

and 100.1 g (1.2 mol) of hexene-1 were heated at 115° for 72 hr. Each tube contained 0.03 ml of 0.1 *M* chloroplatinic acid. A glc analysis of the crude product revealed one major and four minor components. Distillation of 83 g of this material gave 23.3 g (41%) of bis(*n*-hexyldimethylsilyl)dimethylsilylamine: bp 110° (1 mm); n_D^{25} 1.4569; neut equiv 368, calcd 359; ir (CCl₄) 2130 (SiH) (CS₂), 900–920 cm⁻¹ (SiN); nmr τ 9.87 (s, 12, SiCH₃), 9.74 (d, 6, HSiCH₃), 8.4–9.6 (26, alkyl-H) 5.44 (m, 0.8, SiH). One of the minor components was isolated from a separate experiment with trisdimethylsilylamine and hexene-1 and identified as bis(*n*-hexyldimethylsilyl)trimethylsilylamine: bp 115° (1 mm); n_D^{25} 1.4611; neut equiv 373, calcd 373; ir (CS₂) 1250–1260 (multiplet SiMe), 840 (SiMe₃), 910 cm⁻¹ (SiN).

The residue from the distillation of the above 83 g of material was analyzed by a combination of glc and mass spectra. Three peaks in the glc had a *m/e* ratio of 429 for a molecular ion corresponding to Si₃C₂₃H₆₅N. This corresponds to Hex₃Me₃HSi₃N.

A solution of 17 g of this residue in 50 ml of ethanol with \approx 100 mg of ammonium chloride was refluxed for 10 days. The volatiles were removed *in vacuo* and a glc of the resulting products had a large peak corresponding to hexyldimethylethoxysilane and smaller peaks for hexylmethylethoxysilane and dihexylmethylethoxysilane as indicated by coinjection with authentic samples.

Registry No.—Bis-[2-(dimethylaminodimethylsilyl)-ethyldimethylsilyl]amine, 25938-29-8; 2-(methyldimethoxyethyl)propylamine, 25938-30-1; *sym*-bis(3,3-dimethoxypropyl)tetramethyldisilazane, 26344-26-3; bis-(*n*-hexyldimethylsilyl)dimethylsilylamine, 25938-32-3; bis-(*n*-hexyldimethylsilyl)trimethylsilylamine, 25938-28-7.

A Novel Reaction of Saturated Aliphatic Acids with Aromatic Compounds in the Presence of Palladium(II) Chloride. The Formation of Cinnamic Acid Derivatives

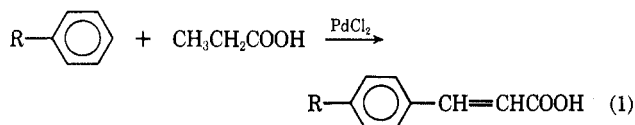
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Received December 23, 1969

Saturated aliphatic acids with α and β hydrogens, such as propionic, *n*- and isobutyric acid, reacted with aromatic compounds and palladium(II) salts in the presence of alkali metal carboxylates to give cinnamic acid derivatives. The addition of some solvents, such as an acid anhydride, tetrachloroethylene, or acetonitrile, resulted in significant differences in products formed. A mechanism involving the formation of an intramolecular π complex of palladium acrylate (D) has been suggested for the dehydrogenation step.

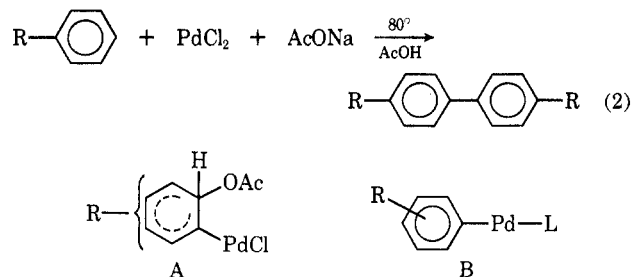
In a previous communication,¹ we reported on the novel carboxyvinylation of aromatic compounds by saturated aliphatic acids and palladium(II) chloride to give cinnamic acid derivatives.



As is well known, aromatic α,β -unsaturated acids can be synthesized by the reaction of aromatic aldehydes, ketones, or olefins with appropriate agents.² Also, with palladium(II) chloride, various cinnamates are successfully obtained from the reactions of unsaturated esters with benzenes.³ However, our work is unique in

that cinnamic acids are formed in one step from aromatic compounds and saturated aliphatic acids. This reaction is very interesting, since the formation of α,β -unsaturated aliphatic acids *via* dehydrogenation of saturated aliphatic acids by metal salts is unknown.

The reaction of aromatic compounds with palladium(II) chloride has been reported by van Helden and Verberg⁴ to give biphenyl derivatives. They proposed that the reaction proceeds *via* dimerization of a π -cyclohexadienyl complex (A). Davidson and Triggs⁵ suggested the presence of unstable phenylpalladium(II) complex (B) by analogy with the reaction of aromatic compounds with other metal acetates. Furthermore,

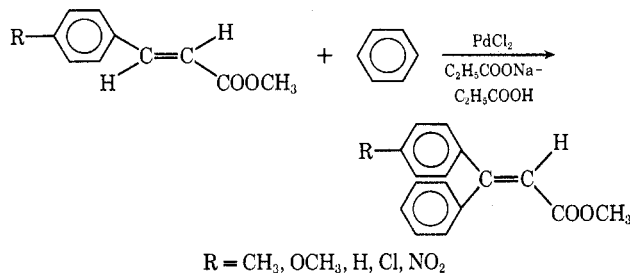


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(1) S. Nishimura, T. Sakakibara, and Y. Odaira, *Chem. Commun.*, 313 (1969).

(2) (a) W. Perkin, *J. Chem. Soc.*, **21**, 53, 181 (1868); **31**, 388 (1877). (b) J. Johnson, *Org. React.*, **1**, 210 (1942). (c) E. Knoevenagel, *Chem. Ber.*, **31**, 2596 (1898); O. Doebner, *ibid.*, **33**, 2140 (1900). (d) S. Reformatsky, *ibid.*, **20**, 1210 (1887); R. Shriner, *Org. React.*, **1**, 1 (1942). (e) M. Kharasch, S. Kane, and H. Brown, *J. Amer. Chem. Soc.*, **64**, 333 (1942).

(3) Unpublished work. Various aromatic α,β -unsaturated esters were phenylated by palladium(II) chloride to give β -phenylcinnamates in 40–50% yields.



it was reported that some olefins reacted with aromatic compounds in the presence of palladium(II) acetate to give phenylated olefins.⁶ That these reactions proceed *via* a similar phenylpalladium(II) complex (B) is supported by the reaction of *N,N*-dimethylbenzylamine-palladium complex with styrene to form a stilbene deriv-

(4) R. van Helden and G. Verberg, *Recl. Trav. Chim. Pays-Bas*, **84**, 1263 (1965).

(5) J. Davidson and C. Triggs, *Chem. Ind. (London)*, 457 (1966).

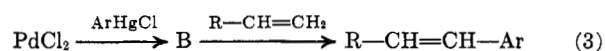
(6) Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi, *Tetrahedron Lett.*, 633 (1968).

TABLE I
 REACTION OF CARBOXYLATE IONS WITH AROMATIC COMPOUNDS IN THE PRESENCE OF Pd^{II} SALTS

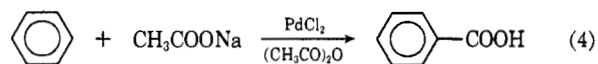
Pd ^{II} salt	Reagents				Solvent	Products, % ^a
	Sodium carboxylate	Aromatic compound	Aliphatic acid			
PdCl ₂	C ₂ H ₅ COONa	PhH	C ₂ H ₅ COOH	None	None	PhPh (11), Ph ₂ C=CHCOOH (9.2), Ph ₂ C=CH ₂ (2.5), PhHC=CHCOOH (0.7), PhCOOH (0.2)
PdCl ₂	C ₂ H ₅ COONa	PhH	C ₂ H ₅ COOH	(C ₂ H ₅ CO) ₂ O	(C ₂ H ₅ CO) ₂ O	PhHC=CHCOOH (28), PhHC=CHPh (3.2)
Pd(OOCC ₂ H ₅) ₂	None	PhH	C ₂ H ₅ COOH	None	None	PhPh (16), PhCOOH (2.1), Ph ₂ C=CHCOOH (1.4)
PdCl ₂	<i>n</i> -C ₃ H ₇ COONa	PhH	<i>n</i> -C ₃ H ₇ COOH	None	None	CH ₃ (Ph)C=CHCOOH (12), PhCOOH (<1), PhCH ₂ (Ph)C=C(Ph)COOH (2.5)
PdCl ₂	<i>n</i> -C ₃ H ₇ COONa	PhH	<i>n</i> -C ₃ H ₇ COOH	(<i>n</i> -C ₃ H ₇ CO) ₂ O	(<i>n</i> -C ₃ H ₇ CO) ₂ O	PhCOOH (21), CH ₃ (Ph)C=CHCOOH (<0.5)
PdCl ₂	<i>n</i> -C ₃ H ₇ COONa	PhH	<i>n</i> -C ₃ H ₇ COOH	Cl ₂ C=CCl ₂	Cl ₂ C=CCl ₂	PhCOOH (28), CH ₃ (Ph)C=CHCOOH (9.2), PhPh (trace)
Pd(<i>n</i> -OOCC ₃ H ₇) ₂	<i>n</i> -C ₃ H ₇ COONa	PhH	<i>n</i> -C ₃ H ₇ COOH	None	None	PhPh (39), PhCOOH (7.9), CH ₃ (Ph)C=CHCOOH (5.4)
PdCl ₂	<i>i</i> -C ₃ H ₇ COONa	PhH	<i>i</i> -C ₃ H ₇ COOH	None	None	PhHC=C(CH ₂ Ph)COOH (8.0), PhCOOH (0.8), PhHC=C(CH ₃)COOH (6.2)
PdCl ₂	<i>i</i> -C ₃ H ₇ COONa	PhCH ₃	<i>i</i> -C ₃ H ₇ COOH	None	None	CH ₃ C ₆ H ₄ (H)C=C(CH ₃)COOH (4.4), CH ₃ C ₆ H ₄ (H)C=C(CH ₂ C ₆ H ₅ CH ₃)COOH (0.8)
PdCl ₂	<i>i</i> -C ₃ H ₇ COONa	PhH	<i>i</i> -C ₃ H ₇ COOH	(<i>i</i> -C ₃ H ₇ CO) ₂ O	(<i>i</i> -C ₃ H ₇ CO) ₂ O	PhCOOH (19), PhHC=C(CH ₃)COOH (<0.5), PhPh (trace)
PdCl ₂	<i>i</i> -C ₃ H ₇ COONa	PhH	CH ₃ COOH	None	None	PhPh (75), PhHC=C(CH ₃)COOH (2.1), PhCOOH (1.4), PhHC=C(CH ₂ Ph)COOH (0.9)
PdCl ₂	<i>i</i> -C ₃ H ₇ COONa	PhH	CH ₃ COOH	CH ₃ CN	CH ₃ CN	PhPh (55), PhCOOH (8.6), PhHC=C(CH ₃)COOH (0.7)
Pd(<i>i</i> -OOCC ₃ H ₇) ₂	<i>i</i> -C ₃ H ₇ COONa	PhH	<i>i</i> -C ₃ H ₇ COOH	None	None	PhHC=C(CH ₃)COOH (13), PhHC=C(CH ₂ Ph)COOH (8.8)
Pd(<i>i</i> -OOCC ₃ H ₇) ₂	None	PhH	None	None	None	PhPh (98)

^a Yield based on Pd^{II} salt charged (mol/mol).

ative.⁷ Recently, it has been shown by Heck⁸ that the complex (B) is an effective arylating agent of olefins. The reaction of palladium(II) chloride with aromatic compounds, therefore, has been generally considered to contain a complex (B) as a reactive intermediate.



As already reported by us,⁹ some coordinative solvents had a significant influence on the reaction of aromatic compounds with palladium(II) chloride. For example, in the presence of acetic anhydride, benzene reacted with sodium acetate and palladium(II) chloride to yield benzoic acid.



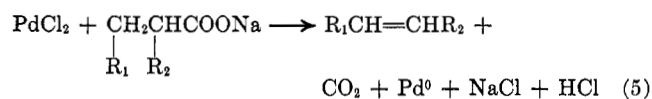
In the present carboxyvinylation of aromatic compounds, an analogous solvent effect should be also expected. Accordingly, further investigation has been made of the solvent effect to establish the limitation and scope of this reaction.

Results and Discussion

In a typical carboxyvinylation experiment, the aromatic compound and sodium carboxylate were reacted in the presence of palladium(II) chloride and the corresponding carboxylic acid for several hours. During the reaction, palladium black precipitated, showing that Pd^{II} was reduced to Pd⁰. The reaction was terminated when the precipitation of metallic

palladium and gas evolution ceased. The results of product analyses in various systems are shown in Table I.

In the absence of aromatic compounds, the reaction of palladium(II) chloride with sodium propionate or butyrate in propionic acid or butyric acid and the corresponding acid anhydride, gave ethylene and propylene, respectively, in addition to carbon dioxide. The absence of ethane and propane suggests that the reaction does not proceed *via* the formation of alkyl radical as has been observed for other metal carboxylates.¹⁰ It is well known that palladium has a strong affinity for hydrogen and that alkylpalladium-phosphine complexes with a β hydrogen in the alkyl group are easily decomposed *via* β -hydride abstraction by palladium to give olefin and Pd-H.¹¹ An analogous β -hydride abstraction by palladium may be involved in the above olefin-forming reaction *via* decarboxylation of carboxylate ion.



As shown in the carboxyvinylation in isobutyric acid, both palladium(II) chloride and palladium(II) isobutyrate gave cinnamic acid derivatives, in the presence of sodium isobutyrate. On the other hand, the reaction of palladium(II) isobutyrate with benzene, without isobutyrate ion, gave biphenyl almost quantitatively as the sole product (Table I). Similarly, the use of palladium(II) propionate without sodium propionate

(7) J. Tsuji, *Accounts Chem. Res.*, **2**, 144 (1969).

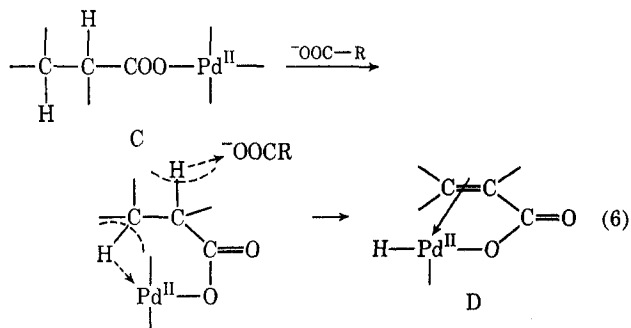
(8) R. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).

(9) T. Sakakibara, S. Nishimura, and Y. Odaira, *Tetrahedron Lett.*, 1019 (1969).

(10) (a) J. Kochi, *J. Amer. Chem. Soc.*, **87**, 3609 (1965). (b) R. Sheldon and J. Kochi, *ibid.*, **90**, 6658 (1968). (c) J. Kochi and T. Betha, *J. Org. Chem.*, **33**, 75 (1968).

(11) G. Calvin and G. Coates, *J. Chem. Soc.*, 2008 (1960).

gave biphenyl rather than the olefinic acids. The presence of sodium carboxylate, therefore, is considered to be essential for carboxyvinilation. If hydride abstraction by palladium is involved in the formation of olefinic acids from saturated aliphatic acids, then an α hydrogen, activated by an adjacent carboxyl group, might be abstracted as proton by a nucleophile, such as carboxylate ion. Thus, a suggested mechanism for dehydrogenation is as follows.



The complex (D), possessing an unstable Pd-H bond, might rapidly decompose to unsaturated acid and Pd⁰.

The reaction of acrylic acid with benzene gave cinnamic acid in the presence of palladium(II) chloride and sodium acetate in acetic acid solvent. The forma-



tion of di- or triphenylated acrylic acids may be explained as further arylation of cinnamic acids. As supporting evidence, cinnamic acid derivatives reacted with benzene in the presence of palladium(II) chloride and sodium propionate in propionic acid to give β -phenylcinnamic acids, along with decarboxylated products (Table II).

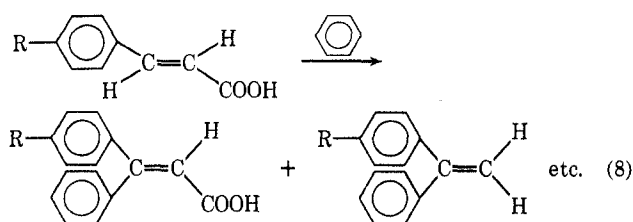


TABLE II

PHENYLATION OF CINNAMIC ACID DERIVATIVES^a

R	Products, % ^b		
H			
CH ₃	9.5	17.4	None
CH ₃ O	11.6	5.8	6.8
Cl	12.8	7.2	7.7
	23.9	6.9	9.2

^a Cinnamic acid derivative (0.02 mol), benzene (0.5 mol), palladium(II) chloride (0.02 mol), and sodium propionate (0.1 mol) were reacted at 100° for 6 hr in propionic acid (110 ml).

^b Yield based on Pd^{II} chloride charged (mol/mol).

As shown in Table I, the addition of some solvents, such as acid anhydrides, tetrachloroethylene, or acetonitrile, remarkably influenced the distribution of products formed. For example, addition of butyric

anhydride to the reaction of sodium butyrate and benzene with palladium(II) chloride accelerated carboxylation to give benzoic acid and propylene, while suppressing carboxyvinilation of aromatic compounds. Similarly, addition of propionic anhydride completely suppressed further arylation of cinnamic acids formed. Since tetrachloroethylene and acetonitrile had a similar effect, these solvents may coordinate strongly to palladium and thus promote elimination of olefin from the aliphatic acid-palladium complex (C) or suppress further arylation of cinnamic acids. Further study of the formation of unsaturated acids from saturated aliphatic acids is in progress.

Experimental Section

Materials.—Commercially available palladium(II) chloride (a guaranteed reagent by Tokyo Kasei Kogyo Co. Ltd.) was powdered and used without further purification. Carboxylic acids and anhydrides were distilled and dried by sodium sulfate before use. Thiophene-free aromatic compounds were used after drying by Na wire. Sodium and potassium propionate were dried under reduced pressure at 130°, and sodium butyrate at 50°, over phosphorus pentoxide overnight. Palladium(II) carboxylates were prepared according to the method of Stephenson, *et al.*¹²

All melting points are uncorrected. The ir spectra were recorded with a Japan Spectroscopic Model IR-G spectrophotometer; the nmr spectra with a Nippon Denshi Model JNM-3H60 spectrometer; the mass spectra with a Hitachi Model RMU-6E mass spectrometer.

Nmr spectral data for the various cinnamic acid derivatives isolated are given in Table III.

Reaction of Benzene with Sodium Propionate and Propionic Acid.—In a 200-ml four-necked flask, a stirred mixture of benzene (39.0 g, 0.5 mol), sodium propionate (9.6 g, 0.1 mol), palladium(II) chloride (3.5 g, 0.02 mol), and propionic acid (98.4 g, 1.33 mol) was heated at 100° for 6 hr under an atmosphere of dried nitrogen. The evolved gas was introduced to a manometric gas trap. The initial brown mixture gradually turned black as metallic palladium formed. After 4 hr, gas evolution almost stopped; 49 ml of gas was collected at the end of reaction. Metallic palladium was removed by filtration, and the solvent was removed under reduced pressure; 150 ml of 15% aqueous sodium carbonate was added to the residue and the mixture was extracted with five portions of diethyl ether (100 ml). The organic layer (K) was washed with water and dried by sodium sulfate overnight. The combined aqueous layer was acidified with concentrated hydrochloric acid and extracted again with diethyl ether, and the organic layer (L) was dried over sodium sulfate. The gaseous product was analyzed by gas chromatography, using a 3-m, 20% acetylacetone on Neopac 1A column (0°, He carrier). Carbon dioxide was detected, but neither ethane nor ethylene. The ether layer (K): after a removal of ether, neutral products were isolated as solids (588 mg), which consisted of biphenyl (58%), 1,1-diphenylethylene (27%), and unidentified products (15%), by glc analysis using a 1.5-m, polyethylene glycol 20M on Celite 545 column (250°) and a 1.5-m silicone DC550 on Celite 545 column (200°, H₂ carrier). The ether layer (L): after a removal of ether and propionic acid by distillation, acidic products were obtained as solids (439 mg). A portion was esterified by diazomethane and the products were identified as a mixture of methyl β -phenylcinnamate (94.3%), methyl cinnamate (4.5%), and methyl benzoate (1.2%) by glc analysis. Another part of the solid products was recrystallized twice from aqueous ethanol to yield β -phenylcinnamic acid, mp 156–157.5° (lit.¹³ mp 162°); the amide gave mp 145–147° (lit.¹⁴ mp 154°).

In the Presence of Propionic Anhydride.—Benzene (39 g, 0.5 mol), sodium propionate (9.6 g, 0.1 mol), palladium(II) chloride (3.5 g, 0.02 mol), and propionic acid (98.4 g, 1.3 mol) were re-

(12) T. Stephenson, S. Morehouse, A. Powell, J. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).

(13) H. Rupe and E. Busolt, *Chem. Ber.*, **40**, 4539 (1907).

(14) S. Work, D. Bryant, and C. Hauser, *J. Amer. Chem. Soc.*, **86**, 872 (1964).

TABLE III
 NMR SPECTRAL DATA FOR CINNAMIC ACID DERIVATIVES ISOLATED

Product	Registry no.	Solvent, %	Phenyl H	Vinyl H	Others H (-CH ₂ , -CH ₂ -, >CH-)
PhHC=CHCOOH	621-82-9	CDCl ₃ (2.0)	2.55 (s, 5)	2.20 (d, 1) 3.55 (d, 1)	
Ph ₂ C=CHCOOH	606-84-8	CDCl ₃ (4.5)	2.74 (s, 10)	3.71 (s, 1)	
CH ₃ (Ph)C=CHCOOH	1199-20-8	CDCl ₃ (3.3)	2.66 (s, 5)	3.89 (s, 1)	7.42 (s, 3)
PhCH ₂ (Ph)C=C(Ph)COOH	25908-00-3	CDCl ₃ (2.7)	2.71 (s, 5)		6.42 (s, 2)
	25860-60-6 (amide)		2.88 (s, 5) 3.20 (s, 5)		
PhHC=C(CH ₃)COOH	1199-77-5	CDCl ₃ (3.3)	2.57 (s, 5)	2.16 (s, 1)	7.81 (s, 3)
PhHC=C(CH ₂ Ph)COOH	4361-83-5	CCl ₄	2.72 (s, 5) 2.85 (s, 5)	2.03 (s, 1)	6.10 (s, 2)
<i>p</i> -CH ₃ C ₆ H ₄ (H)C=C(CH ₃)COOH	25860-59-7	CDCl ₃ (3.0)	2.57-2.89 (q, 4)	2.22 (s, 1)	7.63 (s, 3) 7.83 (s, 3)

acted in propionic anhydride (90 ml) at 97° for 7.5 hr. Gaseous products (28 ml) were carbon dioxide and ethylene. After work-up as described above, a neutral ether solution (K) and an acidic ether solution (L) were obtained. Distillation of K under the reduced pressure (9 mm) gave white crystals (80 mg) as a sublimate on the neck of the Claisen flask, mp 121-122.5° (lit.¹⁵ mp 124°), recrystallized from ethanol. A mixture melting point with a specimen of *trans*-stilbene was undepressed. The ir of the distillation residue showed characteristics of acid anhydride. The residue was hydrolyzed by potassium hydroxide in ethanol under reflux for 2 hr and, after usual treatment, white crystals (143 mg) were isolated; the melting point and ir and nmr spectra were identical with those of cinnamic acid. The acidic residue (480 mg) from L was recrystallized from water, after treatment with activated carbon to give white crystals, mp 130-131°; a mixture melting point with a specimen of cinnamic acid was undepressed. The amide gave mp 140-141° (lit.¹⁶ mp 142°).

Reaction of Benzene with Sodium *n*-Butyrate and *n*-Butyric Acid.—A stirred mixture of benzene (117 g, 1.5 mol), sodium *n*-butyrate (33.2 g, 0.3 mol), palladium(II) chloride (3.5 g, 0.02 mol), and *n*-butyric acid (132 g, 1.5 mol) was heated under reflux (87.5°) for 8 hr. Evolved gas (22.5 ml) was carbon dioxide. The neutral residue (K) and the acidic residue (L) were isolated in yields of 446 mg and 362 mg, respectively. β -Methylcinnamic acid was isolated by recrystallization of L: leaflets from ligroin; mp 96-97° (lit.¹⁷ mp 98°); ir 2500-2800, 1750, and 1225 (COOH), 1618 (C=C), 1575, 690-710, and 770 cm⁻¹ (-Ph). After esterification of L with diazomethane, glc analysis showed the presence of methyl *n*-butyrate (1.5%), methyl benzoate (1.8%), methyl β -methylcinnamate (91%), and unidentified products (5.7%), which probably consisted of diphenylated olefinic acid methyl esters. α -Phenyl- β -benzylcinnamic acid was isolated from K, probably due to slow neutralization of the acid. The acid (151 mg) was separated as an insoluble substance with petroleum ether (bp 40-55°) from aromatic olefins, which mainly contained triphenylated propylene

(by ir and mass analysis), and crystallized from acetonitrile as colorless crystals, whose further purification was made by sublimation: mp 196-197°; ir 2500-2800, 1670, and 1225 (COOH), 1580, 1560, 780, 760, 720, and 693 cm⁻¹ (-Ph's); *m/e* 314 (M⁺), 269 (M - 45); potassium permanganate solution was discolored under heating; the nmr data are shown in Table III.

Anal. Calcd for C₂₂H₁₈O₂: C, 84.05; H, 5.77. Found: C, 83.86; H, 5.60.

Reaction of Benzene with Sodium Isobutyrate and Isobutyric Acid.—A mixture of benzene (117 g, 1.5 mol), sodium isobutyrate (33.2 g, 0.3 mol), palladium(II) chloride (3.6 g, 0.02 mol), and isobutyric acid (132 g, 1.5 mol) was heated under reflux for 7 hr. The evolved gas (53 ml) was carbon dioxide. An acidic residue (L) (675 mg) and a neutral residue (K) (233 mg) were obtained. Fractional crystallization of L gave α -benzylcinnamic acid: needles from ethanol, mp 155-156° (lit.¹⁸ mp 158°); the amide gave mp 148-150°.

Anal. Calcd for C₁₆H₁₄O₂: C, 80.64; H, 5.92. Found: C, 80.38; H, 5.87.

Glc analysis of esterified L showed the presence of methyl α -benzylcinnamate (65%), methyl α -methylcinnamate (32%), and methyl benzoate (3%). Neutral products were mainly mono-, di-, or triphenylated propylene isomers, judging from the results of ir, glc, and mass analyses.

Phenylation of Cinnamic Acid Derivatives in Propionic Acid.—All products were identified by melting point and ir, nmr, and mass spectra. All new compounds were characterized by elementary analyses.

Registry No.—Palladium(II) chloride, 7647-10-1.

Acknowledgment.—The authors are indebted to Dr. E. Fujita and Mrs. M. Sakurai for the nmr measurements, to Miss J. Maenaka and Mrs. N. Ishii for the elemental analyses, and also to Mr. H. Moriguchi for the mass analyses.

(15) A. Michaelis and H. Lauge, *Chem. Ber.*, **8**, 1313 (1875).

(16) T. Poster, *ibid.*, **38**, 2320 (1905).

(17) R. Stoermer, F. Grimm, and E. Laage, *ibid.*, **50**, 968 (1917).

(18) A. Michael and E. Palmer, *J. Amer. Chem. Soc.*, **7**, 69 (1885).