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Electroorganic Chemistry. XXXIV. Novel Intramolecular Cyclization through Anodic Oxidation of Enol Acetates

Tatsuya Shono,* Ikuzo Nishiguchi, Shigenori Kashimura, and Masahisa Okawa
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606

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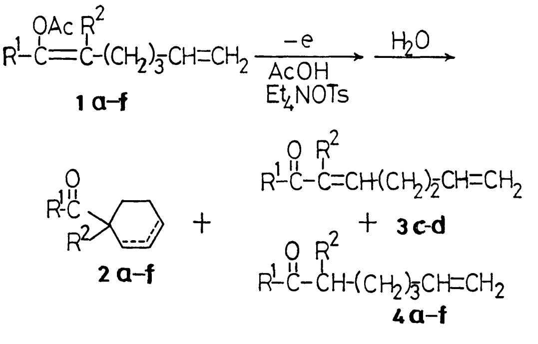
Synopsis. The anodic oxidation of 1-acetoxy-1,6-heptadiene homologues in acetic acid gave mainly intramolecular cyclization products, cyclohexenyl ketones. The cyclization takes place through the electrophilic attack of the cationic center generated from the enol ester moiety to the double bond.

It has been demonstrated by our recent studies[1,2] that the anodic oxidation of enol acetates leads to the selective formation of α,β-unsaturated enones or α-acetoxy ketones under suitably arranged conditions. Although the nature of radical cations, the first intermediates formed from the starting esters, is not necessarily clear, the product determining intermediate in the reaction may possess cationic character at the β-carbon atom of the enol acetate moiety. Thus, it seems interesting to examine the intramolecular cycloaddition between the cationic species generated by anodic oxidation of enol acetates and an olefinic bond in a reasonable position, and the formation of new carbon–carbon bond at the adjacent position to the carbonyl group.

Results and Discussions

Anodic oxidation of enol acetates **1a**—**f** in acetic acid containing tetraethylammonium *p*-toluenesulfonate as a supporting electrolyte was carried out in an undivided cell equipped with carbon rod electrodes under constant current conditions. After 4 *F*/mol of electricity was passed, the usual work-up and distillation afforded three types of products, namely the expected cyclized ketones **2a**—**f**, the conjugated enones **3c**, **d**, and the ketones **4a**—**f**[3] formed by hydrolysis of the starting enol acetates.



The results are summarized in Table 1. All the products were isolated by preparative gas chromatography, and characterized through IR, NMR, and MS analyses. Further identification of **2a**—**e** was accomplished by the comparison of spectroscopic and gas chromatographic behaviors of the corresponding saturated ketones **5a**—**e** obtained by the hydrogenation of **2a**—**e** with those of authentic samples.[4—8] Although the position of the double bond in the cyclohexenyl ring of **2a**—**f** was not definitely determined, spectroscopic and gas chromatographic analyses clearly indicated that each of **2a**—**f** was a single isomer.

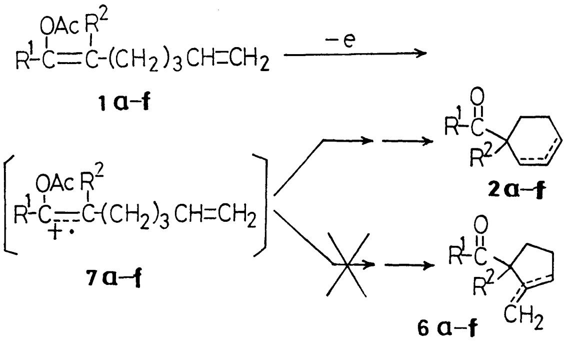
Table 1. Anodic oxidation of enol acetates **1a**—**f**

	Enol acetates 1 R¹	R²	Anodic potential (V *vs.* SCE)	Product (Yield[a,b] %) 2	3	4
a	CH_3	H	1.8—1.9	35(47)	—	25
b	CH_3	CH_3	1.8—1.9	40(47)	—	15
c	$-(CH_2)_3-$		1.8—2.0	25(28)	33(37)	10
d	$-(CH_2)_4-$		1.8—2.0	19(22)	12(14)	13
e	$-(CH_2)_5-$		1.6—1.8	18(32)	—	44
f	$-(CH_2)_6-$		2.2—2.4[c,d]	30(50)	—	40

a) Isolated. b) The number in the parentheses shows the yield calculated on the basis of the consumed **1**. Unconsumed starting esters were recovered as the ketones **4**. c) The reaction was continued until 10 *F*/mol of electricity was passed. d) Anodic oxidation of **1f** in a divided cell gave a mixture of **2f** and **4f** in 35 and 53% yields, respectively.

Extensive studies[9—11] have already been carried out on the intermolecular anodic coupling of electron-rich olefins, though the nature of the key intermediate has been not always clear. It has well been established, however, that in the intramolecular cyclization of 5-hexenyl cations or radicals, electrophilic reaction gives predominantly six-membered ring[12] products, while five-membered ring products are the main products in homolytic reaction.[13,14]

Hence, the exclusive formation of **2a**—**f** rather than **6a**—**f** from **1a**—**f** may indicate that the cyclization takes place through the electrophilic attack of the cationic center generated from the enol ester moiety to the double bond.[15]



This result may also suggest that the radical cations **7a**—**f** generated by the first electron transfer from **1a**—**f**, do not show any reactivity as a free radical.

Experimental

Preparation of Enol Acetates ***1a—f***. Nonconjugated olefinic ketones, 7-octen-2-one (**4a**),[17] 3-methyl-7-octen-2-one (**4b**),[18] 2-(4-pentenyl)cyclopentanone (**4c**),[19] 2-(4-pentenyl)cyclohexanone (**4d**),[20] 2-(4-pentenyl)cycloheptanone (**4e**), and 2-(4-pentenyl)cyclooctanone (**4f**), were prepared through β-keto ester condensation.[21,22] Enol acetates **1a**—**f** were prepared from the corresponding ketones **4a**—**f** according to the procedure similar to the method of Bedoukian[23] or House.[24] Satisfactory NMR, IR, and mass spectra were obtained for **1a**—**f** as shown below. **1a**, bp 90 °C/30 Torr; IR (neat), 3080, 3010, 1750, 1640, 1160, 910 cm^{-1}; NMR (CCl_4), δ 6.1—4.9 (3H, m, $-CH=CH_2$), 4.7—4.5 (1H, m, $\rangle C=CH-$), 2.10 (3H, s, $COCH_3$), 2.4—1.3 (9H, m, $-CH_3$ and $-CH_2-$); MS, *m*/*e* 168 (M^+). **1b**, bp 110 °C/35 Torr; IR (neat), 3080, 1750, 1640, 1140, 910 cm^{-1}; NMR (CCl_4), δ 6.2—4.6 (3H, m, $-CH=CH_2$), 2.10 (3H, s, $COCH_3$), 1.75 (3H, s, $-CH_3$), 1.7—0.9 (6H, m, $-CH_2-$); MS, *m*/*e* 182 (M^+). **1c**, bp 90 °C/2 Torr; IR (neat), 3080, 1750, 1640, 1220, 910 cm^{-1}; NMR (CCl_4), δ 6.2—4.6 (3H, m, $-CH=CH_2$), 2.05 (3H, s, $COCH_3$), 2.7—1.0 (12H, m, $-CH_2-$); MS, *m*/*e* 194 (M^+). **1d**, bp 85—87 °C/20 Torr; IR (neat), 3080, 1750, 1630, 1220, 910 cm^{-1}; NMR (CCl_4), δ 6.2—4.7 (3H, m, $-CH=CH_2$), 2.05 (3H, s, $COCH_3$), 2.0—1.9 (14H, m, $-CH_2-$); MS, *m*/*e* 208 (M^+). **1e**, bp 100—102 °C/2 Torr; IR (neat), 3080, 1740, 1630, 1210, 900 cm^{-1}; NMR (CCl_4), δ 6.3—4.8 (3H, m, $-CH=CH_2$), 2.10 (3H, s, $COCH_3$), 2.6—1.1 (16H, m, $-CH_2-$); MS, *m*/*e* 222 (M^+). **1f**, bp 95—98 °C/0.7 Torr; IR (neat), 3080, 1750, 1640, 1220, 910 cm^{-1}; NMR (CCl_4), δ 6.2—4.8 (3H, m, $-CH=CH_2$), 2.10 (3H, s, $COCH_3$), 2.5—1.1 (18H, m, $-CH_2-$); MS, *m*/*e* 236 (M^+).

General Procedure for the Anodic Oxidation of Enol Acetates ***1***. Into a 30 ml undivided electrolysis cell equipped with carbon rod electrodes and a reference electrode (SCE) was placed a solution of 0.01 mol of an enol acetate and 0.01 mol of tetraethylammonium *p*-toluenesulfonate in 10 ml of glacial acetic acid. Stirred with a magnetic bar and cooled with running water, the solution was electrochemically oxidized at the constant current of 200 mA. After 4 *F*/mol of electricity was passed, the reaction mixture was poured into 100 ml of a cold saturated potassium carbonate solution and extracted with three 50 ml portions of ether. The combined ethereal solution was dried over anhydrous magnesium sulfate and evaporated. The residue was distilled *in vacuo*. The isolated yield of the products, **2a**—**f**, **3c**, **d**, and **4a**—**f**, are summarized in Table 1. **2a**, bp 90—93 °C/30 Torr; IR (neat), 3020, 1710, 735 cm^{-1}; NMR (CCl_4), δ 5.6—5.5 (2H, m, $-CH=CH-$), 2.10 (3H, s, $-COCH_3$), 2.3—1.4 (7H, m, $-CH_2-$ and $\rangle CH-$); MS, *m*/*e* 124 (M^+). **2b**, bp 80—83 °C/20 Torr; IR (neat), 3020, 1705, 740 cm^{-1}; NMR (CCl_4), δ 5.6—5.5 (2H, m, $-CH=CH-$), 2.10 (3H, s, $-COCH_3$), 2.4—1.2 (6H, m, $-CH_2-$), 1.09 (3H, s, $-CH_3$); MS, *m*/*e* 138 (M^+). **2c**, 60—62 °C/2.0 Torr; IR (neat), 3020, 1725, 760 cm^{-1}; NMR (CCl_4), δ 5.5—5.4 (2H, m, $-CH=CH-$), 2.5—1.3 (12H, m, $-CH_2-$); MS, *m*/*e* 150 (M^+). **2d**, bp 60—63 °C/0.5 Torr; IR (neat), 3020, 1700, 760 cm^{-1}; NMR (CCl_4), δ 5.6—5.5 (2H, m, $-CH=CH-$), 2.5—1.4 (14H, m, $-CH_2-$); MS, *m*/*e* 164 (M^+). **2e**, bp 81—83 °C/0.5 Torr; IR (neat), 3010, 1700, 770 cm^{-1}; NMR (CCl_4), δ 5.7—5.5 (2H, m, $-CH=CH-$), 2.7—1.2 (16H, m, $-CH_2-$); MS, *m*/*e* 178 (M^+). **2f**, bp 91—93 °C/0.5 Torr; IR (neat), 3020, 1695, 760 cm^{-1}; NMR (CCl_4), δ 5.7—5.5 (2H, m, $-CH=CH-$), 2.7—1.2 (18H, m, $-CH_2-$); MS, *m*/*e* 192 (M^+). **3c**, bp 120 °C/25 Torr; IR (neat), 3080, 1690, 1630, 910 cm^{-1}; NMR (CCl_4), δ 7.1—7.0 (1H, m, $=CH-$ of enone), 6.0—4.7 (3H, m, $-CH=CH_2$), 2.6—0.9 (10H, m, $-CH_2-$); MS, *m*/*e* 150 (M^+). **3d**, bp 130 °C/20 Torr; IR (neat), 3080, 1670, 1640, 910 cm^{-1}; NMR (CCl_4), δ 7.2—7.1 (1H, m, $=CH-$ of enone), 6.1—4.9 (3H, m, $-CH=CH_2$), 2.7—1.0 (12H, m, $-CH_2-$); MS, *m*/*e* 162 (M^+).

Hydrogenation of **2a**—**f** was carried out by a standard method. The products, saturated ketones **5a**—**e** showed identical spectroscopic and gas chromatographic behavior with authentic samples.[4—8] Spiro[5.7]tridecan-6-one (**5f**) was characterized by IR, NMR, MS, and elemental analyses. **5f**, bp 85—87 °C/0.5 Torr; IR (neat), 1700 cm^{-1}; NMR (CCl_4), δ 2.5—2.2 (2H, m, $-COCH_2-$), 2.1—0.9 (20H, m, $-CH_2-$); MS, *m*/*e* 194 (M^+). Found: C, 80.18; H, 11.42%. Calcd for $C_{13}H_{22}O$: C, 80.35; 11.41%.

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