

ORGANIC SYNTHESIS BY MEANS OF NOBLE METAL COMPOUNDS
XX. DECARBONYLATION OF ACYL CHLORIDE AND ALDEHYDE CATALYZED BY
PALLADIUM AND ITS RELATIONSHIP WITH THE ROSENMUND REDUCTION.¹

Jiro Tsuji, Kiyotaka Ohno and Tsunesuke Kajimoto
Basic Research Laboratories, Toyo Rayon Company, Ltd.

Kamakura, Japan

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We have found that olefin-palladium chloride complex is carbonylated to give β -chloro acyl chloride.² In addition, we have found that metallic palladium is a versatile catalyst for carbonylation of various olefinic compounds. For example, simple olefins³ and nonconjugated cycloolefins⁴ can be converted in ethanol into saturated esters, and allylic compounds⁵ and conjugated dienes⁶ form β, γ -unsaturated esters. In these catalytic carbonylations, the presence of metallic palladium and hydrogen chloride was found to be essential, and the formation of acyl-palladium complex as an intermediate is assumed by analogy with the mechanism of the carbonylation catalyzed by cobalt and nickel carbonyls,⁷ although there is no direct evidence that palladium forms isolable palladium carbonyl.

It is known that insertion reaction of carbon monoxide to form acyl-complex is reversible depending on the pressure of carbon monoxide and temperature.⁸ Therefore, it is expected that acyl halide might be decarbonylated to olefin in the absence of carbon monoxide and at certain temperature, if any kind of acyl-palladium bond is formed from acyl halide and metallic palladium. This proved to be the case. It was found that olefin was formed from acyl chloride with the evolution of carbon monoxide and hydrogen chloride at 200° in the presence of a catalytic amount of metallic palladium such as palladium on carbon. The most

efficient catalyst was found to be palladium chloride which was reduced to black metallic palladium soon after it was heated in acyl chloride. For example, when decanoyl chloride was heated with palladium chloride at 200° in a distilling flask, evolution of carbon monoxide and hydrogen chloride stopped in one hour during which time a mixture of nonene isomers(1,2,3 and 4 nonenes) was distilled. When it was impossible to form olefin, alkyl or aryl chloride was the product; chlorobenzene was obtained from benzoyl chloride in a low yield. Results are shown in Table I. Thus it was established that metallic palladium catalyzes both carbonylation of olefin to acyl halide and decarbonylation of acyl halide into olefin.

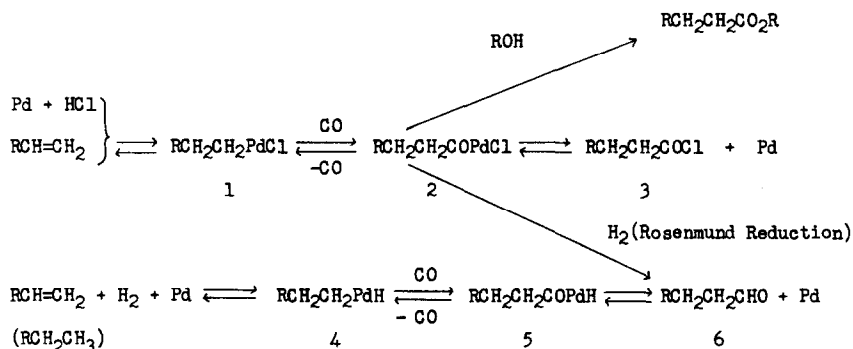
Table I. Decarbonylation of acyl halides.

acyl halide	g.	catalyst g.	reaction time,hr.	temp.	CO+HCl ml.	product	yield %
$\text{CH}_3(\text{CH}_2)_8\text{COCl}$	20	1%Pd/C 1	10	200	2960	nonenes	58
$\text{CH}_3(\text{CH}_2)_8\text{COCl}$	5	PdCl_2 0.1	1.5	200	1050	nonenes	90
$\text{CH}_3(\text{CH}_2)_6\text{COBr}$	5	PdCl_2 0.2	1.5	200	750	heptenes	80
$\text{C}_6\text{H}_5(\text{CH}_2)_2\text{COCl}$	10	PdCl_2 0.2	1.0	210	1780	styrene	53
$\begin{matrix} \text{CH}_2\text{CH}_2\text{COCl} \\ \text{CH}_2\text{CH}_2\text{COCl} \end{matrix}$	8	PdCl_2 0.2	0.5	180	545	cyclopentanone	30
$\text{C}_6\text{H}_5\text{CH}_2\text{COCl}$	20	1%Pd/C 1	3	220	2283	benzylchloride	42
$\text{C}_6\text{H}_5\text{COCl}$	10	1%Pd/C 1	24	200	100	chlorobenzene	5

We have observed that metallic palladium is active for the formation of aldehyde from olefin, hydrogen and carbon monoxide(oxo reaction).¹ From the consideration of reversibility of the carbonylation reaction, it is expected that aldehyde should also be decarbonylated with metallic palladium. Actually decarbonylation of some specific aldehydes in the presence of palladium has

already been known for some time without mentioning any reasonable mechanism.⁹ We have confirmed that the decarbonylation of aliphatic aldehyde is a general reaction forming a mixture of olefin and corresponding paraffin. For example, decanal was converted into nonane and nonene at 200° with evolution of carbon monoxide and hydrogen. Again metallic palladium was active for the formation and decarbonylation of aldehyde.

From these experimental results, we would like to propose the following mechanism for the reaction between olefins and carbon monoxide in the presence of palladium.



In this scheme, the formation of acyl-palladium complexes(2 and 5) is an essential point. It seems possible that both aldehyde and acyl chloride form the acyl-palladium bond when they are contacted with palladium. Although there is no direct evidence of complex formation, we have observed that metallic palladium partially dissolved in acyl chloride when they were mixed and heated. The decarbonylation of the acyl-palladium complexes(2 and 5) to alkyl-palladium complexes(1 and 4) is a reasonable reaction to occur under the present reaction conditions. Finally, the alkyl-palladium bonds(1 and 4) are split to afford the reaction products.

The procedure of converting an acyl halide into an aldehyde is known as the

Rosenmund reduction. From the reaction mechanism proposed above, the Rosenmund reduction offers an interesting connection between the two reaction paths shown above. The first step of the Rosenmund reduction seems to be the formation of the acyl-palladium complex(2) which does not decarbonylate at the reflux temperature of xylene. Instead, by the action of hydrogen, the acyl-palladium complex(2) is split to form an aldehyde(6). A similar idea was independently suggested by Chiusoli et al.¹⁰ who obtained phenol from 2,5-hexadienoyl chloride by their attempted Rosenmund reduction. The formation of phenol is related to the formation of cyclopentanone from adipoyl chloride shown in the Table.

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