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REACTION OF CARBOMETHOXYMERCURIC CHLORIDE WITH π-OLEFIN- AND π-ALLYL-$PdCl_2$ COMPLEXES

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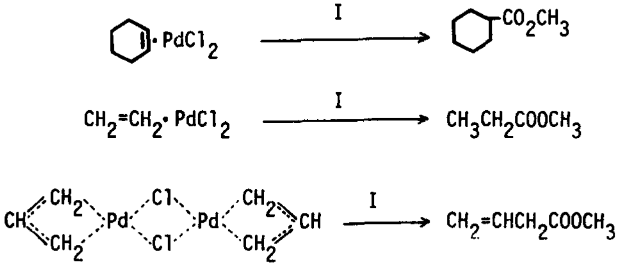
It has been known that a methanolic solution of mercuric acetate absorbs carbon monoxide to form carbomethoxymercuric acetate, $CH_3\underset{\underset{O}{\|}}{C}OHg\underset{\underset{O}{\|}}{C}OCH_3$, and the treatment of this mercuric compound with sodium chloride produces carbomethoxymercuric chloride, $ClHg\underset{\underset{O}{\|}}{C}OCH_3$ (I)$^{1)}$. At higher temperatures, I is not so stable and decomposes to generate carbon monoxide$^{1)}$. Consequently, it may be interestingly expected that I behaves as a new carbonylating agent.

The present communication reports our findings in the reactions of I with π-olefin- and π-allyl-$PdCl_2$ complexes. As the olefin component, cyclohexene and ethylene were employed. In these reactions the carbomethoxy group of I is transferred to the olefin and allyl ligand of the palladium complexes to produce the methyl esters of alkanoic and alkenoic acids, respectively.



A typical experiment of reaction of π-cyclohexene-$PdCl_2$ complex is as follows. To a 50 ml stainless steel tube, 0.97 g (3.8 mmoles) of π-cyclohexene-$PdCl_2$ complex,$^{2)}$ 1.0 g (3.4 mmoles) of I,$^{1)}$ and 4 ml of tetrahydrofuran as solvent were added. The tube was closed and heated without stirring in an oil bath at 90°C for 18 hrs. The reaction mixture was immediately distilled under a pressure of 3 mmHg at about 90°C. The total distillate was subjected to gas chromatography analysis. Methyl cyclohexanecarboxylate was the main product, which was isolated by preparative gas chromatography and identified by nmr spectrum analysis and by the comparisons of infrared spectrum and the retention time of gas chromatography with the authentic sample. The experimental results are summarized in the following table.

TABLE I. Reaction of Carbomethoxymercuric Chloride with π-Cyclohexene-Palladium Chloride Complex

π-Cyclohexene-$PdCl_2$ complex (mmoles)	$PdCl_2$ (mmoles)	Cyclohexene (mmoles)	$ClHgCO_2CH_3$ (mmoles)	Solvent (ml)	Yield of methyl cyclohexane-carboxylate[a)] (%)
3.8	—	—	3.4	tetrahydrofuran, 4	13
3.6	—	—	3.4	benzene, 4	10
0.4	—	3.0	3.4	tetrahydrofuran, 4	trace
—	3.4	3.4	3.3	benzene, 4	4
—	—	3.4	3.5	tetrahydrofuran, 4	trace

a) The yield of methyl cyclohexanecarboxylate is based on carbomethoxymercuric chloride.

Methyl cyclohexanecarboxylate was produced properly in the equimolar reaction of I with π-cyclohexene-$PdCl_2$ complex. A small amount of π-complex showed no catalyst activity. When a mixture of cyclohexene and palladium chloride was used instead of the isolated π-complex, poorer result was obtained. In gas chromatography analysis, other carbonylated products were detected only in small amounts, which were not identified in the present study.

In the reaction of I with ethylene, the isolated complex of ethylene-$PdCl_2$ was not employed. I was reacted with ethylene in the presence of equimolar amount of $PdCl_2$. Thus, to a 50 ml stainless steel tube, 1.0 g (3.4 mmoles) of I, 0.6 g (3.4 mmoles) of $PdCl_2$ and 4 ml of chlorobenzene as solvent were added, to which ethylene was compressed up to 15 kg/cm^2. The reaction mixture was heated at 70°C for 22 hrs. Methyl propionate was obtained in a yield of 6%, which was identified by the comparison of the retention time of gas chromatography with the authentic sample.

Transfer of carbomethoxy group to allyl ligand of π-allyl-$PdCl_2$ complex was also observed. A mixture of 0.98 g (3.3 mmoles) of I, 0.64 g (3.5 mmoles) of π-allyl-$PdCl_2$ complex³⁾ and 4 ml of tetrahydrofuran as solvent was heated at 90°C for 19 hrs. Methyl 3-butenoate was formed in a yield of 14%, which was isolated by preparative gas chromatography and identified by the comparison of infrared spectrum and the retention time of gas chromatography with the authentic sample.

The results of the present study have a significant bearing on the character of reactivity of I, i.e., the carbomethoxy group of I is transferred to olefin of π-olefin-complex and to allyl ligand of π-allyl complex. In this study, the product yield is not so high. It seems likely that decomposition of the π-olefin complex to chlorinated hydrocarbons decreases the yield of alkanoic acid ester. Syntheses of saturated carboxylic esters by the palladium compound catalyzed reaction of olefins and compressed carbon monoxide gas in an alcoholic solution of hydrogen chloride⁴⁾ and formation of unsaturated carboxylic esters in the reaction of π-allyl-$PdCl_2$ complex with compressed carbon monoxide gas in an alcohol⁵⁾ have been reported.

Further works are required to clarify the reaction paths, especially the source of hydrogen atom which has added to olefin, and the mechanistic relationship to the above mentioned reports.

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