

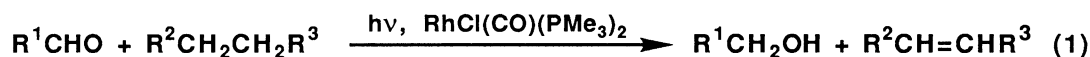
## Reduction of Carbonyl Compounds using Alkane as a Hydrogen Source

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Aldehydes are effectively reduced to corresponding alcohols at room temperature using alkane as a hydrogen donor by the catalysis of  $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$  under irradiation. Chemoselective reduction of aldehyde in the presence of ketone is achieved.

Activation of C-H bond of alkane under mild conditions has attracted increasing attention in these days. We have recently reported the dehydrogenation of alkanes to alkenes catalyzed by  $\text{RhCl}(\text{CO})(\text{PR}_3)_2$  under irradiation.<sup>1)</sup> In these reactions, hydridorhodium species are postulated as intermediates of the catalysis. Here we wish to report the utilization of the hydrido complexes to the reduction of aldehydes (Eq. 1).<sup>2)</sup>



Since cyclooctane is the most reactive substrate in the dehydrogenation by the  $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ -h $\nu$  system,<sup>1a)</sup> hydrogenation of carbonyl compounds to alcohols was investigated using cyclooctane as a hydrogen donor (Table 1). The reactions were carried out under a slow stream of nitrogen through the gas phase. Cyclohexanecarbaldehyde was reduced to cyclohexanemethanol in good yield at room temperature (87% and 359 turnovers after 48 h) (Run 1). In an early stage of the reaction, more than 80% of the hydrogen abstracted from cyclooctane was used for the formation of cyclohexanemethanol. The rest of hydrogen was liberated to the gas phase as dihydrogen. The reaction at a higher temperature reduced the efficiency of hydrogen transfer. The reaction mixture should be irradiated through a short-cut filter (UV-35; 10% transmittance at 325 nm). The presence of shorter wavelength (UV-33; 10% transmittance at 305 nm) resulted in the occurrence of photo-assisted decarbonylation of the aldehyde (Run 2). Although a very small amount of alcohol was produced even without the rhodium complex (Run 3), the catalyst is essential to get a good yield. The present reduction system is interesting in two points. Firstly, in spite of extensive study of photoreactions of carbonyl compounds, the example of simple reduction is still limited.<sup>3)</sup> Secondly, Wilkinson type catalyst,  $\text{RhCl}(\text{PR}_3)_3$  is known to be inactive for hydrogenation of aldehyde under such mild conditions as the present system; the catalyst is deactivated *via* the formation of  $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ .<sup>4)</sup>

Other substrates such as 3-phenylpropanal and octanal were also effectively reduced to the corresponding alcohols under the same conditions (Runs 4 and 5). Norrish Type II photoreaction of aldehyde was negligible when irradiated through UV-35. On the other hand, very interestingly, a ketone like 2-octanone was hardly reduced and was quantitatively recovered after 24 h irradiation (Run 6). A competitive reaction between octanal and 2-octanone also proved the large difference of the reaction rates (Run 7). Thus, the

present reaction is attractive in view of chemoselectivity as well as the use of alkane as a hydrogen source. The reaction of conjugated carbonyl compounds such as acetophenone or benzaldehyde gave poor yields of the desired products because of the consumption of the starting materials *via* various photo-assisted side reactions (*e.g.* oxetane formation with cyclooctene).<sup>5)</sup>

In summary, we have demonstrated the possibility to utilize alkane as a hydrogen source in the reduction of aldehyde. The method gives high catalytic turnover, yield, and chemoselectivity.

Table 1. Reduction of carbonyl compounds using cyclooctane as a hydrogen donor<sup>a)</sup>

| Run | Substrate                              | Time / h | Conv. / % | Yield / % <sup>b)</sup> |                           | Efficiency of H <sub>2</sub> transfer <sup>d)</sup> |
|-----|--|----------|-----------|-------------------------|---------------------------|---|
|     |  |          |           | Alcohol                 | Decarbonyl. <sup>c)</sup> |   |
| 1   | Cyclohexane-carbaldehyde               | 24       | 73        | 69                      | 1                         | 46  |
|     |  | 48       | 94        | 87                      | 1                         | 36  |
| 2   | Cyclohexane-carbaldehyde <sup>e)</sup> | 24       | 78        | 45                      | 17                        | 45  |
| 3   | Cyclohexane-carbaldehyde <sup>f)</sup> | 24       | 25        | 1                       | 16                        | --  |
| 4   | 3-Phenylpropanal                       | 24       | 56        | 45                      | 2                         | 59  |
|     |  | 48       | 78        | 67                      | 3                         | 50  |
| 5   | Octanal                                | 24       | 72        | 70                      | 1                         | 47  |
|     |  | 48       | 93        | 89                      | 1                         | 31  |
| 6   | 2-Octanone                             | 24       | 1         | 1                       | 0                         | 1   |
| 7   | {Octanal <sup>g)</sup>                 | 48       | 84        | 74                      | 1                         | 30  |
|     | {2-Octanone                            |          | 3         | 3                       | 0                         | 1   |

<sup>a)</sup>Substrate 0.1 cm<sup>3</sup>, cyclooctane 2.0 cm<sup>3</sup>, RhCl(CO)(PMe<sub>3</sub>)<sub>2</sub> 0.0020 mmol, irradiated by a high pressure mercury lamp through UV-35 filter at room temperature. <sup>b)</sup>GC yields based on substrates charged. <sup>c)</sup>Decarbonylated products (mainly alkane). <sup>d)</sup>100 x Alcohol/cyclooctene. <sup>e)</sup>Irradiated through UV-33 filter. <sup>f)</sup>Reaction without RhCl(CO)(PMe<sub>3</sub>)<sub>2</sub>. <sup>g)</sup>Used as a mixture.

#### References

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