

The Selective Catalytic Conversion of Cycloalkanes into Cycloalkenes using a Soluble Rhenium Polyhydride System

Denise Baudry,* Michel Ephritikhine,* Hugh Felkin, and Rupert Holmes-Smith

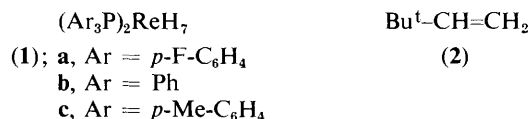
Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

Selective catalytic dehydrogenation (up to 9 turnovers) of cycloalkanes C_nH_{2n} ($n = 6, 7,$ and 8) to the corresponding cycloalkenes is achieved, under mild conditions ($30\text{--}80^\circ\text{C}$), using dilute (*ca.* 3 mM) solutions of the bis(phosphine)rhenium heptahydrides $(Ar_3P)_2ReH_7$ ($Ar = p\text{-F-C}_6\text{H}_4, \text{Ph},$ and $p\text{-Me-C}_6\text{H}_4$) in the cycloalkane, with an olefin as the hydrogen acceptor.

A few soluble transition metal systems have recently been discovered which, when activated either thermally^{1,2} (*e.g.*, by reaction with an olefin which removes two or more hydride ligands) or photochemically³ (*e.g.*, by dissociation of H_2 or CO), afford highly reactive, co-ordinatively unsaturated, intermediates capable of inserting into alkane C–H bonds. Thus, the key step in the conversion of cycloalkanes C_nH_{2n} ($n = 6, 7,$ and 8) into the corresponding cycloalkenes using the bis(phosphine)rhenium heptahydrides $(Ar_3P)_2ReH_7$ (**1a–c**), in the presence of 3,3-dimethylbut-1-ene (**2**) as a hydrogen acceptor, is thought to involve the insertion of a 14e intermediate such as $(Ar_3P)_2ReH_3$ into a C–H bond of the cycloalkane.^{†‡}

Consideration of the various possible reactions occurring in this system suggested to us that the dehydrogenation of cycloalkanes might be made *catalytic* [with respect to (**1**)] simply by using low concentrations of the reagents (**1**) and (**2**). We now report that this is indeed the case.

† We have recently re-examined these reactions and found that, in some cases, the yields of cycloalkenes are higher than those we reported previously [30–80% based on (**1**)]² especially in reactions involving the heptahydride (**1a**), which now appears to be a more efficient reagent than both (**1b**) and (**1c**). The reasons for this disparity, which may be due to use of purer starting materials [hydrocarbon or (**1**)] or to subtle differences in experimental procedure, will be discussed in our full paper.



Our best results have been obtained with the heptahydride (**1a**) and cyclo-octane. This system is far more reactive than we previously suspected. Thus, when a pale buff, deoxygenated, solution of (**1a**) (3.3 mM) and the olefin (**2**) (50 mM) in cyclo-octane was made up at *ca.* 20°C and then placed in a bath preheated to 30°C , within 5 min the colour had changed to pale amber and cyclo-octene (0.7 mM, 0.2 turnover) had already been formed. After 10 min, the concentration of cyclo-octene had reached its maximum (5.3 mM, 1.6 turnovers). This system therefore functions catalytically even at 30°C . The number of turnovers was greater [9 mol of cyclo-octene[‡] per mol of (**1a**) after 10 min] when the bath was preheated to 80°C . Under similar conditions (bath preheated to 80°C), cyclohexane gave cyclohexene[‡] (3.2 turnovers) and cycloheptane gave cycloheptene (4 turnovers). The heptahydrides (**1b**)⁴ and (**1c**)⁵ were rather less effective [*e.g.*, cyclo-octene, 6 turnovers using (**1b**), cyclohexene, 1.4 turnovers using (**1c**)].

‡ In these experiments, the cycloalkene was identified by g.c.–m.s. In the others, identification of the products was by g.c. retention times. The yields were determined by g.c.

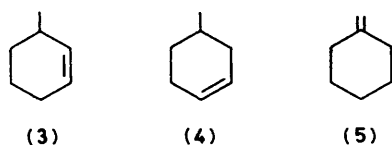


Table 1. Proportions of olefins formed in the dehydrogenation of methylcyclohexane by L_2ReH_7 (1) and $Bu^t-CH=CH_2$ (2) at 80 °C.

L	Olefin (%)		
	(3)	(4)	(5)
$(p-F-C_6H_4)_3P^{a,b}$	29	65	6
$Ph_3P^{a,c}$	28	63	9
Et_3P^d	27	45	28

^a $[L_2ReH_7] = 2$ mM, $[(2)] = 20$ mM, 10 min. ^b 3 turnovers.
^c 1 turnover. ^d $[(Et_3P)_2ReH_7] = 5$ mM, $[(2)] = 50$ mM, 2 h; 0.2 turnover.

All these reactions were totally selective; no other dehydrogenation products (*e.g.*, benzene from cyclohexane) could be detected.

The relatively large free energy of hydrogenation of the olefin (2) (21.9 kcal/mol⁶) (1 kcal = 4.18 kJ) is not a determining factor in these reactions, since the dehydrogenation of cyclo-octane [using (1a)] was still catalytic (5 turnovers instead of 9) with cyclohexene (free energy of hydrogenation 18.7 kcal/mol⁶) as the hydrogen acceptor instead of (2).

Methylcyclohexane gave a mixture of olefins. The results (Table 1) are interesting for several reasons: (a) they show that the various olefins, once formed, are not all interconverted by these rhenium hydride systems, since 1-methylcyclohexene (the most stable of the four isomers⁷) is present in no more than trace amounts; (b) they show that radical intermediates cannot be involved, since the major products (3- and 4-methylcyclohexene) cannot have arisen from the tertiary 1-methylcyclohexyl radical which would have been formed preferentially in a radical process;⁸ (c) they show that adventitious traces of a rhenium colloid cannot be responsible for these dehydrogenations, since a common intermediate such as

this would have led to the formation of the same mixture of olefins from all three heptahydrides; and (d) they suggest that the 'intrinsic' reactivity sequence is $Me > CH_2 > CH$, and that this is counteracted by a strong steric effect which directs the reagents, especially those containing bulky phosphines (Ar_3P), away from the more hindered sites (*i.e.*, Me, 2- CH_2 , and 6- CH_2 in methylcyclohexane).

Even though the total number of turnovers achieved by this system under present conditions is limited, the results reported here establish for the first time that the selective, non-radical, catalytic functionalisation of an unstrained hydrocarbon by means of a soluble transition-metal catalyst is a feasible process.

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References

- A. E. Shilov, *Sov. Sci. Rev. Sect. B, Chem. Rev.*, 1982, **4**, 71; R. H. Crabtree, J. M. Mihelcic, and J. M. Quirk, *J. Am. Chem. Soc.*, 1979, **101**, 7738; R. H. Crabtree, M. F. Mellea, J. M. Mihelcic, and J. M. Quirk, *ibid.*, 1982, **104**, 107; D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1980, 1243; D. Baudry, M. Ephritikhine, H. Felkin, and J. Zakrzewski, *ibid.*, 1982, 1235.
- D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1982, 606.
- M. A. Green, J. C. Huffman, K. G. Caulton, W. K. Rybak, and J. J. Ziolkowski, *J. Organomet. Chem.*, 1981, **218**, C39; A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352; J. K. Hoyano and W. A. G. Graham, *ibid.*, p. 3723; W. D. Jones and F. J. Feher, *Organometallics*, 1983, **2**, 562.
- J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1969, 1963.
- M. Freni, D. Giusto, and P. Romiti, *Gazz. Chim. Ital.*, 1975, **105**, 435.
- 'Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds' (API Research Project 44), Carnegie Press, Pittsburgh, 1953.
- I. A. Yursha, G. Ya. Kabo, and D. N. Andreevskii, *Neftekhimiya*, 1974, **14** (5), 688; *Chem. Abstr.*, 1975, **82**, 57332g.
- W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Am. Chem. Soc.*, 1972, **94**, 1632.