Stereoselectivity of Metathesis of Various Acyclic Olefins with Chromium-, Molybdenum-, and Tungsten-Based Catalysts

M. Leconte and J. M. Basset*

Contribution from the Institut de Recherches sur la Catalyse, 69626 Villeurbanne Cedex, France. *Received August 25, 1978*

Abstract: The stereoselectivity of metathesis of *cis*- and *trans*-RCH=CHCH$_3$ has been determined by the trans/cis ratios of 2-butenes (C$_4$) at 0% conversion; the catalytic systems used were M(NO)$_2$X$_2$(PPh$_3$)$_2$ + EtAlCl$_2$ (M = Mo, W; X = Cl, Br, I) (**1**); M(CO)$_5$(PPh$_3$) + EtAlCl$_2$ + O$_2$ (M = Mo, W) (**2**); (arene)M(CO)$_3$ + EtAlCl$_2$ (arene = benzene, mesitylene; M = Cr, Mo, W) (**3**). For **1**, M = Mo, X = Cl, and R = Et, the trans/cis ratios of C$_4$ are equal to 0.20 and 12.5, respectively, for a cis and a trans olefin; increasing the bulkiness of R above R = Et results in a significant decrease of selectivity (and activity); with a cis olefin, the trans/cis ratio of C$_4$ increases when the bulkiness of R increases above a certain size (trans/cis ratio of C$_4$ = 0.44 for R = *t*-Bu and **1**, M = Mo, X = Cl); with a trans olefin, the trans/cis ratio of C$_4$ decreases when the bulkiness of R increases above a certain size (trans/cis ratio of C$_4$ = 8.3 for R = *t*-Bu and **1**, M = Mo, X = Cl). This effect does not seem to be the result of an electronic effect of the R group since similar stereoselectivities are obtained with **1**, M = Mo, R = *t*-Bu, phenyl, or benzyl; changing the coordination sphere of the precursor catalyst (**1**, M = Mo, W; X = Cl, Br) does not result in a meaningful variation of stereoselectivity. For *cis*- and *trans*-2-pentene, a comparison was made between the trans/cis ratios of C$_4$ and the trans/cis ratios of C$_6$: for **1**, M = Mo, W; X = Cl, Br, the trans/cis ratio of C$_6$ is always higher than the trans/cis ratio of C$_4$. This result, which seems to be related to 1–2 a–e $\rightleftharpoons$ e–a repulsive interaction in the metallocyclobutane transition state, is corroborated by the stereoselectivities of the metathesis of α olefins propylene, 1-butene, and 1-pentene: for **1**, M = Mo, X = Cl, the trans/cis ratio of the products increases in the order 2-butene (1.1) < 3-hexene (1.42) < 4-octene (2.0). The stereoselectivity of metathesis of acyclic olefins is explained on the basis of many competitive interactions occurring during olefin coordination to the metallocarbene and in the metallocyclobutane transition state: 1–3 diaxial interaction, 1–2 equatorial–axial interaction, and olefin–metal (and/or its ligands) interaction $\underline{M_4{-}C_1{-}C_2{-}C_3}$. Comparison of the stereoselectivities between Cr, Mo, and W was carried out with R = Et and **1** (M = Mo, W; X = Cl), **2** (M = Mo, W), and **3** (M = Cr, Mo, W; arene = mesitylene). The variations of stereoselectivity observed (Cr > Mo $\gg$ W) may be explained on the following basis: the Mo–C distance is smaller than the W–C distance in the metallocyclobutane; this would result in an increase of the 1–3-diaxial interaction.

The stereochemistry of olefin metathesis has been the subject of recent publications[1-6] which tried to rationalize the behavior of tungsten-based or molybdenum-based calatysts with acyclic olefins. Most tungsten-based catalysts exhibit a very weak stereoselectivity corresponding to an almost random coordination and/or reaction of the olefin with the metallocarbene.[2] However, steric factors are not completely negligible even in the case of tungsten-based catalysts since cis olefins and trans olefins exhibit respectively a slight cis or trans stereoselectivity.[7,8] Many hypotheses have been advanced to account for the stereoselectivities observed: steric effects during the coordination of the olefin to the metallocarbene,[2] stability of the various conformations of the "metallocyclobutane" transition state, steric effect of the ligands on the tungsten or steric effect of a surface,[8] opening of the carbon–metal bond in the metallocyclobutane forming a substituted metallopropyl cation in which the remaining bonds rotate.[1] If model reactions of W(CO)$_5$CH(C$_6$H$_5$) and W(CO)$_5$C(C$_6$H$_5$)$_2$ with olefins have suggested the validity of the minimized 1-3 diaxial repulsive interaction in the metallocyclobutane intermediate leading to cyclopropane derivatives,[6,9] the observed stereoselectivities are in this particular case much higher than in olefin metathesis as though the same intermediates were not involved in both reductive elimination leading to cyclopropane and ring cleavage leading to metathesis. Besides, recent results obtained with various olefins of the type *cis*- or *trans*-RCH=CHCH$_3$ have indicated that increasing the bulkiness of R results in a decrease of stereoselectivity with tungsten-based catalysts[5] (trans/cis ratio of C$_4$ tends toward unity for R = *tert*-butyl). This result is not explained either on the basis of the 1,3 minimized diaxial repulsive interaction of the metallocyclobutane only[2,3] or on an asymmetric ligand arrangement in the coordination sphere of tungsten.[2] Obviously more data related to the influence of the structure of the olefin on the resulting stereoselectivity were needed before reaching any valid conclusion.

We report in this paper a series of experiments carried out with various chromium, molybdenum, and tungsten catalysts. Chromium- and molybdenum-based catalysts were selected because they give rise to much higher selectivities than most tungsten-based catalysts,[2,7] and consequently the use of these group 6 transition metal compounds would lead to more significant conclusions. The various olefins used were selected with respect to the information they could supply with regard to 1-3, 1-2, or 3-4 interactions in the metallocyclobutane which is supposed to be the intermediate step in the carbene mechanism of metathesis.[10]

Results and Discussion

1. Determination of the Stereoselectivity in Metathesis of Acyclic Olefins. In a previous paper,[2] we proposed a model of olefin coordination (or reaction) to the metallocarbene. This model accounts for the simultaneous occurrence of formal metathesis, degenerate metathesis, and cis–trans isomerization which are found to occur simultaneously in metathesis of olefins.[2,10,11] From this kinetic model it was possible to derive a mathematical equation which could apply to metathesis of any internal olefin. When applied to *cis*-2-pentene metathesis it was observed that a linear relationship could be observed by plotting *trans-/cis*-C$_4$ (C$_4$ = 2-butene) vs. *trans-/cis*-C$_5$ (C$_5$ = 2-pentene).

The linear relationship observed indicates in fact that cis–trans isomerization of the starting olefin as well as cis–trans isomerization of the products is a competitive reaction during propagation. The extrapolation of the experimental data to 0% conversion seems to be a very good measure of the stereoselectivity of the reaction. In Figure 1, we have plotted a typical result obtained in *cis*-2-pentene metathesis with a zerovalent complex of tungsten (W(CO)$_5$PPh$_3$, C$_2$H$_5$AlCl$_2$, O$_2$), with a hexavalent complex of tungsten (WCl$_6$, C$_2$H$_5$OH, C$_2$H$_5$AlCl$_2$, data taken from Calderon[7a]), and with a nitrosyl complex of molybdenum (Mo(NO)$_2$Br$_2$(PPh$_3$)$_2$, C$_2$H$_5$AlCl$_2$). In a very

0002-7863/79/1501-7296$01.00/0

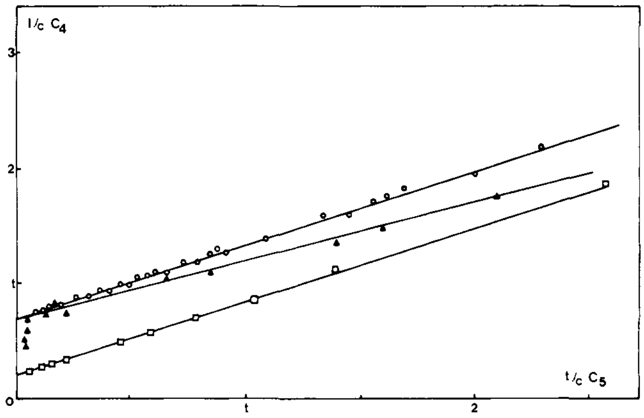


Figure 1. Determination of the stereoselectivity of metathesis of *cis*-2-pentene with the catalytic systems: ○, $W(CO)_5PPh_3 + EtAlCl_2$; ▲, $WCl_6 + EtOH + EtAlCl_2$; □, $Mo(NO)_2Br_2(PPh_3)_2 + EtAlCl_2$.

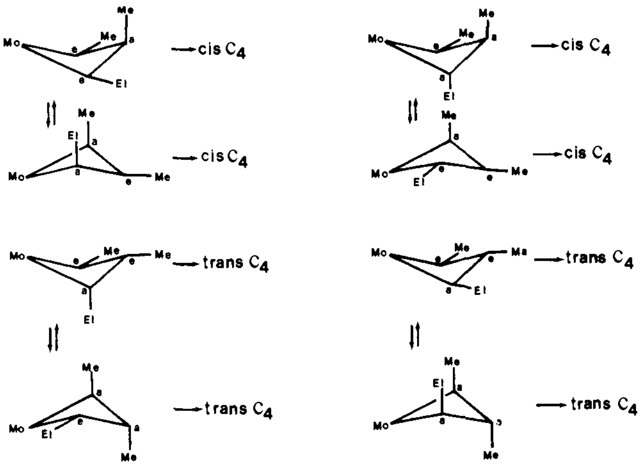


Figure 2. Metallocyclobutanes involved in *cis*-2-pentene (left) and in *trans*-2-pentene (right) metathesis.[23]

wide range of conversions, a linear relationship is observed and the intercepts at a trans/cis ratio of C_5 equal to zero (that is, for a 0% conversion) give a very precise value of the stereoselectivity of the propagation step. If one considers the real experimental data obtained at very low conversion (Figure 1), it appears in some cases that there is some deviation between these values and those obtained by the extrapolation procedure. The reason for such deviations probably has many origins. Determinations at low conversion involve low concentrations of products and high experimental errors. It has been shown[2,10g] also that initiation, which corresponds to the formation of the first metallocarbene catalyst, is probably very complex and may produce some metallocarbene fragments different from those observed during propagation, resulting in a different stereoselectivity. It may happen that the olefins produced at low conversion are the result of the *first* turnover of the catalyst. Consequently the stereoselectivity observed at very low conversion measured that from initiation and not from the desired propagation step. Therefore, in any case, we have considered the extrapolated values rather the values obtained at low conversion.

It must be pointed out here that a kinetic model very similar to our model was also used by Grubbs et al.[10g] in the case of metathesis of *cis,cis*-2,8-decadiene. By plotting *trans-/cis*-C_4 vs. *trans-/cis*-C_{10} (2,8-decadienes = C_{10}) they obtained a linear, calculated, and experimental relationship over a large range of conversion. The real stereoselectivities were obtained as in our case by extrapolation of the linear plot to a trans/cis ratio of C_{10} equal to zero.

As a consequence of the above considerations, it is necessary to carry out a detailed kinetic analysis before drawing any conclusion with respect to real stereoselectivity in metathesis. This requirement is particularly true with some catalysts of poor activity ($W(CO)_5C(Ph)_2$)[1] or with some olefins of low reactivity, e.g., bulky olefins; in the latter case, the cis-trans isomerization of the olefin produced by metathesis may occur much faster than metathesis of the bulky olefin itself so that values close to thermodynamic ratios may be reached at low conversion without giving information about the stereoselectivity of the propagation step. Let us mention also that in the case of some trans olefins it was not possible to measure the cis/trans ratio of the starting olefin with enough accuracy at the beginning of the reaction. The stereoselectivities were then determined by plotting the trans/cis ratios of the products vs. percent conversion of "formal metathesis" and by extrapolation to 0% conversion.

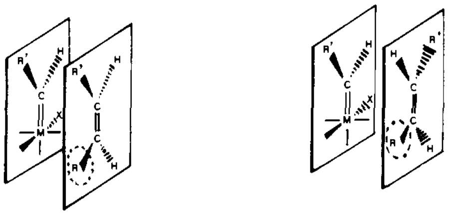
2. Influence of the Cis or Trans Nature of the Olefin on the Stereoselectivity. Among the parameters which play a role in determining stereoselectivity, the most commonly considered is the influence of the cis or trans nature of the starting olefin on the distribution of the geometric isomers in the products. In most cases, a cis olefin gives preferentially a cis olefin and a trans olefin a trans olefin.[1-7] This phenomenon, which is quite general, will be verified during metathesis of almost any olefin considered later in this paper. However, the retention of the configuration of the starting olefin is rather small with many tungsten-based catalysts. With molybdenum and chromium the stereoselectivities are much more pronounced (vide supra) and *in most cases* there is also retention of the cis or trans configuration of the starting olefin. It is also worth mentioning here that stereoselectivities observed with trans olefins are higher than those observed with cis olefins, using molybdenum and chromium catalysts (vide supra).

The explanation for the retention of configuration of the starting olefin must be deduced from the possible conformations of the metallocyclobutanes using the analogy with 1,3-disubstituted cyclobutane derivatives.[12] In this type of compound, it has been shown that the order of stability of the various isomers was the following: cis-e,e > trans-e,a > cis-a,a.

In Figure 2 we have summarized the four possible transition states observed in *cis*-2-pentene metathesis (left) and in *trans*-2-pentene metathesis (right). Among the various interactions which may be considered (1-2, 1-3, 3-4, 2-4) (i), only the 1-3 or 3-4 interactions are able to supply a satisfactory explanation for the retention of configuration. The possible 2-4 repulsive interaction between an axial substituent in the 2 position and the transition metal or its ligands is the same in the transition states leading to cis olefins and in the transition states leading to trans olefins: it is a "nonstereoselective interaction". The possible 1-2 equatorial-axial or axial-equatorial interaction between two substituents in 1-2 position is a stereoselective interaction; if such interaction occurred alone, it would favor the transition states with two R group in equatorial-equatorial, axial-axial position. Regardless of the cis or trans nature of the olefin, the favored isomer in the products should be a trans isomer, which is usually not the case; we will see later that this effect really occurs to a certain extent, but in most cases it is not the major effect, especially when the substituents in 1-2 position are small (methyl). The possible 3-4 interaction is able to account for the retention of configuration if one assumes an asymmetric ligand distribution around the metallocarbene; representative configurations for reactions of cis and trans olefins are given in Figure 3. In this model, the bulkiness of the ligands on the transition metal induces the R′ groups of the coordinated carbene as well as the R group of the olefins away from the ligands.

Table I. Influence of the Substituents in α Position to the Double Bond. Metathesis of *cis*- or *trans*-RCH=CHCH$_3$ with Tungsten Catalyst (W(CO)$_5$PPh$_3$ + EtAlCl$_2$ + O$_2$)

cis olefin	trans/cis ratio of 2-butene at 0% convn	trans olefin	trans/cis ratio of 2-butene at 0% convn
	equilibrium: 3.0		equilibrium: 3.0
cis-2-pentene	0.73 ± 0.02	*trans*-2-pentene	1.25 ± 0.05
cis-2-hexene	0.79 ± 0.02	*trans*-2-hexene	1.25 ± 0.05
		trans-2-heptene	1.25 ± 0.05
		trans-2-octene	1.25 ± 0.05
		trans-1-phenyl-2-butene	1.21 ± 0.05
cis-4-methyl-2-pentene	1.02 ± 0.05	*trans*-4-methyl-2-pentene	1.16 ± 0.05
cis-4,4-dimethyl-2-pentene	1.00 ± 0.02	*trans*-4,4-dimethyl-2-pentene	1.10 ± 0.1



cis favored coordination of a cis olefin   trans favored coordination of a trans olefin

Figure 3.

It is impossible at this stage to rule out completely such a model. However, it is possible to predict on the basis of such a model the steric behavior of various olefins: by increasing the R size of cis or trans olefins RCH=CHR′, one should progressively increase the stereoselectivity, especially when R′ is small (we will see later on that this prediction is not verified). The stereoselectivity of α olefins should lead to cis olefins (we will see later on that this is not verified).

Let us consider now the 1-3 diaxial interaction. It appears that among the four transition states observed in *cis*-2-pentene metathesis, the most favored metallocyclobutane is the one with one methyl and one ethyl group in 1-3 diequatorial position; this conformation leads to *cis*-C$_4$. In the case of *trans*-2-pentene metathesis, the most favored metallocyclobutane is the one with three substituents (two methyl and one ethyl group) in 1-2-3 triequatorial position; this leads to *trans*-C$_4$. The consideration of the minimized 1-3 diaxial interaction was already considered by Katz,[1,10b] Casey,[3] and us.[2]

As a conclusion, the retention of configuration observed in metathesis of acyclic olefins can be explained either on the basis of the 1-3 diaxial interaction or on the basis of a 3-4 effect, assuming in the latter case an asymmetric ligand distribution around the metallocarbene. We will see later on that the results rule out the second hypothesis.

3. Influence of the Substituents in α Position to the Double Bond on the Stereoselectivity. This study was carried out with various olefins of the type *cis*- or *trans*-RCH=CHCH$_3$ in which R was equal to H, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, isopropyl, *tert*-butyl, phenyl, or benzyl. The stereoselectivities were determined by the trans/cis ratio of 2-butenes (C$_4$) extrapolated to zero conversion.

The results reported in Table I were obtained with a zerovalent complex of tungsten, W(CO)$_5$PPh$_3$, associated with an organoaluminum compound and molecular oxygen. This catalytic system, which is highly active in metathesis,[13] exhibits a weak stereoselectivity regardless of the cis or the trans nature or the olefin.

First it is noteworthy that the *trans*-/*cis*-2-butene ratio obtained starting from either *trans*- or *cis*-2-pentene is less than the equilibrium ratio. It is also interesting to note that the length of the unsubstituted R group (R ≠ H) has no effect on the stereoselectivity; similar conclusions were recently obtained by Grubbs et al.[10g] The most important phenomenon occurs for highly crowded olefins: for R = isopropyl or *tert*-butyl, the trans/cis ratios of 2-butene tend toward unity regardless of the cis or trans nature of the olefin; simultaneously, the rate of metathesis is highly decreased. For R = H, it was not possible to get reliable data for the stereoselectivity owing to a strong degenerate metathesis (in the case of these tungsten-based catalysts, the conversion to C$_4$ was too low to get an accurate value of the stereoselectivity of the propagation).

More drastic changes of stereoselectivities were obtained with molybdenum-based catalysts (Tables II and III). With the olefins of the type *cis*- or *trans*-RCH=CHCH$_3$, no steric effect occurs for R = H (*trans*-/*cis*-C$_4$ is equal to unity); in the case of the molybdenum-based catalysts used, conversions were high enough to get very reliable data on the stereoselectivity of the propagation step. For R ≠ H, cis and trans olefins exhibit respectively a high cis or trans stereoselectivity. The stereoselectivity is much more pronounced for trans olefins than for cis olefins (trans/cis ratios of C$_4$ are equal to 12.5 and 0.20 for *trans*-2-pentene and *cis*-2-pentene, respectively). Increasing the size of the R group, the reactivity of the olefin was observed to decrease considerably. This effect was quite noticeable for R = isopropyl or *tert*-butyl, indicating that the steric effect of R not only induces a different stereoselectivity but also a different reactivity.

As for tungsten-based catalysts, with a cis olefin the trans/cis ratio of C$_4$ increases when the bulkiness of R increases above a certain size; with a trans olefin the trans/cis ratio of C$_4$ decreases when the R size increases above a certain size. Unexpectedly, increasing the size or the R group above a certain value decreases the stereoselectivity. This variation does not seem to be the result of an electronic effect of the R group since similar stereoselectivities are obtained for *trans*-RCH=CHCH$_3$ when R = *tert*-butyl, phenyl, or benzyl. These results rule out first the model of asymmetric ligand arrangement as being responsible for the stereoselectivity of metathesis. One should obtain a continuous increase of stereoselectivity by increasing the bulkiness of R. Propylene should also exhibit a cis stereoselectivity whereas a ratio of unity, lower than equilibrium, is obtained. Figure 4 suggests in fact that two types of effect are competing: one tends to lead to a retention of configuration, whereas the other tends to attenuate this retention by increasing the R size. This is particularly true for a very bulky R group. The first effect seems to be the 1-3 diaxial repulsive interaction, whereas the second effect is probably a repulsion between the R group and the transition metal and/or its ligands. Such an effect will also account for the marked decrease of the rate of metathesis observed with bulky R groups. One may assume that, when the R size increases above a certain value, besides the 1-3 diaxial interaction, another type of repulsive interaction occurs, during coordination and/or reaction, between the R group of the olefin *cis*- or *trans*-RCH=CHCH$_3$ and molybdenum, tungsten, and/or their ligands (Figure 5).

With a symmetric ligand arrangement around the metal-

Table II. Influence of the Substituents in α Position to the Double Bond. Metathesis of *cis*-RCH=CHCH$_3$. Values of the Trans/Cis Ratios of C$_4$

olefin	catalyst Mo(NO)$_2$Cl$_2$(PPh$_3$)$_2$	 Mo(NO)$_2$Br$_2$(PPh$_3$)$_2$	 Mo(NO)$_2$I$_2$(PPh$_3$)$_2$
propene	1.1 ± 0.1	0.95 ± 0.10	
cis-2-pentene	0.20 ± 0.02	0.205 ± 0.02	0.17 ± 0.05
cis-2-hexene	0.22 ± 0.02		
cis-4-methyl-2-pentene	0.42 ± 0.02	0.38 ± 0.02	
cis-4,4-dimethyl-2-pentene	0.44 ± 0.02	0.41 ± 0.02	

Table III. Influence of the Substituents in α Position to the Double Bond. Metathesis of *trans*-RCH=CHCH$_3$. Values of the Trans/Cis Ratios of C$_4$

olefin	catalyst Mo(NO)$_2$Cl$_2$(PPh$_3$)$_2$	 Mo(NO)$_2$Br$_2$(PPh$_3$)$_2$	 Mo(NO)$_2$I$_2$(PPh$_3$)$_2$
trans-2-pentene	12.5 ± 0.5	12.5 ± 0.5	10 ± 2
trans-2-hexene	11.1 ± 0.5		
trans-2-heptene	12.5 ± 0.5		
trans-2-octene	10.9 ± 0.5		
trans-4,4-dimethyl-2-pentene	8.3 ± 0.5		
trans-1-phenyl-1-propene	8.0 ± 0.5		
trans-1-phenyl-2-butene	8.2 ± 0.5	7.9 ± 0.5	

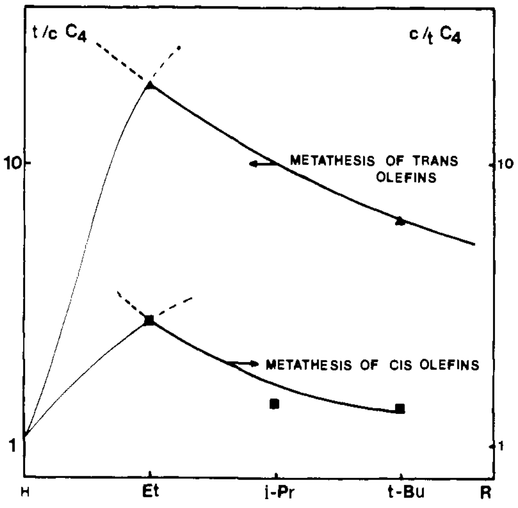


Figure 4. Influence of R on the stereoselectivity of metathesis of *cis*- and *trans*-RCH=CHCH$_3$ (molybdenum-based catalyst).

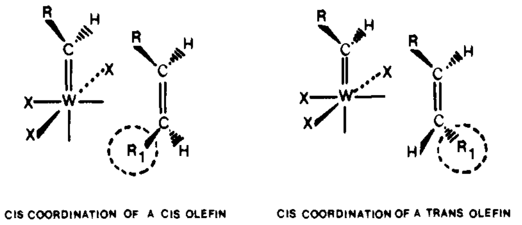


Figure 5.

locarbene, this repulsion is nonstereoselective: whether a cis olefin coordinates and/or reacts in a cis or trans position with respect to the metallocarbene will be equally probable, since the main steric effect will occur between the R group and the group 6 metals and/or their ligands. The same applies to a trans olefin: equally probable coordination and/or reaction of the olefin with respect to the metallocarbene. It is therefore logical to observe a decrease of stereoselectivity with a bulky cis or trans olefin. This "nonstereoselective" repulsive 3-4 interaction starts to compete with the 1-3 diaxial interaction for rather bulky olefins. Besides, it is possible that the bulkiness of the olefin makes the transition state more difficult to be reached, favoring thus the rotation of the carbene about the metal-carbon double bond. This would result in a decrease of stereoselectivity.

A limiting situation is the case of propylene, for which trans/cis ratio is equal to unity within experimental error (*trans*-/*cis*-C$_4$ = 1.1 ± 0.1). Here the absence of stereoselectivity indicates the very small 1-3 diaxial interaction: no substituent in the 3 position.

At this point, it is necessary to consider the absence of effect of the ligands on the transition metal which should be of stereochemical importance (e.g., the halogens): theoretically, increasing the size of such ligands should result in the same "nonstereoselective" effect as increasing the size of the R group (for the 3-4 interaction). However, it is not surprising that such an effect does not occur since there are only small variations of covalent radii between Cl, Br, and I, compared to large modification of bulkiness in the R groups considered in the present study. Another explanation would be to consider that the halogens are not present on the coordination sphere of the "living" catalyst owing to the double alkylation of the metal by the cocatalyst, this alkylation resulting in the first metallocarbene.[21,22]

Finally, it is also possible that there is a rapid exchange of halogen between Mo(NO)$_2$X$_2$(PPh$_3$)$_2$ and EtAlCl$_2$ (sixfold excess of the cocatalyst), leading to an absence of effect of the halogen.

For *cis*- and *trans*-2-pentene, retention of the configuration (Table IV) of the starting olefin was also observed with the C$_6$ alkenes produced but the trans/cis ratio of 3-hexenes was always higher than the trans/cis ratio of 2-butenes, whether the catalyst was derived from molybdenum or tungsten.

We have represented in Figure 6 the eight transition states leading to C$_4$ and to C$_6$. Each transition state leading to cis and trans isomers of C$_4$ and C$_6$ has the same substituent in the 1-3 positions (A-A′, B-B′, C-C′, and D-D′) so that the difference of stereoselectivity between C$_4$ and C$_6$ must therefore be attributed to the presence of a substituent of greater size in position 2 (Et vs. Me in position 2).

Two effects may be put forward:

(1) Repulsive 1-2 (a-e or e-a) interactions: when one substitutes methyl for ethyl in the 2 position, C′ and D′ leading to *trans*-C$_6$ are progressively favored.

(2) Repulsive 2-4 (a) interactions: when one substitutes

of the Trans/Cis Ratios of C_4 and C_6 Starting from 2-Pentenes

		catalyst		
	olefin	$W(NO)_2Cl_2(PPh_3)_2$	$Mo(NO)_2Cl_2(PPh_3)_2$	$Mo(NO)_2Br_2(PPh_3)_2$
cis-2-pentene	trans/cis ratio of 2-butenes	0.44 ± 0.02	0.20 ± 0.02	0.205 ± 0.02
	trans/cis ratio of 3-hexenes	0.74 ± 0.05	0.45 ± 0.05	0.43 ± 0.05
trans-2-pentene	trans/cis ratio of 2-butenes	6.2 ± 1.0	12.5 ± 0.5	12.5 ± 0.5
	trans/cis ratio of 3-hexenes	11.4 ± 1.0	25 ± 1.0	25 ± 1.0

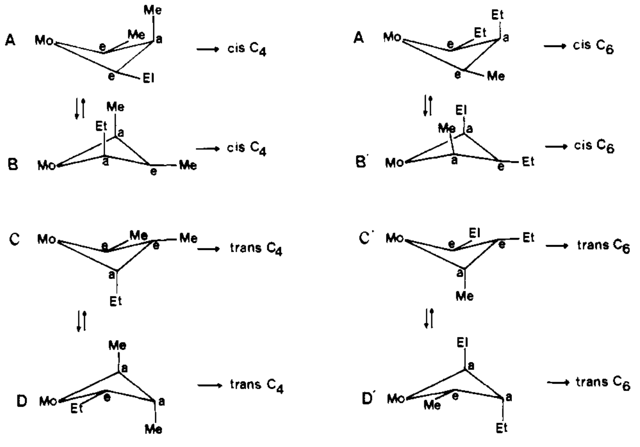


Figure 6. Metathesis of *cis*-2-pentene: (left) transition states leading to C_4; (right) transition states leading to C_6.

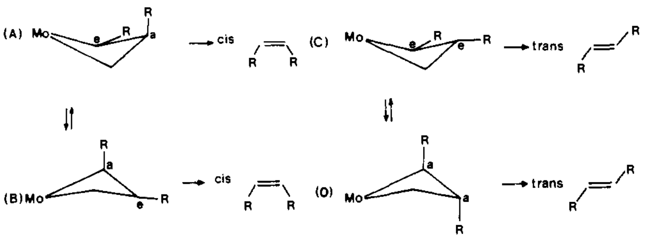


Figure 7. Transition states with α olefins.

methyl for ethyl in the 2 position, B′ and C′ leading respectively to *cis*- and *trans*-C_6 are progressively favored.

Although the above considerations seem to indicate that the 1-2 interaction is more trans stereoselective than the 2-4 interaction, a clear-cut decision was not possible owing to the simultaneous presence of the 1-3 diaxial interaction.

In order to avoid such mechanistic inconvenience the metathesis of various α olefins (propylene, 1-butene, 1-pentene) was carried out. The results given in Table V indicate that the trans/cis ratios of the products increase in the order 2-butene < 3-hexene < 4-octene.

We have given in Figure 7 the various transition states to be considered in the case of α olefins. In any case, the 1-3 diaxial interaction is negligible, since the substituents in position 3 is H. Let us consider the 2-4 effect: upon increasing the R size, transition states B and C leading to cis and trans isomers will be equally favored. Let us consider the 1-2 effect: upon increasing the R size, transition state D or C leading to trans olefin will be progressively favored.

Consequently the transition state in which the two R groups do not interact at all (a-a) is the most stable one. This explains the appearance of more trans isomers in the products with increasing the R size of various α olefins. Again propylene is a remarkable case since the 1-2 effect is very small for two methyl groups in 1-2 position. Propylene is therefore a unique case since it does not show any of the various repulsive effects which progressively appear in the stereochemistry of metathesis of acyclic olefins: 1-3 (a-a), 3-4, and 1-2 (e-a), (a-e).

Table V. Comparison of the Trans/Cis Ratios of C_4, C_6, and C_8 with the α Olefins $RCH{=}CH_2$ (Catalyst: $Mo(NO)_2Cl_2(PPh_3)_2$ + $EtAlCl_2$)

propene	trans/cis ratio of 2-butenes	1.1 ± 0.1 (equilibrium: 3.0)
1-butene	trans/cis ratio of 3-hexenes	1.42 ± 0.05 (equilibrium: 6.0)
1-pentene	trans/cis ratio of 4-octenes	2.0 ± 0.2 (equilibrium: 4.7)

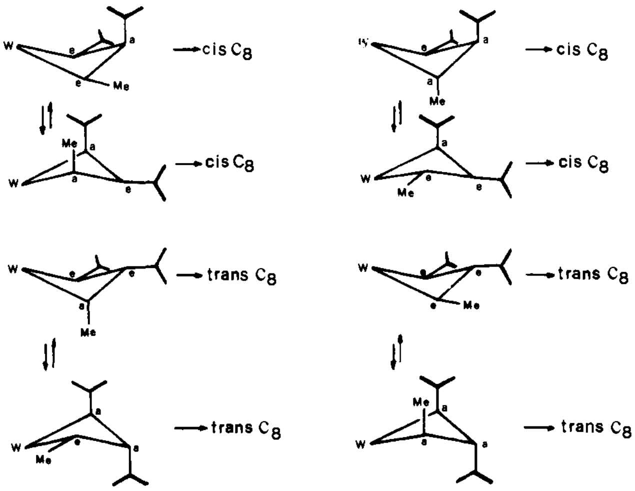


Figure 8. Metathesis of *cis*-4-methyl-2-pentene (left) and *trans*-4-methyl-2-pentene (right).

At this point, it is necessary to consider to what extent the various effects observed are competing. *In most cases*, there is a retention of the configuration of the starting olefin: with the cis olefins, the 1-3 diaxial interaction will be more effective than the 1-2 (e-a or a-e) interaction; with the trans olefins, the two simultaneous interactions will favor the formation of trans products. This accounts for the fact that trans olefins exhibit a higher degree of stereoselectivity than cis olefins.

For very bulky olefins, the 1-3 diaxial interaction in the transition state leading to C_4 can be progressively erased by a 3-4 interaction with a substituent on the metal.

Finally, there are also some cases for which the 1-2 interaction may become more important than the 1-3 interaction: recently, Calderon and co-workers[14] reported that metathesis of 4-methyl-2-pentene yielded *trans*-2,5-dimethyl-3-hexene with a trans/cis ratio equal to 99, regardless of the cis or trans nature of the starting olefin. (The equilibrium ratio was independently established to be 13.2.)

If one considers the various transition states leading to *cis*- or *trans*-C_8 starting from *cis*- or *trans*-C_6 (Figure 8), it appears that the 1-3 diaxial interaction is negligible compared with the 1-2 interaction: the transition state where the two isopropyl groups are in (a-a, e-e) position is then favored. This is a *limiting case* where the 1-2 interaction prevails over any other interaction.

4. Influence of the Nature of the Transition Metal on the Stereoselectivity of Metathesis. It has been known for a long

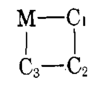
Table VI. Influence of Group 6 Transition Metal on the Stereoselectivity of Metathesis of *cis*- and *trans*-2-Pentene

transition metal M	*cis*-2-pentene						*trans*-2-pentene	
	M(CO)$_3$(mesitylene)^b		M(CO)$_5$PPh$_3$^{b}		M(NO)$_2$Cl$_2$(PPh$_3$)$_2$^{b}		M(NO)$_2$Cl$_2$(PPh$_3$)$_2$^{b}	
	t-/*c*-C$_4$	*t*-/*c*-C$_6$	*t*-/*c*-C$_4$	*t*-/*c*-C$_6$	*t*-/*c*-C$_4$	*t*-/*c*-C$_6$	*t*-/*c*-C$_4$	*t*-/*c*-C$_6$
W	0.80	1.1	0.73	0.88	0.44	0.74	6.2	11.4
Mo	0.60		0.60		0.20	0.45	12.5	25
Cr	0.45							
	0.42^a							

^{a} With Cr(CO)$_3$(benzene). ^{b} Catalyst.

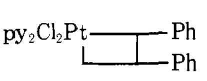
time[15] that molybdenum complexes were more stereoselective than tungsten complexes but no systematic and comparative studies had been carried out with a single substrate and a set of group 6 transition metal complexes exhibiting the same ligands. This study was carried out with various Cr, Mo, and W complexes. The olefins used were *cis*- and *trans*-2-pentene. It must be pointed out here that a very wide range of catalytic activities was encountered with group 6 transition metals. Most chromium complexes were found to be almost inactive except for the arene complexes (arene)Cr(CO)$_3$, associated with EtAlCl$_2$ (arene = benzene, mesitylene). Whatever the set of complexes used (Table VI), the stereoselectivities observed with *cis*- or *trans*-2-pentene follow the same trend: they decrease in the order Cr > Mo ≫ W, chromium being the most stereoselective. If one assumes the same mechanism for a given set of ligands, then the variations observed must be ascribed to the nature of the transition metal itself.

A simple explanation for the very low stereoselectivities observed with the tungsten-based catalysts would be to consider that, in the transition state i, the M-C$_1$ and M-C$_3$ bond length

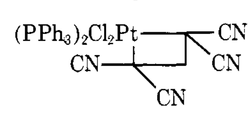


i

would increase from Cr to W. This would increase the C$_1$-C$_3$ distance and decrease the 1-3 repulsion interaction. At this point there is no X-ray structure available for (C$_5$H$_5$)$_2$WC$_3$H$_6$[16] or related compounds which could indicate the degree of puckering of such a tungstacyclobutane derivative. Nevertheless there are some data available for some platinacyclobutane derivatives which were synthesized first by Chatt and co-workers.[17] In PtCl$_2$py$_2$C$_3$H$_6$ (Figure 9), the C$_2$ carbon of the cyclobutane is only 12°5 above the plane defined by Pt, C$_1$, C$_3$, N$_1$, and N$_2$ (N$_1$ and N$_2$ belong to the pyridine ligands). With the substituted complexes ii and iii the



ii



iii

C$_2$ carbon is about 28 and 26° above the plane. Obviously more model compounds are necessary to fully account for the tendency observed with group 6 transition metals.

Conclusion

As a conclusion, the results related to the stereochemistry of metathesis of acyclic olefins can be rationalized in the following way.

(1) The retention of configuration of the starting olefin can be explained on the basis of a 1-3 diaxial interaction in the metallocyclobutane transition state (i).

(2) The lowering of stereoselectivity and activity observed with bulky olefins (formation of 2-butenes from RCH=CHCH$_3$) is due to a nonstereoselective repulsive interaction between the R group of the olefin and the transition metal and/or its ligands.

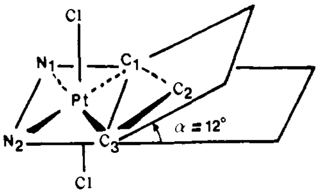


Figure 9. X-ray structure of PtCl$_2$py$_2$C$_3$H$_6$ according to ref 17b.

(3) The favored formation of trans isomers by metathesis of α olefins indicates the presence of a repulsive 1-2 (e-a, a-e) interaction in the metallocyclobutane transition state. This 1-2 interaction accounts for the higher degree of stereoselectivity observed in metathesis of trans olefins compared with cis olefins. It also explains why for a given olefin the trans/cis ratio of the produced heavy olefin is higher than the trans/cis ratio of the produced light olefin (at 0% conversion).

All these effects are superimposed and contribute to various degrees to the resulting stereochemistry. Nevertheless there are some limit cases. Propylene does not give any significant 1-3 nor 1-2 interaction. *cis*- or *trans*-4-methyl-2-pentene affords only *trans*-2,5-dimethyl-3-hexene,[14] due to a 1-2 (a-e, e-a) interaction which is higher than the 1-3 (a-a) interaction.

Variations of stereoselectivity between Cr, Mo, and W are explained on the basis of a decreased 1-3 interaction in the metallocyclobutane transition state when going from Cr to W.

Experimental Section

1. Materials. (a) Olefins. All the olefins used are commercial samples. Liquid olefins were dried over 5-Å molecular sieves and kept under argon. Propene and *cis*- and *trans*-2-butene were supplied by Air Liquide, 1-butene by Phillips. 1-pentene, *trans*-2-pentene, *cis*- and *trans*-2-hexene, *trans*-2-heptene, *trans*-2-octene, *cis*- and *trans*-4,4-dimethyl-2-pentene, *trans*-1-phenyl-1-propene, and *trans*-1-phenyl-2-butene were purchased from Fluka AG. *cis*-2-Pentene was obtained from Merck and *cis*- and *trans*-4-methyl-2-pentene from Riedel-de Haën AG.

(b) Catalysts, M(CO)$_5$L Complexes. These complexes were obtained by mixing stoichiometric amounts of M(CO)$_6$ and the corresponding ligand in a sealed tube and heating at the desired temperature according to a procedure already described.[18]

M(CO)$_3$L$_3$ Complexes. W(CO)$_3$(mesitylene) and Cr(CO)$_3$(benzene) were purchased form Strem Chemicals Inc.; Mo(CO)$_3$(mesitylene) and Cr(CO)$_3$(mesitylene) were supplied by Research Organic/Inorganic Chemical Corp.

M(NO)$_2$X$_2$(PPh$_3$)$_2$ Complexes (M = Mo, W; X = Cl, Br, I). These catalysts were synthesized according to a procedure described by Johnson.[19,20]

(c) Cocatalysts. EtAlCl$_2$ was supplied by the Ethyl Corp. It was purified by vacuum distillation, diluted in anhydrous chlorobenzene, and stored under argon.

(d) Solvent. Chlorobenzene was a commercial Merck product. It was distilled twice from P$_2$O$_5$ under argon. It was stored under argon over 5-Å molecular sieves.

(e) Gases. All the gases used (argon and oxygen) were dried over 5-Å molecular sieves.

2. Apparatus and Procedure. The apparatus used for kinetics experiments included a batch reactor in glass with valves allowing argon purges, evacuation, and introduction of the various reagents. Various gases syringes as well as burets allowed given amounts of olefin, O_2, alkylaluminum, or solvent to be introduced into the reactor. A sampling valve was connected to the reactor in order to analyze the gaseous phase or liquid phase at any time during the reaction. Analysis of the olefins required was performed on an Intersmat IGC 120 flame ionization chromatograph.

In the case of the $M(CO)_{6-x}L_x$ catalyst, the precursor complex was introduced into the reactor, which was then evacuated and carefully purged with argon before the solvent was introduced. Then, the olefin, O_2, and the cocatalyst were introduced. In the case of $M(NO)_2X_2(PPh_3)_2$, the catalyst and cocatalyst were allowed to react for 30 min before introducing the olefin.

3. Experimental Conditions. All the experiments were carried out at 25 °C. In all cases 60 mL of chlorobenzene was used. Owing to the various activities observed, the olefin, catalyst and cocatalyst amounts could vary with the catalytic systems. The following experimental conditions were used.

$W(CO)_5PPh_3$, $EtAlCl_2$, O_2: W = 0.167×10^{-2} mol/L, olefin/W = 100, Al/W = 4, O_2/W = 0.5 except for the metathesis of 4,4-dimethyl-2-pentene, where Al/W = 8 and O_2/W = 2.

$Mo(CO)_5PPh_3$, $EtAlCl_2$, O_2: Mo = 0.333×10^{-2} mol/L, olefin/W = 50, Al/Mo = 3, O_2/Mo = 3.

$M(CO)_3$(mesitylene), $EtAlCl_2$, O_2: M = W, W = 0.167×10^{-2} mol/L, olefin/W = 100, Al/W = 2; M = Mo, Mo = 0.167×10^{-2} mol/L, olefin/Mo = 100, Al/Mo = 10, O_2/Mo = 10; M = Cr, Cr = 0.333×10^{-2} mol/L, olefin/Cr = 50, Al/Cr = 4, O_2/Cr = 1.

$M(NO)_2X_2(PPh_3)_2$ (M = W. Mo; X = Cl, Br, I), $EtAlCl_2$: M = 0.167×10^{-2} mol/L, olefin/M = 100, Al/M = 6 except in the case of $Mo(NO)_2I_2(PPh_3)_2$ and branched olefins: Al/M = 10.

Acknowledgments. The authors are very grateful to CNRS and ELF ERAP for supporting this work.

References and Notes

(1) T. J. Katz and W. H. Hersh, *Tetrahedron Lett.*, **6**, 585 (1977).
(2) J. L. Bilhou, J. M. Basset, R. Mutin, and W. F. Graydon, *J. Am. Chem. Soc.*, **99**, 4083 (1977).
(3) C. P. Casey, L. D. Albin, and T. J. Burkhardt, *J. Am. Chem. Soc.*, **99**, 2533 (1977).
(4) K. J. Ivin, D. T. Laverty, J. J. Rooney, and P. Watt, *Recl. Trav. Chim. Pays-Bas*, **96**, M54 (1977).
(5) M. Leconte, J. L. Bilhou, W. Reimann, and J. M. Basset, *J. Chem. Soc., Chem. Commun.*, 341 (1978).
(6) C. P. Casey and H. E. Tuinstra, *J. Am. Chem. Soc.*, **100**, 2270 (1978).
(7) (a) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Am. Chem. Soc.*, **90**, 4133 (1968); (b) G. Dall'asta, *Rubber Chem. Technol.*, **47**, 511 (1974); (c) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968); (d) W. B. Hughes, *Chem. Commun.*, 431 (1969).
(8) J. M. Basset, J. L. Bilhou, R. Mutin, and A. Theolier, *J. Am. Chem. Soc.*, **97**, 7376 (1975).
(9) C. P. Casey and S. W. Polichnowski, *J. Am. Chem. Soc.* **99**, 6097 (1977).
(10) (a) J. L. Herisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970); (b) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592 (1975); (c) R. H. Grubbs, D. D. Carr, C. Hoppin, and P. L. Burk, *ibid.*, **98**, 3478 (1976); (d) T. J. Katz and R. Rothchild, *ibid.*, **98**, 2519 (1976); (e) C. P. Casey and T. J. Burkhardt, *ibid.*, **96**, 7808 (1974); (f) W. J. Kelly and N. Calderon, *J. Macromol. Sci. Chem.*, **9**, 911 (1975); (g) R. H. Grubbs and C. R. Hoppin, *J. Am. Chem. Soc.*, **101**, 1499 (1979); (h) P. Günther, F. Haas, G. Marwede, K. Nützel, W. Oberkirch, G. Pampus, N. Schön, and J. Witte, *Angew. Makromol. Chem.*, **14**, 87 (1970); (i) G. Dall'asta and G. Motroni, *Ibid.*, **16**, 51 (1971); (j) R. J. Minchak and H. Tucker, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **13**, 885 (1970).
(11) J. M. Basset, G. Coudurier, R. Mutin, and H. Praliaud, *J. Catal.*, **34**, 152 (1974).
(12) S. Wolfe and W. Hangbo, *Tetrahedron Lett.*, **49**, 4365 (1975).
(13) J. M. Basset, Y. Ben Taarit, J. L. Bilhou, R. Mutin, A. Theolier, and J. Bousquet, *Proc. Int. Congr. Catal. 6th Chem. Soc. Ed.*, **1**, 47 (1976).
(14) N. Calderon, J. P. Lawrence, and E. A. Ofstead, *Adv. Organomet. Chem.*, **17**, 449 (1979).
(15) (a) E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Am. Chem. Soc.*, **92**, 528 (1970); (b) W. B. Hughes, *Chem. Commun.*, 431 (1969).
(16) M. Ephritikhine, M. L. H. Green, and R. E. Mackenzie, *J. Chem. Soc., Chem. Commun.*, 620 (1976).
(17) (a) D. M. Adams, J. Chatt, R. Guy, and N. Sheppard, *J. Chem.Soc.*, 738 (1961); (b) R. G. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. Russel, *J. Organomet. Chem.*, **33**, 247 (1971); (c) K. G. Powell and F. J. McQuillin, *Tetrahedron Lett.*, 3313 (1971); (d) J. P. Wisser, *J. Chem. Soc., Chem. Commun.*, 1266 (1974).
(18) R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).
(19) B. F. G. Johnson, *J. Chem. Soc. A*, 475 (1967).
(20) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).
(21) M. Leconte and J. M. Basset, to be published.
(22) R. H. Grubbs and C. R. Hoppin, *J. Chem. Soc., Chem. Commun.*, 634 (1977).
(23) Note that all drawings and discussion assume for clarity a greater degree of ring puckering than is observed in X-ray structure.[17b]

Allenes and Acetylenes. 22. Mechanistic Aspects of the Allene-Forming Reductions (S_N2' Reaction) of Chiral Propargylic Derivatives with Hydride Reagents[1]

Alf Claesson* and Lars-Inge Olsson[2]

Contribution from the Department of Organic Pharmaceutical Chemistry, Biomedical Center, University of Uppsala, Box 574, S-751 23 Uppsala, Sweden.

Received May 29, 1979

Abstract: Four chiral 3-decyn-2-yl derivatives (**1a–d**, Scheme I) were treated in THF with various aluminum hydride reagents selected to give high yields of 2,3-decadiene. The preferred mode of substitution was deduced from the known absolute configurations of starting material and product. The effect of the temperature on the stereoselectivity was also studied and the thermodynamic parameters were calculated. The use of hydroxy, tertiary amine, or bromide as the leaving group (in compounds **1a**, **1c**, and **1d**, respectively) yielded the allene in a preferred overall syn mode of substitution, the degree of which increased with temperature. The mesylate (**1b**) with lithium trimethoxyaluminum hydride yielded the allene in an anti displacement which was more preferred at lower temperatures. The mechanisms of these reductions are discussed. The chiral allenic alcohols (**11** and **12**) were also prepared via lithium aluminum hydride reductions of chiral acetylenic derivatives (Schemes III and IV).

Introduction

The stereochemical course of the allene-forming 1,3-substitution reactions (S_N2') of chiral propargylic derivatives presents a problem which is analogous to the S_N2' reactions in allylic systems. These reactions of allylic derivatives have been of synthetic and mechanistic interest for years.[3,4] However, it is only during the last 3 or 4 years that definitive experimental evidence of the stereochemistry, in cyclic as well as acyclic systems, has been collected. It is now apparent that

0002-7863/79/1501-7302$01.00/0