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Electrochemical Carboxylation of α,β-Unsaturated Ketones with Carbon Dioxide

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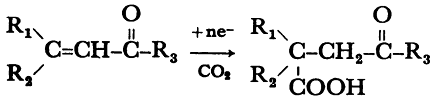
Synopsis. Several aromatic and aliphatic α,β-unsaturated ketones were converted to the corresponding γ-keto acids by the electrochemical reduction in acetonitrile in the presence of CO_2. The yields of the keto acid were 73—82% when the enones have at least one aromatic substituent. In the case of aliphatic enones, the yields of the carboxylation reaction were 67% for 2-cyclohexen-1-one and 44% for 3-buten-2-one.

γ-Keto acids or γ-keto esters are useful intermediates for γ-lactones, cyclopentenones, butenolides, 1,3-cyclopentanediones and heterocyclic compounds. Available synthetic methods of γ-keto acid or γ-keto esters usually need multi-stage reactions.[1a–g] In recent years, electrochemical carboxylation of various unsaturated compounds has received considerable attention from synthetic and mechanistic point of views. Among these, reductive carboxylation of α,β-unsaturated ketones has been reported,[2–4] where γ-keto acids were produced. However, the yields were not satisfactory in the earlier works because of the formation of dimeric and polymeric products.

We would like to report the effective transformation of aromatic and aliphatic α,β-unsaturated ketones into γ-keto acid by electrochemical carboxylation with CO_2 in acetonitrile under the controlled potential conditions.



$$\mathrm{R_1R_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}R_3 \xrightarrow[CO_2]{+ne^-} R_1R_2\underset{COOH}{C}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}R_3}$$

1 $R_1=H$, $R_2=Ph$, $R_3=Me$
2 $R_1=H$, $R_2=Ph$, $R_3=Ph$
3 $R_1=Ph$, $R_2=Ph$, $R_3=Ph$
4 $R_1=H$, $R_2R_3=\text{-}(CH_2)_3\text{-}$
5 $R_1=Me$, $R_2R_3=\text{-}(CH_2)_3\text{-}$
6 $R_1=H$, $R_2=H$, $R_3=Me$

Results and Discussion

The α,β-unsaturated ketones, 4-phenyl-3-buten-2-one (**1**), 1,3-diphenyl-2-propen-1-one (**2**), 1,3,3-triphenyl-2-propen-1-one (**3**), 2-cyclohexen-1-one (**4**), 3-methyl-2-cyclohexen-1-one (**5**), and 3-buten-2-one (**6**) were used for starting materials. The polarographic half-wave potential in each case is summarized in Table 1. The aromatic enones **1**—**3** showed two one-electron reduction waves, while the aliphatic enones **4**—**6** exhibited only a single one-electron wave. For all of the compounds studied, the half-wave potentials of both the first and second waves are more positive than that of carbon dioxide (*ca.* −2.5 V).

When carbon dioxide was introduced into the solution of the aromatic enone **2**, the first wave grew as CO_2 concentration increased and the final height of it became approximately two times of that of the original first wave. A similar phenomenon was observed for the aliphatic enone **4**. These facts suggest that at the first wave potential the ECE reaction of an anion radical with CO_2 proposed by Wawzonek[2] may operate to afford the carboxylated product.

When preparative electrolysis of the aromatic enone **2** was carried out at the potential of the first wave, at which the anion radical species is formed, the carboxylated product was obtained less selectively (35%), and considerable amounts of dimeric and polymeric materials were formed, in accordance with the results shown by Wawzonek. When the electrolysis of the enone **2** was made at the potential of the second wave, 2,4-diphenyl-4-oxobutanoic acid was produced in 77% yield (run 2 in Table 1). In this case, by-products were a minor amount of a dihydro compound, 1,3-diphenyl-1-propanone, and traces amounts of dimeric and polymeric materials. Similar results were also obtained with the aromatic enones **1** and **3** (runs 1 and 3). Here, it is worth noting that an introduction of bulky phenyl groups into the enone moiety does not hinder the efficiency of the carboxylation reaction. This is the marked difference from the cases of aliphatic enones. The fact that more selective transformation of the enone **2** into the γ-keto acid was achieved at the second wave potential, at which dianion species is formed, suggests that a pathway arising from the reaction of the dianion with CO_2 is more effective to the carboxylation reaction.

On the other hand, the second reduction waves were not observed for the aliphatic enones **4**—**6**. When the electrolysis of **4** was carried out at −2.40 V, the yield of the keto acid was 43% and considerable amounts of dimeric products of cyclohexenone were formed (50%, run 4). When a methyl group was attached to the 3-position of cyclohexenone ring, the yield of γ-keto acid decreased to 10% (run 10). With the enone **5**, the carboxylation reaction became rather a minor path and a large amount of a mixture of dimeric compounds was obtained in 80% yields. In order to examine the effect of the anion radical concentration on the electrode surface on the competitive pathways of carboxylation and dimerization, we carried out a series of controlled current experiments with 2-cyclohexen-1-one (**4**) (runs 5—9). When the current density, which should relate to the radical concentration on the electrode surface, was chosen to be 20 A dm^{-2}, the yield of the keto acid was only 18% (run 9). By lowering the current density, the yields were definitely improved up to 67% (run 6). With 2-buten-1-one (**6**), the carboxylation also occurred in moderate yield (run 12), but a detailed study has not been done in this case.

TABLE 1. ELECTROLYSES OF α,β-UNSATURATED KETONES WITH CO_2 IN ACETONITRILE

Run	Starting materials (mmol)	Half wave potential	Conditions[a)]	Conversion	Yield of the products[b)]/%			Current[c)] efficiency
		V	V or A dm^{-2}	%	γ-Keto acid	Saturated ketone	Dimeric products	%
1	**1** (7.0)	−1.73 & −2.25	−2.40 V	100	82	Trace	Trace	82
2	**2** (7.0)	−1.50 & −2.10	−2.20 V	92	77	18	Trace	71
3	**3** (7.0)	−1.62 & −1.96	−2.10 V	95	73	5	Trace	70
4	**4** (7.0)	−2.20	−2.40 V	100	43	4	50	43
5	**4** (1.0)		7.3 A dm^{-2}	97	58	Trace	12	55
6	**4** (1.0)		11.0 A dm^{-2}	95	67	Trace	16	64
7	**4** (1.0)		14.7 A dm^{-2}	100	38	Trace	31	38
8	**4** (1.0)		17.0 A dm^{-2}	100	26	Trace	30	26
9	**4** (1.0)		20.6 A dm^{-2}	100	18	Trace	18	18
10	**5** (7.0)	−2.32	−2.50 V	64	10	—	80	6
11	**6** (1.0)	−2.00	3.7 A dm^{-2}	—	35	—	—	35
12	**6** (1.0)		3.7 A dm^{-2}	—	44	—	—	22

a) Electricity was 2.0 F mol^{-1} for runs 1—11, and 4.0 F mol^{-1} for run 12. b) Based on reacted ketones. c) Current efficiency of carboxylation.

Experimental

General. Guaranteed grade enones were purified by distillation or recrystallization before use. Acetonitrile was purified in the usual way.[5)] The base solution used for polarographic measurements and preparative electrolyses was always acetonitrile containig 0.1 mol dm^{-3} tetraethylammonium perchlorate. All the potential values cited are referred to a saturated calomel electrode using acetonitrile as the solvent.[6)] Preparative electrolyses were carried out in a divided cell with a mercury pool cathode at 5—10°C under the controlled potential conditions. A solution of a enone (10 mmol dm^{-3}) was placed into the cathode compartment and saturated with bubbling CO_2. In some experiments, the electrolyses were made under the controlled current. The electrolyzed solution was evaporated to remove the solvent and the residue was taken into a small amount of water, acidified, and extracted with ether throughly. The condensed extract was subjected to product analyses. The γ-keto acids were isolated by silica-gel column chromatography or preparative GLC after esterifications. Reaction conditions and results are summarized in Table 1. All the spectroscopic data, melting points, and elemental analyses agreed with those of the authentic samples.

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