

The Anodic Oxidation of trans-Cinnamic Acid. I.

The Formation of Ketone and Aldehyde Derivatives*

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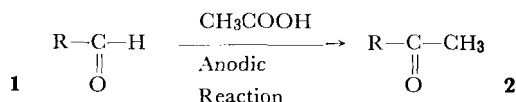
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The electrochemical oxidation of trans-cinnamic acid in a mixed aqueous solution of acetic acid and methanol containing potassium hydroxide was studied. The separation of ketones and aldehydes from the neutral materials using Girard reagent P gave benzaldehyde, tolualdehydes, acetophenone, methylacetophenones, propiophenone, phenacyl acetate, and phenacyl alcohol. The mechanism of the anodic reaction of trans-cinnamic acid has been discussed.

As a manner of our study of the anodic reaction, acetic acid has been electrolyzed in the presence of various organic substrates, chiefly aldehydes,^{1),2)} ketones,^{2),3)} acetals,²⁾ glycidates,³⁾ and cyclopropanecarboxylic acids.⁴⁾ These attempts provided us with a chance to discover a new type of anodic methylation of aldehydes, in which the hydrogen atom attached to the carbonyl of aldehyde (1) is replaced by methyl group giving ketone (2).^{1),2)}



In the present paper, the features of the decomposition of trans-cinnamic acid and of the recombination of generated radicals and ionic fragments in the course of the anodic reaction of acetic acid in aqueous methanol containing potassium hydroxide were investigated. Recently, the electrochemical oxidation of acetic acid in the presence of 3,3-diphenylacrylic acid⁵⁾ and maleic acid half-ester⁶⁾ has been attempted.

Results and Discussion

According to the manner of the separation

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of the products as is shown in Scheme I, the produced neutral materials were separated by the chemical procedure into two groups: one is the ketone and aldehyde component, the other is the non ketone and aldehyde component. The constituents of the ketone and aldehyde component were isolated by the fractional distillation as is shown in Table III in the Experimental Section and were identified by their retention times of vpc, physical constants, formation of derivatives, and comparison with their authentic samples as are listed in Table IV in the Experimental Section. The

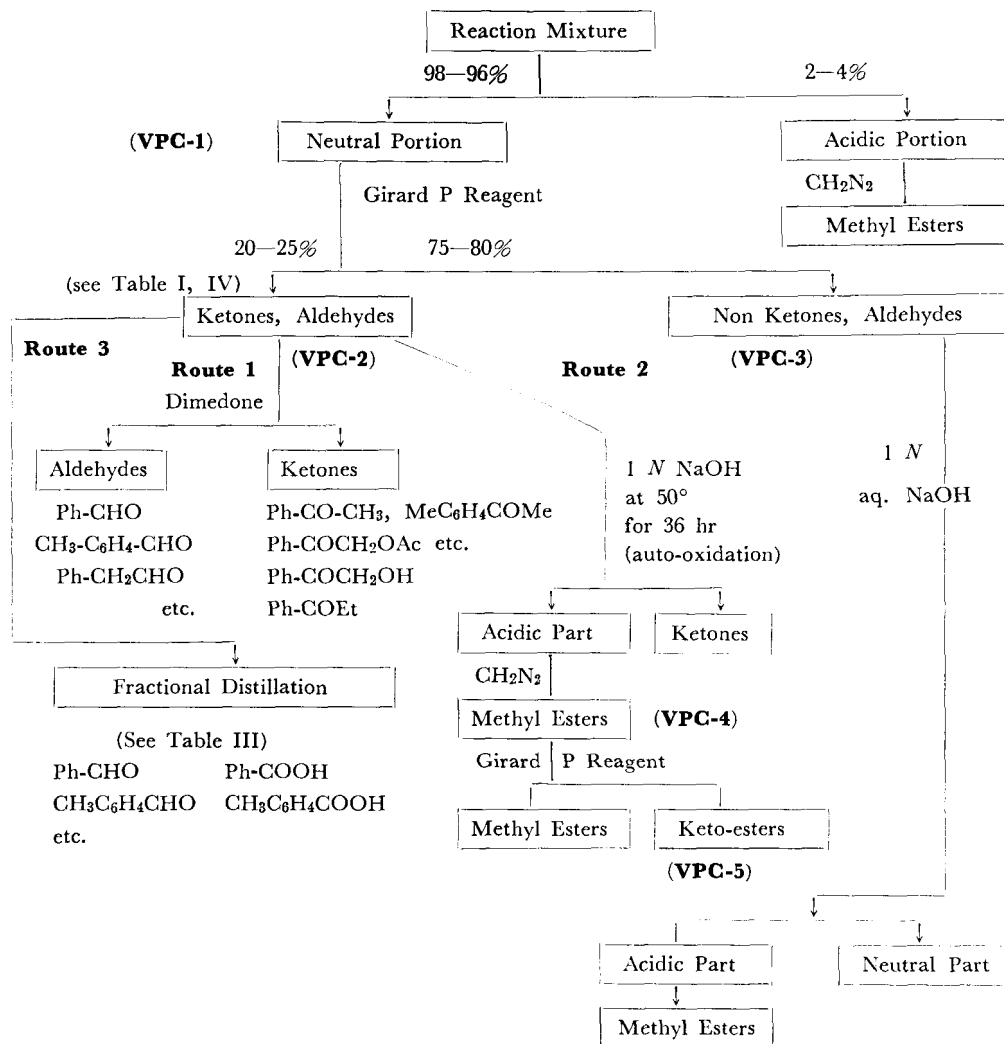
Table I Constituents of the Ketone and Aldehyde Component

Retention Time *)		Relative Peak Area*%)	Constituent
min	sec		
6	20	11.85	Benzaldehyde
8	00	7.12	Acetophenone
8	30	3.20	<i>p</i> -Tolualdehyde
11	30	3.22	<i>p</i> -Methylacetophenone
24	12	7.12	Phenacyl Acetate
40	40	1.00	Phenacyl Alcohol

*) Hitachi F6-D gas chromatograph, Golay column Z-45, carrier gas Ne (0.3 Kg/cm², 60ml/min), Column temp. 140–200°C (1.25°/min), injection 300°C. Detector FID.

***) Neutral Materials (100%).

Scheme I Mode of Separation

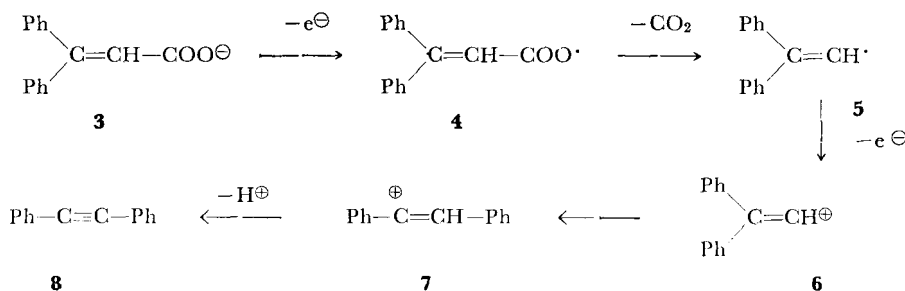


major constituents of the ketone and aldehyde component of the anodic reaction of trans-cinnamic acid are summarized in Table I.

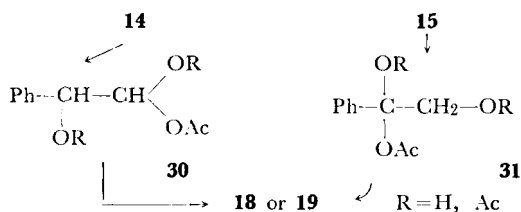
Kochl suggested⁵⁾ a mechanism, where the anodic oxidation of 3,3-diphenylacrylic acid commenced in the usual Kolbe manner, through the unstable intermediates (4, 5, 6, and 7) to give acetylenic compound (8). And, reason-

able evidences of the presence of the intermediates (4, 5, 6, and 7) are obtained by the isolation of 4-phenylcoumarin, 1,1-diphenylpropene, benzil, benzoin, and benzoin acetate.

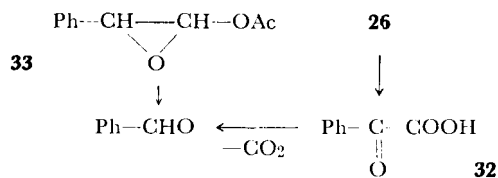
In the present study, similar consideration may be possible, since the discharge of trans-cinnamic acid may occur to give radical and cationic intermediates (10, 11, 12, and 13),



Thus, the attack of anodically produced acetoxy radicals to aromatic alkenes in the dilute solution may be unlikely. The direct acetoxylation of the methyl group of acetophenone may give the acetate (**19**). Indeed, the expected reaction occurred, when the anodic reaction of acetophenone was carried out in the similar reaction condition, but it gave only ca. 0.1% yield of **19**.³⁾ Thus, this route should be excluded from the principal role of the formation of **19**. Ultimately, it seems conceivable that the acetoxy derivatives (**14** and **15**) might be converted into **18** and **19** via polyhydroxy or acetoxy compounds (**30** and **31**).



Benzaldehyde and acetophenone are key constituents of the ketone and aldehyde component, obtained by the anodic reaction of trans-cinnamic acid. Most of acetophenone and its derivatives must be formed by the anodic methylation of benzaldehyde.¹⁾ However, as for the formation of benzaldehyde, our evidence gives no real suggestion. It appears likely that a keto-acid (**32**), which may be obtained by the anodic oxidation of the acetate (**26**), may be subjected to decarboxylation to form benzaldehyde, on one hand, and the anodic oxidation of both the acetolysis products of the epoxy intermediates (**33**) and polyacetates (**30** and **31**), followed by the fission of α , β -carbon bond, may give benzaldehyde, on the other. An evidence for that was provided by the isolation of keto-acid in a manner described in Scheme I, whose infrared spectrum is shown in IR Chart I. The latter assumption is supported by the result of the anodic reaction of sodium β -phenylglycidate.³⁾ The vinyl



acetates (**14** and **15**) are also seemed to be precursors of benzaldehyde.⁵⁾

Experimental Section

Apparatus.— The electrochemical cell consisted of a cylindrical glass vessel, 7 cm long in diameter and 14 cm high, fitted with a gas lead pipe, a thermometer, and a magnetic stirrer. The vessel was immersed in a water bath, cooled with circulating cold water. The electrodes were two platinum foils ($1.2 \times 2.0 \text{ cm}^2$) spaced about 2 mm apart and the current direction was changed in every 30 sec by means of a commutator. The products were analyzed by vpc (Hitachi F6-D gas chromatograph) using Golay column (Z-45).

Materials.— Analytical grade trans-cinnamic and acetic acids, methanol, ethanol, and inorganic reagents were used. The commercially available compounds were used as a reference, but the following reference compounds were prepared. Phenacyl alcohol,¹⁰⁾ mp 87° , phenacyl acetate,¹¹⁾ $102\text{--}164^\circ$ (2 mm), *p*-methylacetophenone,¹²⁾ 100° (10 mm), propiophenone,¹³⁾ $60\text{--}70^\circ$ (2 mm), and α -tolualdehyde,¹⁴⁾ 80° (10 mm), were synthesized.

Electrolysis of trans-Cinnamic Acid in an Aqueous Acetic Acid-Methanol-Potassium Hydroxide Solution.— A typical reaction procedure is shown in Table II. Thus,

Table II Reaction Procedure

	Experimental
trans-Cinnamic Acid	0.2 mole
H ₂ O	300 ml
CH ₃ OH	150 ml
CH ₃ COOH	120 g
KOH	16.8 g
Cell Voltage	8–12 V
Current	0.7–0.8 (A/cm ²)
Time	50 hrs
End Point	4–5 (pH)
Commutator	Every 30 sec

a mixed solution of trans-cinnamic acid, acetic acid, water, methanol, and potassium hydroxide was electrolyzed at Pt electrodes for 50 hrs. at $25\text{--}30^\circ$, with terminal voltage 8–12 V at a current of 1.7–2.2 A, magnetically stirring, and changing the current direction in every 30 sec by means of a commutator. The resulting reaction mixture was diluted with 300 ml of water and extracted with ether. The extracts were washed with aqueous saturated sodium

chloride and concentrated *in vacuo*. The separation of the products was carried out in the manner as is shown in Scheme I. The results of the fractional distillation of the ketone and aldehyde component are indicated in Table III. The methods of the characterization and identification of each constituents of the ketone

Table III The Fractional Distillation of a Mixed Solution of Ketone and Aldehyde Component (11g)^{*)}

Fract. No.	B. p. (°C/30 mmHg)	Yield (g)
1	-82	0.5
2	82-84.5	0.5
3	84.5-85	0.5
4	85-87	0.5
5	87-88.5	0.5
6	88.5-92	0.25
7	92-94	0.45
8	96-99	0.35
9	99-103	0.47
10	103-109	0.35
11	109-120	0.35
12	120-122	0.30
13	122-124	0.20
14	124-	0.20
15	124-	0.50
16	Residue	1.70

*) The fractional distillation was carried out by the use of the Taika-Kogyo Model TA-SB₁ with a spinning band-type distillation apparatus.

**) Major constituent: 1 Benzaldehyde, 2 Acetophenone, 3 *p*-Tolualdehyde, 4 Propiophenone, 5 Phenacyl Alcohol, 6 Phenacyl Acetate.

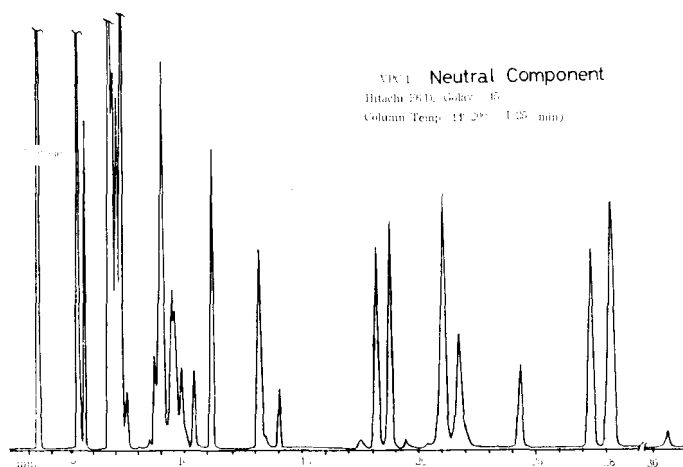
Table IV The Isolation and Identification of the Constituents

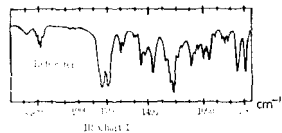
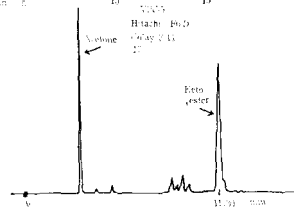
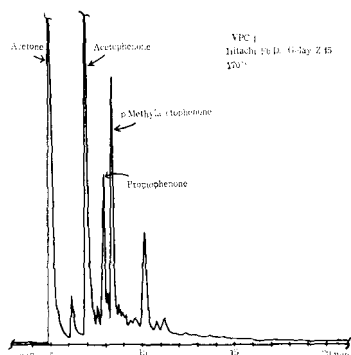
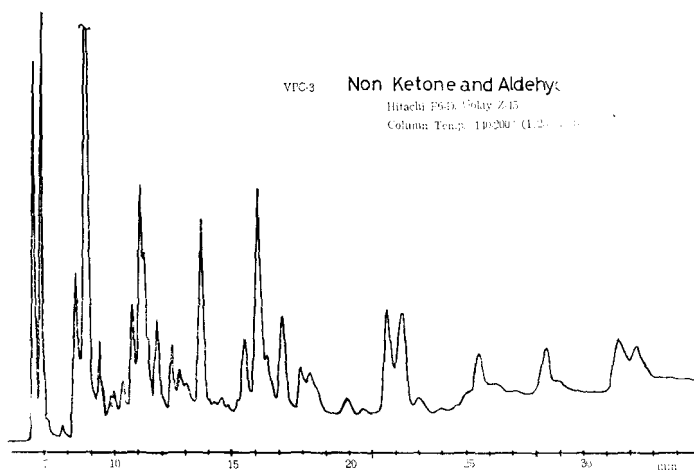
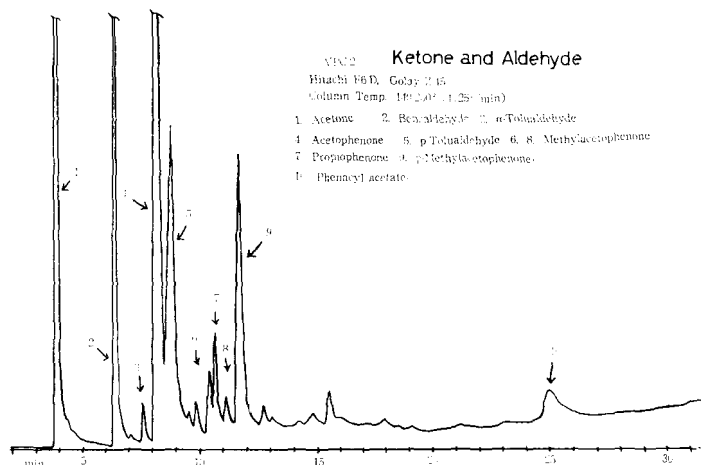
Compound	Methods
Benzaldehyde	Fractional Distillation (F. D.) No. 1-4, IR, VPC, 2,4-DNPH (mp. 237°), Formation of Benzoic Acid.
Acetophenone	F. D. No. 3-6, VPC, 2,4-DNPH (mp. 250°), IR
<i>p</i> -Tolualdehyde	F. D. No. 6-7, <i>p</i> -Toluic Acid.
Propiophenone	F. D. No. 7-8, VPC
Phenacyl Alcohol	F. D. No. 10-11, IR, VPC, Mp. 87°. 2,4-DNPH (mp. 216°), Microanalysis.
Phenacyl Acetate	F. D. No. 12-15, IR, VPC, Bp. 102-4°/2mm., 2,4-DNPH (mp. 186°), Microanalysis.

and aldehyde component are summarized in Table IV. The gas chromatographs of the components described in Scheme I are shown in VPC Charts 1, 2, 3, 4, and 5. The infrared spectrum of the keto-esters (**32**) is shown in IR Chart I.

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