Tetrahedron Letters No. 15, pp 1391 - 1392, 1972. Pergamon Press. Printed in Great Britain.

SELECTIVE HYDROGENATION OF ALLENES WITH CHLOROTRIS-(TRIPHENYLPHOSPHINE) RHODIUM CATALYST

M.M. Bhagwat and D. Devaprabhakara
Department of Chemistry
Indian Institute of Technology Kanpur-16, India

(Received in Japan 22 February 1972; received in UK for publication 2 March 1972)

So far there have been few attempts to obtain selectivity for homogeneous hydrogenation of alkynes and dienes to the intermediate alkene.[1-3] However, there are no reports of such reduction of allenes. The present work concerns the homogeneous hydrogenation of some acyclic and cyclic allenes to the intermediate alkene using chlorotris(triphenylphosphine)rhodium catalyst. The results are shown in the Table.

TABLE

Allene	Product[(a)]	% Conversion[(b)]
1,2-Nonadiene	_cis_-2-Nonene	66
3-Ethyl-1,2-pentadiene	3-Ethyl-2-pentene	50
4,5-Nonadiene	_cis_-4-Nonene	30
2,4-Dimethyl-2,3-pentadiene	2,4-Dimethyl-2-pentene	12
1,2-Cyclononadiene	_cis_-Cyclononene	40
1,2,6-Cyclononatriene	_cis,cis_-1,5-Cyclononadiene	10
1,2-Cyclotridecadiene	Cyclotridecene (_cis_ 85%, _trans_ 15%)	65

(a) The reaction products were separated by preparative GLC and compared with authentic samples; (b) GLC analysis.

$RhCl(PPh_3)_3$ was prepared in the usual manner from $RhCl_3$,3 H_2O and PPh_3.[1] $RhCl(PPh_3)_3$ (9.25 mg, 0.01 mmol) and 15 ml of dry benzene were placed in a standard microhydrogenation vessel, containing a teflon-coated magnet, and the apparatus was flushed out with H_2 gas. On stirring the solution became homogeneous in less than 1 min. The temperature of the reaction vessel was then raised to

60 ± 1° and the solution was saturated with hydrogen. The allene (2 mmol) was injected into the reaction vessel *via* serum cap and the hydrogenation was carried out at 1 atmosphere for 24 hr. The hydrogen gas uptake was measured at intervals to find the extent of the reaction. The GLC analysis indicated a yield in the range 90-95% (based on the allene consumed) in each case. In no case was the isomerization of the allene or the formation of the saturated hydrocarbon observed under these conditions.

The following conclusions can be drawn from the data presented in the Table. (a) The partial homogeneous reduction of allenes is either stereospecific or highly stereoselective. (b) Highly substituted acyclic allenes are reduced slower than least substituted acyclic allenes. (c) In case of unsymmetrical acyclic allenes (1,2-nonadiene and 3-ethyl-1,2-pentadiene) the least substituted carbon-carbon double bond undergoes preferential reduction to form highly substituted olefin. (d) The results with cyclic allenes (1,2-cyclononadiene and 1,2-cyclotridecadiene) suggest that a nine-membered cyclic allene offers more steric hindrance than a thirteen-membered cyclic allene during hydrogenation. This may be attributed to the difference in flexibility of the two rings. The molecular models of these cyclic allenes show that the ring is more rigid in a nine-membered ring than in a thirteen-membered ring. (e) The slow reduction of 1,2,6-cyclononatriene may be due to its coordinating ability[4] with the catalyst just like *cis,cis*-1,5-cyclooctadiene. (f) Finally, the formation of only olefinic products suggests that the allenes have high competition figure in allene/alkene mixture.

The synthetic exploitation of this reduction procedure, the reaction kinetics and the possible isomerization of the allenes and the initial reduction products during the reduction process are currently under study.

Acknowledgement: We thank the CSIR, New Delhi for an award of J.R.F. to M.M.B.

REFERENCES

1. J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, *J.Chem.Soc.A*, 1711 (1966).
2. F.H. Jardine, J.A. Osborn and G. Wilkinson, *J.Chem.Soc.A*, 1574 (1967).
3. J.P. Candlin and A.R. Oldham, *Discussions of the Faraday Society*, *46*, 60 (1968).
4. G. Nagendrappa, G.C. Joshi and D. Devaprabhakara, *J.Organometal.Chem.*, *27*, 421 (1971).