$$\frac{k_n}{k_{H_2O}} = \frac{(1 - n + nl^{1-\alpha})^2(1 - n + nl^{1+2\alpha}k_{D_2O}/k_{H_2O})}{(1 - n + nl)^3} \quad (22)$$

α parameter, corresponding to the exponent α of the Brönsted correlations, are known.

For enol ketonization eq 22 must also be obeyed. In Figures 4 and 5, $(k_{-1})_n/(k_{-1})_{H_2O}$ for different H_2O-D_2O mixtures is compared with the curves calculated for different arbitrary values of α. The values of $(k_{-1})_n/(k_{-1})_{H_2O}$ have been determined from the variations of $(k_{-1}/(k_2^{Br_2})_g)_n/(k_{-1}/(k_2^{Br_2})_g)_{H_2O}$ with two different assumptions: (a) the constant $(k_2^{Br_2})_g$ is independent of n (Figure 4)[32] and (b) the bromination constant varies linearly with the fluidity $(1/\eta)^{36}$ of the H_2O-D_2O mixtures (Figure 5).[32] Depending on which of these hypotheses is taken, the experimental points are either above or below the curve calculated for $\alpha = 0.5$, showing that the isotope effect on the enol bromination rate is probably overestimated by hypothesis (b). However, in

(36) The viscosities of a mixture of two solvents A and B are generally calculated from Bingham's law $(1/\eta = x_A/\eta_A + x_B/\eta_B)$ where η_A, η_B, x_A, and x_B are the viscosities and the molar fraction of A and B. This law has been found to be approximately valid for H_2O-D_2O mixtures: G. Jones and H. L. Fornwalt, *J. Chem. Phys.*, **4**, 30 (1936).

view of the experimental errors, no more definite conclusion can be drawn. The value of $\alpha = 0.5$ is consistent with the observed variations in r. These results confirm the parallelism of the mechanisms of enol ketonization and the hydrolysis of the corresponding ethers.

Experimental Section

Reagents. Sulfuric and perchloric acids were R. P. (Prolabo-France). Heavy water (Spin et Technique-Paris) was at least 99.8% pure. Solutions of D_2SO_4 (Fluka) were prepared in an inert atmosphere. The deuterium content of the acetone-d_6 (Spin et Technique — 99% min) was checked by mass spectroscopy (at 70 eV) on a Thompson 206C apparatus. The peak at m/e 63 is attributed to $CD_2HCOCD_3^+$, and that at 62 to the fragmentation ion $CD_3COCD_2\cdot^+$ (by analogy with the spectrum of acetone which has a similar peak of the same relative magnitude at 57 and attributed to $CH_3COCH_2\cdot^+$). The CD_2HCOCD_3 fraction was determined by comparison with the peak at 65, which corresponds to CD_3COCD_3 molecules in which one of the atoms is ^{13}C.

Kinetic Measurements. The amperometric method for the determination of rates was similar to that previously described.[11] For measurements in deuterated media, argon was passed over the solution before the introduction of the acetone and then interrupted to avoid evaporation of acetone and halogen during the reaction.

Electroorganic Chemistry. XII.[1] Anodic Oxidation of Enol Esters

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Abstract: Electrochemical oxidation of a number of enol esters was carried out at a carbon rod anode in acetic acid. The products consisted of four types of compounds: conjugated enones, α-acetoxy carbonyl compounds, *gem*-diacetoxy compounds, and triacetoxy compounds. The product distribution was influenced by the structure of the starting compound. The oxidation of the enol ester prepared from α-alkylcycloalkanone gave the conjugated enone exclusively. The product structure, the current–potential relationship, and the polarographic oxidation potential suggest a mechanism involving an initial electron transfer from the enol ester to the anode followed by proton ejection or nucleophilic attack of the solvent.

In our continuing study on the anodic oxidation of a series of aliphatic compounds, the main research interest focussed on the formation and reaction of the unstable electron-deficient intermediates which are difficult to generate in solution by the usual chemical methods.

It has been clarified that the anodic oxidation of an olefin is initiated by an electron transfer from the unsaturated bond to the anode and that the lowering of the oxidation potential of the unsaturated system is a favorable factor in the anodic oxidation.[2]

Thus, an enol ester, easily obtainable from the corresponding ketone, is expected to show the oxidation potential which is accessible by the anodic oxidation technique, and the active intermediate anodically gen-

erated from an enol ester should show quite interesting chemical behavior.[3]

Indeed, the anodic oxidation of enol esters gave a novel and remarkable synthesis of α-acyloxy or α,β-unsaturated carbonyl compounds.

Results

Preparative Oxidation of Enol Acetates. The preparative oxidation of enol acetates (**1–14**) was carried out at room temperature in acetic acid containing

(1) Paper XI: T. Shono and M. Mitani, *Tetrahedron*, **28**, 4747 (1972).

(2) (a) T. Shono and A. Ikeda, *J. Amer. Chem. Soc.*, **94**, 7892 (1972); (b) V. D. Parker and L. Eberson, *Chem. Commun.*, 340 (1969).

(3) Typical reactions of enol esters: H. C. Brown and R. L. Sharp, *J. Amer. Chem. Soc.*, **90**, 2915 (1968); A. Suzuki, K. Ohmori, and M. Itoh, *Tetrahedron*, **25**, 3707 (1969); D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967); R. J. P. Allan, J. McGee, and P. D. Ritchie, *J. Chem. Soc.*, 4700 (1957); R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5535 (1968).

Table I. Product of Anodic Oxidation of Enol Ester in Acetic Acid[a]

Enol ester	Anode potential (V vs. sce)	Type a	Product (% yield) Type b	Type c	Type d
1	1.9		1b (23)	1c (8)	1d (7)
2[b]	d		2b (27)		
3	1.8	3a (trace)	3b (20)		
4	2.1	4a (55)	4b (3)		
5[b]	1.9		5b (41)		
6	2.0		6b (73)		
7[b]	d		7b (53)		
8	1.8	8a (9) (0.9)[c]	8b (21) (39)[e]		
9	1.4	9a (49)			
10	1.4	10a (58)[c]			
11	d	11a (3.3)	11b (37)		
12	2.0	12a (57)			
13	1.4	13a (48)			
14	2.1	14a (68)			

[a] Supporting electrolyte was Et₄N–OTs. [b] Mixture of cis and trans isomers. [c] Aqueous solution (10%) of tetraethylammonium hydroxide was used as a supporting electrolyte. [d] The anode potential was not measured, but it was estimated to be about 1.8–2.0 V vs. SCE. [e] The isolated yield was improved to 97% after 2.5 faraday/mol of electricity was passed.

tetraethylammonium p-toluenesulfonate (Et₄N–OTs) as a supporting electrolyte. The electrode was a carbon rod and the anode potentials were in the range of 1.4–2.1 V vs. SCE. The products consisted of four types of compounds: conjugated enones (type a), α-acetoxy carbonyl compounds (type b), gem-diacetoxy compounds (type c), and triacetoxy compounds (type d). The results are summarized in Table I, in which the yields shown were not optimized but were measured at the time when 2 faraday/mol of electricity was passed. The yield may be improvable, and an almost quantitative yield was observed in one case (e.g., 10).

The anodic oxidation of the enol acetate in a solvent other than acetic acid was investigated in acetonitrile and in propionic acid using 1-cyclohexenyl acetate (8) as a typical substrate. Interestingly, α-acetoxycyclohexanone was obtained as one of the products in both solvent systems, and, unlike the result in acetic acid, the addition of water brought about a remarkable increase in the yield of α-acetoxycyclohexanone. The results are indicated in Table II.
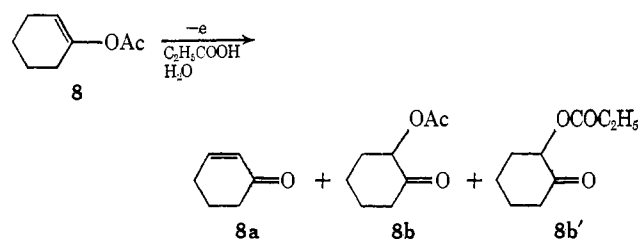
**Table II.** The Anodic Oxidation of 1-Cyclohexenyl Acetate (8)[a]

Run	Solvent (mol)	H₂O, mol	Faraday/ mol	Product yield, % 8a[b]	8b[c]	8b[d]
1	AcOH (0.50)	e	2.0	8.5	20.5	
2	AcOH (0.50)	0.45	2.0	5.1	20.2	
3	CH₃CN (0.70)	e	1.0	4.3	3.3	
4	CH₃CN (0.50)	0.40	1.0	7.3	19.9	
5	C₂H₅COOH (0.50)	e	1.3	1.0	4.0	5.3
6	C₂H₅COOH (0.45)	0.25	1.0	9.0	12.9	15.5

[a] Supporting electrolyte was Et₄N–OTs. [b] 2-Cyclohexenone. [c] α-Acetoxycyclohexanone. [d] α-Propionyloxycyclohexanone. [e] Commercial anhydrous solvent was used.

Current–Potential Curve and Polarographic Oxidation Potential. The current-potential curve shown in Figure 1 clearly demonstrates that the addition of 1-cyclohexenyl acetate to the solvent system brings about a notable increase in current suggesting that the oxidation reaction is initiated by the electron transfer from the enol ester to the anode. A similar current–potential relationship was observed in the oxidation of the other enol acetates. The half-wave oxidation potentials of enol acetates in acetonitrile (Table III) suggest that these acetates are oxidizable in acetic acid since the related olefins showing similar oxidation potentials are anodically oxidizable in acetic acid.[2a]

Discussion

On the bases of the current–potential relationship, the structures of products, and the mechanism of the anodic oxidation of olefins, the general reaction route may be depicted as shown in Scheme I, in which the initiation step is the one-electron oxidation of the enol ester to generate a cation radical, and the second electron is eliminated in concert with the proton ejection of the nucleophilic attack of the solvent.
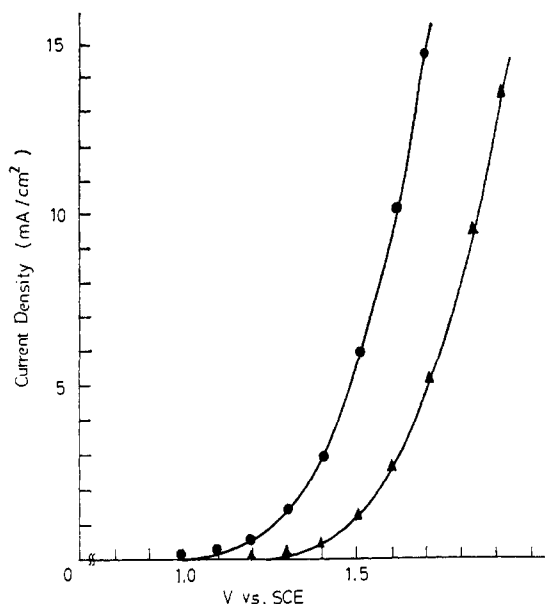
Figure 1. Current–potential curve of 1-cyclohexenyl acetate (8): (▲) AcOH–Et₄N·OTs (0.16 *M*) system, (●) AcOH–Et₄N·OTs (0.16 *M*)–8 (1.60 *M*) system.

Table III. Half-Wave Oxidation Potential of Enol Acetates and Related Olefins[a,b]

Enol acetate	$E_{1/2}$, V *vs.* SCE	Enol acetate and olefin	$E_{1/2}$, V *vs.* SCE
1	1.82	10	1.72
2[c]	2.09	12	1.48
3	1.83	13	1.46
4	1.63	14	1.44
5[c]	1.74	A	2.17
6	1.59	B	1.48
7[c]	1.57	C	1.96
8	1.93	D	2.14
9	1.60	E	1.70

[a] The concentration of enol acetate and olefin was 2×10^{-4} *M*. [b] Supporting electrolyte, lithium perchlorate. [c] Mixture of cis and trans isomers.
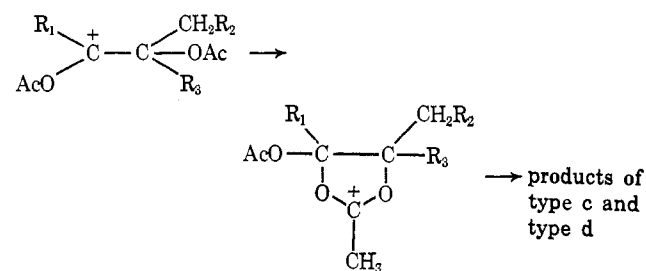
Scheme I
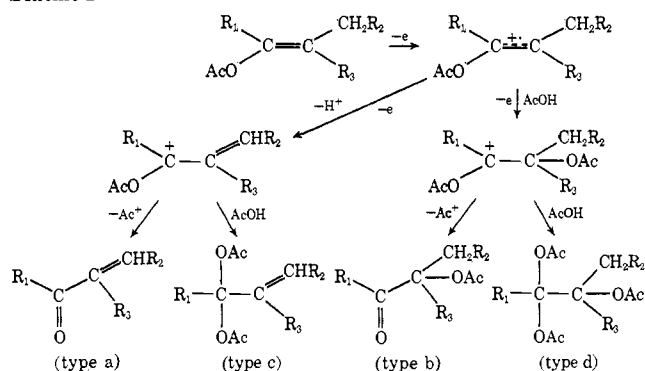
Although any product which suggests the formation of a radical intermediate[4] was not detected, the proton elimination or the solvent attack prior to the transfer of the second electron may not be denied.

In the cationic intermediates bearing acetoxy group on the neighboring position of the positive center, the

(4) H. Schäfer and E. Steckhan, *Angew. Chem.*, 81, 532 (1969).

participation of the acetoxy group may be possible as shown below.


→ products of type c and type d

The elimination of acetyl cation[5] shown in Scheme I is in agreement with the fact that the formation of acetic anhydride was observed in the reaction mixture. The thermal or electrolytic transformation of the type b product to the type a seems improbable, since the compound 9b[6] prepared independently was thermally stable
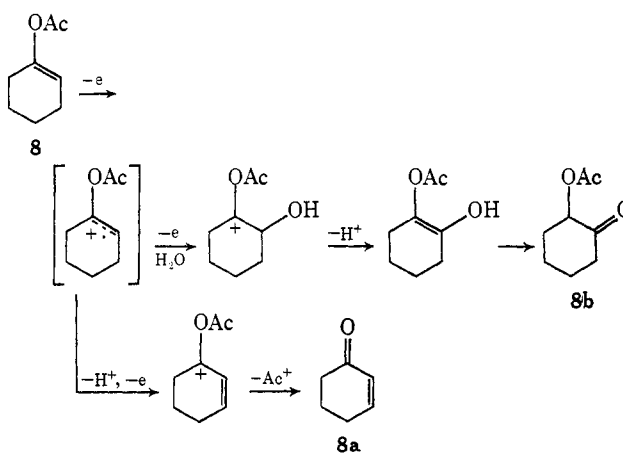

9b
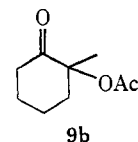
and inert for the anodic oxidation under the same condition. Thus, the reaction route of the electrooxidation of 1-cyclohexenyl acetate in acetic acid could be shown as Scheme II.

Scheme II
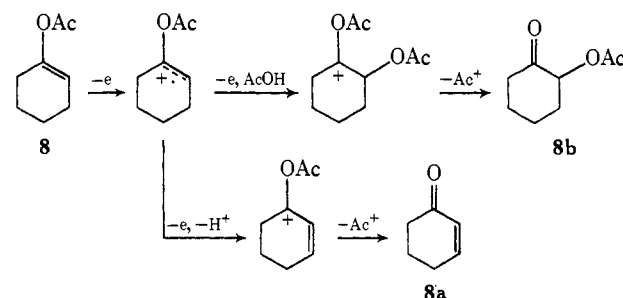
Scheme III

The curious result that α-acetoxycyclohexanone was obtained even in the solvent system of acetonitrile–water or propionic acid–water, where the concentration

(5) V. D. Parker, *Chem. Commun.*, 610 (1969).
(6) E. W. Warnhoff and W. S. Johnson, *J. Amer. Chem. Soc.*, 75, 495 (1953); K. L. Williamson, R. T. Keller, G. S. Fonken, J. Symuszkoviez, and W. S. Johnson, *J. Org. Chem.*, 27, 1612 (1962). The compound 9b was separated from its mixture with 2-methyl-6-acetoxycyclohexanone by preparative gas chromatography.

of acetate ion as a nucleophile would be negligible, may be explained by the attack of water to the initially generated cation radical as shown in Scheme III.

The remarkably low yield of α-acetoxycyclohexanone in the almost anhydrous acetonitrile or propionic acid may endorse this pathway. However, this reaction route may be minor in acetic acid, since the oxidation of enol acetates **2** and **5** in acetic acid did not give the products **15** and **16** which suggest the existence of this pathway.
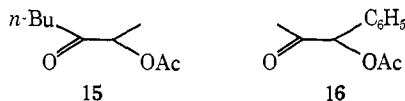
Although the factors which control the distribution of the four types of products are not clarified as yet, the main factor controlling the reaction pathway in the series of the cycloaliphatic enol acetates may be the steric hindrance of the α-alkyl group.

The α-alkyl group would obstruct the introduction of an acetoxy group in this α position. This kind of steric hindrance seems common in the anodic substitution reaction.[2a]

The exclusive and almost quantitative formation of α,β-unsaturated ketone from the enol acetate of α-alkylcycloalkanone shows the noteworthy synthetic potentialities.

Experimental Section

Materials. In the preparative experiments, commercial glacial acetic acid was used. Acetonitrile was distilled from phosphorous pentoxide three times before use in the polarographic experiments. 1-Acetoxy-2-methylpropene (**1**),[7] 2-acetoxy-2-heptene (**2**),[8] 1-acetoxy-1-phenylpropene (**5**),[8] 1-cyclohexenyl acetate (**8**),[8] and 1-acetoxycyclopentene (**11**)[9] were prepared by the reported methods. The other acetates were prepared according to the similar procedure as the method[8] of Bedoukian.

Procedures. The preparative experiments were carried out according to the following standard procedure. Into a 100-ml electrolysis cell fitted with two carbon electrodes were placed 0.05 mol of the enol ester, 0.005 mol of Et₄N-OTs, and 0.50 mol of glacial acetic acid. The constant current (0.1 A) was passed through the cell which was externally cooled with water. After 2 faraday/mol of electricity was passed, water was added to the reaction mixture and it was extracted with three portions of ether. The combined ethereal layer was washed with aqueous sodium bicarbonate and water successively and then dried on magnesium sulfate overnight. Magnesium sulfate was removed by filtration and the residue was distilled.

All products were isolated by glc and identified with spectroscopic methods and elemental analyses and/or by comparison with authentic samples. The identification of acetic anhydride which is formed in the anodic oxidation reactions in acetic acid was also performed by the same method.

Electrolysis of 1. Products consisted of 2-methyl-2-acetoxypropionaldehyde (**1b**), 2,2-diacetoxy-1-methylpropene (**1c**), and 2-methyl-1,1,2-triacetoxypropane (**1d**). Yields are shown in Table I. **1b**: ir 2820, 2720 (aldehyde), 1730, 1260, and 1140 cm⁻¹ (ester); nmr (CCl₄) τ 0.30 (s, 1, CHO), 7.97 (s, 3, CH_3CO), and 8.43 (s, 6, CH_3). *Anal.* Calcd for C₆H₁₀O₃: C, 55.37; H, 7.75. Found: C, 54.96; H, 7.86. **1c**: ir 3100, 1650 (olefin), 1760, 1240, 1200, and 1000 cm⁻¹ (ester); nmr (CCl₄) τ 3.06 (s, 1, CH), 4.85 (d, 2, CH_2=), 7.95 (s, 6, CH_3CO), and 8.20 (s, 3, CH_3). *Anal.* Calcd for C₈H₁₂O₄: C, 55.80; H, 7.03. Found: C, 55.51; H, 7.03. **1d**: ir 1760, 1240, and 1020 cm⁻¹ (ester); nmr (CCl₄) τ 3.24 (s, 1, CH(OAc)₂), 7.93 (s, 6, CH_3OCO), 8.05 (s, 3, CH_3OCO), and 8.52 (s, 6, CH_3). *Anal.* Calcd for C₁₀H₁₆O₆: C, 51.72; H, 6.94. Found: C, 52.00; H, 7.18.

Electrolysis of 2. 3-Acetoxy-2-heptanone (**2b**) was generated exclusively. **2b**: ir 1740 (carbonyl), 1730, and 1250 cm⁻¹ (ester); nmr τ 5.10 (t, 1, CHOAc), 7.94 (s, 3, CH_3OCO), 7.95 (s, 3, CH₃CO), and 8.00-9.20 (m, 9, CH_3, CH_2, CH_2, CH_2). *Anal.* Calcd for C₉H₁₆O₃: C, 62.76; H, 9.36. Found: C, 62.89; H, 9.58.

Electrolysis of 3. Products were 2,4-dimethyl-2-acetoxy-3-pentanone (**3b**) and trace amounts of 2,4-dimethyl-1-penten-3-one (**3a**). **3a**: ir 3100, 1630 (olefin), and 1670 cm⁻¹ (carbonyl); nmr (CCl₄) τ 4.2 (d, 2, CH_2=), 6.80 (m, 1, CHCO), 8.13 (s, 3, CH_3C=), 8.90 (d, 6, CH_3). **3b**: ir 1730, 1260, 1150, 1040, and 1020 cm⁻¹ (ester and carbonyl); nmr (CCl₄) 7.07 (m, 1, CHO), 7.96 (s, 3, CH_3OCO), 8.52 (s, 6, CH_3CO), and 8.95 (d, 6, CH_3). *Anal.* Calcd for C₉H₁₆O₃: C, 62.76; H, 9.36. Found: C, 63.02; H, 9.46.

Electrolysis of 4. Products, 1-cyclohexenyl methyl ketone (**4a**) and a small amount of 1-acetoxy-1-acetylcyclohexane (**4b**), were obtained. **4a**: ir 3060, 1640 (olefin), 1665, and 1250 cm⁻¹ (ester); nmr (CCl₄) τ 3.20 (m, 1 CH=), 7.50-8.05 (m, 4, CH_2C=), 7.80 (s, 3, CH_3CO), and 8.40 (m, 4, CH_2). **4b**: ir 1720 and 1240 cm⁻¹ (ester); nmr (CCl₄) τ 7.90 (s, 3, CH_3CO), 8.00 (s, 3, CH_3OCO), and 7.60-8.80 (m, 10, CH_2). *Anal.* Calcd for C₁₀H₁₆O₃: C, 65.19; H, 8.75. Found: C, 65.15; H, 8.67.

Electrolysis of 5. The product was 1-phenacyl-1-acetoxyethane (**5b**) exclusively. **5b**: ir 3080, 1600 (phenyl), 1740 (ester), and 1700 cm⁻¹ (carbonyl); nmr (CCl₄) τ 2.10 (m, 2, ortho H), 2.54 (m, 3, meta and para H), 4.10 (q, 1, CHOCO), 7.90 (s, 3, CH_3CO), and 8.50 (d, 3, CH_3). *Anal.* Calcd for C₁₁H₁₂O₃: C, 68.73; H, 6.29. Found: C, 68.98; H, 6.41.

Electrolysis of 6. 2-Phenacyl-2-acetoxypropane (**6b**) was given in an excellent yield. **6b**: ir 3090, 1600 (phenyl), 1740 (ester), and 1690 cm⁻¹ (carbonyl); nmr (CCl₄) τ 2.08 (m, 2, ortho H), 2.63 (m, 3, meta and para H), 8.16 (s, 3, CH_3OCO), and 8.35 (s, 6, CH_3). *Anal.* Calcd for C₁₂H₁₄O₃: C, 69.88; H, 6.84. Found: C, 69.72; H, 6.59.

Electrolysis of 7. 2-Acetoxy-2-phenacylbutane (**7b**) was generated exclusively. **7b**: ir 3080, 1600 (phenyl), 1740 (ester), and 1690 cm⁻¹ (carbonyl); nmr (CCl₄) τ 2.10 (m, 2, ortho H), 2.65 (m, 3, meta and para H), 7.60-8.20 (m, 2, CH_2), 8.17 (s, 3, CH_3OCO), 8.40 (s, 3, CH_3), and 8.50 (t, 3, CH_3); mass spectrum peak, m/e 177 (P − 43), 105 (P − 115).

Electrolysis of 8. Products consisting of 2-cyclohexenone (**8a**) and 2-acetoxycyclohexanone (**8b**) were obtained. **8a** showed the same infrared spectrum as an authentic sample;[10] mass spectrum peak, m/e 96. **8b**: ir 1750 and 1720 cm⁻¹ (ester); nmr (CCl₄) τ 4.96 (m, 1, CHOCO), 7.40-8.60 (m, 8, CH_2), and 7.90 (s, 3, CH₃-OCO). *Anal.* Calcd for C₈H₁₂O₃: C, 61.52; H, 7.75. Found: C, 61.33; H, 7.85.

Electrolysis of 9. 2-Methyl-2-cyclohexenone (**9a**) was generated exclusively. **9a**: ir 3040 (olefin) and 1670 cm⁻¹ (carbonyl); nmr (CCl₄) τ 3.30 (m, 1, CH=), 7.40-8.40 (m, 6, CH_2), and 8.30 (s, 3, CH_3). *Anal.* Calcd for C₇H₁₀O: C, 76.32; H, 9.15. Found: C, 76.20; H, 9.21.

Electrolysis of 10. 2-Methenone (**10a**) was obtained quantitatively after 2.5 faraday/mol of electricity was passed. **10a**: ir 3050 (olefin), and 1670 cm⁻¹ (carbonyl); nmr (CCl₄) τ 3.47 (m, 1, CH=), 6.80-8.30 (m, 6, CH_2 and CH), and 9.00 (d, 9, CH_3). *Anal.* Calcd for C₁₀H₁₆O: C, 78.89; H, 10.59. Found: C, 78.80; H, 10.72.

Electrolysis of 11. A mixture of two products, 2-cyclopentenone (**11a**) and 2-acetoxycyclopentanone (**11b**), was obtained. **11a** was identified spectroscopically by comparison with an authentic sample.[11] **11b**: ir 1740 and 1240 cm⁻¹ (ester); nmr (CCl₄) τ 5.1 (t, 1, COCHOCO), 7.40-8.50 (m, 6, CH_2), and 7.93 (s, 3, CH_3OCO). *Anal.* Calcd for C₇H₁₀O₃: C, 59.14; H, 7.09. Found: C, 58.91; H, 7.21.

Electrolysis of 12. The electrolysis product was 2-methyl-2-cyclopentenone (**12a**). **12a**: ir 3060, 1640 (olefin), and 1700 cm⁻¹ (carbonyl); nmr (CCl₄) τ 2.77 (m, 1, CH=), 7.30-7.80 (m, 4, CH_2), and 8.28 (d, 3, CH_3); mass spectrum parent peak, m/e 96.

Electrolysis of 13. 2-Ethyl-2-cyclopentenone (**13a**) was obtained exclusively. **13a**: ir 3060, 1630 (olefin), and 1700 cm⁻¹ (carbonyl); nmr (CCl₄) τ 2.80 (m, 1, CH=), 7.30-8.10 (m, 6, CH_2), and 8.90 (t, 3, CH_3). *Anal.* Calcd for C₇H₁₀O: C, 76.32; H, 9.15. Found: C, 76.04; H, 9.40.

Electrolysis of 14. 2-Isopropyl-2-cyclopentenone (**14a**) was obtained. **14a**: nmr (CCl₄) τ 2.80 (m, 1, CH=), 7.20-7.80 (m, 5, CH_2 and CH), and 8.90 (d, 6, CH₃); mass spectrum parent peak,

(7) P. Z. Bedoukian, *J. Amer. Chem. Soc.*, **66**, 1326 (1944).
(8) P. Z. Bedoukian, *J. Amer. Chem. Soc.*, **67**, 1430 (1945).
(9) L. Goodman, A. Benitez, C. D. Anderson, and B. R. Baker, *J. Amer. Chem. Soc.*, **80**, 6582 (1958).

(10) W. F. Gannon and H. O. House, *Org. Syn.*, **40**, 41 (1960).
(11) C. H. Depuy and K. L. Eilers, *J. Org. Chem.*, **24**, 1380 (1959).

m/e 124. *Anal.* Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.10; H, 9.93.

Electrolysis of 8 in AcOH Containing Et₄NOH. A mixture of 7.0 g (0.05 mol) of **8**, 1.5 g of 10% aqueous Et₄NOH, and 30.0 g (0.50 mol) of acetic acid was electrolyzed. The isolated yields of **8a** and **8b** were 0.9 and 31%, respectively.

Electrolysis of 8 in AcOH–H₂O. Two kinds of solvents (commercial glacial acetic acid and 55% aqueous acetic acid) were used. Products, **8a** and **8b**, were obtained in each case. The yields of **8a** and **8b** were determined by vpc after 2 faraday/mol of electricity was passed (see Table II).

Electrolysis of 8 in CH₃CN. The reactions were carried out in two kinds of solvents (100% acetonitrile and 55% aqueous acetonitrile). The products, **8a** and **8b**, were identified by comparison of vpc retention times and ir spectra with those of authentic samples. The yields of **8a** and **8b** were determined by vpc (Table II).

Electrolysis of 8 in CH₃CH₂CO₂H. Two kinds of solvents (100% propionic acid and 65% aqueous propionic acid) were used. Products were **8a**, **8b**, and **8b′**. Compounds **8a** and **8b** were identified by comparison of vpc retention times and ir spectra with those of authentic samples. **8b′**: ir 1720 and 1180 cm⁻¹ (ester); nmr (CCl₄) τ 4.95 (m, 1, C*H*OCO), 7.30–8.50 (m, 10, C*H₂*), and 8.80 (t, 3, C*H₃*). *Anal.* Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.73; H, 8.48.

Polarographic Oxidation Potential. All polarographic data were obtained at room temperature on an Yanaco P-8DP (Yanagimoto Co. Ltd). Oxidations were carried out in dry acetonitrile at a rotating platinum electrode with 0.1 M LiClO₄ as a supporting electrolyte using an aqueous saturated calomel reference electrode. The concentration of substrates was 2×10^{-4} M and an H-type electrolysis cell was used. All enol esters showed one oxidation wave. The results are shown in Table III.
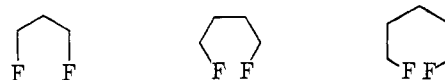
Substituent Effects on Through-Space ¹⁹F–¹⁹F Coupling in the 1,8-Difluoronaphthalene System

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Abstract: F–F coupling constants for a series of 4-substituted 1,8-difluoronaphthalenes were determined from measurements of the ¹⁹F nmr spectra of these compounds. Arguments are presented that the observed variation of J_{FF} with substituent reflects primarily a steric effect of the C-4 substituent on the F–F distance and hence on the through-space F–F coupling in this system.

Through-space interactions[2,3] are believed to be chiefly responsible for the especially large fluorine-fluorine nuclear spin–spin coupling constants that have been observed for intramolecularly crowded fluorines in many different systems of the three structural types shown below.[4] A few selected examples of through-space F–F coupling are indicated in Figure 1.

(1) Taken in part from the Senior Honors Paper of M.-C. F., Bryn Mawr College, 1969.

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(3) For recent theoretical views of these interactions, see (a) M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969); (b) K. Hirao, H. Nakatsuji, H. Kato, and T. Yonezawa, *ibid.*, **94**, 4078 (1972); (c) K. Hirao, H. Nakatsuji, and H. Kato, *ibid.*, **95**, 31 (1973); (d) F. B. Mallory, *ibid.*, **95**, 7747 (1973).

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An earlier study[4h] of a series of substituted 4,5-difluorophenanthrenes (see Figure 1) revealed that J_{FF} was quite insensitive to the nature of the substituent although the fluorine chemical shifts varied considerably. As a generalization of this result, it was suggested that the lack of response of the value of J_{FF} to changes in substituent, when ¹⁹F chemical shifts are significantly influenced by those changes, might be a distinguishing criterion for through-space F–F coupling.[4h] We report herein our studies of F–F coupling in a series of 4-substituted 1,8-difluoronaphthalenes, the results of which have led us to propose that the above-mentioned criterion should be qualified.

Syntheses. The 4-substituted 1,8-difluoronaphthalenes **1–8** were synthesized by the reactions outlined in
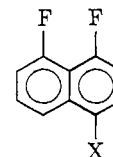
1, X = H   5, X = NO₂
2, X = Br   6, X = NH₂
3, X = CN   7, X = NHCOCH₃
4, X = CH₃ 8, X = Cl

Scheme I. The best route that we found for the synthesis of **1** involves a Schiemann reaction starting with the readily available 1,8-diaminonaphthalene. Initially