

TRANSFER HYDROGENATION OF ALDEHYDES CATALYZED BY
DIHYDRIDOTETRAKIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

Hideaki IMAI, Takeshi NISHIGUCHI, and Kazuo FUKUZUMI
Department of Applied Chemistry, Faculty of Engineering,
Nagoya University, Chikusa-ku, Nagoya 464

In the hydrogen transfer reaction catalyzed by dihydrido-tetrakis(triphenylphosphine)ruthenium(II), aldehydes and ketones are reduced to corresponding alcohols by ethers, hydroaromatic compounds, a tert-amine and alcohols under mild conditions.

It has been reported¹⁾ that aldehydes and ketones are reduced by prim- and sec- alcohols in the presence of $\text{CoH}_3(\text{PPh}_3)_3$,²⁾ $\text{RuCl}_2(\text{PPh}_3)_3$,³⁾ several iridium complexes⁴⁾ and Raney nickel,⁵⁾ and that benzil is reduced to benzoin in the presence of Palladium Carbon.⁶⁾

We report here that ethers, a tert-amine, hydroaromatic compounds and alcohols reduced aldehydes and ketones under mild conditions, using $\text{RuH}_2(\text{PPh}_3)_4$ as a catalyst.

When capronaldehyde (1.0 M), a hydrogen donor (2.0 M) and the catalyst (0.02 M) were heated at $36.5 \pm 0.5^\circ$ for 72 hr in bromobenzene, n-hexanol and a dehydrogenation product were obtained. The identification and the evaluation of yield of products were carried out by glc analysis, and the results are shown in the Table. 2,5-Dihydrofuran, tri-n-propylamine, benzil alcohol and cyclohexanol showed excellent hydrogen-donating abilities. This result suggests that these compounds donate hydrogen rapidly and the resulted dehydrogenation products are relatively resistant to reduction. Other compounds gave almost the same amount of n-hexanol.

In the reaction of 2,5-dihydrofuran or dioxane, following results were obtained. (1) The amount of n-hexanol was equal to that of the dehydrogenation product. (2) The total amount of the survived donor and the dehydrogenated donor was equal to that of the charged donor. (3) The total amount of n-hexanol and capronaldehyde was equal to that of the charged aldehyde. In the absence of the hydrogen donor, only 0.02 M of n-hexanol was obtained by hydrogen transfer from the catalyst (0.02 M). These results show that following reactions proceeded without any side reaction.

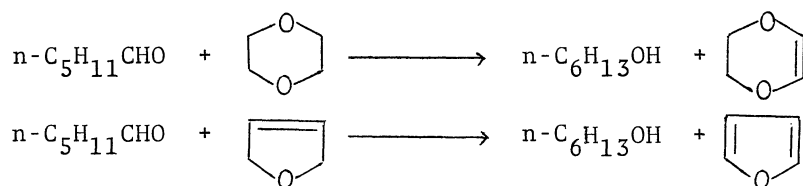


Table. Transfer hydrogenation of capronaldehyde

Hydrogen donor	Yield of n-hexanol, %	Dehydrogenation products
2,5-Dihydrofuran	30	Furan
Dioxane	10	Dioxene
Tetrahydrofuran	9	Furan
Di-n-propyl ether	9	----- ^a
Diisopropyl ether	9	----- ^a
Di-n-butyl ether	8	----- ^a
Tetrahydropyran	8	2,3-Dihydropyran
Ethyl n-butyl ether	6	----- ^a
Tri-n-propylamine	25	----- ^a
Benzyl alcohol	23	Benzaldehyde
Cyclohexanol	18	Cyclohexanone
Ethanol	13	Acetaldehyde
2-Propanol	10	Acetone
1,2-Dihydronaphthalene	12	Naphthalene
Tetralin	11	Naphthalene, 1,2-Dihydronaphthalene
Cyclohexene	9	Benzene

a) Dehydrogenation product was not identified.

In the reaction of some alcohols and hydroaromatic compounds, such as benzyl alcohol, 2-propanol, tetralin and cyclohexene, similar quantitative relationship was confirmed. It is noteworthy that non-cyclic ethers gave hydrogen in homogeneous catalysis, because such a phenomenon seems not to be reported. When prim- and sec-amines were used as donors, n-hexanol was not detected and capronaldehyde disappeared. In the case of tert-amine, the alcohol was obtained in good yield, but the amount of the surviving aldehyde was smaller than the theoretical one. These results show the existence of side reactions between the aldehyde and amines. Other aliphatic aldehydes and ketones were also reduced in similar systems.

References

- 1) G. Brieger and T. J. Nestrik, Chem. Rev., 1974, 5, 567.
- 2) E. Malunowicz, S. Tyrlik, and Z. Lasocki, J. Organometal. Chem., 1974, 72, 269.
- 3) Y. Sasson, P. Albin, and J. Blum, Tetrahedron Lett., 1974, 10, 833.
- 4) E. L. Eliel, T. W. Doyle, R. O. Hutchins, and E. C. Gilbert, Org. Syn., 1970 50, 13; M. Gullotti, R. Ugo, and S. Colonna, J. Chem. Soc. (C), 1971, 2652; Y. M. Y. Haddad, H. B. Henbest, J. Husbands, T. R. B. Mitchell, and J. T. Grimshaw, J. Chem. Soc. Perkin I, 1974, 596.
- 5) E. C. Kleiderer and E. C. Kornfeld, J. Org. Chem., 1948, 13, 455.
- 6) E. A. Braude, R. P. Linstead, K. P. H. Wooldridge, and P. W. D. Mitchell, J. Chem. Soc., 1954, 3595.

(Received June 6, 1975)