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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 $RhCl(CO)(PMe_3)_2$ 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 $RhCl(CO)(PR_3)_2$ under irradiation.[1)] 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).[2)]

$$R^1CHO + R^2CH_2CH_2R^3 \xrightarrow{h\nu,\ RhCl(CO)(PMe_3)_2} R^1CH_2OH + R^2CH{=}CHR^3 \quad (1)$$

Since cyclooctane is the most reactive substrate in the dehydrogenation by the $RhCl(CO)(PMe_3)_2$-hν system,[1a)] 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.[3)] Secondly, Wilkinson type catalyst, $RhCl(PR_3)_3$ 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 $RhCl(CO)(PR_3)_2$.[4)]

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).[5]

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[a]

Run	Substrate	Time / h	Conv. / %	Yield / %[b] Alcohol	Yield / %[b] Decarbonyl.[c]	Efficiency of H_2 transfer[d]
1	Cyclohexane-carbaldehyde	24	73	69	1	46
		48	94	87	1	36
2	Cyclohexane-carbaldehyde[e]	24	78	45	17	45
3	Cyclohexane-carbaldehyde[f]	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[g]	48	84	74	1	30
	2-Octanone		3	3	0	1

a)Substrate 0.1 cm^3, cyclooctane 2.0 cm^3, $RhCl(CO)(PMe_3)_2$ 0.0020 mmol, irradiated by a high pressure mercury lamp through UV-35 filter at room temperature. b)GC yields based on substrates charged. c)Decarbonylated products (mainly alkane). d)100 x Alcohol/cyclooctene. e)Irradiated through UV-33 filter. f)Reaction without $RhCl(CO)(PMe_3)_2$. g)Used as a mixture.

References

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2) As for transfer hydrogenation of alkene with alkane, see M. J. Burk and R. H. Crabtree, *J. Am. Chem. Soc.*, **109**, 8025 (1987) and references cited therein. See also Refs. 1a and 1c.
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