Unusual Stereoselectivities in Olefin Metathesis

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Summary The stereoselectivity of metathesis of various olefins (*cis*- or *trans*-RCH=CHMe) decreases with increasing bulk of the R groups; this corresponds to an increased randomness of the various modes of olefin co-ordination to the metallo-carbene intermediate.

We report new data which indicate that, unexpectedly, the stereoselectivity of metathesis of various olefins of the type *cis*- or *trans*-RCH=CHMe decreases with increasing bulk of the R group, corresponding to an increased randomness of the various modes of olefin co-ordination and/or reaction with the metallocarbene intermediate.[1,2] We also report data which indicate that some tungsten-based catalysts of low activity appear to exhibit a higher degree of stereoselectivity than the highly active catalysts.

The *trans/cis* ratio of the but-2-ene produced at 0% conversion in the metathesis of various olefins over catalysts of different activities was obtained from plots of the *trans/cis* ratio of the but-2-ene either against the *cis/trans* ratio of the starting olefin or against conversion.[2,3] Extrapolation to 0% conversion gave the stereoselectivity with good accuracy. Owing to the low reactivity of some *trans*-olefins, especially for R = Pr^i, the *trans/cis* ratio of the but-2-ene could vary considerably at low conversion and reach the thermodynamic composition even for very low conversions of the starting olefin.[4]

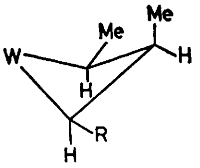
TABLE. Stereoselectivities in the metathesis of the *cis*- or *trans*-olefins RCH=CHMe (and in the polymerisation of *endo*-5-methylbicyclo[2.2.1hept-2-ene[a])

cis-Olefins		*trans*-Olefins	
R	*trans/cis* ratio of but-2-ene	R	*trans/cis* ratio of but-2-ene
H	$0{\cdot}73 \pm 0{\cdot}02^b$	Bu^n	$1{\cdot}25 \pm 0{\cdot}05^{b,c}$
Et	$0{\cdot}73 \pm 0{\cdot}02^b$	Et	$1{\cdot}25 \pm 0{\cdot}05^{b,c}$
Pr^n	$0{\cdot}79 \pm 0{\cdot}02^b$	Pr^n	$1{\cdot}25 \pm 0{\cdot}05^{b,c}$
Pr^i	$1{\cdot}02 \pm 0{\cdot}05^b$	Pr^i	$1{\cdot}16 \pm 0{\cdot}05^{b,c}$
Bu^t	$1{\cdot}00 \pm 0{\cdot}02^e$	n-Pentyl	$1{\cdot}25 \pm 0{\cdot}05^{b,c,f}$
Pr^n	$0{\cdot}60 \pm 0{\cdot}05^d$	Pr^n	$4{\cdot}0 \pm 0{\cdot}1^d$

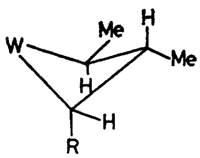
[a] *trans/cis* ratio of double bonds in the polymer chain formed from polymerization of *endo*-5-methylbicyclo[2.2.1]hept-2-ene, 0·75 for WCl_6–$EtAlCl_2$ as catalyst and 0·19 for WCl_6–$EtAlCl_2$–CH_2=$CHCO_2Et$ (ref. 6.) [b] Conditions: $W(CO)_5PPh_3$–$EtAlCl_2$–O_2; olefin, 10 mmol; olefin/W 100; Al/W 4; O_2/Al 0·125; 25 °C. [c] 1·25 ± 0·10 with $W(CO)_3$(*p*-xylene)–$EtAlCl_2$; olefin 10 mmol; olefin/W 100; Al/W 2. [d] $W(CO)_4Cl_2$; 100 °C. [e] As for (b) except Al/W 8; O_2/Al 0·25. [f] 1·25 ± 0·10 as for (c) but with Al/W 4.

The results obtained (Table) depend on the catalytic systems used. The highly active catalytic systems $W(CO)_{6-x}L_x$–$EtAlCl_2$–O_2, which show very high turnover numbers ($N > 60{\cdot}000$ mol olefin/mol tungsten/h for L = PPh_3 and $x = 1$)[5] show weak stereoselectivity towards *cis*- or *trans*-olefin. Surprisingly, increasing the bulk of the R group decreases the difference in stereoselectivity for the *cis*- and the *trans*-olefin. The length of unsubstituted R group has no effect on stereoselectivity. For R = Pr^i or Bu^t the *trans/cis* ratios of the but-2-ene formed tend towards unity regardless the *cis*- or *trans*-nature of the starting olefin. Interestingly a *trans/cis* ratio of 0·75 was obtained by Rooney[6] in the polymer resulting from the polymerisation of *endo*-5-methylbicyclo[2.2.1]hept-2-ene, and the ethyl acrylate increases drastically the *cis*-content of the polymer. $W(CO)_4Cl_2$, which is of low activity and which even at 100 °C shows a very low turnover number comparable to that of $W(CO)_5CPh_2$,[4] shows a stereoselectivity which is quite different from that of the highly active catalysts, especially with *trans*-hex-2-ene.

The unexpected stereoselectivities observed with crowded *cis*- or *trans*-olefins cannot be easily rationalised on the basis of various conformations of intermediate metallocyclobutanes.[7] In the intermediate states (I) and (II) leading respectively to *cis*-but-2-ene and *trans*-but-2-ene, increasing the bulk of R should result in a greater 1,3 diaxial interactions in (II) and therefore *cis*-but-2-ene formation should be favoured, from (I).

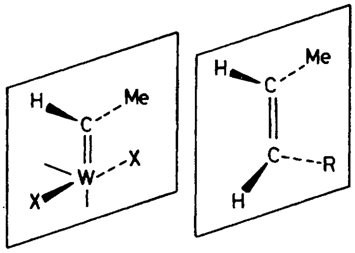


(I)



(II)

The loss of stereoselectivity upon increasing the size of the R group can be explained by steric interactions between the bulky R groups and tungsten (or ligands on tungsten); assuming a symmetrical arrangement of ligands X around the metallo-carbene it is clear that equally probable *cis*- or *trans*-co-ordination of a *cis*- or a *trans*-olefin would become more and more likely with increasing bulk of R (Figure).



FIGURE

For small R the stereochemistry is mainly determined by the favoured conformation of the metallo-cyclobutane (R = H, Et, *etc.*) whereas for bulky R the stereoselectivity is progressively lost (R = Pr^i, Bu^t, *etc.*).

The results presented here, along with those of Katz,[4] Calderon,[8] Pampus,[9] Dall'Asta,[10] Rooney,[6] and Tucker[11] suggest that metathesis of cyclic and acyclic olefins may show drastic changes of stereoselectivities. With cyclic olefins some catalysts lead to high molecular weight *cis*-polyalkenes without chain termination[11] *via* intramolecular or intermolecular co-ordination of the acyclic double bond or *via* a chain termination agent such as an α-olefin.[11] A tentative explanation would be to consider that catalysts of low stereoselectivity possess around the metallo-carbene intermediate more than one empty co-ordination site for olefin co-ordination; this would explain the molecular weight regulation by acyclic olefins in the case of cyclopentene polymerisation.[11] Highly stereoselective catalytic systems would be co-ordinatively more saturated, which would explain the effect of some promotors such as ether[9] or ethyl acrylate.[6]

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