

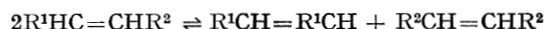
Stereochemistry of the Homogeneous Disproportionation of Pent-2-ene

By WILLIAM B. HUGHES

(Research and Development Division, Phillips Petroleum Co., Bartlesville, Oklahoma 74003)

Summary Disproportionation of pent-2-ene with a soluble molybdenum catalyst shows unique stereo-selectivity which can be rationalized in terms of a molybdenum-diolefin complex intermediate.

A NOVEL homogeneous catalyst system for olefin disproportionation (equation) has recently been reported.¹ The



catalyst is obtained by treating a molybdenum complex of the type $L_2Mo(NO)_2Cl_2$ [$L=Ph_3P; C_5H_5N; Ph_3PO, etc.$] with an alkylaluminum compound. Homogeneous catalysts based on tungsten have also been reported.^{2,3}

A definite correlation exists between the total concentration of *cis*-olefins in the reaction mixture and the percent conversion in the disproportionation reaction. Two separate reactions of *cis*-pent-2-ene were carried out using different catalyst concentrations so that the rates were quite different (reaction I had 14% conversion in 10 min., reaction II had 48% conversion in 10 min.). However, a plot of percent total *cis*-olefins ($C_4 + C_5 + C_6$) against percent conversion for the two reactions gave essentially the same curve. The fact that the rate of disproportionation and the rate of isomerization decrease simultaneously implies that the two processes are intimately connected and probably occur on the same catalyst (*vide infra*).

The observed stereoselectivity of the disproportionation

TABLE 1

Starting pent-2-ene	Equilibrium distribution of olefins in the disproportionation of pent-2-ene at 0°					
	<i>t</i> -but-2-ene	<i>c</i> -but-2-ene	<i>t</i> -pent-2-ene	Mole % <i>c</i> -pent-2-ene	<i>t</i> -hex-3-ene	<i>c</i> -hex-3-ene
<i>trans</i>	16.7	5.7	42.6	8.3	23.6	3.2
<i>cis</i>	17.9	6.0	40.9	9.0	22.6	3.7

The stereochemistry of the homogeneous disproportionation of pent-2-ene using the catalyst system $py_2Mo(NO)_2Cl_2-EtAlCl_2$ has been studied. The results of this study, in marked contrast to those obtained in the tungsten systems,^{2,3} reveal that the molybdenum catalyst exhibits a high degree of stereoselectivity.

At 0° in chlorobenzene, the above system converts pent-2-ene into but-2-ene and hex-3-ene, reaching a maximum conversion of *ca.* 50%. The distribution of *cis*- and *trans*-isomers of the three olefins also attains an equilibrium value independent of the isomeric nature of the starting pent-2-ene. The equilibrium distribution among all olefins and between each *cis-trans*-pair is shown in Table 1. The data of Table 1 agree fairly well with calculated values using ΔF_f° data and indicate that the final composition is thermodynamically controlled. However, examination of the reactions in their early stages reveals that the initial isomer distributions in the products are dependent upon the isomeric nature of the starting-pent-2-ene, *i.e.* they are kinetically controlled. The *cis/trans*-ratios for the three olefins in the first 4 min. of the disproportionation of *cis*- and of *trans*-pent-2-ene are shown in Table 2.

The data of Table 2 clearly shows that *cis*-pent-2-ene disproportionates preferentially to *cis*-but-2-ene and *cis*-hex-3-ene, and that *trans*-pent-2-ene reacts to yield preferentially *trans*-but-2-ene and *trans*-hex-3-ene.

TABLE 2

Starting olefin	Time (min.)	Disproportionation of <i>cis</i> - and of <i>trans</i> -pent-2-ene at 0°		
		but-2-ene	<i>cis/trans</i> -Ratio pent-2-ene	hex-3-ene
<i>cis</i>	2	4.4	28.8	2.3
	4	2.7	7.2	2.0
<i>trans</i>	2	0.1	0.04	0.0
	4	0.2	0.08	0.1

reaction may be explained in terms of a metal-olefin complex model. We suggest that the two reactant pent-2-ene molecules occupy *cis*-positions about an octahedrally co-ordinated molybdenum atom (Figure 1).

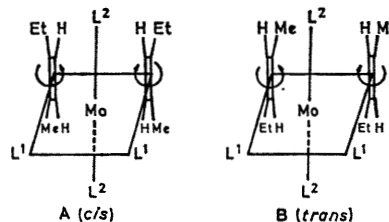


FIGURE 1

The most stable configurations sterically for a Mo-bisolefin complex containing two *cis*- and two *trans*-pentenes

are those shown in Figures 1A and 1B, respectively. The metal-olefin bonding is as usually depicted⁴ with the olefinic bond perpendicular to the plane of the Mo and ligands L¹. The σ -component of the Mo-olefin bond is formed by overlap of metal σ -type acceptor orbitals with olefin π^b -orbitals (Figure 2A).

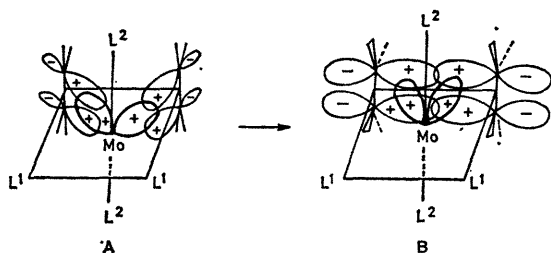


FIGURE 2

For positive overlap of the olefin π^b -orbitals to occur, which results in product σ -bonds and hence disproportionation, the two olefins must rotate in a disrotatory manner

(Figure 2B). In the case of two *cis*-pent-2-enes reacting (Figure 1A) this leads to *cis*-but-2-ene and *cis*-hex-3-ene; in the case of two *trans*-pent-2-enes (Figure 1B) to *trans*-but-2-ene and *trans*-hex-3-ene. This agrees with the experimental results.

Inspection of the molybdenum-bisolefin complexes (Figure 1) reveals that a 180° rotation about the Mo-olefin bond of one of the pentenes gives a configuration which yields two pentene molecules upon disproportionation, *i.e.* there is no net reaction. However, it is possible in this manner to interconvert two *cis*-pent-2-enes into two *trans*-pent-2-enes. This is consistent with the experimentally observed close relationship between disproportionation and isomerization. The configurations leading to isomerization are sterically unfavoured and suggest that isomerization should proceed at a slower rate than disproportionation.

Complexation and decomplexation of all olefins in the various configurations provide a pathway for the eventual attainment of thermodynamic equilibrium both with respect to *cis*- and *trans*-olefins and C₅ and C₄ + C₆ olefins.

(Received, February 12th, 1969; Com. 193.)

¹ E. A. Zuech, *Chem. Comm.*, 1968, 1182.

² N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, 1968, **90**, 4133.

³ J. L. Wang and H. R. Menapace, *J. Org. Chem.*, 1968, **33**, 3794.

⁴ J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.