oxides in quantitative yields (Table I).

General Procedure for Oxidation of Phosphines and Arsines with Sulfuryl Chloride Fluoride. A slight excess of sulfuryl chloride fluoride (11 mmol) is added to a stirred solution of the phosphine or arsine (10 mmol) in dichloromethane (25 mL) at room temperature. The reaction mixture was stirred for 1 h, and then it was quenched with 10% aqueous sodium bicarbonate solution (25 mL) and extracted with dichloromethane (2 × 20 mL). The organic extract was dried over anhydrous sodium sulfate and the solvent evaporated. The crude products were purified by crystallization.

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Registry No. **1a**, 603-35-0; **1b**, 1038-95-5; **1c**, 6224-63-1; **1d**, 6163-58-2; **1e**, 1159-54-2; **1f**, 4731-53-7; **1g**, 998-40-3; **1h**, 1486-28-8; **1i**, 603-32-7; **2a**, 791-28-6; **2b**, 797-70-6; **2c**, 6151-88-8; **2d**, 6163-63-9; **2e**, 4576-56-1; **2f**, 78-50-2; **2g**, 814-29-9; **2h**, 2129-89-7; **2i**, 1153-05-5; SO_3, 7446-11-9; $ClSO_2F$, 13637-84-8.

Electrochemistry of Cyclopentadienones

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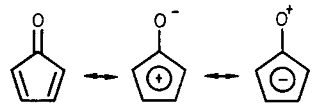
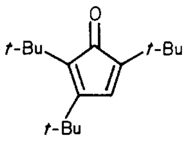
Received September 7, 1982

Although electrochemical techniques have been used occasionally for the demonstration of interesting properties of molecules (for example, in Breslow's classic demonstration of the relative antiaromaticity of cyclobutadiene derivatives[1]), there has evolved only little general appreciation of the power of cyclic voltammetry for the solution of problems in physical organic chemistry. We report in this note an electrochemical study of some cyclopentadienone derivatives that demonstrates how a simple electrochemical experiment can provide a rapid characterization of the molecular orbitals relevant to the chemical behavior of these compounds.

The extent of delocalization in annulenones is an important test for theories of aromaticity. Whether [5]-annulenone, cyclopentadienone 1, behaves as a normal enone or as a significantly polarized species (as in resonance contributor **1a**, where normal carbonyl polarization generates a potentially antiaromatic cyclopentadienyl cation, or as in contributor **1b**, where a cyclopentadienyl anionic delocalized systems ensues) is a question of theoretical interest.



1 1a 1b



2

Although electrochemical characterization of 1 would provide valuable information regarding the energies of the relevant frontier orbitals, the well-established proclivity of the parent cyclopentadienone to dimerization[2,3a] precludes its direct study. Alkylation with bulky substituents provides a steric barrier to such cycloaddition reactions, however, and permits study of the monomeric derivatives. We report here our investigation of the redox potentials of 2,3,5-tri-*tert*-butylcyclopentadienone (2)[3b] and several of its simple derivatives.[3c] In this series, we find an irreversible oxidation (E_{pa} = +1.68 V vs. SCE for 2) and two quasi-reversible one-electron reductions (−1.48 and −2.41 V vs. SCE for 2), the first of which occurs at a potential much less negative than one would expect from localized models (Figure 1).[4]

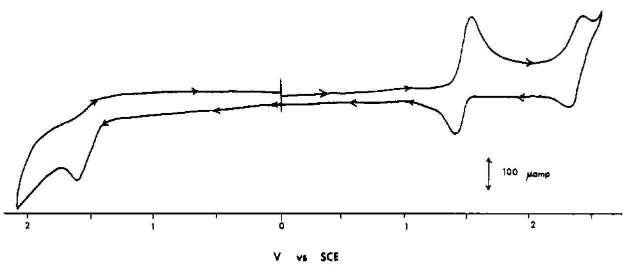


Figure 1. Cyclic voltammogram of 2: 5 × 10^{-3} M in acetonitrile containing 0.1 M tetrabutylammonium perchlorate; room temperature; scan rate 500 mV/s; glassy carbon working electrode; platinum coil counterelectrode.

Some information about the molecular orbitals of substituted cyclopentadienones is available. For example, Garbisch and co-workers had earlier studied the absorption spectra, and hence the HOMO–LUMO gaps, of alkylated derivatives of 1.[5] In a more definitive study, Schweig, Maier, and co-workers found photoelectron spectroscopic evidence for a strong inductive effect of the carbonyl group (which is probably partially compensated by the effect of the alkyl groups) on the lowest energy ionization ($\pi(a_2)$ MO with a node along the C=O bond).[6] Since cyclic voltammetry can, in principle, provide valuable information regarding the energies of both the HOMO and LUMO, we wished to compare the electrochemical descriptions of these orbitals with those obtained by these other techniques. It is clear, however, from both absorption data and from ionization potentials, that substituent effects must be quantitatively examined before conclusions can be made regarding the energy of the LUMO of 1.

The reduction potentials of compound 2 and some related model systems are listed in Table I.

These values allow for an evaluation of the LUMO energy of 1, a value not previously available for this family of compounds. The quasi-reversible reduction of 2 occurs at potentials much less negative than might be expected from model compounds. We can estimate a reasonable value for a localized (resonance contributor 1) model for the electronic properties of 1 in the following way. To a first approximation, a localized 1 might be expected to exhibit redox behavior analogous to that observed in a

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[†] Department of Chemistry.

[‡] Institut für Organische Chemie.

(1) Breslow, R.; Grubbs, R.; Murahashi, S. I. *J. Am. Chem. Soc.* **1970**, *92*, 4139.

(2) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261.

(3) (a) Maier, G.; Lage, H. W.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 976. (b) Maier, G.; Bosslet, F. *Tetrahedron Lett.* **1972**, 1025. (c) Franz, L. H. Dissertation, Giessen, 1982.

(4) Cyclic voltammetry was performed in a standard three-electrode cell with a Princeton Applied Research Model 173 potentiostat equipped with a Universal Programmer. The current–voltage curves were recorded on a Houston Instruments *x*–*y* recorder. Experimental conditions are listed in the caption for Figure 1.

(5) Garbisch, E. W., Jr.; Sprecher, R. F. *J. Am. Chem. Soc.* **1966**, *88*, 3434; *Ibid.* **1969**, *91*, 6785.

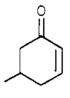
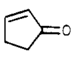
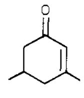
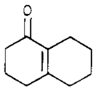
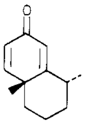
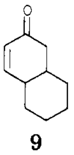
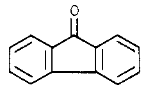
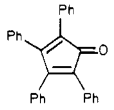
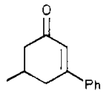
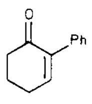
(6) Schäfer, W.; Schweig, A.; Maier, G.; Sayrac, T. *J. Am. Chem. Soc.* **1974**, *96*, 279.

(7) House, H. O.; Huber, L. E.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 8471.

(8) Given, P. H.; Peover, M. E. *J. Chem. Soc.* **1960**, 465.

0022-3263/83/1948-1762$01.50/0

Table I. Half-Wave Reduction Potentials for Some Enones and Dienones

compd	$E_{1/2}$, V vs. SCE	reference
2	−1.48, −2.41	this study
 **3**	−2.18	this study
 **4**	−2.07	7
 **5**	−2.16	7
 **6**	−2.22	7
 **7**	−2.34	7
 **8**	−2.01	7
 **9**	−2.15	7
 **10**	−1.29	7
 **11**	−0.83, −1.40	8
 **12**	−1.71	7
 **13**	−1.96	7

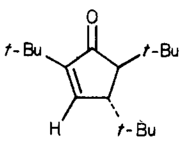
cyclohexadienone, e.g., **3**,[9] where contiguous interaction of a cyclic π system is not possible. A correction must be made for the geometric changes inherent in comparing six- and five-membered rings, however. Fortunately, extensive work by House and co-workers allows for easy determination of ring size and substituent effects on cyclohexenone reduction potentials.[7] We correct the observed reduction potential of **2** by using a value of −0.09 V (**4** vs. **5**) for the ring-size correction, −0.15 V (**4** vs. **6**) for β-alkylation, and −0.12 V (**6** vs. **7**) for α-alkylation. Even allowing for an unusual positive shift in the reduction potential for alkyl-eclipsing steric interactions (+0.17 V as in **3** vs. **8**; +0.07 V as in **6** vs. **9**), we estimate a upper limit for the potential for the first reduction of localized **2**, no more positive than −2.49 V, at least 1 V more negative than observed here. Our observed value is nearly as positive as that reported for the extensively delocalized fluorenone **10** ($E_{1/2}$ = −1.29 V).[7]

The only other monocyclic cyclopentadienone derivative whose electrochemistry has been studied is tetraphenylcyclopentadienone (**11**), a compound in which, like fluorenone, extensive delocalization into the adjacent π system is likely. Using analogous reasoning, together with the values for phenyl substitution (**4** vs. **12** and **4** vs. **13**),[10] we calculate a reduction potential for a localized version of **11** which is 0.86 V more negative than observed.

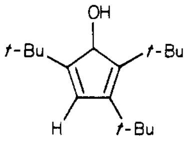
That these approximations for substituent effects represent reasonable estimates for the potential shifts is established by comparison of the effects observed upon further substitution of the cyclopentadienone derivatives[3] listed in Table II. In fact, the shifts observed upon further alkylative substitution with sterically bulky groups (**2** vs. **14**, **15**, or **16**) suggest that the allowance made for these effects in the above estimations render our crude estimate of the effect of delocalization a lower limit. Our estimation of the effect on the reduction potential of α-phenyl substitution is reasonably confirmed in this series (**14** vs. **17** or **18**) and the shift observed with pentafluorophenyl substitution (**19**) can undoubtedly be attributed to inductive effects within the substituent. The additional irreversible reduction in **20** probably involves reductive cleavage of the vinyl halide rather than reduction of the cyclopentadienoid π system.

In both **2** and **11** we attribute the unexpected ease of reduction to contributions of resonance contributor **1a** and/or **1b**, less of an effect being observed when charge can be effectively dispersed onto adjacent substituents. These reduction potentials fully support the inference from photoelectron spectroscopy that polar contributors are important in describing the electronic character of **1**.[6] Thus, either the cyclic delocalized four-electron system induced by normal carbonyl polarization in **1a** or the inverted carbonyl polarization induced by electronic requirements for ring aromaticity in **1b** renders cyclopentadienone much more reducible than a localized model would predict.

Characterization of isolated products obtained upon electroreduction of cyclopentadienones should, under nonequilibrating conditions, allow assignment of the LUMO character. Preparative electrolytic reduction of **2**, however, gives rise to a mixture dominated by the thermodynamic product, enone **21**,[11] and an uncharacterized acetonitrile adduct ($C_{19}H_{31}NO$). Specifically, no hydrodimer analogous to **16** or alcohol **22** could be detected in the product mixture. Parallel results were also observed in the preparative reduction of **11**.[8] Since previous studies have established



21



22

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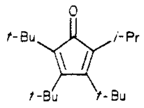
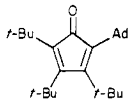
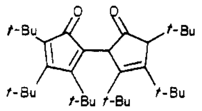
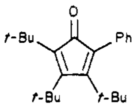
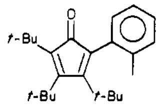
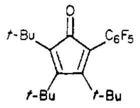
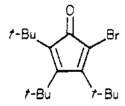
[9] Zimmerman, H. E.; Hackett, P.; Juers, D. F.; McCall, J. M.; Schröder, B. J. Am. Chem. Soc. 1971, 93, 3653.

[10] No correction has been made for eclipsing of phenyls at adjacent positions since nearly no difference in reduction potential is observed in the cis and trans isomers of enones.[7]

[11] Maier, G.; Pfriem, S.; Schäfer, U.; Malsch, K. D.; Matusch, R. Chem. Ber. 1981, 114, 3965.

Table II. Redox Potentials of Some Monomeric Cyclopentadienones

compd	reduction potential, ($E_{1/2}$, V vs. SCE)	oxidation peak potential (E_{pa}, V vs. SCE)	HOMO-LUMO gap λ_{max}, nm	
			calcd	found
 **14**	−1.94, −2.81	+1.20	395	430
 **15**	−1.83, −2.52	+1.24	404	434
 **16**	−1.85, −2.14	+1.37, +1.78	385	430
 **17**	−1.49, −2.30	+1.46	420	430
 **18**	−1.51, −2.37	+1.45	419	432
 **19**	−1.37, −2.35	+1.71	402	420
 **20**	−1.40, −1.56, −2.22	+1.48	430	434

that the LUMO of cyclopentadienone, in analogy to fulvene, is of b_1 character, initial protonation should occur on oxygen, giving rise to a hydroxycyclopentadienide anion, protonation and enolization of which could lead to the observed product.

Valuable information regarding electronic transitions can also be obtained from the cyclic voltammetric trace shown in Figure 1. For example, easy calculation of the HOMO-LUMO gap for this molecule can be accomplished by measuring the separation between the oxidative peak potential and the reductive half-wave potential. This difference, 3.16 V, converts to an expected absorption maximum for 2 of 392 nm (cf. 420 nm observed[3b]). Although irreversible peak potentials lack thermodynamic significance, their use in such calculations often gives reasonable results, as is observed here. Similarly, the frequently observed linearity of the relationship between the solution-phase oxidation peak potential and the gas-phase ionization potential[12] allows for easy prediction of HOMO energies. Using the peak potential from Figure 1, we calculate an ionization energy of 8.5 eV (cf. 8.50 eV observed in the photoelectron spectrum of 2,5-di-*tert*-butylcyclopentadienone[6]).

Finally, since the net effect observed upon alkylation was a shift to a more negative potential, it seems clear that inductive interactions of the alkyl groups dominate over hyperconjugative effects.

Experimental Section

Apparatus. Ultraviolet and visible spectra were recorded on a Cary 14 spectrometer in spectral-grade hexane.

Both cyclic voltammetry and preparative electrolyses were performed with a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a Universal Programmer. The current-voltage curves were recorded on a Houston Instruments x-y recorder, and current flow was monitored using a PAR Model 179 digital coulometer. The electrochemical cell was a standard three-electrode cell modified by a side arm for adding solids. The cell was equipped with a glassy carbon working electrode (0.05 cm^2), a platinum coil counterelectrode, and a silver wire reference electrode.

Electrochemistry. Vacuum-dried electrolyte (tetrabutylammonium perchlorate, Southwest Analytical) was placed in the electrochemical cell before it was attached to a vacuum line for overnight evacuation under modest warming (ca. 50 °C). Sufficient solvent was then added to the cell by syringe to make a 0.1 M electrolyte solution. The mixture was then degassed by repeated freeze-pump-thaw cycles, and the solvent window was scanned (between −3.5 and +2.5 V) to ensure the absence of air, water, or other impurities. The cyclopentadienone of interest was then injected to make a solution of approximately 5 mM concentration. All peak potential measurements were conducted at room temperature.

Electrolysis of 2. Preparative electroreduction of 2 (104 mg) was accomplished on a platinum disk electrode in methanolic

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[12] Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308.

acetonitrile (1:10) made 0.2 M in Bu_4NClO_4. A constant potential of −1.6 V vs. SCE was applied to the resulting solution at room temperature until 2 Faraday/mol had been taken up. After electrolysis, the reduction mixture was taken up in ether and stripped of solvent. The infrared spectrum of the crude product mixture showed no absorption in the OH stretch region. The components of the mixture were isolated by preparative gas–liquid chromatography (5 ft × 0.25 in. 20% SE-30 on 100-mesh Chromosorb P, 150 °C). The first fraction exhibited spectral properties identical with those of an authentic sample of **21**.[11] The second fraction was characterized by high-resolution mass spectrometry (Du Pont CEC 21-110 instrument) as an acetonitrile adduct of **2**. The absence of hydrodimer was established by the absence of a peak upon injection of the crude mixture at the retention volume of an authentic sample of the analogous hydrodimer **16**.

Acknowledgment. We are grateful to the National Science Foundation and to the Robert A. Welch Foundation for financial support of this research. M.A.F. is grateful for support as an Alfred P. Sloan Research Fellow and as a Camille and Henry Dreyfus Teacher–Scholar.

Registry No. **2**, 36319-95-6; **3**, 1073-14-9; **14**, 80451-50-9; **15**, 85293-79-4; **16**, 85293-80-7; **17**, 80451-51-0; **18**, 85293-81-8; **19**, 85293-82-9; **20**, 66808-99-9; **21**, 85293-83-0.

Conversion of Aldehydes into Geminal Diacetates[1]

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S. N. Rajadhyaksha, and Harold W. Pinnick*

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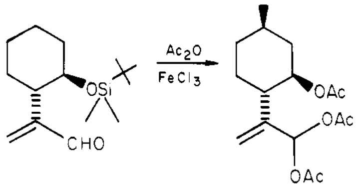
Received June 28, 1982

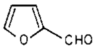
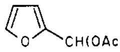
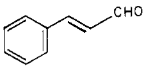
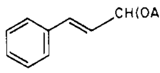
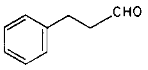
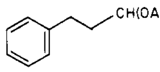
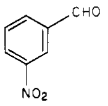
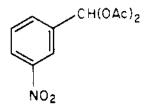
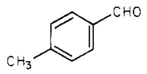
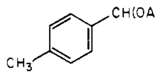
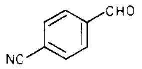
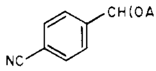
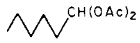
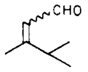
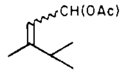
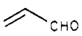
Aldehydes react with anhydrides under acid catalysis to give geminal diacetates, but the yields are usually poor.[2,3] There is keen interest in the development of an efficient method for preparing these compounds because the derived enol acetate is a particularly useful product,[4] especially when the aldehyde is α,β-unsaturated so that the enol acetate is an acetoxybutadiene.[5] This elimination reaction has been accomplished with either weak base[4,5b] or acid catalysis.[6]

During a study aimed at the synthesis of α-methylene lactones,[7] a new preparation of a geminal diacetate was discovered (eq 1).[8] This provides an interesting protecting group for aldehydes[9] because this functionality should have moderate stability to acid and yet should be removable under very mildly basic conditions. This nicely complements the commonly used acetal aldehyde protecting groups.[9]



(1)

Table I. Geminal Diacetates from Aldehydes

aldehyde	diacetate	% yield[a,b]	acetal CH chemical shift, ppm
C_6H_5CHO	$C_6H_5CH(OAc)_2$	79[c]	7.67
CH_3CH_2CHO	$CH_3CH_2CH(OAc)_2$	57	6.72
		60[c]	7.70
		60[c]	7.33[d]
		89	6.85
		93[c]	7.73
		93[c]	7.63
		85[c]	7.32
		63	6.65
		70	7.35
	$CH_2{=}CHCH(OAc)_2$	64	7.03

[a] The percent yields are not maximized. In most cases, the value given is from a single experiment. [b] All yields refer to pure isolated products. [c] Solids. [d] This value is approximate because of overlapping aromatic signals.

In order to examine the feasibility of these systems as protecting groups and synthetic intermediates, we explored the scope of this reaction by examining a variety of aldehydes (see Table I). Both aromatic and aliphatic aldehydes give good, although unmaximized, yields of the corresponding geminal diacetates. For example, benzaldehyde gives α,α-diacetoxytoluene in 79% yield, and 1,1-diacetoxyhexane is obtained in 65% yield from hexanal. In addition, aromatic aldehydes bearing either electron-donating or -withdrawing groups work with equal facility (the yields from benzaldehyde, *m*-nitrobenzaldehyde, *p*-tolualdehyde, and *p*-cyanobenzaldehyde all lie in the range 79–93%). Furthermore, all of these reactions are remarkably fast. All systems were complete in less than 30 min in contrast to the results of Miller.[3] Finally, α,β-unsaturated aldehydes also react. Elimination of acetic acid from these systems bearing a γ hydrogen leads to 1-acetoxybutadienes.[4,5]

The stability of these geminal diacetates has been studied. Thus, they are stable when stirred with either methanol overnight or 10% aqueous HCl in methanol for 30 min. Furthermore, neither 10% aqueous sodium carbonate and ether for 70 min nor sodium bicarbonate in aqueous THF for 4 h has any effect. Complete conversion

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(1) Protecting Groups in Organic Synthesis. 8. For part 7, see: Barot, B. C.; Pinnick, H. W. *J. Org. Chem.* **1981**, *46*, 2981.

(2) Thiele, J.; Winter, E. *Justus Liebigs Ann. Chem.* **1960**, *311*, 355.

(3) A recent paper outlines the use of phosphorus trichloride as a catalyst for this reaction with good results: Michie, J. K.; Miller, J. A. *Synthesis* **1981**, 824. This paper contains an excellent historical account of this reaction.

(4) For example, see: (a) Wichterle, O.; Hudlicky, M. *Czech. Collect. Chem. Commun.* **1947**, *12*, 564. (b) Georgieff, K. K.; Dupre, A. *Can. J. Chem.* **1960**, *38*, 1070. (c) Blanc, P. Y. *Helv. Chim. Acta* **1961**, *44*, 1.

(5) These are especially useful in Diels–Alder reactions. For example: see Snider, B. B.; Amin, S. G. *Synth. Commun.* **1978**, *8*, 117.

(6) (a) Hagemeyer, H. J.; Hull, D. C. *Ind. Eng. Chem.* **1949**, *41*, 2920. (b) McDonald, E.; Suksamrarn, A.; Wylie, R. D. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1893.

(7) Bal, B. S.; Pinnick, H. W. *Heterocycles* **1981**, *16*, 2091.

(8) Acetic anhydride and ferric chloride convert *tert*-butyldimethylsilyl ethers into acetate esters: Ganem, B.; Small, V. R., Jr. *J. Org. Chem.* **1974**, *39*, 3728.

(9) For other protecting groups for aldehydes, see: Greene, Theodora W. "Protective Groups in Organic Synthesis"; Wiley: New York, 1981.

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