Tetrahedron Letters No.13, pp. 1019-1022, 1969. Pergamon Press. Printed in Great Britain.

A NEW CARBOXYLATION OF AROMATIC COMPOUNDS BY PALLADIUM(II) CHLORIDE

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(Received in Japan 16 January 1969; received in UK for publication 10 February 1969)

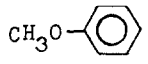
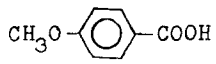
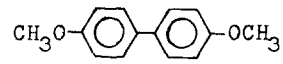
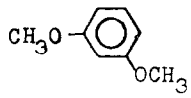
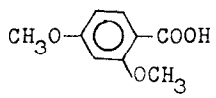
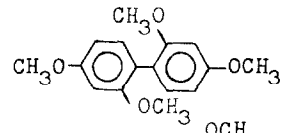
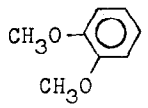
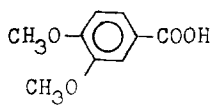
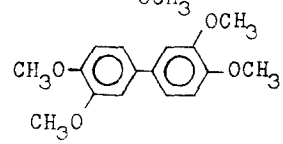
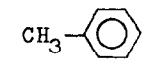
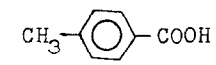
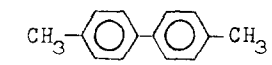
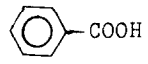
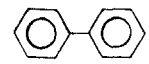
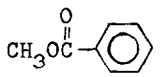
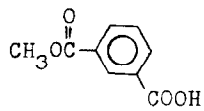
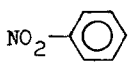
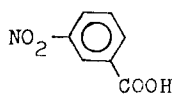
Since Smidt et al. established a commercially feasible process for acetaldehyde production from ethylene, many workers have investigated the reaction of unsaturated compounds with palladium salts. However, the direct introduction of carboxyl group into an aromatic ring by palladium(II) chloride has never been made. Although Henry recently reported a synthetic method of aromatic acids by Pd(II)-catalyzed CO insertion, this reaction yields an aroyl chloride as a primary product (1). We report here a novel carboxylation of aromatic compounds by palladium(II) chloride as a preliminary communication.

Heating a mixture of 0.50 mole of benzene, 0.02 mole of palladium(II) chloride and 0.10 mole of sodium acetate in the mixed solvent of 0.70 mole of acetic anhydride and 1.3 mole of acetic acid at 100° for 5 hours under the nitrogen atmosphere, gave a 27.4 % yield of benzoic acid in addition to a 19.0 % of biphenyl. For characterization, this reaction was applied for various benzene derivatives, and the results are summarized in Table I.

As shown in Table I, the formation of aromatic acids and of biphenyls were competitive, and the nature of substituent groups influenced on the isomer distribution of aromatic acids formed. Thus the para-isomers were mainly obtained from benzene derivatives with electron-donating substituents, such as methyl

TABLE I

Formation of Aromatic Acids and Biphenyls from Benzene Derivatives

Reagents[a] Benzene Derivatives	Products, (%)[b] Aromatic Acids		Biphenyls	
		(10.8)[c]		(12.0)[c]
		(11.8)[c]		(1.2)[c]
		(13.6)[c]		(34.0)[c]
		(10.6)[c]		(3.4)[c]
		(18.5)		(3.0)
		(6.2)[c]	ND[d]	
		(5.7)[c]	ND[d]	

a. A mixture of $PdCl_2$ (0.02 mole), sodium acetate (0.10) and benzene derivatives (0.25), was reacted in the mixed solvent of acetic anhydride (0.20) and acetic acid (0.88) at 100° for 5 hours.

b. Yield based on $PdCl_2$.

c. Other isomers were not identified but their yields were much smaller.

d. Not determined.

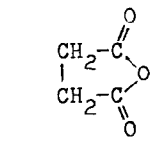
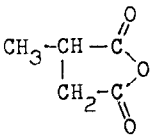
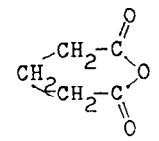
or methoxyl group, while the meta-isomers predominated with electron-withdrawing substituents, such as methoxycarbonyl or nitro group. These results indicate

that the carboxylation is seemingly an aromatic electrophilic substitution reaction by the carboxyl group. The biphenyl formation by oxidative coupling has already been reported by van Herden et al. (2, 3). However, in our experiments, it is noteworthy that the oxidative coupling reaction was extremely suppressed by the addition of acetic anhydride and the carboxylation predominantly occurred.

Also in the presence of cyclic acid anhydrides, the aromatic acid was certainly formed but the biphenyl derivative was the main product as shown in Table II.

TABLE II

Formation of Aromatic Acids and Biphenyls with Various Acid Anhydrides

Reagents[a]		Products	(%)[b]
Acid Anhydride	R-C$_6$H$_4$	R-C$_6$H$_4$-COOH	R-C$_6$H$_4$-C$_6$H$_4$-R
	R = H	1.8	55.0
	OCH_3	2.0	16.0
	H	Small	52.0
	H	4.1	26.0

a. $PdCl_2$ (0.02 mole), sodium acetate (0.10), aromatic compounds (0.25), acid anhydride (0.20) and acetic acid (1.3) were mixed and heated at 100° for 5 hours.

b. Yield based on $PdCl_2$.

The carboxylation of aromatic compounds was facilitated by some kind of solvents. For example, with acetonitrile instead of acid anhydride, the formation of aromatic acid was considerably notable; a mixture of benzene (0.125 mole), palladium(II) chloride (0.01), sodium acetate (0.05) and acetonitrile (0.10) in acetic acid (0.66) was heated at 93° for 15 hours under the nitrogen

atmosphere to afford benzoic acid (8.4 %) and biphenyl (11.6 %).

A carboxylation did take place also with lithium or potassium acetate but did not occur in the absence of metal acetate. The yield of aromatic acid decreased in the order of sodium, lithium and potassium acetate.

A further detailed work will be shortly published on the mechanism of carboxylation of aromatic compounds by palladium(II) chloride.

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2. R. van Helden and G. Verberg, Rec. Trav. chim., 84, 1263 (1965).
3. J. M. Davidson and C. Triggs, Chem. Ind. (London), 457 (1966).