Electrochemical Syntheses. V. The Direct Synthesis of Methyl Esters of α, β-Unsaturated Carboxylic Acids from Some Arylated Olefins and Carbon Monoxide*

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Although various reactions of olefins with carbon monoxide in the presence of proton-catalysts(1) and/or metal-carbonyls(2) or their-complexes(3) have been reported, the synthesis of α, β-unsaturated carboxylic acids or esters from olefins and carbon monoxide has been unsuccessful as yet.

The present investigation deals with the first direct synthesis of methyl esters of α, β-unsaturated carboxylic acids from olefins and carbon monoxide by a unique electrochemical method in the presence of a certain platinum carbonyl compound.

In the last previous paper(7) in this series,(4-7) the present authors have shown that the anodic oxidation of methanol in the presence of arylated olefins produced α, β-dimethoxylated derivatives, and that the reaction involved a methoxy radical as an intermediate. In order to utilize the radicals produced in the electrolysis for organic synthesis, the electrolysis was carried out in these systems in the presence of carbon monoxide; consequently, we have observed that the platinum used as a cathode was easily dissolved into the solution during the electrolysis of methanol containing sodium methoxide, thus giving a certain platinum carbonyl compound. We have also found that this carbonyl compound reacted with olefins catalytically as well as electrolytically in the presence of carbon monoxide to give a methyl ester of the corresponding α, β-unsaturated carboxylic acid as the main product. In order to provide some information with regard to the reaction mechanism and the synthetic usefulness of this curious electrochemical reaction, various experiments were carried out regarding the formation of the platinum carbonyl compound, its catalytic action on carboxylations of olefins, the influence of the concentration of the carbonyl compound, and the effect of the steric factor in olefins. Thus, styrene, α-methylstyrene and 1, 1-diphenylethylene were chosen as the starting olefins.

Results and Discussion

1) The Carbomethoxylation of Olefins (Method A).—The electrolyses were carried out

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* Reported at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

1) M. Orchin and I. Wender, "Catalysis," Vol. V, Reinhold Publ. Corp., New York, N. Y. (1957), p. 6.

2) C. W. Bird, *Chem. Revs.*, **62**, 283 (1962); W. Reppe, *Ann.*, **582**, 38 (1953).

3) M. A. Bennett, *Chem. Revs.*, **62**, 611 (1962); N. Kutepof and H. Kindler, *Angew. Chem.*, **72**, 802 (1960).

4) T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1659 (1963).

5) T. Inoue, K. Koyama and S. Tsutsumi, This Bulletin, **37**, 1597 (1964).

6) T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka and S. Tsutsumi, *Tetrahedron Letters*, No. **21**, 1409 (1963).

7) T. Inoue and S. Tsutsumi, This Bulletin, **38**, 661 (1965).

by using two platinum-plate electrodes in a cylindrical glass cell placed in an autoclave under a pressure of 70 kg./cm^2 of carbon monoxide. The apparatus used is shown in Fig. 1. The current was controlled at nearly 1.0 amp., the temperature being kept at -10—-15°C. The electrolysis of a methanolic solution containing sodium methoxide and styrene for 9 hr. gave methyl *trans*-cinnamate (I) as the main product in a 14% yield based on the styrene used; it also gave methyl β-methoxy-β-phenyl propionate (II) (3.6%), methyl β-phenyl propionate (III) (3.1%), dimethyl *meso*-β,γ-diphenyl adipate (IV) (a trace) and styrene glycol dimethyl ether (V) (5.6%), and unreacted styrene (57%). However, during the course of this electrolysis, the platinum plate used as a cathode (1.3 g.) was dissolved into the solution, and the electrolyzed solution turned a greenish-blue. The results obtained under various conditions are summarized in Table I, where the yield is calculated from the results of gas chromatographic analysis. When the electrolysis was carried out by using copper or carbon as the cathode and a platinum plate as the anode, styrene glycol dimethyl ether (V) was obtained as the sole product (23%), as is shown in Table I.

The electrolysis in the presence of α-methylstyrene instead of styrene for 9 hr. gave methyl *trans*-β-methyl cinnamate (VI) (14.8%), methyl 3-phenyl-3-butenoate (VII) (4.9%), methyl β-methyl-β-phenyl propionate (VIII) (1%) and α-methylstyrene glycol dimethyl ether (IX) (2.2%). When 1, 1-diphenylethylene was used, methyl β-phenyl cinnamate (X) was also obtained in a 17.2% yield as the main product, as is shown in Table II. In these electrolyses, the platinum used as a cathode was also dissolved into the electrolyzed solution.

2) One Platinum Compound.—When the electrolysis of methanol containing sodium methoxide was carried out by using two platinum-plate electrodes in the absence of olefins under the pressure of carbon monoxide, the platinum used as the cathode was also easily dissolved into the solution, giving a certain platinum carbonyl compound; this compound was then isolated by the removal

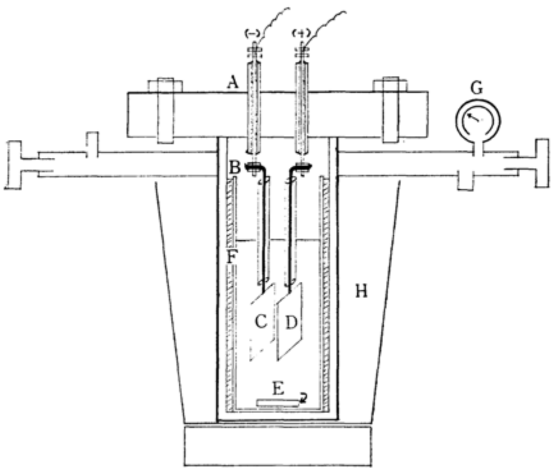


Fig. 1. Apparatus.

A: Autoclave (500 cc.)
B: Cylindrical glass cell
C: Cathode, Pt (2×3 cm^2) or Cu (2×3 cm^2)
D: Anode, Pt (2×3 cm^2)
E: Magnetic stirrer
F: Methanol solution
G: Gauge
H: Ice-salt

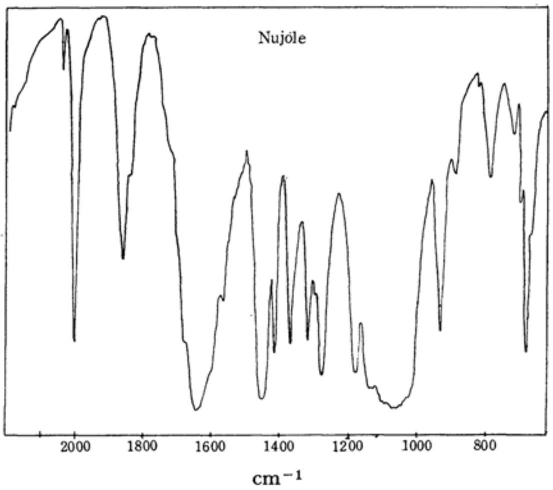


Fig. 2. IR spectrum of platinum carbonyl compound isolated.

TABLE I. CARBOMETHOXYLATION OF STYRENE BY METHOD A

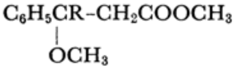
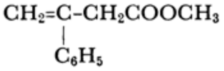
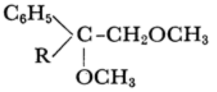
Expt. No.	$C_6H_5CH=CH_2$ g. (mol.)	CO kg./cm^2	Cathode material	Amp.·hr.	Wt. of Pt lost from cathode g.	Product, g.			
						I	II	III	V
1	52 (0.5)	70	Pt	9.6	1.95	3.5	0.6	0.5	1.8
2	26 (0.25)	70	Pt	9.6	1.77	3.5	0.7	0.5	2.1
3[a]	15.6(0.15)	70	Pt	8.6	1.32	3.4	1.0	0.7	1.4
4	52 (0.5)	45	Pt	9.3	0.34	1.8	0.3	0.2	3.3
5	52 (0.5)	45	C	9.2	—	—	—	—	4.2
6	26 (0.25)	70	C	12.2	—	—	—	—	9.3

* CH_3OH, 80 g. (2.5 mol.); metallic sodium, 1.0 g.; anode, Pt, 2×3 cm^2.

** A current was controlled at nearly 1.0±0.1 amp.

a) Metallic sodium, 0.5 g. was used.

TABLE II. CARBOMETHOXYLATION OF ARYLATED OLEFINS BY METHOD A

$C_6H_5CR{=}CH_2$, g. (mol.)	R=H 15.6 (0.15)	$R{=}CH_3$ 17.7 (0.15)	$R{=}C_6H_5$ 18.0 (0.1)
Wt. of Pt lost from cathode, g.	1.32	3.31	1.74
Amp.·hr.	8.6	8.4	8.6
Product, g. (%)[a]			
$C_6H_5CR{=}CHCOOCH_3$	3.4 (14.0)	3.9 (14.8)	4.1 (17.2)
 $C_6H_5CR(OCH_3){-}CH_2COOCH_3$	1.0 (3.6)	—	—
		 $CH_2{=}C(C_6H_5){-}CH_2COOCH_3$ 1.3 (4.9)	
$C_6H_5CHRCH_2COOCH_3$	0.7 (3.0)	trace	trace
 $(C_6H_5)(R)C(OCH_3){-}CH_2OCH_3$	1.4 (5.6)	0.6 (2.2)	1.8 (7.4)

* CH_3OH, 80 g. (2.5 mol.); metallic sodium, 0.5 g.; anode and cathode, 2×3 cm^2; CO, 70 kg./cm^2; current, 1.0±0.1 amp.; temperature, −10—−15°C.

a) Based on olefins used.

TABLE III. CARBOMETHOXYLATION OF ARYLATED OLEFINS BY METHOD B

Expt. No.	$C_6H_5CR{=}CH_2$ g. (mol.)	Pt-carbonyl compound g. (wt. of Pt)	Amp.·hr.	$RCOOCH_3$ (total)	Product, %[a]			
					V	I	II	III
	R=H							
1	15.6 (0.15)	0.9	16.4	23	32	14	8	1
2	15.6 (0.15)	1.5	16.6	35	23	21	13	1
3	15.6 (0.15)	2.8	16.8	43	10	17	16	10
	$R{=}CH_3$				IX	VI	VII	VIII
4	17.7 (0.15)	0.9	16.5	24	33	16	7	1
5	17.7 (0.15)	2.9	16.8	31	9.3	18	11	2
	$R{=}C_6H_5$				XI	X		
6	18.0 (0.10)	1.0	16.4		25	30		

* CH_3OH, 90 g.; metallic sodium, 0.5 g.; anode, Pt, 2×3 cm^2; cathode, copper plate, 2×3 cm^2; current, 1.0±0.1 amp.; time, 16 hr.; CO, 70 kg./cm^2; temperature, −10—−15°C.

a) Based on olefins used.

of methanol from the electrolyzed solution under a dry nitrogen atmosphere. This carbonyl compound was very sensitive to air and was greenish-blue. Its infrared spectrum has the characteristic absorption bands at about 2015 (v. s.) and 2145 cm^{-1} (w.) (terminal carbonyl group), and at about 1860 (m. s.) and 1840 cm^{-1} (m. s.) (the bridged carbonyl group); it also has strong absorption bands at about 1642, 1280 and 1180 cm^{-1}, as is shown in Fig. 2. Although the structure of this carbonyl compound has not yet been completely elucidated, the latter strong absorption bands may be due to the ester group attached to platinum metal, as has been reported in other metal-carbonyl compounds.[8]

3) The Carbomethoxylation of Olefins in the Presence of the Platinum Carbonyl Compound (Method B).—At first, the platinum carbonyl compound was produced in methanol containing sodium methoxide by electrolysis in a cylindrical glass cell in a manner similar to the procedure described above 2); then, after the plate of cathode had changed to copper(2×3 cm^2), electrolyses were carried out in the presence of olefins and carbon monoxide for 16 hr. (1.0 amp., −10—−15°C).

In these electrolyses, methyl esters of α, β-unsaturated carboxylic acids were also obtained as the main products. Examples of the yields of these unsaturated esters and of other products are given in Table III.

4) The Carbomethoxylation of Styrene in the Presence of Platinous Potassium Chloride.—When the electrolysis was carried out in the presence of platinous potassium chloride or sodium cholride under similar conditions 3), it gave as products I (1%), II (3.3%) and V (18%).

The products obtained from these reactions were identified by the infrared spectroscopic, gas chromatographic and elemental analysis and, some of them, by NMR data; they were also identified as free acids by mixed melting points determinations with authentic specimens.

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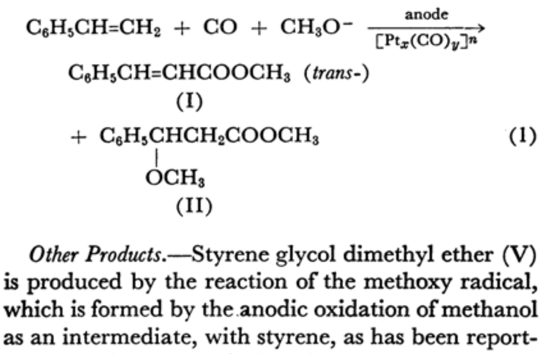
[8] T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

The Participation of the Platinum Carbonyl Compound.—In these electrochemical reactions, the formation of unsaturated esters proceeds by the catalytic action of the platinum carbonyl compound, which is cathodically generated from the platinum used as the cathode and from sodium methoxide in the presence of carbon monoxide. The above statement was supported by the following experimental results: (a) Without the platinum carbonyl compound, the electrolysis of styrene using copper or carbon as the cathode and platinum as the anode gave styrene glycol dimethyl ether (V), and the formation of esters I—IV was not observed, as is shown in Table I (R-5 and 6); on the other hand, in the presence of the platinum carbonyl compound, these esters were mainly obtained, as Tables I—III show. (b) The electrolysis under a nitrogen atmosphere with catholyte and anolyte which contained the platinum carbonyl compound and styrene in each separated compartment resulted in the formation of the esters I and II from the anode compartment, although no product was detected from the cathode compartment. (c) With the increase in the concentration of the platinum carbonyl compound, the yield of these esters increased. On the contrary, the yield of styrene glycol dimethyl ether (V) decreased, as is shown in Table III. (d) The formation of these esters may proceed catalytically as well as electrolytically in the presence of the platinum carbonyl compound and carbon monoxide, for the electrolysis of styrene (0.15 mol.) give I (0.031 mol.), II (0.020 mol.) and III (0.003 mol.) in the presence of a catalytic amount of the platinum carbonyl compound (0.007 mol.), as Table III-R-2 shows.

Thus, it can be considered that the esters I and II are produced by the anodic reaction of styrene with the platinum carbonyl compound and carbon monoxide:



$$\begin{array}{l} C_6H_5CH{=}CH_2 + CO + CH_3O^- \xrightarrow[{[Pt_x(CO)_y]^n}]{\text{anode}} \\ \quad C_6H_5CH{=}CHCOOCH_3 \ (\textit{trans-}) \\ \qquad\qquad (I) \\ \quad + \ C_6H_5\underset{\displaystyle OCH_3}{\underset{|}{C}}HCH_2COOCH_3 \qquad (1) \\ \qquad\qquad (II) \end{array}$$

Other Products.—Styrene glycol dimethyl ether (V) is produced by the reaction of the methoxy radical, which is formed by the anodic oxidation of methanol as an intermediate, with styrene, as has been reported before.[7] Methyl β-phenyl propionate (III) and dimethyl *meso*-β, γ-diphenyl adipate (IV) are probably produced by the cathodic reduction of the methyl cinnamate (I) generated in the first step at a low concentration of the platinum carbonyl compound, since I was partly reduced to III and IV in, respectively, the absence of and presence of the platinum carbonyl compound under conditions similar to those described above 3), and since it is well known that cinnamic acid or its derivatives are easily reduced to propionic acid and adipic acid or their derivatives at mercury cathode.[9]

Mechanistic Aspects.—In this new electrochemical reaction, the above-mentioned carbomethoxy platinum carbonylate was assumed to be the active species for the carboxylation, preserving the olefinic double bond, of olefins. The experimental evidence for the above assumption included the facts that the carbomethoxy platinum carbonylate was isolated in the solid state, the infrared spectrum of which showed the presence of the ester group attached to platinum-metal, the terminal and the bridged carbonyl group, and that it reacted with olefins upon electrolysis to give methyl esters of α, β-unsaturated carboxylic acids. Although the precise mechanism of the formation of this carbomethoxy platinum carbonylate is still open to question, it may be considered, as a possible rationalization, that the cathodically-generated platinum carbonyl compound immediately reacts with the methoxy radical or sodium methoxide via the anodic process to give the carbomethoxy platinum carbonylate (Eq. 2 or 3):

$$CH_3O^- \xrightarrow[\text{anode}]{-e} CH_3O\cdot \qquad (2)$$

$$\begin{array}{l} [Pt_x(CO)_y]^n + CH_3O\cdot \longrightarrow Pt_x(CO)_{y-1}COOCH_3 \\ \text{or} \hspace{16em} \uparrow \quad (3) \\ [Pt_x(CO)_y]^n \xrightarrow[\text{anode}]{-e} [Pt_x(CO)_y]^{n-1} \xrightarrow{CH_3ONa} \end{array}$$

Equation 2 may be expected, since the environment around the electrode might have a particularly high concentration of the methoxy radical. The reaction scheme of Eq. 3 may be analogous to the formation of carbomethoxy manganese and rhenium carbonyl compound using manganese or rhenium carbonyl and sodium methoxide,[8] but in our case the reaction of Eq. 3 proceeded via the anodic process.[10] In any case, it is interesting that the platinum carbonyl or its derivatives, the preparation of which by other methods was difficult, was easily prepared by the electrochemical method.[11]

Thus, the esters of α, β-unsaturated carboxylic acids may be considered to be produced by the addition of the Pt–$COOCH_3$ group in the platinum carbonyl compound to the olefinic double bond via the electrode process, followed by further anodic oxidation or decomposition with sodium methoxide, as is indicated below:

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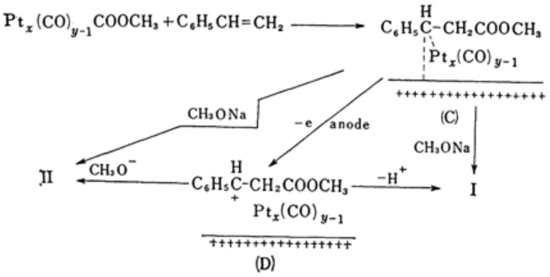
[9] C. L. Wilson and K. B. Wilson, *Trans. Electrochem. Soc.*, **84**, 153 (1943); C. L. Wilson, ibid., **92**, 369 (1947).

[10] This statement is supported by the experiment in which nickel carbonyl was easily oxidized at the anode surface by the electrolysis of methanol containing sodium methoxide.

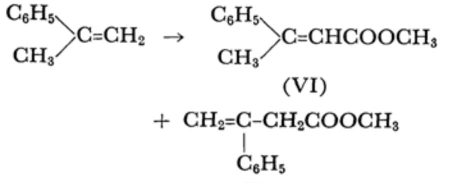
[11] For example, the synthesis of manganese cyclopentadienyl tricarbonyls has been reported by the electrolysis of a mixture of a manganese compound, a cyclopentadiene, carbon monoxide and a transition metal-carbonyl. (Ethyl Corp., Brit 845074 (1960); *Chem. Abstr.*, **55**, 4205 (1961).)



The addition of the metal-carbon σ-bond to the olefinic double bond has recently been reported by several workers. For example, acyl and alkyl cobalt- and manganese-carbonyl compounds react with olefins,[12] diene[13] and fluoro-olefins.[14]

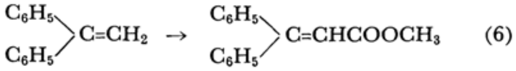
The complex C may be decomposed in the presence of sodium methoxide to give I and II as final products, as has been shown in other metal-carbonyl complexes.[12,13] Alternatively, the possibility of the oxidation of C to carbonium ions, which are then converted to I and II as final products, cannot be excluded, since it has been reported that benzylic carbonium ions can be easily produced as intermediates in electrolysies.[15,16]

The Electrolyses of α-Methylstyrene or 1, 1-*Diphenylethylene.*—When α-methylstyrene was used instead of styrene, methyl 3-phenyl-3-butenoate (VII), besides methyl *trans*-β-methyl cinnamate (VI) as the main product, was obtained in a fairly high yield, as Table III shows. The NMR spectrum of



$$(C_6H_5)(CH_3)C{=}CH_2 \rightarrow (C_6H_5)(CH_3)C{=}CHCOOCH_3 \text{ (VI)} + CH_2{=}C(C_6H_5){-}CH_2COOCH_3 \text{ (VII)} \qquad (5)$$

VII (CCl_4 as the solvent) showed peaks at 2.75 (C_6H_5), 4.55 (CH_2=), 4.85 (CH_2=), 6.47 (OCH_3) and 6.59 τ (–CH_2–); the peak areas were in the ratio of 5 : 1 : 1 : 3 : 2, as was to be expected from the presumed structure. In addition, VII could be easily hydrolyzed with an aqueous alkali solution to give *trans*-β-methyl cinnamic acid in the same way as methyl vinyl acetate.[17] The formation of these esters of unsaturated products VI and VII can be reasonably explained by α- or γ-proton elimination from the intermediate complex C or the carbonium ion D in according to the hypothetical scheme described above. Similar electrolysis in the presence of 1, 1-diphenylethylene gave methyl β-phenyl cinnamate (X) and 1, 1-diphenylethylene glycol dimethyl ether (XI).



$$(C_6H_5)_2C{=}CH_2 \rightarrow (C_6H_5)_2C{=}CHCOOCH_3 \qquad (6)$$

(X)

In these electrolyses, however, the corresponding methyl β-methoxy carboxylates were not detected in the products from α-methylstyrene or in 1, 1-diphenylethylene, while methyl β-methoxy-β-phenyl propionate (II) was obtained from styrene, as has been mentioned above, and the corresponding dimethyl ether derivatives were obtained from these olefins. This may be due to the steric factor (CH_3–, C_6H_5–) with methoxide ions approaching the complex C or carbonium ion D as intermediates. More confirmations, however, are required with respect to this matter.

It is interesting to note that methyl esters of α, β-unsaturated carboxylic acids were directly synthesized from olefins and carbon monoxide in fairly high yields in the presence of the platinum carbonyl compound.

Experimental

All melting points and boiling points are uncorrected. The electrolyses were carried out with the apparatus shown in Fig. 1.

Materials. — Styrene and α-methylstyrene were carefully purified in a usual manner,[18] stored in an ice-box, and distilled before use. 1, 1-Diphenylethylene was prepared by the dehydration of the alcohol formed by the action of phenylmagnesium bromide and ethyl acetate[19]; b. p. 97—97.5°C/0.5 mmHg, n_D^{15} = 1.6098. Methanol was purified in a manner described earlier.[4] These materials were confirmed to be pure by gas chromatography. Carbon monoxide (99.5% pure) was purchased from the Takatiho Co. The platinum plate (99.99% pure, 2×3 cm^2, 0.3 mm. thick) used as an electrode was prepared by carefully treating commercial material with dilute nitric acid and with distilled water; it was weighed before and after use. Commercially-available platinous potassium chloride was used.

The Anodic Oxidation of Methanol in the Presence of Styrene and Carbon Monoxide (Method A).—The reaction conditions and the yields of the products are summarized in Table I. R-3 may be illustrated as follows: Metallic sodium (0.5 g., 0.022 mol.) was dissolved in 80 g. of absolute methanol (2.5 mol.) in a cylindrical glass cell, and then 15.6 g. of freshly distilled styrene (0.15 mol.) was added to the mixture. After dry nitrogen had been bubbled through the mixture for about 1 hr., the cell was placed in an autoclave and the platinum plate as cathode was weighed. Carbon monoxide was then introduced (70 kg./cm^2), and the mixture was electrolyzed at −10—−15°C for 9 hr., with the current

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[12] R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3116 (1963).

[13] R. F. Heck, ibid., **85**, 3383 (1963).

[14] J. B. Wilford, P. M. Treichel and F. G. A. Stone, *J. Organometallic Chem.*, **2**, 119 (1964); J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 93 (1965).

[15] W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430 (1964).

[16] E. J. Corey, N. L. Bauld, R. T. Lalonde, J. Casanova and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960); F. D. Mango and W. A. Bonner, *J. Org. Chem.*, **29**, 1367 (1964).

[17] R. P. Linstead and E. G. Noble, *J. Chem. Soc.*, **1934**, 614.

[18] A. Weissberger, "Technique of Organic Chemistry," Vol. VII, Interscience Publ., New York (1955), p. 331.

[19] "Organic Syntheses," Coll. Vol. I (1956), p. 226.

maintained at nearly 1.0 amp. (current density, ca. 8.3 amp./cm^2). The electrolyzed solution turned a greenish-blue, and 1.32 g. of the platinum used as a cathode was dissolved into the electrolyzed solution. After the methanol had been removed from the reaction mixture under 25—30 mmHg pressure, the residue was poured into water (50 ml.), neutralized with 3 N hydrochloric acid, and extracted with ether; the extract was then dried over magnesium sulfate. After the ether had been removed, the oily residue (17.5 g.) was fractionated by distillation under diminished pressure into the following fractions:

Fraction	B. p.	Weight, g.
1	~50°C/25—28 mmHg	4.1
2	70—120°C/0.7 mmHg	6.9
3	120—150°C/0.7 mmHg	1.0
4	Residue	2.0

By gas chromatographic analysis (conditions: column, Poly Ethylene Glycol 6000, 3 m. and Poly Ester DA., 3 m.; column temperature, 190°C; carrier gas, H_2), it was shown that Fraction 1 was unreacted styrene, while Fractions 2 and 3 were mixtures of styrene glycol dimethyl ether, methyl β-methoxy-β-phenyl propionate, methyl β-phenyl propionate, and methyl *trans*-cinnamate. The total amounts of these products were as follows: styrene glycol dimethyl ether, 1.4 g.; methyl β-methoxy-β-phenyl propionate, 1.0 g.; methyl β-phenyl propionate, 0.7 g.; methyl *trans*-cinnamate, 3.4 g. (14% yield based on the styrene used.)

Fraction 2 was submitted to preparative gas chromatography (column, Poly Ethylene Glycol 6000, 3 m.; column temperature, 190°C; carrier gas, N_2), and the respective products were isolated:

(a) methyl *trans*-cinnamate, m. p. 35—36°C.

Founds: C, 74.25; H, 6.46. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22%.

The infrared spectrum of this ester showed the chracteristic bands at about 1735 (C=O) and 1640 cm^{-1} (C=C), and it was identical with that of an authentic sample. The hydrolysis of this ester with an aqueous alkali solution gave *trans*-cinnamic acid (m. p. 132—133°C) from ligroin; a mixed melting point determination with an authentic sample showed no depression.

Found: C, 72.67; H, 5.57. Calcd. for $C_9H_8O_2$: C, 72.96; H, 5.44%.

(b) Methyl β-methoxy-β-phenyl propionate, b. p. 125—127°C/12—13 mmHg. The infrared spectrum of this compound showed the characteristic bands at about 1750 (C=O) and 1100 cm^{-1} (C–O–C), and it was identical with that of an authentic sample prepared as described below; the hydrolysis of this ester with a cold 3 N potassium hydroxide solution gave β-methoxy-β-phenyl propionic acid, m. p. 98—98.5°C, from ligroin. A mixed melting point determination with an authentic sample showed no depression.

Found: C, 66.66; H, 6.77. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%.

With a boiling aqueous alkali solution, this ester was easily hydrolyzed to give *trans*-cinnamic acid, m. p. 132—133°C; a mixed melting point determination with an authentic sample showed no depression.

(c) Methyl β-phenyl propionate, b. p. 132—135°C/30 mmHg, $n_D^{15}=1.4997$. The hydrolysis of this compound with a boiling alkali solution gave β-phenyl propionic acid, m. p. 47.5—48°C, from petroleum ether; a mixed melting point determination with an authentic sample showed no depression.

Found: C, 72.18; H, 6.75. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71%.

The infrared spectrum of this acid showed the characteristic band at about 1730 cm^{-1} (C=O), and it was identical with that of an authentic sample.

(d) Styrene glycol dimethyl ether, b. p. 75—76°C/2 mmHg.

Found: C, 72.49; H, 8.88. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.

The infrared spectrum of this ether showed the characteristic absorption band at 1105 cm^{-1} (C–O–C), it was identical with that of an authentic sample prepared as described earlier.[7)]

Fraction 3 was chromatographed over silica gel (2.5×45 cm). After the elusion of methyl *trans*-cinnamate (0.1 g.) with benzene, elusion with methanol gave a material which was then hydrolyzed with a methanolic alkali solution to give *meso*-β,γ-diphenyl adipic acid, m. p. 270—272°C, from methanol; a mixed melting point determination with an authentic sample prepared as described below showed no depression.

Found: C, 72.48; H, 6.14. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08%.

The infrared spectrum of this acid was identical with that of an authentic sample.

The Anodic Oxidation of Methanol in the Presence of Styrene, Carbon Monoxide and the Platinum Carbonyl Compound (Method B).—The reaction conditions and the yields of the products are summarized in Table III.

R-2 may be illustrated as follows: Metallic sodium (0.5 g., 0.022 mol.) was dissolved in 90 g. of absolute methanol in a cylindrical glass cell, and dry nitrogen was bubbled through the mixture for about 1 hr. The cell was placed in an autoclave, carbon monoxide was introduced (70 kg./cm^2), and then the mixture was electrolyzed at −10—−15°C for 5 hr. (1.0 amp., 16—45 V.), using two weighed platinum plates. The platinum used as a cathod (1.5 g.) was dissolved into the solution in order to give a certain platinum carbonyl compound; the solution then turned to greenish-blue. After the carbon monoxide had been removed, the plate of cathode was changed to a copper one (2×3 cm^2), and then 15.6 g. of freshly-distilled styrene (0.15 mol.) was added to the electrolyzed solution. Carbon monoxide was again introduced (70 kg./cm^2) and the mixture was electrolyzed for 16 hr. under the conditions described above. The electrolyzed solution was worked up in a manner similar to the procedure described above (method A), and the oily residue was fractionated by distillation under reduced pressure into the following fractions:

Fraction	B. p.	Weight, g.
1	~39°C/15—17 mmHg	2.5
2	64—75°C/0.3 mmHg	3.5
3	75—85°C/0.3 mmHg	10.5
4	85—125°C/0.3 mmHg	1.8
5	Residue	3—4

By gas chromatographic analysis (conditions: described above), it was shown that Fraction 1 was unreacted styrene, while Fractions 2—4 were mixtures of styrene glycol dimethyl ether (5.7 g.), methyl β-phenyl propionate (0.4 g.), methyl β-methoxy-β-phenyl propionate (3.9 g.) and methyl *trans*-cinnamate (5.0 g., 21% yield). The hydrolysis of the Fraction 5 (residue) with an aqueous alkali solution gave a small amount of *meso*-β,γ-diphenyl adipic acid (0.1 g.).

The Anodic Oxidation of Methanol in the Presence of α-Methylstyrene, Carbon Monoxide and Platinum Carbonyl Compound (Method B). —According to the procedure described above, the platinum carbonyl compound (2.9 g., wt. of Pt) was produced in a methanol solution containing sodium methoxide (metallic sodium (0.5 g.) in 90 g. of methanol) by electrolysis for 13.5 hr., and then freshly-distilled α-methylstyrene (17.7 g., 0.15 mol.) was added to the mixture. The electrolysis of the mixture was carried out, by using copper copper plate as a cathode, under the pressure of carbon monoxide (70 kg./cm^2) for 16 hr. (1.0 amp., −10—−15°C). The electrolyzed solution was worked up in a manner similar to the procedure described above (method A), and the oily residue was fractionated by distillation under reduced pressure into the following fractions:

Fraction	B. p.	Weight, g.
1	~49°C/12—13 mmHg	4.9
2	65—85°C/2—3 mmHg	2.0
3	85—125°C/2—3 mmHg	7.4
4	125—185°C/2—3 mmHg	1.0
5	Residue	5.9

By gas chromatographic analysis (conditions: column, Poly Ester DA, 3 m.; temperature, 182°C; carrier gas, H_2), it was shown that Fractions 1—4 were mixtures of methyl *trans*-β-methyl cinnamate, methyl 3-phenyl-3-butenoate, methyl β-methyl-β-phenyl propionate, α-methylstyrene glycol dimethyl ether and acetophenone and that the total amount of these products were as follows: methyl *trans*-β-methyl cinnamate, 4.5 g. (18% yield, based on the α-methylstyrene used); methyl 3-phenyl-3-butenoate, 2.7 g.; methyl β-methyl-β-phenyl propionate, 0.6 g.; α-methyl-styrene glycol dimethyl ether, 2.5 g.; acetophenone, 1.1 g. Fractions 3 and 4 were chromatographed over silica gel (2.5× 45 cm.). Elusion with benzene led to the isolation of the following products:

(a) Methyl *trans*-β-methyl cinnamate, b. p. 80—81°C/0.8 mmHg, m. p. 28—29°C; from ligroin.

Found: C, 74.88; H, 6.97. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86%.

The infrared spectrum of this unsaturated ester showed the characteristic absorption bands at about 1735 (C=O) and 1642 cm^{-1} (C=C), and it was identical with that of an authentic sample. The hydrolysis of this ester with an aqueous alkali solution gave *trans*-β-methyl cinnamic acid, m. p. 96.5—97.5°C, from ligroin; a mixed melting point determination with an authentic sample prepared as described below showed no depression.

Found: C, 74.22; H, 6.22. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22%.

(b) Methyl 3-phenyl-3-butenoate, b. p. 125—126°C/12—13 mmHg.

Found: C, 75.17; H, 6.89. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86%.

The infrared spectrum of this ester showed the characteristic absorption bands at about 1755 (C=O) and 1645 cm^{-1} (C=C), and the NMR spectrum of this unsaturated ester (CCl_4 as solvent) showed peaks at 2.75(C_6H_5), 4.55(CH_2=), 4.85(CH_2=), 6.47(OCH_3) and 6.59 τ(-CH_2-); the peak areas were in the ratio of 5 : 1 : 1 : 3 : 2, as would be expected from the structure. The hydrolysis of this ester with a 3 N potassium hydroxide solution gave *trans*-β-methyl cinnamic acid, m. p. 96.5—97.5°C; a mixed melting point determination with an authentic sample showed no depression.

(c) α-Methylstyrene glycol dimethyl ether, b. p. 67—69°C/1.5 mmHg, n_D^{14}=1.5022.

Found: C, 73.57; H, 9.27. Calcd. for $C_{11}H_{16}O_2$: C, 73.39; H, 8.95%.

The infrared spectrum of this dimethyl ether showed the characteristic absorption bands at about 1110 and 1128 cm^{-1} (C-O-C), and it was identical with that of an authentic sample prepared as earlier.[7]

Methyl β-methyl-β-phenyl propionate was identified by gas chromatographic analysis (conditions as described above). From Fraction 2, acetophenone was identified as its 2,4-dinitrophenylhydrazone: m. p. 237—238°C; a mixed melting point determination with an authentic sample was not depressed.

Found: C, 56.17; H, 3.93. Calcd. for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03%.

The Anodic Oxidation of Methanol in the Presence of 1,1-Diphenylethylene, Carbon Monoxide and the Platinum Carbonyl Compound (Method B).—After the platinum carbonyl compound (1.0 g., wt. of Pt) had been produced in methanol containing sodium methoxide (metallic sodium 0.5 g in 90 g. of methanol) by electrolysis for 3 hr., 18.0 g. of freshly-distilled 1,1-diphenylethylene was added to the mixture; then the mixture was electrolyzed by using copper plate as the cathode for 16 hr. under carbon monoxide pressure (70 kg./cm^2). The electrolyzed solution was worked up in a manner similar to that described above, and the oily residue was fractionated by distillation under diminished pressure into the following fractions:

Fraction	B. p.	Weight, g.
1	~125°C/0.2 mmHg	2.5
2	125—145°C/0.2 mmHg	17.3
3	Residue	2—3

10.0 g. of a mixture of Fractions 1 and 2 was chromatographed over silica gel (2.5×50 cm.). Elution with benzene led to the isolation of methyl β-phenyl cinnamate (4.0 g.), 1,1-diphenylethylene glycol dimethyl ether (2.5 g.), unidentified products (3.5 g.) and unreacted 1,1-diphenylethylene (0.5 g.): (a) methyl β-phenyl cinnamate, b. p. 133—134°C/0.3 mmHg.

Found: C, 80.83; H, 6.19. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92%.

The infrared spectrum of this ester showed the characteristic absorption bands at about 1745 (C=O) and 1625 cm^{-1} (C=C). The hydrolysis of this ester with an alcoholic alkali solution gave β-phenyl cinnamic acid, m. p. 161—162°C, from methanol; a mixed melting point determination with an authentic sample prepared as described below showed no depression.

Found: C, 80.54; H, 5.15. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39%.

(b) 1,1-Diphenylethylene glycol dimethyl ether, m. p. 64.5—65.5°C, from ligroin; a mixed melting point determination with an authentic sample prepared as described earlier[7] showed no depression.

Found: C, 79.06; H, 7.25. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

9.5 g. of the mixture of Fractions 1 and 2 was hydrolyzed with a 10% potassium hydroxide - ethanol solution to give 3.5 g. of β-phenyl cinnamic acid with a m. p. of 158—161°C.

The Anodic Oxidation of Methanol in the Presence of Styrene, Carbon Monoxide and Platinous Potassium Chloride. — Metallic sodium (0.5 g.) was dissolved in 90 g. of absolute methanol in a cylindrical glass cell, and then 3.0 g. of platinous potassium chloride and 33 g. of freshly-distilled styrene were added to the mixture. The mixture was electrolyzed by using carbon as the cathode and platinum as the anode for 17 hr. under a carbon monoxide pressure of 70 kg./cm². The reaction mixture was worked up in a manner similar to the procedure described above, and the oily residue was distilled under diminished pressure to give the following fractions:

Fraction	B. p.	Weight, g.
1	~49°C/20 mmHg	8.7
2	~75°C/1 mmHg	6.2
3	75—100°C/1 mmHg	5.8
4	100—145°C/1 mmHg	2.5
5	Residue	5.5

By gas chromatographic analysis (conditions: column, Poly Ethylene Glycol 6000, 3 m.; column temperature, 177°C; carrier gas, H_2), it was shown that the total amount of the products were as follows: styrene-glycol dimethyl ether, 9.3 g.; methyl β-methoxy-β-phenyl propionate, 1.8 g.; methyl *trans*-cinnamate, 0.4 g.; unidentified products, 3.5 g.

Fraction 3 was hydrolyzed with a cold 3 N potassium hydroxide solution to give 1.7 g. of β-methoxy-β-phenyl propionic acid with a m. p. of 97—98.5°C from ligroin; a mixed melting point determination with an authentic sample showed no depression.

The Syntheses of the Authentic Samples.— *trans*-Cinnamic acid and β-phenyl propionic acid or their esters were commercial; they were then purified from ligroin.

Methyl β-methoxy-β-phenyl propionate was prepared by the reaction of methyl α-acetoxymercury-β-methoxy-β-phenyl propionate, which had been prepared by the action of methyl *trans*-cinnamate with mercury acetate in methanol,[20] with hydrogen sulfide and ammonia[20]; b. p. 125—127°C/12—13 mmHg. β-Methoxy-β-phenyl propionic acid was obtained by the hydrolysis of methyl β-methoxy-β-phenyl propionate with a cold aqueous alkali solution; m. p. 97—98°C (lit.,[20] m. p. 98°C). *meso*-β,γ-Diphenyl adipic acid was prepared by the electrolytic reduction of *trans*-cinnamic acid at the mercury cathode[21]; m. p. 270—272°C (lit.,[21] m. p. 270—273°C). *trans*-β-Methyl cinnamic acid was synthesized from *t*-butyl acetate[22] and acetophenone by the action of lithium amide[23]; m. p. 97.5—98°C (lit.,[23] m. p. 98—98.5°C). Methyl β-methyl-β-phenyl propionate was prepared by the electrolytic reduction of methyl *trans*-β-methyl-cinnamate[24]; b. p. 133—134°C/22 mmHg. β-Phenyl cinnamic acid was prepared by the reaction of 1,1-diphenylethylene with oxalyl chloride[25]; m. p. 161—162°C (lit.,[25] m. p. 162°C).

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