

## The Activation of C–H Bonds in Cycloalkanes by Rhenium Complexes

Denise Baudry,\* Michel Ephritikhine,\* and Hugh Felkin

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

Cycloalkanes  $C_nH_{2n}$  ( $n = 6, 7, 8$ ) are dehydrogenated at  $\leq 80^\circ C$  to the corresponding cycloalkenes by  $(Ar_3P)_2ReH_7$  in the presence of 3,3-dimethylbutene.

The activation of C–H bonds in alkanes by transition-metal complexes is receiving increasing attention, and systems which

achieve this have recently been developed<sup>1</sup> or discovered by chance.<sup>2</sup> Here we report on the dehydrogenation, under mild

conditions, of cycloalkanes by the bisphosphine rhenium heptahydrides (**1**) in the presence of 3,3-dimethylbutene (**2**) as a hydrogen acceptor. With cyclopentane, the heptahydride (**1b**)<sup>3</sup> has been shown previously<sup>2</sup> to lead to the cyclopentadienyl dihydride (**6b**);<sup>4</sup> we now find that *with the higher homologues (4, n = 6, 7, 8) this system directly affords the corresponding cycloalkenes (8)*.

Thus, when cyclohexane (5 ml) was refluxed with (**1b**) (0.28 mmol) and (**2**) (2.8 mmol) for 1 h, cyclohexene was formed (0.07 mmol; 25% yield based on **1b**). Similarly, after heating at 80 °C for 1 h, cycloheptane gave cycloheptene (30%), and cyclo-octane gave cyclo-octene (65%).†

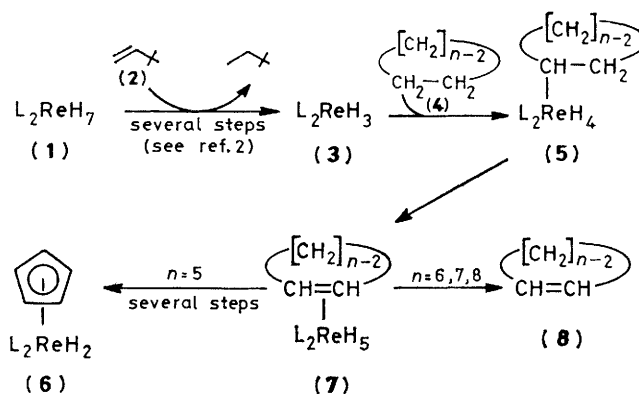
There appears to be a general trend towards more efficient dehydrogenation with more electron-releasing ligands in the heptahydride (**1**). This applies both to the formation of the cyclopentadienyl dihydrides (**6**) [the yields (by n.m.r.) of (**6a**),‡ (**6b**),<sup>4</sup> and (**6c**)§ were 10, 25,<sup>2</sup> and 45%, respectively] and to the formation of cyclo-octene [50, 65, and 80% yield, respectively, using (**1a**), (**1b**) and (**1c**)].

Processes involving radicals (*i.e.*, abstraction of H· from the cycloalkane), or free metal particles (*e.g.*, colloidal rhenium), do not seem to be responsible for these dehydrogenations. Finely divided rhenium metal is very reactive and burns to the heptaoxide;<sup>6</sup> the yield of cyclo-octene (65%) from cyclo-octane and (**1b**) was unaffected, however, when the reaction was carried out in the presence of air, and cyclo-octene was still formed (30% yield) even when pure oxygen was bubbled through the mixture during the reaction. Furthermore, no bicyclohexyl, which would be expected in a reaction involving cyclohexyl radicals,<sup>7</sup> could be detected in the reaction mixture from cyclohexane and (**1b**). Finally, it is interesting to note that the dehydrogenation of cyclohexane stops at cyclohexene, whereas a reaction involving metallic rhenium would have been expected to lead to benzene.<sup>8§</sup>

† In each of these experiments, the cyclo-olefin was separated from the excess of cycloalkane as its complex with AgSbF<sub>6</sub>, and identified by its mass spectrum and g.l.c. retention time. The yields reported were obtained by g.l.c. and are thought to be accurate to within about ± 5%. The organometallic component of the reaction mixture, which is soluble in acetone and dichloromethane, has not yet been characterised.

‡ Authentic samples of (**6a**) [ $\tau$ (CD<sub>2</sub>Cl<sub>2</sub>): 5.8 (5H, s,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) and 20.5 (2H, t,  $J$  40 Hz, ReH<sub>2</sub>)] and (**6c**) [ $\tau$ [(CD<sub>3</sub>)<sub>2</sub>CO]: 5.85 (5H, s,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 7.75 (18H, s, Me), and 20.5 (2H, t,  $J$  40 Hz, ReH<sub>2</sub>)] were prepared by the reaction<sup>4</sup> between cyclopentadiene and (**1a**) [ $\tau$ (CH<sub>2</sub>Cl<sub>2</sub>): 15.1 (t,  $J$  18 Hz)] and (**1c**).<sup>5</sup>

§ A small amount (*ca.* 10%) of benzene was detected (g.l.c.) in the reaction between cyclohexane and (**1b**); this, however, must have been formed from (**1b**) and not from cyclohexane, since the dehydrogenation of cyclohexane using (**1c**) gave cyclohexene, toluene, and no benzene.



**Scheme 1.** Postulated mechanism for the reaction between the heptahydrides (**1**) and cycloalkanes (**4**). L = a, (*p*-F-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P; b, Ph<sub>2</sub>P; c, (*p*-Me-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P.

We therefore believe that these dehydrogenations proceed essentially according to the mechanism outlined in Scheme 1, the key step (3 → 5) being the (reversible) oxidative addition of the cycloalkane to a co-ordinatively unsaturated intermediate such as (3), followed by (reversible)  $\beta$ -elimination (5 → 7). Presumably, the larger cycloalkenes (**8**,  $n > 5$ ) are more labile as ligands than cyclopentene, and dissociate from the metal before further reaction can occur, whereas cyclopentene undergoes further dehydrogenation to the cyclopentadienyl dihydrides (**6**).

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## References

- 1 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; A. H. Janowicz and R. G. Bergman, *ibid.*, 1982, **104**, 352; and references therein.
- 2 D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1980, 1243.
- 3 J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1969, 1963.
- 4 D. Baudry and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1980, 249; D. Baudry, M. Ephritikhine, and H. Felkin, *J. Organomet. Chem.*, 1982, **224**, 363.
- 5 M. Freni, D. Giusto, and P. Romiti, *Gazz. Chim. Ital.*, 1975, **105**, 435.
- 6 R. D. Peacock, in 'Comprehensive Inorganic Chemistry,' Pergamon Press, Oxford, 1973, Vol. 3, p. 907.
- 7 J. A. Sofranko, R. Eisenberg, and J. A. Kampmeier, *J. Am. Chem. Soc.*, 1980, **102**, 1163.
- 8 H. Pines, 'The Chemistry of Catalytic Hydrocarbon Conversions,' Academic Press, New York, 1981.