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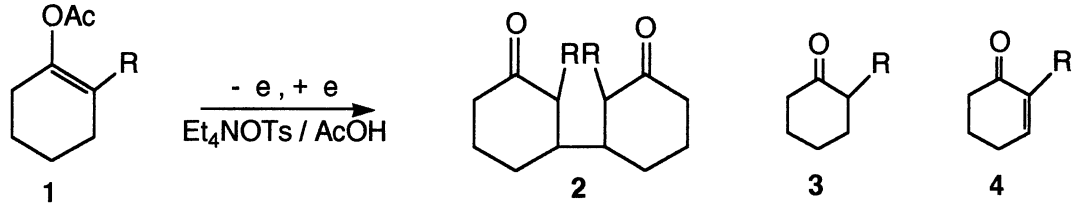
Selective Dimerization by Paired Electrolysis of Enol Acetate

Hirofumi MAEKAWA, Kazuharu NAKANO, Tsuneaki HIRASHIMA, and Ikuzo NISHIGUCHI*
Osaka Municipal Technical Research Institute,
1-6-50, Morinomiya, Jyoto-ku, Osaka 536

Electrolysis of enol esters of cyclic ketones possessing an alkyl group at the α-position using graphite carbon electrodes (EGM62 or EG10 : Nippon Carbon Co. Ltd.) brought about selective dimerization at the β-position of the ketones to give the corresponding 1,6-diketones in good to moderate yields. It was found that initial anodic formation of α,β-unsaturated ketones was successively followed by cathodic hydrodimerization (paired electrolysis) in an undivided cell.

It has been reported that anodic oxidation of enol esters in acetic acid containing Et_4NOTs as a supporting electrolyte using graphite carbon electrodes (provided by YUASA Battery Co. Ltd.) gave α,β-unsaturated ketones in good yields.[1)]

In this study, we wish to present selective and facile formation of 1,6-diketones **2**, dimerization products at the β-position of cyclic ketones **3** possessing an alkyl group at the α-position, by paired electrolysis of enol acetates **1** of **3** in AcOH using graphite carbon electrodes (EGM62 or EG10 from Nippon Carbon Co. Ltd.) as an anode and a cathode of an undivided cell.



1 **2** **3** **4**

The typical procedure is as follows : A solution of 1-acetoxy-2-methylcyclohexene (**1a**, R=Me) (2 g, 13 mmol) and Et_4NOTs (2 g, 6.6 mmol) as a supporting electrolyte dissolved in glacial acetic acid (30 ml) was introduced into an undivided cell equipped with graphite carbon electrodes (EGM62). Electrolysis was carried out at room temperature with magnetic

stirring under constant current condition (current density : 50-60 mA cm^{-2}) until the starting material was completely consumed (2.5-4.0 F mol^{-1}). After the reaction , the crude solution was subjected to usual work-up and the products were isolated by column chromatography. A dimerization product (**2**a, R=Me)[2] possessing a new C-C bond at the β-position[3] was obtained in 65% yield accompanying with formation of a small amount of 2-methylcyclohexanone (**3**a) and 2-methylcyclohex-2-enone (**4**a) as the by-products.

The present electrolysis was found to be largely dependent upon the nature of electrodes and upon the presence of a metallic ion such as Fe^{II}, Fe^{III}, Co^{II}, Cu^{II} as shown in Table 1 and Table 2, respectively.

Table 1. Effects of Electrodes in Anodic Oxidation of **1**a

run	Current density /A cm^{-2}	Anode	Cathode	Supplied electricity /F mol^{-1}	Yield / %			
					1a	**2**a	**3**a	**4**a
1	0.053	C(EG10)	C(EG10)	3.0	–	56	6	trace
2	0.053	C(EGM62)	C(EGM62)	3.0	–	65	4	trace
3	0.053	C(YUASA)	C(YUASA)	2.9	–	–	–	90
4	0.053	C(EG10)	Pt	3.0	–	–	–	77
5	0.053	C(EG10)	Fe	3.0	6	–	3	58
6	0.053	C(EG10)	Cu	3.0	7	–	3	59
7	0.053	C(EG10)	Al	3.5	–	trace	–	69
8	0.053	C(EG10)	Ni	3.5	3	trace	10	44

Thus, use of graphite carbon electrodes from YUASA, which was found to contain some amount of Fe metal or Fe ion by fluorescent X-ray analysis, led to exclusive formation of the α,β-unsaturated ketone **4**a in electrolysis of the enol acetate **1**a as reported before[1] (Table 1: run 3) while the dimer **2**a was obtained as the main product when EG10 or EGM62 was used (Table 1:runs 1,2).

Furthermore, the presence of a small amount of any of those metal salts (ca. 0.4-1.0 mol%) brought about exclusive formation of the α,β-unsaturated ketone **4**a as the main product instead of the dimerization product **2**a, which was yielded only in a trace amount (Table 2).

It may be noteworthy that the reaction using a metal cathode, such as Pt, Fe, Cu, Al, or Ni instead of EGM62 or EG10, also gave α,β-unsaturated ketones **4** as the main products (Table 1: runs 4-8).

Table 2. Effects of the Metal Salts (Anode, Cathode, EG10)

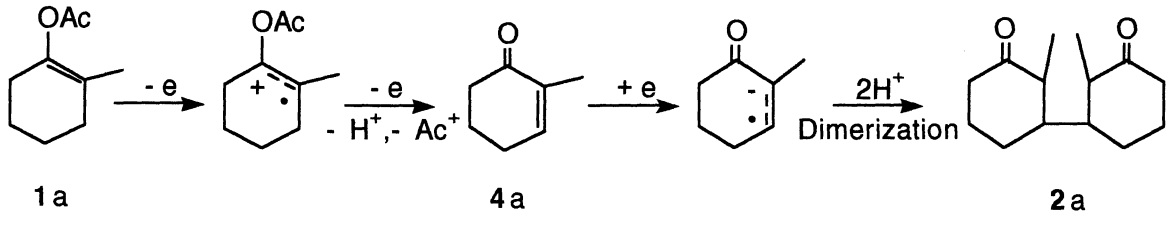
Additives	mol %	Supplied electricity / Fmol^{-1}	Yield / %			
			1a	2a	3a	4a
None	0	3.5	–	56	6	trace
$Fe_2(SO_4)_3 \cdot nH_2O$	10	2.5	–	–	trace	84
	5	2.5	–	–	trace	87
	1	2.5	–	trace	trace	80
	0.5	2.5	–	trace	8	46
$Co(OAc)_2 \cdot 4H_2O$	0.4	2.5	–	–	trace	85
$FeSO_4 \cdot 7H_2O$	0.4	2.5	–	trace	trace	86
$CuSO_4$	0.6	2.5	–	–	trace	80

Therefore, exclusive formation of **4**a in the presence of the metal salt as shown in Table 2, may be elucidated by electrochemical metal plating on a graphite cathode EG10.

On the other hand, anodic oxidation of **1**a using EGM62 type of carbon electrodes as an anode and a cathode, and a ceramic cylinder as a diaphragm of a divided cell resulted in the formation of **4**a (38%) and **3**a (5%) while none of the dimer **2**a was detected even by gas chromatographic analysis.

These experimental facts may indicate that anodic oxidation of **1**a to **4**a takes place regardless of the nature of graphite carbon anode, and subsequent electroreductive hydrodimerization of the resulting α,β-unsaturated ketone **4**a proceeds only when EG10 or EGM62 were used as a cathode, as shown in Scheme 1.[4)]

The present electrolysis provides a very rare example of successive occurrence of direct electrochemical oxidation followed by reduction in one cell, called *"paired electrolysis"*.[5)] Paired electrolysis is much favorably effective because of no need of the isolation of the intermediate and the economy of the electricity.

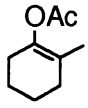
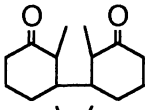
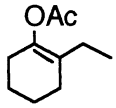
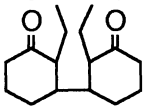
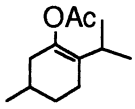
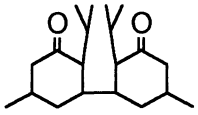
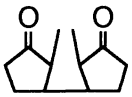


1a 4a 2a

Scheme 1.

Finally, it was shown that this paired electrolysis can be applied to direct formation of 1,6-diketones **2**a-d through selective dimerization at the β-positions of enol acetates **1** as listed in Table 3.

Table 3. Variety of the Substances

Substance **1**	Supplied electricity / F mol^{-1}	Product **2**	Yield of dimers **2** / %
	3.5	 **2a**	56 (65)[a]
	2.5	 **2b**	57
	3.8	 **2c**	58
	4.0	 **2d**	55

a) The reaction is carried out using EGM62 as the electrodes.

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References

1) T.Shono, Y.Matsumura, and Y.Nakagawa, *J. Am. Chem. Soc.*, **96**, 3532 (1974). T.Shono, M.Okawa, and I.Nishiguchi, *ibid.*, **97**, 6144 (1975).

2) The stereochemistry of the dimers is a mixture of meso and dl isomers (about 1:1). NMR and IR spectrum of **2a** are as follows. ^{1}H NMR ($CDCl_3$) ; δ 1.40-2.62 (m. 16H), 1.14 (d. 3H, J = 7.2 Hz), 1.14 (d. 3H, J = 6.4 Hz), IR (KBr) ; 2950, 1710, 1460, 1320 cm^{-1}.

3) J.Grimshaw and R.J.Haslett, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 395.

4) Although any clear-cut explanation has not been available as yet, large apparent porosity and high hydrogen overvoltage of the electrodes, EG10 or EGM62 seem to bring about much adsorption of **4**a on the cathode favorable to electroreductive hydrodimerization.

5) M.M.Baizer, T.Nonaka, K.Park, Y.Saito, and K.Nobe, *J. Appl. Electrochem.* **14**, 197 (1984).

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