STEREOCHEMISTRY OF METATHESIS CATALYSED BY W(VI) COMPOUNDS

H. T. DODD and K. J. RUTT

Faculty of Natural and Life Sciences, Brighton Polytechnic, Moulsecoomb, Brighton BN2 4GJ (U.K.)

Summary

The trans/cis ratios in butene and hexene products arising from the metathesis of cis- and trans-pent-2-ene have been measured at zero conversion for a series of catalysts of the type $W(OAr)_4Cl_2$. With cis-pent-2-ene, the results for all the catalysts were similar and comparable with those of other workers using different W(VI) catalysts. The trans/cis ratios for reactions of trans-pent-2-ene show a marked dependence on the nature of the OAr ligand attached to the catalyst. Those ligands bearing ortho substituents give rise to a much greater cis selectivity. A possible explanation of this result is given in terms of specific ligand interactions.

Introduction

Several studies have been made of the stereoselectivity of alkene metathesis using *cis* and *trans* substrates [1 - 4] since, in principle, they could elucidate the contribution of steric factors in the mechanism of metathesis. The results, using acyclic alkenes, have been remarkable for the consistency of the *trans/cis* ratios obtained for the products at zero conversion with a wide variety of catalysts. Several explanations for this have been offered [5 - 7].

We have been attempting to assess the importance of electronic and steric effects in the metathesis of acyclic alkenes using a series of catalysts of the type $W(OAr)_4Cl_2$, employing mainly $Et_3Al_2Cl_3$ as the catalyst [8, 9]. We report here the results of measurements of the *trans/cis* ratios in butene and hexene products derived from the metathesis of both *cis*- and *trans*-pent-2-ene using these catalytic systems.

Results

The catalysts employed were of the type $W(OAr)_4Cl_2$ where OAr represents a phenoxide ring bearing the following substituents: H; 4-Cl; 4-Br;

$W(OC_6H_{5-n}X_n)_4Cl_2$ catalyst employed where X =	W/Al/alkene ratio used in reaction	<i>trans/cis</i> -C ₄ ratio observed in products	trans/cis-C ₆ ratio observed in products	
Н	1:6:150	1.37	3.85	
4-Cl	1:6:400	1.39	3.23	
4-Br	1:6:400	1.23	3.13	
4-Me	1:6:50	1.38	3.92	
4-OMe	1:6:50	1.36	3.77	
2-Me	1:6:200	0.60	1.13	
trans-2,4-Me ₂	1:6:100	0.62	1.25	
cis-2,4-Me ₂	1:6:100	0.63	1.41	
2,4,6-Me ₃	1:6:150	0.64	2.03	
2,4,6-Cl ₃	1:5:200	0.64	1.32	

Initial $trans/cis-C_4$ and $-C_6$ ratios arising from the metathesis reaction of trans-pent-2-ene in the presence of W(VI) catalysts

4-CH₃; 4-CH₃O; 2-CH₃; 2,4-(CH₃)₂ (*cis* and *trans* complexes); 2,4,6-(CH₃)₃; and 2,4,6-Cl₃.

The stereoselectivities of the catalysts were measured by analysis of the geometric isomers present during metathesis of *cis*- or *trans*-pent-2-ene. As expected, the conversions were accompanied by geometric isomerisation of all the alkenes present, yielding at equilibrium the distribution of geometric isomers expected thermodynamically. For *cis*-pent-2-ene, the initial *trans/cis* ratios for the products of metathesis were obtained by plotting the *trans/cis* ratios for C₄ or C₆ alkenes against the *trans/cis* ratio for C₅ alkenes and then extrapolating the linear graph to *trans/cis*-C₅ = 0. For *trans*-pent-2ene a similar procedure using *cis/trans* ratios was employed. For *cis*-pent-2ene with a W/Al/alkene ratio of 1:6:200, the isomer ratios in the products were similar for all the catalysts, the values obtained being about 0.71 for *trans/cis*-butene and 1.2 for *trans/cis*-hexene. When much lower W/alkene ratios of 1:50 were used, the values of *trans/cis*-C₄ and -C₆ were raised to 1.1 and 2.1, respectively.

With trans-pent-2-ene, the results for individual catalysts were independent of the W/Al/alkene ratio. Moreover the catalysts fall into two distinct groups. The first category showed the typical characteristics found by other workers [3], with a variety of catalysts having trans/cis-C₄ $\simeq 1.37$ and trans/cis-C₆ $\simeq 3.7$. The second category, which was made up of phenoxo-tungsten catalysts bearing ortho substituents on the aromatic ring, gave an initial stereochemistry much more favourable towards cis products. These two types of behaviour are shown in Table 1.

Discussion

The stereochemistries of the catalysts employed with cis-alkenes are similar to those observed by other workers [2-4], at least at W/Al/alkene

TABLE 1



Fig. 1. Favoured orientation of W=CHR and approach of *trans* R'CH=CHR minimising X....R interactions for 2,6-disubstituted phenoxotungsten intermediates.

ratios commonly employed. The reason for the different behaviour at low alkene concentrations is uncertain, particularly since the *trans*-alkene does not show this effect.

In the metathesis of *trans*-pent-2-ene, the marked difference in stereoselectivity when the catalyst bears *ortho* substituents on the aromatic ring suggests that a specific ligand interaction is occurring. We propose that the reaction involved an intermediate such as that shown in Fig. 1. The ligand *trans* to the alkylidene is left vacant for the sake of clarity. Model studies suggest that the phenoxide rings take up a tilted, propellor-type configuration to minimise interactions between the *ortho* substituents. Steric interactions are a minimum if the configuration of the alkylidene and the approach of the *trans*-alkene are as shown in the figure.

Such a model predicts that a *trans* starting alkene will lead initially to *cis* products. With a *cis* starting alkene, the alkyl-substituent interactions will be non-stereoselective. In the absence of *ortho* substituents, steric restrictions on the approach of the alkene are much reduced.

Experimental

Synthesis of complexes

The preparation and characterisation of all the complexes except dichlorotetrakis(2,4,6-trichlorophenoxo)tungsten(VI) have been reported previously [8]. This latter compound was synthesised via a similar procedure to that used earlier. Purified WCl₆ and 2,4,6-trichlorophenol in a 1:4 molar ratio were refluxed together in CCl₄ for 48 h, the product mixture being filtered and stored at -5 °C. The dark purple needles produced were recrystallised from toluene, washed with light petrol and vacuum dried (yield 32%, m.p. 191 °C). Analysis (%): C, 28.1 (27.7); H, 0.76 (0.78). ¹H NMR in

CCl₄: singlet at 7.44 ppm. Electronic spectrum above 300 nm in chlorobenzene (λ_{max} (nm) [$\epsilon \times 10^4$]: 505 [1.72]; 410 [1.68]; 315 [0.89].

Catalysis experiments

Catalytic runs were performed as described previously, using $Et_3Al_2Cl_3$ as the co-catalyst [8]. The *trans/cis* distributions of starting and product alkenes were determined by GLC on a column (2.5 m × 5 mm) of 15% silicon oil/15% AgNO₃-PhCN on Chromosorb W at 30 °C using a nitrogen carrier gas flow of 40 cm³ min⁻¹.

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