Selective *cis*-Isomerisation of But-1-ene by Homogeneous Catalysis with Triphenylphosphinenickel Complexes

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Summary The treatment of but-1-ene with a mixture of tin(II) chloride and triphenylphosphinenickel complexes prepared from $(PPh_3)_2NiX_2$ (X = Cl, Br, I), PPh_3, and zinc leads to selective *cis*-isomerisation.

WHEN the nickel complexes $(PPh_3)_2NiX_2$ (X = Cl, Br, I), were treated with zinc in the presence of triphenylphosphine in tetrahydrofuran at room temperature, a red-brown solution was obtained which appeared to contain a mixture of Ni^0 and Ni^I, since the solution gave a weak e.s.r. signal typical of Ni^I, and when $(PPh_3)_2NiX_2$ was added, the solution yielded an intense e.s.r. signal of Ni^I. Heimbach found that a solution of the complexes, $Ni(PPh_3)_4$ and $(PPh_3)_2NiX_2$ in ether,[1] contained $Ni(PPh_3)_4$, $(PPh_3)_3NiX$ and species from which PPh_3 had dissociated.

The isomerisation of but-1-ene was catalysed by this solution at 0 °C as shown in the Table. The reactivity and

TABLE *Catalytic isomerisation of but-*1-*ene by* $(PPh_3)_2NiX_2$–PPh_3–Zn *systems and the effects of the addition of* $SnCl_2$[a]

X	Additive (mmol)	Time (min)	Product (mol %) $1\text{-}C_4H_8$	$t\text{-}2\text{-}C_4H_8$	$c\text{-}2\text{-}C_4H_8$	*cis* : *trans*
Cl	—	30	92·9	1·77	5·31	3·0
Br	—	30	97·6	0·51	1·89	3·7
I[b]	—	30	95·9	0·45	3·61	8·1
Cl	$SnCl_2$ 0·27	5	75·4	1·12	23·5	20·9
	0·71	5	64·0	1·26	34·7	27·7
	1·57	5	40·5	1·73	59·1	34·1
	2·97	5	14·4	2·27	83·3	36·8
Br	$SnCl_2$ 2·84	5	47·0	1·22	51·8	42·5
I[b]	$SnCl_2$ 2·92	5	80·6	0·39	19·1	49·3
	Equilibrium value		2·0	74·2	23·8	0·32

[a] The catalytic solution was prepared by adding 1·5 g of Zn to a mixture of 0·5 mmol of $(PPh_3)_2NiX_2$ and 0·75 mmol of PPh_3 in 20 ml of tetrahydrofuran at room temperature and then treating the filtrate with 0·25 mmol of $(PPh_3)_2NiX_2$. The reaction tube was charged with 3 ml of catalyst solution and 2·3 mmol of but-1-ene, sealed, and then brought to 0 °C. [b] 1·0 mmol of PPh_3 was used.

the ratio of *cis*-but-2-ene to *trans*-but-2-ene were dependent upon the halide bonded to the nickel atom, indicating that the catalytically active species contained Ni–X bonds. The stereoselectivity increased with the size of the halide in a similar manner to the isomerisation of but-1-ene with $(PPh_3)_2CoX_2$– and $(PPh_3)_2NiX_2$–$NaBH_4$ catalytic systems.[2]

The addition of $SnCl_2$ to the catalysis solution produced a solution which had a higher catalytic activity and gave an increased *cis*-: *trans*-but-2-ene ratio which increased with increasing concentrations of $SnCl_2$ and was also affected by the halide bonded to nickel. This may be due to co-ordination of $SnCl_2$ to the Ni^{I}–X complex to form Ni^{I}–$SnXCl_2$ analogous to the formation of $(C_5H_5)Ni(PPh_3)(SnCl_3)$ from $(C_5H_5)Ni(PPh_3)Cl$ and $SnCl_2$.[3]

The ratio of *cis*-: *trans*-but-2-enes did not decrease until but-1-ene was almost consumed. The *cis*-selectivity was as high as in the isomerisation of but-1-ene by base catalysts.[4] The characteristic feature of homogeneous catalytic systems is that the scrambling of but-2-ene is very slow compared to the double bond migration of but-1-ene.

$SnBr_2$ was less effective than $SnCl_2$ in both catalytic activity and *cis*-selectivity, and there was no detectable isomerisation of but-1-ene with a nickel–iodide complex and SnI_2.

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