

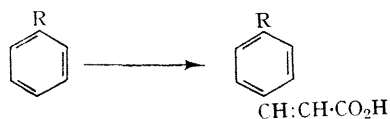
A Novel Carboxyvinylation of Aromatic Compounds by Palladium(II) Chloride

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Summary Benzene and substituted benzenes are converted into cinnamic acid derivatives by carboxyvinylation in the presence of palladium(II) chloride.

As an extension of our earlier work¹ we describe a novel carboxyvinylation of aromatic compounds by palladium(II) chloride in the presence or absence of aliphatic acid anhydrides to give cinnamic acid derivatives.



In a typical experiment, benzene (0.50 mole), sodium

propionate (0.10 mole), palladium(II) chloride (0.02 mole), propionic anhydride (180 ml.), and propionic acid (100 ml.) were heated at 100° for 6 hr. Carbon dioxide and ethylene were evolved and palladium was precipitated. Upon work-up, cinnamic acid (27.9%) and *trans*-stilbene (3.2%) were obtained [yields based on palladium(II) chloride used]. In the analogous carboxyvinylation of monosubstituted alkylbenzenes, (*e.g.* toluene and isopropylbenzene) the corresponding *para*-substituted cinnamic acids were obtained, although in lower yields. In a similar reaction of benzene with palladium(II) propionate in place of palladium(II) chloride and sodium propionate, cinnamic acid (13%) was also formed, together with a trace of *trans*-stilbene. The absence of propionic anhydride in the

reaction of benzene with palladium(II) chloride and sodium propionate led to the formation of further phenylated products. Thus, $\beta\beta$ -diphenylacrylic acid (9.2%) and biphenyl (11.1%) were obtained, together with cinnamic acid (0.7%), benzoic acid (0.2%), and 1,1-diphenylethylene (2.5%). Similarly, with palladium(II) propionate instead of palladium(II) chloride and sodium propionate in the above reactions, the same product was formed.

In attempts to prepare α - or β -methylcinnamic acid derivatives, significant differences in products, depending

on the presence or absence of butyric anhydride, were found. The reaction of benzene with palladium(II) chloride, sodium butyrate, and butyric acid in the absence of butyric anhydride gave β -methylcinnamic acid (26.8%) and benzoic acid (2.5%). In the presence of butyric anhydride in this reaction, such carboxyvinilation was completely suppressed, carboxylation taking place to afford benzoic acid (20%); propene and carbon dioxide were evolved.

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¹ T. Sakakibara, S. Nishimura, and Y. Odaira, *Tetrahedron Letters*, in the press.