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ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS.
XXIX.[1] DECARBONYLATION OF ACID HALIDES AND CARBONYLATION OF ALKYL HALIDES CATALYZED BY RHODIUM COMPLEX.

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We have shown that metallic palladium is an active catalyst for the carbonylation of olefins to form aldehyde and acyl halide, and decarbonylation of these carbonyl compounds.[2] In addition, we have found that chlorotris(triphenylphosphine)rhodium(complex I) is more efficient catalyst for the decarbonylation of carbonyl compounds; aldehydes[3] and acyl halides[4] are decarbonylated smoothly even at room temperature. We have reported the isolation of an acylrhodium complex by the reaction of acyl halide with the complex I as an intermediate of the decarbonylation reaction which gives a very important clue to the mechanism of the decarbonylation reaction.[4] In these decarbonylation reactions, however, an equivalent amount of the complex I is consumed and it is converted into chlorocarbonylbis(triphenylphosphine)rhodium(complex II) as shown below.

$$RCOX + \underset{I}{(PPh_3)_3RhCl} \longrightarrow RX(\text{or olefin} + HCl) + \underset{II}{(PPh_3)_2Rh(CO)Cl} + PPh_3$$

Consideration of a general mechanism of transition metal complex-catalyzed carbonylation and decarbonylation reactions led us to expect that the complex II is a suitable catalyst for the decarbonylation and carbonylation reactions, because the complex II is reasonably stable and four-coordinated and thus can easily expand to form a six-coordinated complex as an intermediate by the reaction of RCOX or RX. This proved to be the case and we found that the complex II is a very efficient catalyst for the decarbonylation of acyl and aroyl halides and carbonylation of some alkyl halides.

The decarbonylation is homogeneous and can be carried out simply by heating halides in the presence of a catalytic amount of the complex II. The activity of this complex is apparently superior to that of palladium. Thus acyl halides are decarbonylated to olefins. In this case, different from palladium catalyzed reaction which forms mainly thermodynamically more stable inner olefins, 1-olefin is obtained as a main product under certain conditions, showing that 1-olefin is the primary product of the decarbonylation. In addition, palladium catalyst is not very effective for the decarbonylation of aroyl halides. On the other hand, the complex II is a very efficient catalyst for the decarbonylation of aroyl halides and other halides which have no β-hydrogen to be abstracted. Simply by heating to 200°, aryl halides can be obtained. Some of the experimental results are shown in the Table. After the reaction, the complex can be used repeatedly. Thus this complex is very useful catalyst in organic syntheses. Not only chlorides, but also bromides can be converted into aryl bromide in high yield.

Table I Decarbonylation reaction.

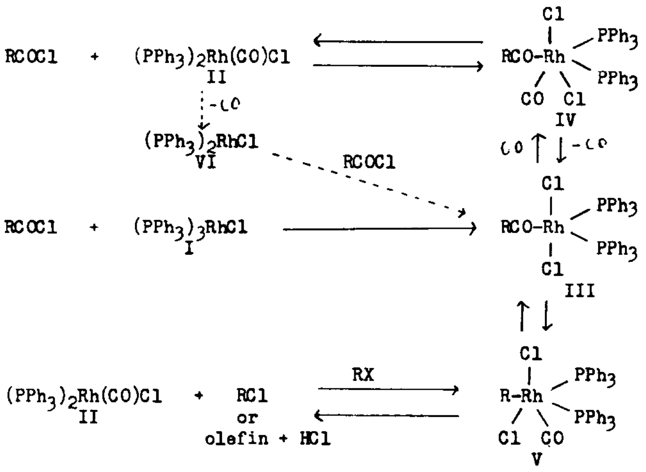
Halide(g)	(PPh$_3$)$_2$RhCOCl	reaction		product (g)	yield. (%)
		temp.	hr.		
PhCH$_2$COCl 8	0.1	200-220	2	PhCH$_2$Cl 3.9	60
PhCOCl 8	0.2	200	4	PhCl 5.1	85
PhCOBr 8	0.2	220	1.5	PhBr 5.9	87
CH$_3$(CH$_2$)$_6$COBr 8	0.1	200	1	1-heptene 71% 2-,3-heptenes 29%	91(total)

Recently the decarbonylation of aroyl chloride with the complex I was reported by Blum.[5] Contrary to the suggestion given in his paper, it is highly probable that the complex II is a true catalyst in the Blum's decarbonylation too.

Furthermore, II was found to be active for the carbonylation of certain alkyl halides. For example, benzyl chloride was carbonylated to phenylacetyl chloride in benzene in the presence of a catalytic amount of II at 150° under carbon monoxide(100 atm.).

$$PhCH_2Cl + CO \xrightarrow{II} PhCH_2COCl$$

From these experiments, it was established that the four-coordinated rhodium complex II is an efficient catalyst for carbonylation and decarbonylation, and the following reaction mechanism can be proposed for these reactions.



In this reaction mechanism, the following comments can be given.

1. We have reported the isolation of the acyl complex III by the reaction of I with RCOCl.[4] This step is irreversible and the complex I can never be recovered under any conditions.

2. When I is treated with CH_3COCl or PhCOCl, complex V, instead of III, is isolated as crystalline substance which has an IR band at 2080 cm^{-1} and is converted into CH_3Cl or PhCl and II.[6]

3. When the decarbonylation reaction of aroyl halide was interrupted by cooling shortly after the decarbonylation started, the complex II was recovered which was contaminated with other complex having an IR band at 2080 cm^{-1} indicating that probably the complex V was formed in a small amount. The isolation of the pure complex V is in progress.

4. The course of the decarbonylation reaction catalyzed by the complex II is: (II + RCOX) $\rightarrow$ IV $\rightarrow$ III $\rightarrow$ V $\rightarrow$ (RX or olefin + II). The step(III $\rightarrow$ IV) is a type of the well established acyl-alkyl conversion. Another possible pass through II — VI — III can not be excluded rigorously.

5. The course of the carbonylation reaction of RX is: (RX + II) $\rightarrow$ V $\rightarrow$ III $\rightarrow$ IV $\rightarrow$ (II + RCOX). The step(II $\rightarrow$ V) has already been proved by Heck.[7]

In this mechanism, the most important point is that the complex II is formed after the carbonylation and decarbonylation, and this complex plays the key role of the reactions.

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