings. We therefore used the analogous linear correlation that exists between the E° values of the α-phenoxyacetophenones and the acetophenones [eqn. (2)] to calculate the standard reduction potential of **1a**.[14] Using the E° value for acetoveratrone given above, we obtain a value of −2.392 V vs. Fc/Fc^+ for **1a**.

$$E^\circ[Ar(CO)CH_2OPh] = -0.152\ V + 0.859E^\circ[ArC(O)CH_3] \quad (2)$$

The similarity of the α-aryloxyacetophenones and the α-aryloxyacetoveratrones was further probed by comparing the ^{13}C shifts of the carbonyl group, Fig. 2. The plot shows an excellent linear correlation. The ^{13}C NMR shift is (to a first approximation) a measure of the electron density of the carbonyl group, and is therefore a measure of the inductive effect of the α-substituents. The slope of 1.24 indicates the substituents on the phenoxy ring have a stronger influence on the electron density at the carbonyl carbon in the acetoveratrones than in the acetophenones. This can be understood as the two electron-donating methoxy groups in the acetoveratrones will tend to push π-electron density towards the carbonyl group (i.e. a synergistic effect of a push–pull system). The higher electron density on the carbonyl group is indicated by the lower value of the ^{13}C carbonyl chemical shifts of the acetoveratrones relative to the corresponding acetophenones. It is interesting to note that the point that corresponds to the *ortho*-methoxyphenoxy compounds falls on the regression line suggesting that the steric interaction between the *ortho*-methoxy group and the benzoyl moiety in the acetophenones and the acetoveratrones is negligible. The main electronic interaction is inductive, analogous to the *meta*- and *para*-substituted compounds.

The α-anilinoacetoveratrones form stable radical anions and thus make it possible to examine the correlation between the ^{13}C shifts and the E° values.[14] The linear correlation in Fig. 3 confirms that the relationship between the ^{13}C shifts of α-anilinoacetophenones and the α-aryloxyacetophenone can be extended to the acetoveratrones (slope = 0.90, $r = 0.993$). As pointed out earlier, the slope less than unity is expected, as the oxygen is less polarizable and more electronegative than nitrogen. Similarly, a linear relationship exists between the E° of the α-anilinoacetoveratrone and the ^{13}C shifts of the carbonyl group that has the same slope as that for the corresponding acetophenones. Thus, we are able to use these correlations to determine the E° values of the α-aryloxyacetoveratrones if we make the plausible assumption (as was done with the acetophenones[14]) that the slope from Fig. 4 can be used in this case. These data are shown in Table 1.

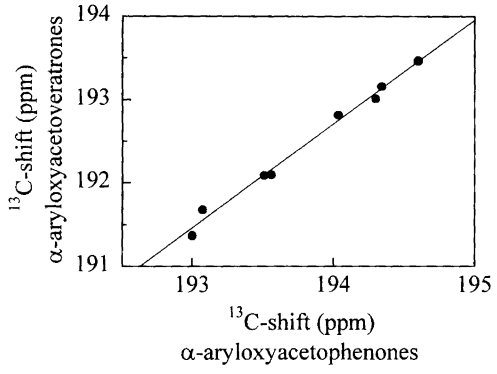


Fig. 2. ^{13}C NMR shifts of carbonyl carbons of α-aryloxyacetoveratrones, **1a–g**, versus the ^{13}C shifts of the corresponding α-aryloxyacetophenones. The slope of the regression line is 1.24 ($r = 0.994$).

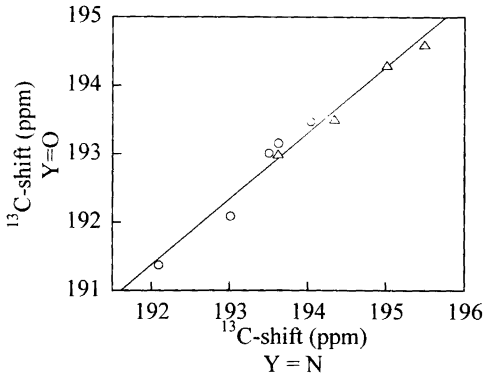


Fig. 3. ^{13}C carbonyl shifts of α-anilinoacetophenones (○, Ref. 16) and α-anilinoacetoveratrones (△), **4a–e**, plotted versus the ^{13}C carbonyl shifts of the corresponding α-aryloxyacetophenones and α-aryloxyacetoveratrones.

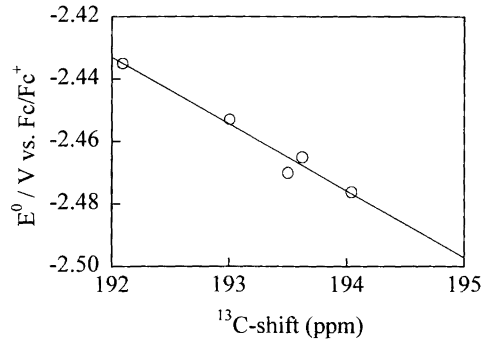
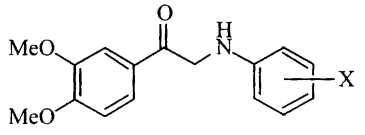


Fig. 4. E° values of α-anilinoacetoveratrones, **4a–e**, plotted versus the ^{13}C shift of the carbonyl groups.



X = H (**4a**), *o*-MeO (**4b**), *p*-MeO (**4c**), *m*-CF_3 (**4d**), *p*-CN (**4e**)

Table 1. Formal reduction potentials, $E°$, and ^{13}C NMR shift of carbonyl carbon of 3,4-di-MeO-$C_6H_3COCH_2$-Y-C_6H_4-X.

	Y = NH		Y = O	
X	$E°$/V vs. Fc/Fc^+ [a]	^{13}C-shift (ppm)[b]	$E°$/V vs. Fc/Fc^+ [c]	^{13}C-shift (ppm)[b]
o-MeO	−2.466	193.62	−2.395	193.16
p-MeO	−2.476	194.04	−2.402	193.47
H	−2.470	193.50	−2.392[d]	193.01
m-MeO	—	—	−2.388	192.82
m-CF_3	−2.453	193.01	−2.372	192.09
m-CN	—	—	−2.363	191.68
p-CN	−2.435	192.09	−2.356	191.37

[a]DMF, 0.1 M TEAP, Hg-electrode, $T = 25$ °C. [b]NMR shift of carbonyl carbon measured against TMS in $CDCl_3$. [c]Estimated from ^{13}C-shift–$E°$ correlation (see the text). [d]Calculated by using eqn. (2).

Cleavage rates of the radical anions. The rate constants for the cleavage of the radical anions of **1a–g** were determined by the same digital simulation procedure using the Rudolf algorithm as we have previously described for the corresponding α-phenoxyacetophenones.[14,15] This procedure is based on simulating the values for the peak shift, $E_p - E°$, and the half-peak width, $E_{p/2} - E_p$, measured over a wide range of scan rates (three orders of magnitude) using a combined ECE/DISP cleavage mechanism. Both the rate constant for the heterogeneous electron transfer, $k°$, and the rate constant for the cleavage are adjusted using an iterative process so that the values of $E_p - E°$ and $E_{p/2} - E_p$ are reproduced. A rate constant of $1 \times 10^{10}\ M^{-1}\ s^{-1}$ (i.e. diffusion controlled) for the DISP reaction was assumed. The results are given in Table 2.

The simulation results obtained using the ECE/DISP mechanism were compared with the results obtained by using either an ECE or a DISP mechanism with the same rate constants. This allowed us to determine whether the experimental results could be rationalized by one of these two limiting mechanisms. The cathodic cleavages were found to be best described by the ECE mechanism when $k > 10^7\ s^{-1}$, as can be seen from the results in Table 2. The combined ECE/DISP mechanism was necessary to describe the cleavage for the other compounds. In none of the cases did the DISP mechanism prove to be applicable. These results are completely consistent with our previous findings for the α-aryloxyacetophenones.[14,15]

Table 2. Cathodic cleavage rates, heterogeneous rate constants and the reduction mechanisms for 3,4-di-MeO-$C_6H_3COCH_2$-OC_6H_4-X.[a]

X	$k/10^6\ s^{-1}$	$k°$/cm s^{-1}	Mechanism
o-MeO	5.0	1.8	ECEDISP
p-MeO	2.5	1.8	ECEDISP
H	5.0	1.8	ECEDISP
m-MeO	7.0	2.0	ECEDISP
m-CF_3	700	2.0	ECE
m-CN	430	1.9	ECE
p-CN	1000	1.5	ECE

[a]2 mM substrate, 8 mM DBP, DMF, 0.1 M TEAP, Hg-electrode, $T = 25$ °C.

A Brønsted plot of the rate constants for the cleavage of the radical anions plotted versus the pK_a in DMF of the corresponding phenol gives a linear correlation. The slope $\alpha = 0.49$ is very close to the value found for the α-aryloxyacetophenones. Thus, it is clear that these fragmentation reactions are under activation control.[16] The point for **1e** is not included in this plot. The rate constant is unusually fast for reasons which are not clear at this time. However, with this one exception, it is possible to combine these data with the data for other α-aryloxyacetophenones in a single free energy plot (Fig. 6). This plot consists of rate constants determined for 25 different compounds that cover almost 10 orders of magnitude in rate constant and 20 kcal mol^{-1} in driving force. The driving force for each reaction was estimated from a thermochemical cycle as previously described.[16] The curvature from $\alpha = 0.5$ at high driving force to $\alpha = 1$ at low driving force has been shown to be due to the

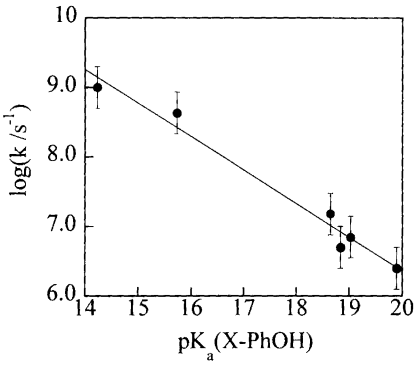


Fig. 5. Rate constants for the cleavage of the α-aryloxyacetoveratrone radical anions versus the pK_a in DMF of the corresponding phenol.

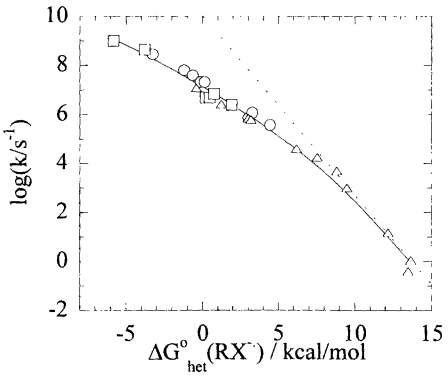


Fig. 6. Plot of the rate constants for cleavage of acetophenone ring substituted α-phenoxyacetophenones (△), phenoxy ring substituted α-phenoxyacetophenones (○), and phenoxy ring substituted α-phenoxyacetoveratrones (□) versus the overall free energy change (driving force) for the process (data from this work and references 14–16). The dotted line represents the limiting slope at $\alpha = 1$.

transition from activation (rate limiting k_3) to 'counter-diffusion' control [i.e. equilibrium in eqn. (3) followed by rate limiting k_4].[16,19] All of the acetoveratrone data fall on this curve confirming that the intrinsic barrier for the cleavage (≈ 8 kcal mol^{-1}) is independent of substituent.

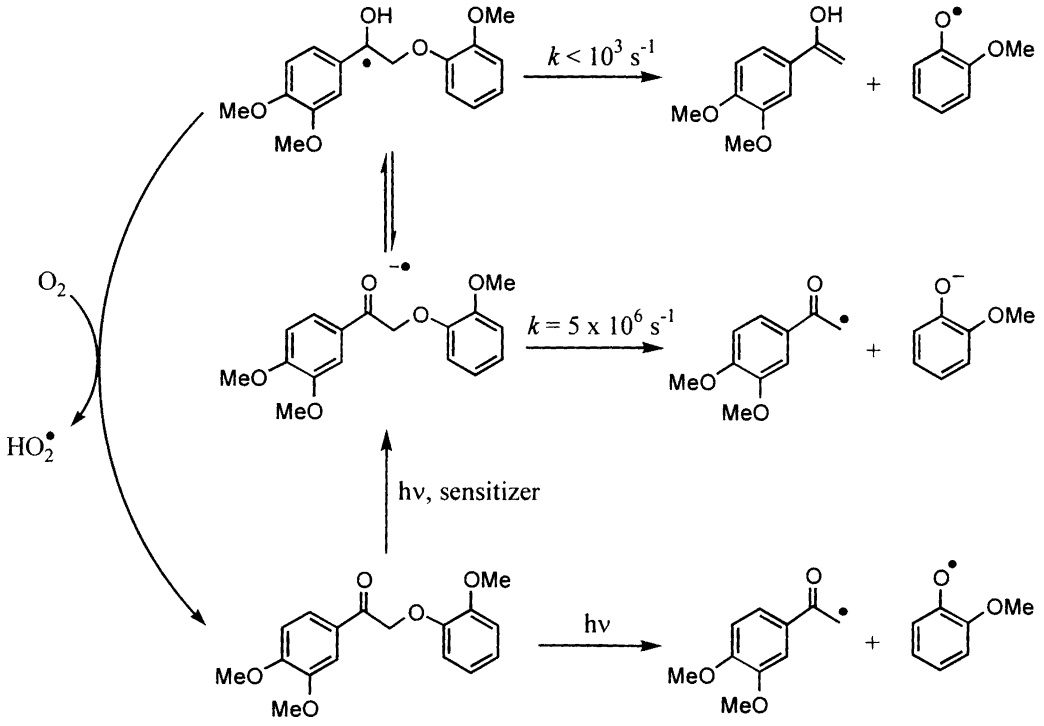
$$RX^{-\cdot} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (R^{\cdot}X^{-})_{cage} \quad (3)$$

$$(R^{\cdot}X^{-})_{cage} \xrightarrow{k_4} R^{\cdot} + X^{-} \quad (4)$$

Implications to the mechanism of photo-yellowing. One of the key reactions believed to lead to the formation of phenoxyl radicals from the degradation of lignin has been the cleavage of β-guaicoxyacetoveratrone ketyl radicals (Scheme 1) formed from hydrogen atom abstraction from the corresponding benzyl alcohols.[20] However, we have questioned the kinetic feasibility of this reaction, expecially in a solid matrix such as paper where diffusional separation will not compete with the strongly exothermic back reaction.[7,21] As paper tends to be somewhat basic, perhaps a more attractive mechanism may be deprotonation to form the radical anion followed by fragmentation to form phenoxide (Scheme 1). The phenoxide ion will be air oxidized to form phenoxyl radicals and ultimately *ortho*-quinones which are the species responsible for the yellow color. Alternatively, we have shown that in air, the ketyl radicals are rapidly converted into the guaiacoxyacetoveratrone with the formation of the hydroperoxyl radical (which in itself will degrade lignin).[7,21] It is likely that this reaction proceeds by addition of oxygen to form an α-hydroxyperoxyl radical followed by elimination of hydroperoxyl.[22] Furthermore, phenoxyl radicals also can be formed by direct photolysis of the ketone,[2-5] or possibly by photoinduced electron transfer from electron-rich alkoxystilbenes that are present in the paper.

Conclusions

The E° value of **1a** has been determined by using a correlation of E° values for acetophenones and α-aryloxyacetophenones. In combination with the ^{13}C shift of the carbonyl group it was possible to estimate the E° values of the remaining α-aryloxyacetoveratrones. The E° values allowed the determination, by digital simulation methods, of the cleavage rates of a series of α-aryloxyacetoveratones which are related to one of the key lignin substructures. The cleavage of these radical anions are under activation control and fall on the same free energy curve with all of the α-aryloxyacetophenone derivatives studied previously. A radical anion mechanism cannot be ruled out as one of the chemical reactions contributing to the photoinduced degradation of lignin leading to photo-yellowing of paper (Scheme 1). The rate constant for fragmentation of α-guaiacoxyacetoveratrone (**1b**) radical anion is from three to five orders of magnitude faster than the β-cleavage of the corresponding ketyl radical. It is likely that the strategies to prevent or inhibit photo-yellowing of paper will have to be re-evaluated to take these other mechanistic possibilities into account.



Scheme 1.

Experimental

N,N-Dimethylformamide (DMF) was distilled from CaH_2 under argon at a reduced pressure. Tetraethylammonium perchlorate (TEAP) was recrystallized three times from ethanol–water (80:20 v/v) and dried at 40 °C in a vacuum oven. Acetoveratrone (**2**) (Aldrich) was used as received. The α-aryloxyacetoveratrones, **1a–g**, were synthesized according to a known procedure.[4,23] The following new α-aryloxyacetoveratrones were synthesized.

α-(m-*Trifluoromethylphenoxy)acetoveratrone* (**1e**). M.p. 144–145 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.94 (s, 3 H), 3.96 (s, 3 H), 5.29 (s, 2 H), 6.92 (d, J=8 Hz, 1 H), 7.10 (dd, J=8 Hz, J=2Hz, 1 H), 7.18–7.25 (m, 2 H), 7.39 (t, J=8 Hz, 1 H), 7.55 (d, J=2 Hz, 1 H), 7.63 (dd, J=8 Hz, J=2 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.99 (–OCH_3), 70.42 (CH_2), 110.11, 111.84, 117.95, 118.14, 122.62, 130.01 (aromatic CH), 123.73 (CF_3, q, J=272 Hz), 127.39 (*C*–CO), 131.83 (*C*–CF_3, q, J=33 Hz), 140.30 (*C*–OMe), 154.02 (*C*–OMe), 158.14 (*C*–OCH_2), 192.09 (C=O). MS (EI$^+$): *m/z* (%) 340 (8), 321 (2), 165 (100), 145 (10), 137 (9), 122 (5), 107 (9).

α-(m-*Cyanophenoxy)acetoveratrone* (**1f**). M.p. 144–145 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.94 (s, 3 H), 3.97 (s, 3 H), 5.31 (s, 2 H), 6.93 (d, J=8 Hz, 1 H), 7.15–7.42 (m, 4 H), 7.53 (d, J=2 Hz, 1 H), 7.62 (dd, J=8 Hz, J=2 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.97 (–OCH_3), 56.07 (–OCH_3), 70.28 (CH_2), 109.76, 110.07, 117.70, 119.93, 122.55, 125.21, 130.37 (aromatic CH), 113.20 (*C*–CN), 118.44 (CN), 127.20 (*C*–C=O), 149.35 (*C*–OMe), 154.14 (*C*–OMe), 158.14 (*C*–OCH_2), 191.68 (C=O). MS (EI$^+$): *m/z* (%) 297 (10), 165 (100), 137 (6), 107 (5).

α-*Methoxyacetoveratrone* (**3**) was synthesized according to a known procedure.[24] M.p. 66–67 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.19 (s, 3 H), 3.63 (s, 3 H), 3.64 (s, 3 H), 4.36 (s, 2 H), 6.58 (d, J=8 Hz, 1 H), 7.22 (s, 1 H), 7.24 (d, J=8 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.83 (–OCH_3), 59.16 (–OCH_3), 74.83 (CH_2), 109.86, 122.18 (aromatic CH), 127.81 (*C*–C=O), 148.97 (*C*–OMe), 153.41 (*C*–OMe), 194.45 (C=O). MS (EI$^+$): *m/z* (%) 210 (8), 180 (2), 165 (100), 137 (11), 122 (6).

α-*(Phenylamino)acetoveratrones* were synthesized from 2-bromo-3′,4′-dimethoxyacetophenone[25] by using a known procedure.[26]

α-*(Phenylamino)acetoveratrone* (**4a**). M.p. 121 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.95 (s, 3 H), 3.96 (s, 3 H), 4.55 (s, 1 H), 4.57 (s, 1 H), 4.92 (br s, 1 H), 6.69–6.78 (m, 3 H), 6.92 (d, J=8 Hz, 1 H), 7.22 (t, J=7 Hz, 2 H), 7.56 (d, J=2 Hz, 1 H), 7.64 (dd, J_1=8 Hz, J_2=2 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 49.71 (CH_2), 56.03 (OMe), 109.93, 110.17, 112.95, 117.63, 122.13 and 129.27 (aromatic CH), 128.06 (*C*–C=O), 147.16 (*C*–NH), 149.23 (*C*–OMe), 153.78 (*C*–OMe), 193.50 (C=O). MS (EI$^+$): *m/z* (%) 271 (23), 165 (20), 106 (100), 77 (20).

α-*(*o-*Methoxyphenylamino)acetoveratrone* (**4b**). M.p. 117–118 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.90 (s, 3 H), 3.96 (s, 3 H), 3.97 (s, 3 H), 4.59 (s, 2 H), 5.42 (br s, 1 H), 6.61 (dd, J_1=8 Hz, J_2=2 Hz, 1 H), 6.75 (td, J_1=8 Hz, J_2=2 Hz, 1 H), 6.82 (dd, J_1=8 Hz, J_2=2 Hz, 1 H), 6.89 (td, J_1=8 Hz, J_2=2 Hz, 1 H), 6.93 (d, J=8 Hz, 1 H), 7.58 (d, J=2 Hz, 1 H), 7.66 (dd, J_1=8 Hz, J_2=2 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 49.77 (CH_2), 55.47 (OMe), 56.09 (OMe), 109.63, 110.04, 110.17, 117.00, 121.11 and 122.17 (aromatic CH), 128.30 (*C*–C=O), 137.34 (*C*–NH), 147.22 (*C*–OMe), 149.24 (*C*–OMe), 153.72 (*C*–OMe), 193.62 (C=O). MS (EI$^+$): *m/z* (%) 301 (34), 165 (8), 136 (100), 121 (30), 107 (6), 93 (6), 77 (13).

α-*(*p-*Methoxyphenylamino)acetoveratrone* (**4c**). M.p. 117 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.76 (s, 3 H), 3.96 (s, 3 H), 3.97 (s, 3 H), 4.55 (s, 2 H), 4.65 (br s, 1 H), 6.68 (d, J=9 Hz, 2 H), 6.83 (d, J=9 Hz, 2 H), 6.93 (d, J=8 Hz, 1 H), 7.57 (d, J=2 Hz, 1 H), 7.64 (dd, J_1=8 Hz, J_2=2 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 50.81 (CH_2), 55.81 (OMe), 56.10 (OMe), 109.98, 110.17, 114.25, 114.98 and 122.18 (aromatic CH), 128.20 (*C*–C=O), 141.65 (*C*–NH), 149.28 (*C*–OMe), 152.32 (*C*–OMe), 153.79 (*C*–OMe), 194.04 (C=O). MS (EI$^+$): *m/z* (%) 301 (31), 165 (12), 136 (100), 121 (7), 108 (6), 92 (6), 77 (10).

α-*(*m-*Trifluoromethylphenylamino)acetoveratrone* (**4d**). M.p. 127 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.96 (s, 6 H), 4.57 (s, 2 H), 5.20 (br s, 1 H), 6.84–6.99 (m, 4 H), 7.29 (t, J=8 Hz, 1 H), 7.57 (s, 1 H), 7.66 (d, J=8 Hz 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 50.49 (CH_2), 56.00 (–OCH_3), 108.69, 109.87, 110.17, 113.90, 116.23, 122.30, 129.58 (aromatic CH), ca. 124 (CF_3; q, J=270 Hz), 127.70 (*C*–CO), 131.50 (*C*–CF_3, q, J=32 Hz), 147.23 (*C*–$NHCH_2$), 149.23 (*C*–OMe), 153.96 (*C*–OMe), 193.01 (C=O). MS (EI$^+$): *m/z* (%) 339 (23), 320 (3), 174 (56), 165 (100), 145 (8), 137 (7).

α-*(*p-*Cyanophenylamino)acetoveratrone* (**4e**). M.p. 200–201 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.97 (s, 3 H), 3.98 (s, 3 H) 4.58 (s, 2 H), 5.51 (br s, 1 H), 6.68 (d, J=9 Hz, 2 H), 6.95 (d, J=9 Hz, 1 H), 7.48 (d, J=9 Hz, 2 H), 7.56 (d, J=2 Hz, 1 H), 7.63 (dd, J_1=8 Hz, J_2=2 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 48.62 (CH_2), 56.15 (OMe), 99.33 (*C*–CN), 109.93, 110.24, 112.60, 122.35 and 133.82 (aromatic CH), 120.30 (CN), 127.51 (*C*–C=O), 149.41 (*C*–OMe), 150.02 (*C*–NH), 154.26 (*C*–OMe), 192.09 (C=O). MS (EI$^+$): *m/z* (%) 296 (16), 165 (100), 131 (28).

Electrochemistry. Cyclic voltammetry was performed with a PAR Model 173 potentiostat equipped with a PAR Model 179 digital coulometer and a Model 175

signal generator. The output from the potentiostat was filtered using a PAR 189 selective amplifier in the low pass mode before being digitized and stored by a Tektronix TDS 620 oscilloscope. The frequency of the selective amplifier (in Hz) was set to 100 times the scan rate (in $V\,s^{-1}$). Noise originating from the power lines (60 Hz) was reduced by triggering the signal generator and oscilloscope from a home built phase-sensitive trigger unit and averaging an even number of scans.

The electrochemical cell contained 5 ml of solution purged by argon. The mercury working electodes were made by electrolytically depositing mercury onto a Pt disk electrode (0.5 mm diam.). The counter electrode was a platinum wire. The reference electrode was made by immersing a silver wire into DMF containing 0.1 M TEAP in a glass tube with a sintered glass bottom. All potentials are reported versus ferrocene/ferrocenium as an internal standard. For further experimental details see Ref. 14.

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