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DECARBONYLATION OF α-AND β-DIKETONES CATALYZED BY RHODIUM COMPOUNDS

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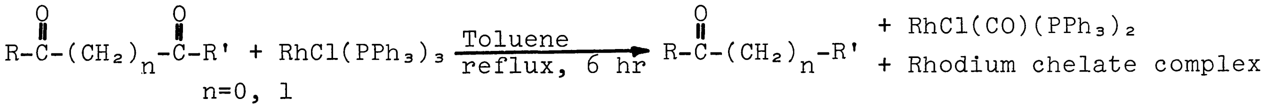
α-and β-Diketones can be easily decarbonylated to monocarbonyl compounds by rhodium complexes at toluene reflux and at room temperature, β-diketones react with rhodium complex to afford chelate complexes without decarbonylation products.

The decarbonylation of aldehydes, acylhalides, isocyanates and ketenes with the transition metal complexes has been the subject of numerous investigations,$^{1,2)}$ whereas, except for cyclohexanone$^{3)}$ little is known concerning the decarbonylation of ketones probably because they might be weakly bound to metal complexes.

In this communication, we wish to report the finding that rhodium compounds effectively catalyze the decarbonylation of α-and β-diketones.

In general method of decarbonylations, mixture of the reactant diketone (20 mmol), rhodium compound (0.50 mmol) in toluene solvent (50 ml) was heated for 6 hr under reflux.



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_n{-}\overset{O}{\overset{\|}{C}}{-}R'} + \mathrm{RhCl(PPh_3)_3} \xrightarrow[\text{reflux, 6 hr}]{\text{Toluene}} \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_n{-}R'} \begin{array}{l} + \mathrm{RhCl(CO)(PPh_3)_2} \\ + \text{Rhodium chelate complex} \end{array}$$

$$n=0,\ 1$$

Acetylacetone reacted with $RhCl(PPh_3)_3$ to give methyl ethyl ketone (405 %), $RhCl(CO)(PPh_3)_2$ (56 %) and acetylacetonato complex (40 %). At room temperature, only the acetylacetonato complex was obtained without decarbonylation products.

The properties of acetylacetonato complex were as follows. Mp: 156-157°C, Anal. Calcd for $C_{28}H_{29}O_4ClPRh$: C, 56.14; H, 4.84; Cl, 5.92%. Found: C, 56.12; H, 4.76; Cl, 5.90%. IR(Nujols): 1565, 1548, 1515, 1445, 1195, 1127, 1100, 1030, 1005, 940, 760, 732, and 705 cm^{-1}. NMR (C_6D_6): 1.9-2.1 (m, phenyl, 6H), 2.3-3.1 (m, phenyl, 9H), 4.64 (s, methin, 1H). 5.26 (s, methin, 1H), 8.00 (s, methyl, 3H), 8.24 (s, methyl, 3H), 8.37 (s, methyl, 3H), and 8.68 τ(s, methyl, 3H). The reduction with $LiAlH_4$ in benzene afforded a quantitative yield of acetylacetone. From the above results, the acetylacetonato complex is to be assigned to $RhCl(acac)_2(PPh_3)$. Four methyl and two methin signals in the NMR data suggest that chloride and triphenylphosphine ligands exist in the cis form.$^{4)}$ The chelalation mechanism is not clear at present but it seems that methylene hydrogens of acetylacetone might become H_2 gas.

To see if the acetylacetonato complex was an intermediate in the decarbonylation, the acetylacetonato complex was heated in toluene with PPh_3 (2:1, P:Rh ratio) for 6 hr under reflux, while neither methyl ethyl ketone nor carbonyl complex was detected. Therefore, the acetylacetonato complex is not an intermediate species. $RhCl(CO)(PPh_3)_2$ obtained was active for the decarbonylation of acetylacetone to give methyl ethyl ketone (150 %).

$RhCl_3 \cdot 3H_2O$ also proved to be effective catalyst for decarbonylation but other metal compounds such as $IrCl_3 \cdot 3H_2O$, $PdCl_2$ and $CoCl_2 \cdot 6H_2O$ were not effective.

Similarly, unsymmetrical β-diketones, methyl acetoacetate and ethyl acetoacetate also gave methyl propionate (200 %) and ethyl propionate (105 %) respectively which were not further decarbonylated to ethers under these conditions. The fact that the propionates were derived from the decarbonylation of acyl groups, not of carboalkoxyl groups seems to be explained by the ease of acyl-alkyl rearrangement with rhodium compounds.1) Dibenzoylmethane gave only chelate complex, $RhCl_2(PPh_3)_2$-(DBM). Mp: 250-255°C. Anal. Calcd for $C_{51}H_{41}O_2Cl_2P_2Rh$: C, 66.46; H, 4.48; Cl, 7.69%. Found: C, 66.45; H, 4.34; Cl, 7.66%. IR(Nujols): 1590, 1532, 1518, 1310, 1225, 1092, 757, 700 cm^{-1}. This complex is insoluble in common solvents.

α-Diketones show also high reactivity for decarbonylation. Unsymmetrical α-diketones are more reactive than symmetrical diketones. Benzil did not react at 110°C but at higher temperature up to 240°C, gave benzaldehyde (13 %) and fluorenone (5 %). Table 1 summarized the results of α-diketone.

Table 1. Decarbonylation of α-Diketones

α-Diketones	Time(hr)	Temp(°C)	Products (Yieldsa))	Complexes
Diacetyl	4	90	Acetone (430 %)	$RhCl(CO)(PPh_3)_2$, 60 %
Pyruvic acid	6	110	Acetic acid (1450 %)	$RhCl(CO)(PPh_3)_2$, 100 %b)
	24	room temp.	Acetic acid (420 %)	$RhCl(CO)(PPh_3)_2$, 100 %b)
Acetylbenzoyl	6	110	Acetophenone (820 %)	$RhCl(CO)(PPh_3)_2$, 23 %

a) Yields are based on catalyst. b) Pyruvic acid was decomposed to give acetaldehyde by heat. $RhCl(PPh_3)_3$ is easily converted to $RhCl(CO)(PPh_3)_2$ in acetaldehyde.

In addition, we have an interest in behavior of acid anhydride and imide containing oxygen and nitrogen atom respectively in place of methylene between two carbonyl groups, toward rhodium complex. Acetic anhydride was easily decarbonylated to methyl acetate (2550 %) but on the other hand diacetyl imide gave acetic acid (195 %) and acetonitrile (230 %) as products of cleavage of C-N bond without decarbonylation products.5)

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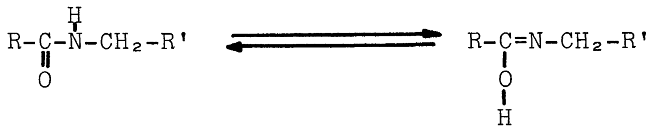
5) J.Blum has already reported the cleavage of C-N bond of monocarbonyl imides and that these reactions might contain next equilibrium.6)



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}\overset{H}{N}{-}CH_2{-}R'} \rightleftharpoons \mathrm{R{-}\underset{\underset{H}{|}}{\underset{O}{|}}{C}{=}N{-}CH_2{-}R'}$$

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