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ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS PART XXXII

SELECTIVE DECARBONYLATION OF α,β-UNSATURATED ALDEHYDES USING RHODIUM COMPLEXES

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We have reported that various aldehydes can be decarbonylated smoothly under mild conditions by the treatment with chlorotris(triphenylphosphine)rhodium (I).[1] This reaction seems to be the best way to decarbonylate aldehydes to yield paraffins.

$$\mathrm{RCHO} + \underset{\text{I}}{\mathrm{ClRh(PPh_3)_3}} \longrightarrow \mathrm{RH} + \underset{\text{II}}{\mathrm{ClRh(PPh_3)_2(CO)}} + \mathrm{PPh_3} \qquad (1)$$

For this decarbonylation, we propose the following mechanism. It is known that the complex I exists as a solvated formally three coordinate species III in a solution.[2] The first step of the reaction is the oxidative addition ($d^8 \longrightarrow d^6$ complex) of an aldehyde to III to form the acyl-rhodium complex IV, followed by acyl-alkyl rearrangement of IV to give V. Finally, RH (or olefins with certain aldehydes) is formed. The similar mechanism has been proposed for the decarbonylation of acyl halides by I.[3]

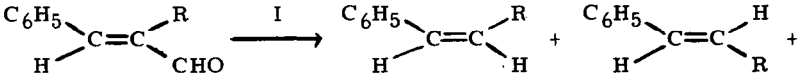
$$\underset{\text{I}}{\mathrm{ClRh(PPh_3)_3}} \xrightleftharpoons{\text{solvent(S)}} \underset{\text{III}}{\mathrm{ClRh(PPh_3)_2S}} \xrightarrow{\mathrm{RCHO}} \underset{\text{IV}}{\mathrm{ClRhH(RCO)(PPh_3)_2}} \longrightarrow$$

$$\underset{\text{V}}{\mathrm{ClRhH(CO)R(PPh_3)_2}} \longrightarrow \underset{\text{II}}{\mathrm{ClRh(CO)(PPh_3)_2}} + \text{RH (or olefins)}$$

Based on this mechanism, it is expected that the decarbonylation should proceed with the retention of stereochemistry of the carbon directly attached to the aldehyde group. In order to investigate the stereoselectivity of the reaction, the decarbonylation of α,β-unsaturated aldehydes, namely α-substituted cinnamaldehydes was studied. As shown in TABLE I, trans α-alkylcinnamaldehydes (trans with respect to CHO and alkyl groups) were decarbonylated smoothly and almost stereoselectively to give the cis olefins. Therefore, it can be said that the decarbonylation proceeds without interferring with the double bond, and this method is useful for the preparation of olefins of definite stereochemistry from unsaturated aldehydes of known stereochemistry.

TABLE I

Decarbonylation of α,β-Unsaturated Aldehydes

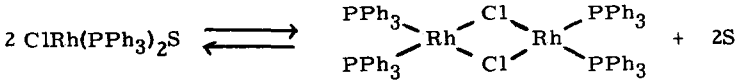


A B

(2)

R	solvent	reaction temp. °C	reaction time min.	total yield of styrenes %	product composition % A	product composition % B	yield of II %
CH_3	xylene	reflux	5	88	91	9	90
CH_3	benzonitrile	160	1	86	96	4	91
C_2H_5	benzonitrile	160	1	82	94	6	88

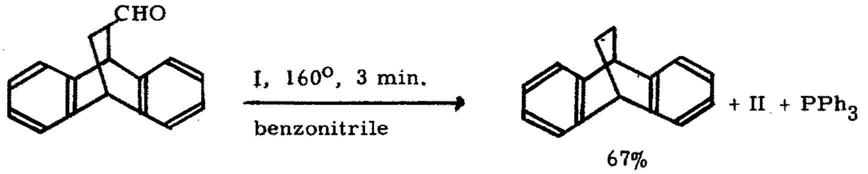
In general, the decarbonylation proceeds in benzene or methylene chloride. However, some aldehydes with steric hindrance shown in equations 4 and 5, are not decarbonylated in these solvents. When the reaction is carried out at higher temperature, for example, in boiling toluene or xylene, the dimeric complex VI tends to precipitate which is not effective for the decarbonylation in these solvents. This difficulty can be overcome by using nitriles such as acetonitrile or benzonitrile as solvent. Strong solvating power of the nitriles to



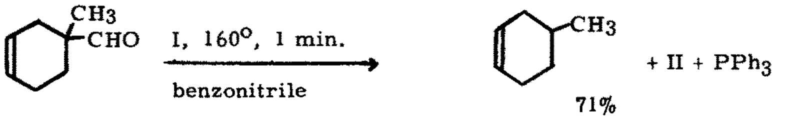
III VI

(3)

form the stable species III (S: nitrile) is certainly responsible for this effect, and it prevents the formation of the dimer VI. For example, the following aldehydes can not be decarbonylated in boiling xylene or methylene chloride. But they can be decarbonylated in benzonitrile.



(4)



(5)

Furthermore, we found that it is possible to convert VI into III by the treatment with the nitriles. This property is very useful for the decarbonylation. As shown in eq. 1, the decarbonylation of aldehydes with I liberates one mole of triphenylphosphine, separation of which from the decarbonylated product gives difficulty in some cases. On the other hand, when the dimeric species VI is used with the nitriles as the solvent for decarbonylation, the catalytic species is III, and hence the decarbonylation proceeds without liberating triphenylphosphine as shown below. After the reaction, most of the solvent is removed and the complex II is quantitatively precipitated by the addition of alcohol. From the filtrate, the decarbonylated product can be isolated without difficulty.

$$\mathrm{RCHO} + \underset{\mathrm{III}}{\mathrm{ClRh(PPh_3)_2S}} \longrightarrow \mathrm{RH} + \underset{\mathrm{II}}{\mathrm{ClRh(CO)(PPh_3)_2}} + \mathrm{S} \qquad (6)$$

By decarbonylation, I is converted into II. On the other hand, we have reported that the decarbonylation of acyl halides can be carried out in the presence of a catalytic amount of the complex II.[3] Similarly, we confirmed that the decarbonylation of aldehydes can be carried out by the use of a catalytic amount of the complex II by heating the reaction mixture at 200° or higher. Some results of the catalytic decarbonylation are shown in TABLE II. The reaction can be applied most satisfactorily to aromatic aldehydes. The stereoselectivity in the catalytic decarbonylation is somewhat lower than in the decarbonylation by the complex I. Catalytic decarbonylation of aldehydes can be cariied out with metallic palladium[4] and the retention of the stereochemistry was reported.[5] The comparative studies of the decarbonylation under the similar conditions were carried out by using either palladium chloride or the complex II. As shown in TABLE II, the rhodium complex gave higher stereoselectivity. In addition, rhodium trichloride can be used for the catalytic decarbonylation of aldehydes.

TABLE II

Catalytic Decarbonylation of Aldehydes

		reaction			
Aldehydes (g.)	catalyst (g.)	temp. °C	time hrs.	product	yield %
p-Cl-C_6H_4CHO 8	II 0.2	220	9	Cl-C_6H_5	71
o-HO-C_6H_4CHO 5	II 0.1	210	8.5	HO-C_6H_5	80
cinnamaldehyde 8	II 0.1	230-240	4	styrene	76
trans-α-ethyl-cinnamaldehyde 10	II 0.3	250-260	3	β-ethyl-styrene	87.5 A. 80* B. 20*
trans-α-ethyl-cinnamaldehyde 10	$PdCl_2$ 0.2	250-260	3	β-ethyl-styrene, n-butyl-benzene	75.6 A. 38.5* B. 49.3* butylbenzene 12.2

* for Aand B, see eq. 2, and Table I.

References

1. J. Tsuji, and K. Ohno, Tetrahedron Letters, 1965, 3969.
2. J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, J. Chem. Soc., (A), 1966, 1711.
3. J. Tsuji, and K. Ohno, Tetrahedron Letters, 1966, 4713.
4. J. Tsuji, K. Ohno, and T. Kajimoto, Tetrahedron Letters, 1965, 4565.
5. N. E. Hoffman, A. T. Kanakkanatt, and R. F. Schneider, J. Org. Chem., **27**, 2687 (1962).