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# IRIDIUM PENTAHYDRIDE COMPLEX CATALYZED DEHYDROGENATION OF ALCOHOLS IN THE ABSENCE OF A HYDROGEN ACCEPTOR

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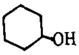
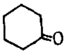
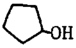
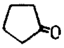
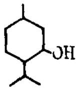
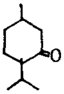
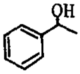
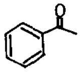
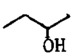
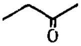
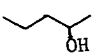
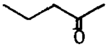
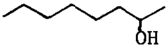
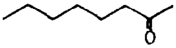
**Abstract:** In the absence of a hydrogen acceptor, alcohols could be dehydrogenated to the corresponding ketones with good yields using $IrH_5(i\text{-}Pr_3P)_2$ as the catalyst.

The catalytic dehydrogenation of saturated compounds is more difficult than its reversed reaction---hydrogenation of unsaturated compounds, since the thermodynamic factor favours the saturated species. A number of catalytic dehydrogenation of alcohols rely for their effectiveness on the continual removal of hydrogen by a hydrogen acceptor or on providing high energy by photochemical method. The most widely studied reaction is the dehydrogenation of secondary alcohols to ketones using ketone or olefin as the hydrogen acceptor. However, the homogeneous systems capable of catalyzing dehydrogenation of alcohols without a hydrogen acceptor are rare. To our knowledge, mainly three homogeneous catalytic systems such as $Rh(III)\text{-}SnCl_2/HCl$[1], $Ru(OOCCF_3)_2(CO)(PR_3)_2/CF_3COOH$[2] and $Rh_2(OAc)_4/PR_3$[3] have been found to dehydrogenate the alcohols into the ketones accompanied with the evolution of hydrogen without an external hydrogen acceptor, but they do require $H^+$ as a hydride ion acceptor. In addition, conversion of primary alcohols to esters is achieved in the presence of $H_2Ru(Ph_3P)_4$[4]. The reaction involves two steps: first, alcohol is dehydrogenated to aldehyde and then the reaction product of aldehyde and alcohol is dehydrogenated to form the ester. The latter step would make the reaction thermodynamically favourable. In this communication, we wish to report the $IrH_5(i\text{-}Pr_3P)_2$ catalyzed dehydrogenation of alcohols to ketones in the absence of a hydrogen acceptor.

The reaction was carried out under mild conditions. Neither external hydrogen acceptor nor $H^+$ as hydride ion acceptor was required. When saturated secondary alcohols and 1-2 mole% of $IrH_5(i\text{-}Pr_3P)_2$ were refluxed in hexamethyldisiloxane at 100°C under nitrogen for 24 h, 90-100% of the saturated ketones were obtained accompanied with the evolution of hydrogen (detected by G.C.). The catalytic turnover number reached 150 for the dehydrogenation of the cyclohexanol using $IrH_5(i\text{-}Pr_3P)_2$ as the catalyst. The results of dehydrogenation of various alcohols are shown in Table 1.

In contrast to the hydrogen transfer of unsaturated alcohols promoted by $IrH_5(i\text{-}Pr_3P)_2$[5] to give the saturated ketones, the steroidal alcohols with hindered double bond were mainly dehydrogenated to yield the unsaturated ketones. When cholest-5-en-3-ol(2) was heated in the presence of a hydrogen acceptor (3,3-dimethylbutene) with 2% of $IrH_5(i\text{-}Pr_3P)_2$, 92% of cholest-4-en-3-one(7) was

Table 1. Dehydrogenation of Saturated Secondary Alcohols in $(Me_3Si)_2O$ at 100°C Under Nitrogen

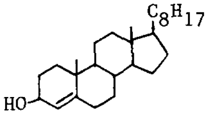
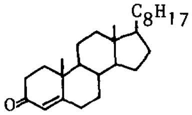
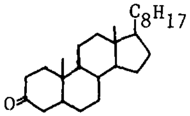
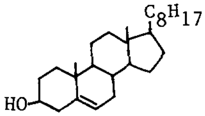
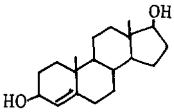
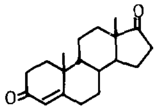
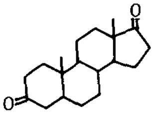
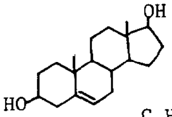
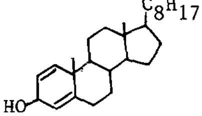
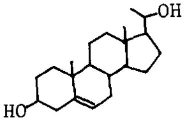
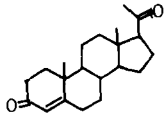
| Alcohols | $IrH_5(i\text{-}Pr_3P)_2$ (mole %) | Time (h) | Products[a] | Yield[b] (%) |
|---|---|---|---|---|
|  | 1 | 24 |  | 100 |
|  | 1 | 24 |  | 100 |
|  | 2 | 28 |  | 90[c] |
|  | 1 | 28 |  | 91[c] |
|  | 1 | 28 |  | 100 |
|  | 1 | 34 |  | 100 |
|  | 2 | 24 |  | 50[c] |

a: All products gave satisfactory $^1H$ NMR, IR and MS data.
b: Determined by G.C..
c: Isolated yield.

isolated and none of **8** was detected. However, when **2** and 2% of $IrH_5(i\text{-}Pr_3P)_2$ were heated in the absence of a hydrogen acceptor in hexamethyldisiloxane in a sealed tube at 100°C for 30 h, 55% of **7** and 13% of cholestan-3-one(**8**) were obtained. If the above reaction was carried out under nitrogen in an open system which would favour the evolution of hydrogen, 83% of **7** and 8% of **8** were formed even without a hydrogen acceptor. The preferential formation of **7** to **8** indicates that the dehydrogenation reaction is easier to occur than the hydrogen transfer reaction in these cases. This may be due to the preferential coordination of the oxygen atom of the hydroxy group to the metal center than the hindered double bond in **2**, which results in affording the dehydrogenated product, whereas cholest-1,4-dien-3-ol(**5**) still underwent the hydrogen transfer reaction normally to give the ketone **7** owing to the facility of the coordination of double bond at the 1-position to the metal center.

Table 2 shows the results of dehydrogenation of some allylic and homoallylic steroidal alcohols. For the allylic steroidal alcohols **1** and **3**, more saturated ketones were formed as compared to the homoallylic alcohols **2** and **4** as a result of the competition of the hydrogen transfer reaction with the dehydrogenation reaction. In the case of **2** and **4**, the dehydrogenation reaction seems faster than the hydrogen transfer reaction because in these cases, the coordination of double bond with the metal would be rather difficult[6]. The different results

Table 2. Dehydrogenation of Steroidal Alcohols in $(Me_3Si)_2O$ at 100°C[a]

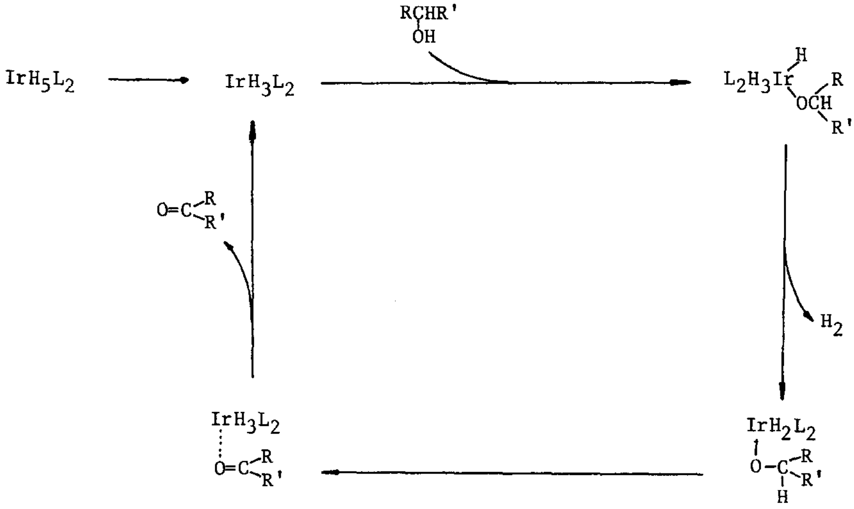
| Alcohols | Time (h) | Products | Yield[b] (%) |
|---|---|---|---|
|  (1) | 20 |  (7) | 52 |
| | |  (8) | 41 |
|  (2) | 24 | **7** | 83 |
| | | **8** | 8 |
|  (3) | 24 |  (9) | 45 |
| | |  (10) | 38 |
|  (4) | 28 | **9** | 83 |
|  (5) | 12 | **7** | 90 |
|  (6) | 33 |  (11) | 81 |

a: The reaction was carried out under nitrogen with 2 mole% of $IrH_5(i\text{-}Pr_3P)_2$ as the catalyst.

b: Isolated yield. All products gave satisfactory $^1H$ NMR, IR and MS data.

obtained either from **1** and **2** or from **3** and **4** implies that the dehydrogenation reaction may occur before the isomerization of the double bond. Otherwise, the same intermediate formed in situ in these reactions would give the same ratio of products.

It was reported recently that the hydrogen ligands of many known polyhydride complexes were proved to be associated with molecular hydrogen ligands in solution, at least to an extent of equilibrium between the dihydride and $\eta^2$-dihydrogen ligands[7-9]. This dynamic equilibrium process probably leads to the continuous evolution of dihydrogen in our catalytic cycle. From the mechanistic point of view, this may be the main difference between this new dehydrogenation reaction using polyhydride system and the dehydrogenation of alcohol in the presence of hydride acceptor. The mechanism of the dehydrogenation of the alcohols catalyzed by $IrH_5(i\text{-}Pr_3P)_2$ is proposed as follows:



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