Tetrahedron Letters,Vol.26,No.16,pp 1999-2000,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

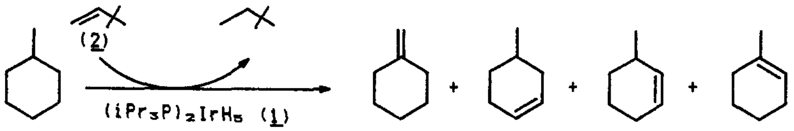
ACTIVATION OF C-H BONDS IN SATURATED HYDROCARBONS. THE SELECTIVE, CATALYTIC FUNCTIONALISATION OF METHYL GROUPS BY MEANS OF A SOLUBLE IRIDIUM POLYHYDRIDE SYSTEM

Hugh Felkin,* Tauqir Fillebeen-Khan, Rupert Holmes-Smith, and Lin Yingrui

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

Summary.- The selective, catalytic conversion of methylcyclohexane into methylenecyclohexane at 100°C, and of n-hexane into 1-hexene at 45°C, has been effected using bis(triisopropylphosphine)iridium pentahydride and an olefin (neohexene) as a hydrogen acceptor; with this system, approximate relative reactivities of C-H bonds in saturated hydrocarbons are: sec-alkyl-H, 1; iso-alkyl-H, 8; n-alkyl-H, >60.

The homogeneous catalytic functionalisation of saturated hydrocarbons has been carried out using soluble transition metal systems (*e.g.*, iron and manganese porphyrins)[1] which catalyse radical reactions and lead to preferential attack upon the weakest C-H bonds in the substrate (*i.e.*, at methine and methylene groups rather than methyl groups). Here we report that the bis(triisopropylphosphine)iridium pentahydride system, which we have previously found to catalyse the conversion of cyclo-octane into cyclo-octene,[2] effects the selective, catalytic functionalisation of saturated hydrocarbons at methyl groups, *i.e.*, it preferentially attacks the strongest C-H bonds.[3] This system appears to involve as its key step the insertion of a coordinatively unsaturated intermediate into a C-H bond of the substrate.[2]



conditions	catalytic turnovers		moles%		
-		-	-	-	-
100°C, 5 min	2.2	71	15	9	6
15 min	3.0	64	16	10	9
1 h	3.6	55	18	12	15
150°C, 65 h	10	1	24	13	62

Scheme. Yields and proportions of olefins formed from methylcyclohexane, 1 (1.6 mM), and 2 (30 mM); the reaction at 150°C was done in a sealed tube.

The products obtained when methylcyclohexane was treated with the pentahydride 1 (1.6 mM) in the presence of neohexene 2 (30 mM) as a hydrogen acceptor[4] are shown in the Scheme. It is apparent that preferential (kinetic) attack occurs at the methyl group, affording methylenecyclohexane, and that this is subsequently slowly isomerised (by 1 or one of its decomposition products). Similarly, the kinetic product formed from n-hexane at 45°C was 1-hexene;[5] this olefin, which constituted 78% of the mixture of hexenes obtained after 5 min (0.3 catalytic turnovers), underwent subsequent rapid isomerisation to a mixture of *cis*- and *trans*-2-hexene. Extrapolation to $t = 0$ of the results in the Scheme shows that the kinetic mixture of olefins formed from methylcyclohexane contains at least 75% of methylenecyclohexane; similar (less precise) extrapolation indicates that the kinetic mixture of olefins formed from n-hexane contains > 90% of 1-hexene.

We have also done some competition experiments with various mixtures of cyclohexane (which gives cyclohexene), methylcyclohexane and n-hexane. The results of these experiments, combined with the results mentioned above, have allowed us to calculate approximate relative reactivities of this iridium hydride system towards various types of C-H bonds. They are: sec-alkyl-H (CH_2 in cyclohexane), 1; iso-alkyl-H (CH_3 in methylcyclohexane), 8; and n-alkyl-H (CH_3 in n-hexane), >60.

The selective, catalytic functionalisation of methyl groups in saturated hydrocarbons does not appear to have been achieved previously. Such a catalytic reaction, if it were developed, might constitute a useful process; long-chain n-alkanes, for example, comprise many very similar methylene groups which are difficult to attack selectively, but only one pair of equivalent methyl groups.[6]

References and footnotes

1. J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1983, 105, 6243-6248; C. L. Hill, J. A. Smegal and T. J. Henly, *J. Org. Chem.*, 1983, 48, 3277-3281; D. Mansuy, M. Fontecave and J.-F. Bartoli, *J. Chem. Soc., Chem. Commun.*, 1983, 253-254; B. Meunier, *Bull. Soc. Chim.*, 1983, II, 345-366.
2. H. Felkin, T. Fillebeen-Khan, Y. Gault, R. Holmes-Smith and J. Zakrzewski, *Tetrahedron Lett.*, 1984, 25, 1279-1282.
3. The selective, stoichiometric functionalisation of methyl groups in n-alkanes via organometallic intermediates has recently been reported: D. Baudry, M. Ephritikhine, H. Felkin, and J. Zakrzewski, *J. Chem. Soc., Chem. Commun.*, 1982, 1235-1236; D. Baudry, M. Ephritikhine, H. Felkin and J. Zakrzewski, *Tetrahedron Lett.*, 1984, 25, 1283-1286; W. D. Jones and F. J. Feher, *Organometallics*, 1983, 2, 562-563; A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, 105, 3929-3939; R. A. Periana and R. G. Bergman, *Organometallics*, 1984, 3, 508-510.
4. R. H. Crabtree, M. F. Mellea, J. M. Mihelcic and J. M. Quirk, *J. Am. Chem. Soc.*, 1982, 104, 107-113.
5. Analyses of the olefin mixtures were done by g.c. These mixtures were also treated with bromine and the identities of the dibromides formed were confirmed by n.m.r. (products from methylcyclohexane) or g.c.-m.s. (products from n-hexane). We are most grateful to Dr. C. Rolando and Mme N. Morin (Ecole Normale Supérieure, Paris) for these g.c.-m.s. analyses.
6. We thank the Comptoir Lyon-Alemand-Louyot (Paris) for a generous loan of iridium.

(Received in France 4 February 1985)