(19) B. C. Challis and J. A. Challis, "The Chemistry of Amides", J. Zabicky, Ed., Interscience, New York, N.Y., 1970, p 731 ff.
(20) See, for example, S. Hanessian, *Tetrahedron Lett.*, 1549 (1967).
(21) (a) J. v. Braun and W. Pinkernelle, *Chem. Ber.*, **67**, 1218 (1934); (b) G. D. Lander, *J. Chem. Soc.*, **81**, 591 (1902).
(22) See, for example, H. W. O. Weissenburger and M. G. van der Hoeven, *Recl. Trav. Chim. Pays-Bas*, **89**, 1081 (1970).
(23) I. Shahak and Y. Sasson, *J. Am. Chem. Soc.*, **95**, 3440 (1973).
(24) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

Electroorganic Chemistry. XXI.[1] Selective Formation of α-Acetoxy Ketones and General Synthesis of 2,3-Disubstituted 2-Cyclopentenones through the Anodic Oxidation of Enol Acetates

Tatsuya Shono,* Masahisa Okawa, and Ikuzo Nishiguchi

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. *Received February 12, 1975*

Abstract: The anodic oxidation of enol acetates in acetic acid gave two types of products, namely α-acetoxy ketones (type A) and α,β-unsaturated enones (type B), and their distribution was remarkably influenced by the character of the supporting electrolyte. In the anodic oxidation of α-alkylated alicyclic enol acetates, the exclusive formation of α,β-unsaturated enones in an excellent yield was achieved by the use of tetraethylammonium tosylate (T salt). On the contrary, the employment of potassium acetate (or triethylamine) instead of T salt brought about the selective formation of α-acetoxy ketones from acyclic and α-nonalkylated alicyclic enol acetates in a sufficient yield. Furthermore, applying this anodic technique, a number of 2,3-disubstituted 2-cyclopentenones were synthesized in the satisfactory overall yield.

In our previous study,[2] it was demonstrated that the anodic oxidation of enol acetates in acetic acid using tetraethylammonium *p*-toluenesulfonate (T salt) as a supporting electrolyte gave α-acetoxy ketones (type A) and/or α,β-unsaturated carbonyl compounds (type B) (see Scheme I). The initiation process of this anodic oxidation has been established to be the electron transfer from enol ester to anode yielding a cationic species. The electrophilic attack of the cationic intermediate to the solvent gave the product of type A, whereas the proton elimination from the intermediate in concert with the second electron transfer yielded α,β-unsaturated enones (type B). The existence of the α-alkyl substituent R on the starting enol acetates was one of the main factors to control the relative rates of these two competitive pathways A and B. For instance, acyclic and α-nonsubstituted alicyclic enol acetates gave preferentially α-acetoxy ketones (type A), whereas α-alkylated alicyclic enol acetates yielded α,β-unsaturated enones (type B) exclusively.

In the present study, we report our new findings that the nature of the supporting electrolyte also possesses a significant influence on the relative rates of these competitive pathways A and B, and the selective formation of α-acetoxy ketones or α,β-unsaturated enones in a good or excellent yield is successfully attainable. Furthermore, a novel and general synthetic method of α-acetoxy ketones[3] or 2,3-disubstituted 2-cyclopentenones[4] including dihydrojasmone was established.

Results and Discussion

As shown in Table I, the use of potassium acetate (or triethylamine) instead of T salt as a supporting electrolyte generally brought about a remarkable improvement in the yield of α-acetoxy ketones (the type A product) in the anodic oxidation of enol acetates in acetic acid. Namely, the selective formation of α-acetoxy ketones **1a**–**4a** in a good yield was observed in the reaction of acyclic and α-nonalkylated alicyclic enol acetates **1**–**4**. Moreover, the introduction of an acetoxy group even to a hindered tertiary position could be achieved in the oxidation of α-alkylated alicyclic enol acetates **5** and **6** which, on the contrary, gave α,β-unsaturated enones **5b** and **6b** exclusively when T salt was used as a supporting electrolyte. When the alkyl substituent of cyclopentenyl acetates is allyl- (**7**), *trans*-2-butenyl- (**8**), or propargyl- (**9**), the anodic oxidation of them using potassium acetate (or triethylamine) gave α-acetoxy ketones **7a**, **8a**, or **9a** in a moderate yield, whereas the substitution of T salt for potassium acetate resulted in the formation of a large

Scheme I

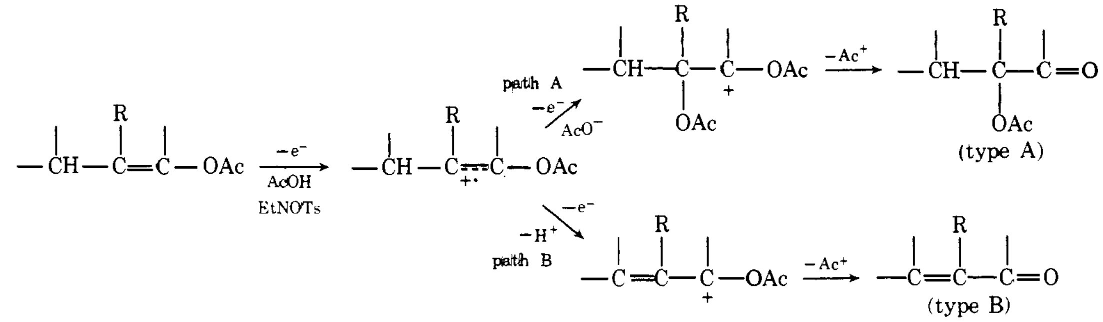
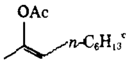
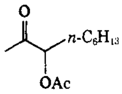
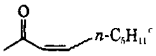
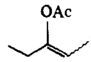
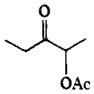
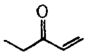
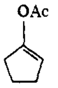
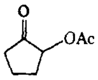
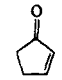
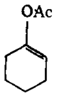
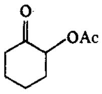
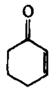
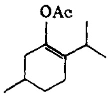
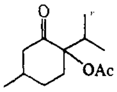
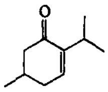
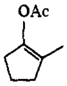
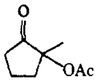
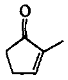
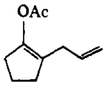
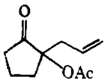
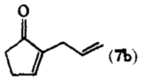
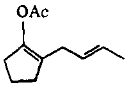
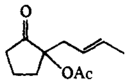
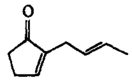
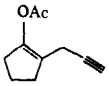
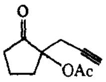
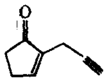


Table I. Products of Anodic Oxidation of Enol Acetates in Acetic Acid[a,b]

	Isolated yield, %, of products					
	Type A			Type B		
Enol acetates	Product	T salt	AcOK[e]	Product	T salt	AcOK[e]
 (1)	 (1a)	24	78	 (1b)	6	0
 (2)	 (2a)	14	66	 (2b)	0	0
 (3)	 (3a)	37	62	 (3b)	3	0
 (4)	 (4a)	25	88	 (4b)	9	0
 (5)	 (5a)	0	60	 (5b)	90	25
 (6)	 (6a)	0	59	 (6b)	90	24
 (7)	 (7a)	0	59	 (7b)	8	12
 (8)	 (8a)	0	43	 (8b)	d	3
 (9)	 (9a)	0	29	 (9b)	0	0

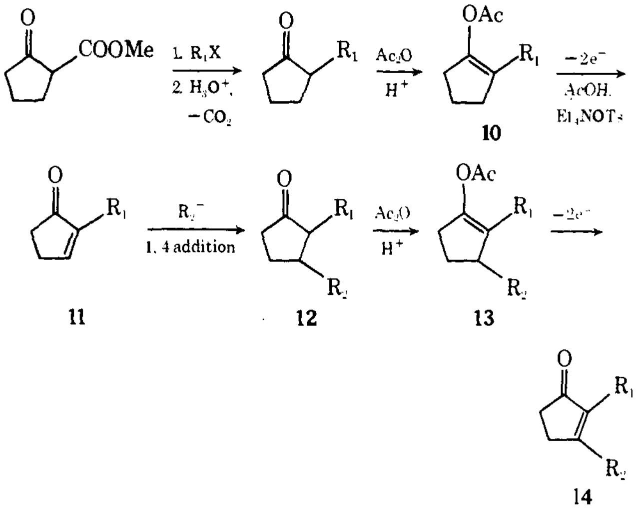
[a] Electrolysis was continued until the starting enol acetates were almost consumed (2–4 F/mol). [b] Electrolysis was carried out using carbon rod electrodes in an undivided cell externally cooled with water. [c] Mixture of cis and trans isomers. [d] Trace. [e] Or triethylamine.

amount of polymeric product accompanying a small amount of α,β-unsaturated enones **7b** or **8b** (none of **9b**).

This remarkable effect of the supporting electrolyte may substantially be attributable to the higher concentration of the acetate ion which may bring about the increase in the rate of the solvolysis of the intermediate cationic species rather than in the rate of proton elimination. A similar phenomenon was observed in the anodic acetoxylation of aromatic compounds,[5] in which the presence of acetate ion was essential for the nuclear acetoxylation, whereas the absence of the acetate ion brought about the formation of a benzylic type intermediate by the proton elimination. Thus, it is quite noteworthy that the selective formation of α-acetoxy ketones or α,β-unsaturated enones could be accomplished from the simple anodic oxidation of enol acetates.

One of the interesting applications of the specific formation of α,β-unsaturated enone from the enol acetate was the general and novel synthesis of 2,3-disubstituted 2-cyclopentenones including jasmone homologs. The synthetic process is shown in the Scheme II, and the isolated yield observed in the three key steps is summarized in Tables II and III. As shown in Tables II and III, the conjugated cyclopentenones **11a–f** and **14g–m** were obtained in good or excellent yields. From the view point of its simple experimental procedure and the considerably wide range of the variety of the substituent introduced to the cyclopentenone skeleton, the synthetic potentiality of the present anodic oxidation method would be remarkable. The overall yields of **14g–m** from 2-carbomethoxycyclopentanone were satisfactory (~15–21%).

Scheme II



Experimental Section

Materials. **2-Acetoxynonene-2 (1)**,[7] **3-acetoxypentene-2 (2)**,[8] **1-acetoxycyclopentene-1 (3)**,[9] **1-acetoxycyclohexene-1 (4)**,[10] **2-methyl-1-acetoxycyclopentene-1 (6)**,[2] **2-isopropyl-1-acetoxycyclopentene-1 (10c)**,[2] and **2-*n*-pentyl-1-acetoxycyclopentene-1 (10d)**[4a]

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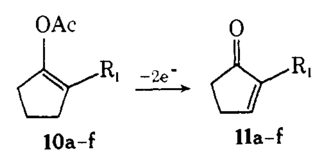
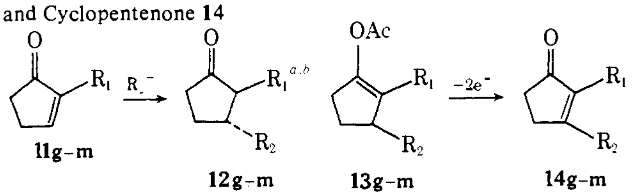
Table II. Isolated Yield of 2-Substituted Cyclopentenone **11**



	R_1	Yield, %
a	CH_3	90
b	n-C_3H_7	70
c	i-C_3H_7	89
d	n-C_5H_{11}	83
e	$(CH_2)_6COOMe$	84
f	$CH_2C_6H_5$	45

Table III. Isolated Yield of 2,3-Disubstituted Cyclopentanone **12** and Cyclopentenone **14**



	R_1	R_2	Yield of **12**, %	Yield of **14**, %
g	CH_3	CH_3	55	74
h	CH_3	i-C_3H_7	68	66
i	CH_3	C_6H_5	55	77
j	i-C_3H_7	CH_3	64	90
k	n-C_5H_{11}	CH_3	55	87[c]
l	n-C_5H_{11}	n-C_5H_{11}	41	80
m	n-C_5H_{11}	CH_2COOMe	70[c]	69

[a] Grignard reagents (for **11g–l**) in the presence of cuprous cyanide or sodium malonate (for **11m**) were used. See ref 6. [b] Presumably trans isomer: R. Pappo and P. W. Collins, *Tetrahedron Lett.*, 2627 (1972); K. F. Bernady and M. J. Weiss, *ibid.*, 4083 (1972). [c] **14k**: dihydrojasmone. **12m**: methyl dihydrojasmonate.

were prepared by the reported methods. The other enol acetates were prepared from the corresponding ketones according to the procedure similar to the method of Bedoukian[10] or House.[11] 2-Monoalkylated cyclopentanones were obtained from the C-alkylation reaction[12] of 2-carbomethoxycyclopentanone with alkyl bromides followed by acid catalyzed hydrolysis,[13] and their structures were characterized through comparison of spectroscopic and gas chromatographic behaviors with those of authentic samples.[4a,10,14-18]

General Procedure of the Anodic Oxidation of Enol Acetates in Acetic Acid Containing Potassium Acetate (or Triethylamine). The preparative experiments were carried out according to the reported standard method[2] except for using potassium acetate (or triethylamine) instead of tetraethylammonium tosylate as a supporting electrolyte. Into 100 ml of undivided electrolysis cell fitted with two carbon rod electrodes were placed 0.05 mol of the enol acetate, 0.005 mol of potassium acetate (or triethylamine), and 50 ml of commercial glacial acetic acid. The constant current (0.1 A) was passed through the cell externally cooled with water. After almost complete consumption (95–100%) of the starting acetates was observed by VPC technique, the reaction mixture was poured into 200 ml of saturated sodium chloride solution and was extracted with three 100-ml portions of ether. The combined ethereal solution was washed with aqueous sodium carbonate and saturated sodium chloride solution successively and then dried over anhydrous magnesium sulfate. After removal of the drying agent through filtration, the residue was distilled on vacuum. All products were isolated by the preparative gas chromatograph and were identified by spectroscopic methods and elemental analyses and/or by comparison with authentic samples. **1b**,[19] **2a**,[20] **3a**,[2] **3b**,[22] **4a**,[2] **4b**,[21] **5b**,[2] **6a**,[23] and **6b**[2] showed the same infrared and NMR spectra as their authentic samples.

1a: bp 75–76° (5 mm); ir 1740 and 1240 (ester), 1720 cm^{-1} (carbonyl); NMR (CCl_4) τ 9.1 (t, 3 H, J = 5 Hz, CH_3CH_2), 8.5–8.9 (m, 10 H, CH_2), 7.9 (s, 6 H, CH_3CO and CH_3COO), 5.1 (t, 1 H, J = 5.8 Hz, >CH–CH_2). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.67; H, 10.09.

5a: bp 81–82° (2 mm); ir 1735 and 1241 (ester), 1720 cm^{-1} (carbonyl); NMR (CCl_4) τ 8.9–9.3 (m, 9 H, CH_3), 7.3–8.5 (m, 8 H, CH_2), 7.98 and 8.03 (s, 3 H, CH_3COO). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.03; H, 9.64.

7b: bp 63–64° (15 mm); ir 3080 and 1630 (olefin), 1690 cm^{-1} (carbonyl); NMR (CCl_4) τ 6.9–8.6 (m, 6 H, CH_2), 4.7–5.2 (m, 2 H, $=CH_2$), 3.6–4.5 (m, 1 H, —CH=), 2.75 (m, 1 H, —CH= of enone); mass spectrum parent peak *m/e* 122.

7a: bp 65–66° (2 mm); ir 3080, 3020 and 1640 (olefin), 1730 (carbonyl), 1250 cm^{-1} (ester); NMR (CCl_4) τ 8.0 (s, 3 H, CH_3COO), 7.4–8.3 (m, 8 H, CH_2) 4.7–5.2 (m, 2 H, $=CH_2$), 3.9–4.7 (m, 1 H, —CH=).

8b: bp 100–101° (20 mm); ir 3020 and 1630 (olefin), 1700 cm^{-1} (carbonyl); mass spectrum parent peak *m/e* 136.

8a: bp 110–111° (4 mm); ir 3045, 1635 and 970 (olefin), 1740 (carbonyl), 1260 cm^{-1} (ester); NMR (CCl_4) τ 8.27 (m, 3 H, CH_3), 8.03 (s, 3 H, CH_3COO), 7.2–8.4 (m, 8 H, CH_2), 4.3–4.7 (m, 2 H, —CH=CH—). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.04; H, 8.22.

9a: bp 84–85° (2 mm); ir 3300 (acetylene), 1730 (carbonyl), 1250 cm^{-1} (ester); NMR (CCl_4) τ 8.03 (s, 3 H, CH_3COO), 7.4–8.2 (m, 9 H, CH_2 and ≡CH). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.37; H, 7.00.

2,3-Disubstituted Cyclopentanones (12g–m). 1,4-Addition of Grignard reagents in the presence of cuprous cyanide to 2-alkylated 2-cyclopentenones (**11a, 11c,** or **11d**) through the reported procedure[6a] gave the corresponding 2,3-disubstituted cyclopentanones (**12g–l**) in a moderate or good yield (Table III). **12m** was prepared from Michael reaction of **11d** with sodium malonate followed by hydrolysis and esterification according to the established method.[6b] **12g**,[24] **12i**,[25] **12k**,[4a] and **12m**[4a] were characterized by comparison of their infrared and NMR spectra with those of authentic samples. **12h, 12j,** and **12l** showed the characteristic carbonyl absorption (1730–1740 cm^{-1}) for cyclopentanone ring in their ir spectra and were used for further reactions without purification.

Anodic Oxidation of Enol Acetates 10a–f or 13g–m to α,β-Unsaturated Enones 11a–f or 14g–m. The general procedure of preparative anodic oxidation in acetic acid containing tetraethylammonium tosylate as a supporting electrolyte was the same as the previously reported standard method.[2] The isolated yields of α,β-unsaturated cyclopentenones **11a–f** and **14g–m** are summarized in Tables II and III. Among them, **11a–f**,[2,4a,26-28] **14g**,[29] **14j**,[30] **14k**,[4a] and **14m**[4a] were identified through comparison of their spectroscopic and gas chromatographic behaviors with those of authentic samples. The other α,β-unsaturated cyclopentenones were assigned by spectroscopic methods and mass spectrum parent peaks.

14h: bp 80–81° (15 mm); ir 1690 (carbonyl), 1640 cm^{-1} (olefin); NMR (CCl_4) τ 8.86 (d, J = 7.0 Hz, 6 H, methyl protons of isopropyl group), 8.38 (m, 3 H, allylic methyl protons), 7.3–8.1 (m, 4 H, $-CH_2-$), 6.97 (m, 1 H, -CH<); mass spectrum parent peak *m/e* 138.

14i: bp 108–110° (2 mm); ir 1682 (carbonyl), 3060, 1620, 760, and 695 cm^{-1} (phenyl and olefin); NMR (CCl_4) τ 8.12 (m, 3 H, CH_3), 7.65 (m, 2 H, CH_2), 6.97–7.40 (m, 2 H, CH_2), 2.58 (m, 5 H, C_6H_5); mass spectrum parent peak *m/e* 172.

14l: bp 117–118° (3 mm); ir 1698 (carbonyl), 1641 cm^{1} (olefin); NMR (CCl_4) τ 8.8 (m, 6 H, CH_3), 8.3–9.1 (m, 12 H, CH_2 of *n*-pentyl group), 7.4–8.2 (m, 8 H, CH_2 of the ring and allylic position); mass spectrum parent peak *m/e* 224.

References and Notes

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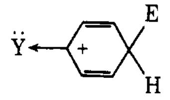
Isoinductive Resonance Substituents for Mechanism Studies. I. Application to the Norbornyl Tosylate Solvolysis Problem

George D. Hartman[1] and T. G. Traylor*

Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92093. *Received March 13, 1975*

Abstract: A series of isoinductive resonance substituents for π-electron donation has been developed. Substituents which donate π-electron density by σ–π conjugation, being carbon substituents, do not vary greatly in inductive effect. One such substituent, $-CH_2Sn(CH_3)_3$, having a $\sigma^+ = -0.92$ and the inductive effect of a methyl group, when substituted at the 1-position accelerates *exo*-2-norbornyl *p*-nitrobenzoate solvolysis by a factor of 6×10^5. This result strongly supports the theory that there is σ delocalization in the transition state for this solvolysis and demonstrates the usefulness of σ–π conjugating substituents in mechanism studies.

The separation of resonance and inductive contributions to the total electron-donating effect of substituents on electron-deficient aromatic systems (e.g., **1**) has been attempted in many ways, most of which have employed Y groups of widely varying electronegativities.[2,3] While this separation into σ^{R+} and σ^I components has met with considerable success in aromatic systems, the extension of this concept to presumed σ-delocalized systems such as cyclopropylcarbinyl or 2-norbornyl cations has led to ambiguity and disagreement.[4-9] This ambiguity apparently stems from the widely varying and unpredictable response of such σ systems to both inductive and resonance effects.



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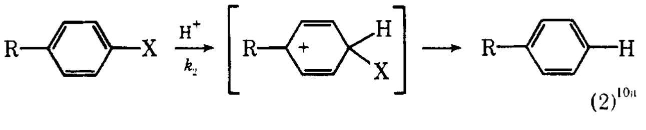
Rather than attempting to develop σ^{R+} for each new system, we decided to devise a series of isoinductive π electron donating substituents with which such separation would be unnecessary. This approach is based upon our observation that σ–π conjugation of bent or polarized σ bonds afford σ^+ values of carbon substituents from $\sigma^+ = -0.2$ to -1.2.[10] For example, $\sigma^+_{p\text{-homocubyl}} = -0.75$,[10h] and $\sigma^+_{p\text{-}CH_2SnMe_3} = -0.92$.[10a] Furthermore, a wide ranging series of σ^+ substituents with σ^+ values increasing in increments of about 0.05 can be easily attached to most chemical systems. But the important quality of these σ–π conjugating substituents is that, because they are all carbon substituents, their inductive effects are almost invariant and very near that of CH_3. Thus, the $\sigma^I{}_R$ values of $-CH_2PbPh_3$, $-CH_2SnMe_3$, and $-CH_3$ are all -0.3 as determined by charge transfer from $PhCH_2R$ to TCNE.[10a,11] A selected list of σ^+ values of σ–π conjugating substituents is shown in Table I.

Because all these substituents have σ^I values near -0.3, we can define an isoinductive σ^+ constant[12]

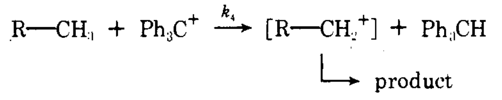
$$\text{isoinductive } \sigma^+ \equiv (\sigma^+)_I \equiv (\sigma^+)_{\sigma^I = -0.3} \equiv \left(\frac{\partial \ln k}{\partial \sigma^+}\right)_{\sigma^I} \tag{1}$$

We have already shown excellent correlation of the σ^+ values of these kinds of substituents (R) in reactions such as 2, 3, and 4.



(2)[10a]

$$R\text{—}CH_2OTos \xrightarrow[R'OH]{k_3} [RCH_2^+] \longrightarrow ROR' \qquad (3)^{10b}$$



$$R\text{—}CH_3 + Ph_3C^+ \xrightarrow{k_4} [R\text{—}CH_2^+] + Ph_3CH \qquad (4)$$
$$\quad\quad\quad\quad\quad \llcorner\!\!\longrightarrow \text{product}$$

In these cases, the electron deficiency was either localized on a carbon p orbital[10h,13] or delocalized in a π system.[10a,b,d]

We now turn to the application of these substituents to presumed σ-delocalized (nonclassical) systems where the usual σ^+ or σ^R values have not been applicable.