

SELECTIVE DEHYDRATION OF 1,3-DIOLS TO KETONES CATALYZED BY RHODIUM COMPOUNDS

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The reaction of 1,3-diols with various rhodium compounds was carried out at 80°C for 48 hr. The dehydration products, mono-ketones were formed selectively in high yields. A  $\text{RhCl}_3$  -  $\text{PPh}_3$  (1:1) catalyst had the highest activity.

It is known that group VIII transition metal complexes have a catalytic activity for the dehydration of alcohols to ethers<sup>1)</sup> and recently we also reported on the formation of diallyl ethers in the disproportionation of allyl alcohols with rhodium catalysts.<sup>2)</sup> In this connection we have found that the application of this rhodium catalysts to various diol compounds results in the exclusive formation of ketones or cyclic ethers and this letter describes a convenient one-step synthesis of unsymmetrical mono-ketones from 1,3-diols. The product pattern of this dehydration is quite different from that in usual dehydrating reagents. Of many group VIII transition metals, rhodium has the highest reactivity for this reaction.

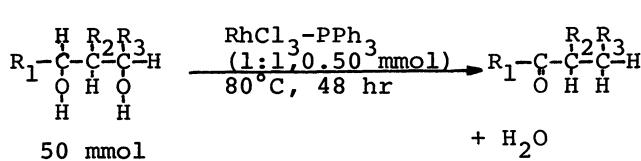


Table I. Dehydration of 1,3-diols with rhodium catalyst

Run	$\text{R}_1$	$\text{R}_2$	$\text{R}_3$ (% based on diol)	Yield of ketone
1	$\text{CH}_3$	H	H	89
2	$\text{C}_2\text{H}_5$	H	H	41
3	$\text{C}_3\text{H}_7$	H	H	36
4	$\text{C}_4\text{H}_9$	H	H	33
5	$\text{C}_5\text{H}_{11}$	H	H	30
6	$\text{CH}_3$	H	$\text{CH}_3$	97
7	$\text{CH}_3$	$\text{CH}_3$	$\text{CH}_3$	64

The result in the reaction of various 1,3-diols with a  $\text{RhCl}_3$  -  $\text{PPh}_3$  catalyst reveals several notable trends: i) the mono-ketones are selectively formed, ii) the yield of ketones decreases with increasing the steric bulk of alkyl substituent( $\text{R}_1$ ) attached to the carbon with hydroxyl group(runs 1-5), Table I), but 1,3-propanediol was unreactive, iii) the hydroxyl group attached to the carbon without alkyl substituent is preferably eliminated(runs 1-5), and iv) the alkyl substituent( $\text{R}_2$ ) at the central carbon between two carbons with hydroxyl groups depresses the reactivity(runs 6,7).

There are many reports on the dehydration of 1,3-diols. For example, in the case of 1,3-butanediol,<sup>3)</sup> 3-buten-1-ol as main product is formed with  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ , 2-buten-1-ol and 2-butenal with  $\text{DMSO}$ ,<sup>4)</sup> and 2-butenal with reduced nickel,<sup>5)</sup> however the selective mono-ketone formation from 1,3-diols is not reported yet as far as we know.

In the reaction of 1,3-butanediol, various group VIII transition metal compounds were tried as the catalyst. Only rhodium compounds have a remarkably catalytic activity. The rhodium- $\text{PPh}_3$  ratio have a great effect on the yield of the product ketones (Fig. I). 1:1 molar ratio of rhodium and  $\text{PPh}_3$  is the best combination, while large excess of additive  $\text{PPh}_3$  suppresses this dehydration,<sup>6)</sup> suggesting that one mole  $\text{PPh}_3$  coordinating intermediate may be the most suitable structure in the point of electronic and steric environment.

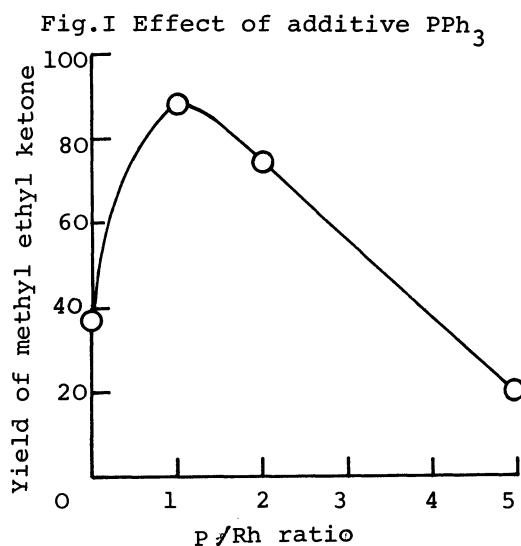
The detailed reaction mechanism is not clear at present, however lower valence state which is reduced by a reactant diol<sup>7)</sup> may be a really active species because dehydrogenated products, e.g., 4-hydroxy-2-pentanone in 2,4-pentanediol could be detected.

In a typical experiment, a mixture of 4.50 g (50 mmol) of 1,3-butanediol, 132 mg (0.50 mmol) of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ , and 131 mg (0.50 mmol) of  $\text{PPh}_3$  was stirred at 80°C for 48 hr. The chromatograph of the resulting solution showed 89 % yield of methyl ethyl ketone,  $\text{H}_2\text{O}$ , and unreacted diol. Extraction and distillation afforded 2.5 g of the ketone.

Under the same conditions as 1,3-diols, 1,4 and 1,5-diols gave the corresponding 5 and 6-membered ring ethers in almost quantitative yields, however 1,2 and 1,6-diols were not reactive. In addition, this rhodium catalysts can be further applied to the dehydration of mono-alcohols to olefins, that is,  $\alpha$ -phenethyl alcohol yielded styrene quantitatively even at room temperature although the  $\text{KHSO}_4$  method necessitates high temperature over 200°C.<sup>8)</sup>

#### References and notes

- 1) a) J.Tsuji, "Advances in Organic Chemistry; Methods and Results", Vol.6, John Wiley & Sons, Inc., p.228. b) Y.Sasson and J.Blum, Chem.Commun., 1974, 309.
- 2) M.Wayaku, K.Kaneda, T.Imanaka, and S.Teranishi, Bull.Chem.Soc.Japan, 48, 1957 (1975).
- 3) M.Mazet reported that the reaction of 2,2-dimethyl-1,3-propanediol derivatives with  $\text{H}_2\text{SO}_4$  gave cyclic acetals and olefins as main products.  
M.Mazet and M.Desmaison-Brut, Bull.Soc.Chim.France, 1971, 2656.
- 4) V.J.Traynelis, W.L.Hergenrother, H.T.Hanson, and J.A.Valicenti, J.Org.Chem., 29, 123 (1964).
- 5) A.Halasz, Ann.Chim., 14, 318 (1940).
- 6) The similar effect of additive phosphine was also observed in reference 2.
- 7) J.A.Osborn, F.H.Jardine, J.F.Young, and G.Wilkinson, J.Chem.Soc.,A, 1966, 1711.
- 8) Organic Syntheses, Collective Vol.3, p.204.



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