

ORGANIC SYNTHESSES BY MEANS OF NOBLE METAL COMPOUNDS
XXI. DECARBONYLATION OF ALDEHYDES USING RHODIUM COMPLEX¹

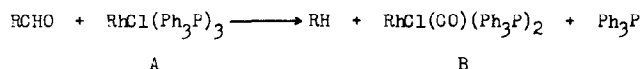
Jiro Tsuji and Kiyotaka Ohno

Basic Research Laboratories, Toyo Rayon Company, Ltd.

Kamakura, Japan

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It is known that acyl halides and aldehydes can be decarbonylated by the catalytic action of metallic palladium at 200^o, and we have proposed a mechanism for the decarbonylation reaction¹. In an effort to find a more efficient decarbonylating agent from a mechanistic viewpoint, we have found that chlorotris(triphenylphosphine)rhodium(A), the syntheses and interesting chemical reactions of which were recently reported,^{2,3} was converted into chlorocarbonylbis(triphenylphosphine)rhodium(B) by the reaction with aldehydes even at room temperature. By this means, aldehydes were decarbonylated smoothly into corresponding paraffins. The reaction can be expressed in the following scheme.



The following illustrates typical decarbonylation reaction. The complex A (2.754 g.), cinnamaldehyde(1.408 g.) and toluene(0.276 g., for chromatographic determination) were mixed in 10 ml of benzene. When the mixture was refluxed for 15 min., the dark red solution turned to yellow and yellow crystals began to separate. The amount of styrene formed was gas chromatographically determined(0.234 g., 77%, based on the complex A). The solvent was removed

and ethanol(10 ml.) was added to ensure the precipitation of the complex B. The complex B was collected by filtration (1.91 g., 93%, m.p. 190-195°, Infrared spectrum, 1980 cm^{-1}). The reaction conditions and products are shown in the Table I.

TABLE I. DECARBONYLATION OF ALDEHYDES.

aldehyde	solvent ^a	reaction		yield of complex B %	product ^b (%)
		temp.	time		
$\text{C}_6\text{H}_5\text{CHO}$	none	reflux	5 min.	80	benzene
$\text{C}_6\text{H}_5\text{CHO}$	none	room temp.	24 hr.	77	benzene
$\text{C}_6\text{H}_5\text{CHO}$	toluene	reflux	2 hr.	92	benzene(83)
$\text{CH}_3\text{CH}_2\text{H}_2\text{CHO}$	benzene	room temp.	2 hr.	65	propane
$(\text{CH}_3)_2\text{CHCHO}$	benzene	room temp.	70 hr.	83	propane
$(\text{CH}_3)_2\text{CHCHO}$	benzene	reflux	30 min.	40	propane
$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	benzene	room temp.	12 hr.	65	styrene
$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	benzene	reflux	15 min.	93	styrene(77)
$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	CH_2Cl_2	room temp.	8 hr.	65	styrene(60)
$p\text{-ClC}_6\text{H}_4\text{CHO}$	benzene	reflux	3 hr.	90	chlorobenzene(85)
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$	benzene	reflux	10 min.	90	ethylbenzene(67)
$o\text{-HCC}_6\text{H}_4\text{CHO}$	toluene	reflux	20 min.	76	phenol(70)

a. When no solvent was used, the reaction was carried out in an excess of aldehyde.

b. Yields were determined by gas chromatography.

Thus, this reaction is a very efficient and specific method of decarbonylation of aldehydes under very mild conditions, and seems to be quite useful in organic syntheses.

Concerning the mechanism of the decarbonylation, it is clear that the

reaction is closely related to the formation of hydrocarbonyl complexes of noble metals by the reaction of certain noble metal salts with alcohols.^{4,5} In this reaction, it is assumed that, although there is no definite evidence, the oxidation of alcohol to aldehyde, followed by the decarbonylation of the latter is involved. Recently it was reported that the complex B was obtained by the reaction of rhodium trichloride, triphenylphosphine and some oxygenated compounds such as alcohols, dimethylformamide and certain ketones.⁶ It is known that one of the three triphenylphosphines of the complex A is reactive due to strong trans effect of triphenylphosphine and can easily be replaced with carbon monoxide or allyl alcohol to form the complex B.³ By the present studies, it is now established that decarbonylation of aldehydes is possible under very mild conditions to form metal carbonyl complex and paraffin.

References

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