Tetrahedron Letters No. 19, pp 1791 - 1792, 1974. Pergamon Press. Printed in Great Britain.

STEREO-SELECTIVE ISOMERISATION OF 3-METHYL-1-PENTENE CATALYSED BY {$Ni[P(OEt)_2Ph]_4$}

G. Strukul, M. Bonivento, R. Ros, and M. Graziani

Istituto di Chimica Generale, Facoltà di Chimica Industriale,
Università di Venezia (ITALY)

(Received in UK 26 February 1974; accepted for publication 4 April 1974)

Double bond migration is catalysed by a variety of coordination compounds, under homogeneous conditions, and this reaction has been extensively studied and reviewed(1). A cocatalyst is frequently required and hydrogen or acids are usually employed for this purpose.

It has been reported(2) that 1-butene is 95% isomerised by {$Ni[P(OEt)_3]_4$} within five minutes in methanolic H_2SO_4 solution. In absence of the acid cocatalyst less than 3% is isomerised after 4.5 days at 25°C. A detailed examination of the mechanism of this isomerisation proved(3) that the reaction proceeds through formation of relatively stable $[HNiL_4]^+$ species, followed by dissociation of the neutral ligand L to give $[HNiL_3]^+$, which must be looked at as the catalytically active complex.

We have now found that 3-methyl-1-pentene is quantitatively isomerised (99% of conversion) by a methanolic solution of {$Ni[P(OEt)_2Ph]_4$}(4) under nitrogen, to a mixture of *cis*- and *trans*-3-methyl-2-pentene (∿2/3 ratio) in the presence of *p*-toluenesulfonic acid as cocatalyst. The isomerisation has been carried out also in the presence of the optically active phosphine (-)R P*(Me)(*n*-Pr)(Ph)(5) ($[\alpha]_D^{20} = -13.7$; c= 3.5 in CH_3OH; 85% optical purity)(6). The reaction was monitored by GLC and the rate of conversion decreases increasing the concentration of the added phosphine (figure 1). If the reaction is stopped at about 50% of conversion by admission of oxygen, which destroys the catalyst, the 3-methyl-1-pentene still present is enriched in the (+)S isomer(7). Although we found that^^

---

^^ optical yields were calculated on the isomerised 3-methyl-1-pentene.

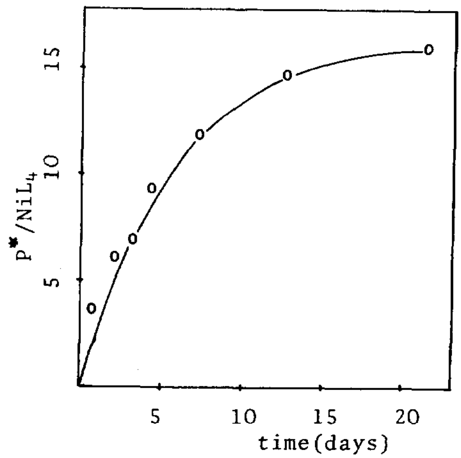

Figure 1.- P^*= (-)R P^*(Me)(*n*-Pr)(Ph); L= $P(OEt)_2Ph$; *time relative to 50%* of conversion.

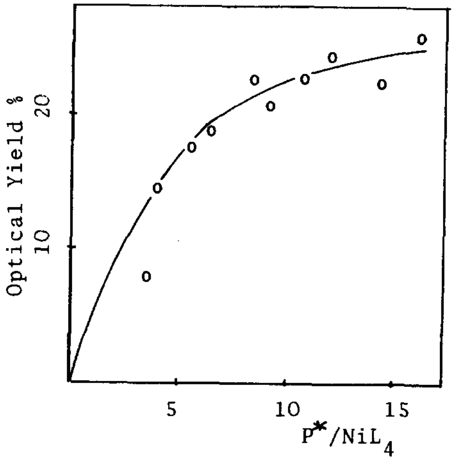

Figure 2.- Symbols as in figure 1; typical reaction conditions: NiL_4= 2.3×10^{-4} mol; 3-methyl-1-pentene= 1.4×10^{-2}mol; *p*-toluenesulfonic acid= 3.15×10^{-4}mol; MeOH = 10 ml; T= 25°C.

the optical yield is independent of the extent of conversion, the value of 50% was selected to get best results in measuring the specific rotation of the solutions (all polarimetric readings were made on a Perkin-Elmer 141 polarimeter with a 10 cm. thermostatted cell). On the other hand the optical yield depends on the concentration of the added phosphine and appears to reach a limiting value at high P^*/NiL_4 ratios (figure 2). This levelling off to a limiting value can be related to saturation in the exchange of the neutral ligand with the optically active phosphine.

References

1.- M. Orchin, Adv. Catalysys, 16, 2 (1966).
2.- R. Cramer and R.V. Lindsay, J. Am. Chem. Soc., 88, 3534, (1966).
3.- C.A. Tolman, J. Am. Chem. Soc., 94, 2994 (1972).
4.- D. Titus, A.A. Orio, and H.B. Gray, Inorg. Synthesis, 13, 117 (1972).
5.- O. Korpiun, R.A. Lewis, J. Chickos and K. Mislow, J. Am. Chem. Soc., 90, 4841 (1968).
6.- R. Luckenbach, Tetrahedron Letters, 2177 (1971).
7.- P. Pino, L. Lardicci and L. Centoni, J. Org. Chem., 24, 1399 (1959).