carbon atom (reactions 21 and perhaps 18), and an undetermined H-substituted ring location (reactions 19, 20, and perhaps also 18).

Conclusions

The reactions of $O(^3P)$ with styrene and of OH with phenylacetylene and styrene show no strong preference for reaction either with the aryl ring or with the unsaturated side chain under the conditions reported here. Qualitative arguments based on frontier electron theory support this lack of preference. We are unable to say conclusively whether the same lack of preference is exhibited in the reaction of $O(^3P)$ with phenylacetylene. Our results for this reaction, however, are consistent with the trends observed in the other three reactions.

Supplementary Material Available: Figures 4–10: ionization efficiency measurements of *m/e* 91 and 92 from $O(^3P)$ + styrene, *m/e* 119 from OH + phenylacetylene, and *m/e* 121, 94, 93, and 91 from OH + styrene (7 pages). Ordering information is given on any current masthead page.

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Consideration of the Mechanism of the Transition Metal Catalyzed Olefin Metathesis Reaction. Metathesis of *cis,cis*-2,8-Decadiene

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Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received July 25, 1978*

Abstract: The analysis of the scrambling pattern of the acyclic olefins resulting from the metathesis of 1,7-diene systems allows a distinction to be made between two general classes of mechanisms of this reaction. This analysis requires no scrambling of the labels in the starting materials or products. These experimental restrictions are firmly established by examining the metathesis of a mixture of *cis,cis*-2,8-decadiene and *cis,cis*-2,8-decadiene-*1,1,1,10,10,10*-d_6. The 2-butene produced in this reaction has a cis/trans ratio of 5 at low conversion. The cis/trans ratio approaches an equilibrium value as the conversion of the diene approaches completion. Extrapolation of a plot of *cis-/trans-*2-butene vs. label ratio to zero stereoisomeric scrambling (trans/cis = 0) gives values of the isotopic label ratio resulting from zero scrambling. The extrapolated value is that expected for a one-carbon chain (carbene) mechanism. These studies allow distinctions between the mechanisms to be made at high (20–30%) conversions.

Introduction

The mechanism of the olefin metathesis reaction has provided one of the most challenging problems in organometallic chemistry.[1] Only within the past 2 years have systems been designed which begin to reveal the important mechanistic features of this reaction.[2-4] Several of these studies have been carried out to determine if the reaction proceeds by a "pairwise" interchange of carbons between two olefins or through a one-carbon chain reaction described as a carbene mechanism. The critical steps of these mechanisms are outlined below.

Of the various studies, only those using terminally labeled 1,7-dienes serve to distinguish between the two mechanisms.[1a,2,4] Owing to the simplicity of the system, all of the various scrambling schemes can be analyzed in an exact fashion. For example, it was shown that metathesis of an equal mixture of 1,7-octadiene-*1,1,8,8*-d_4 and 1,7-octadiene-d_0 should produce the completely randomized ethylene-d_4:-d_2:-d_0 equilibrium mixture of a 1:2:1 ratio if the one-carbon interchange is operative. Alternatively, if the reaction proceeds by a "pairwise" interchange an ethylene-d_4:-d_2:-d_0 ratio of 1: ≤

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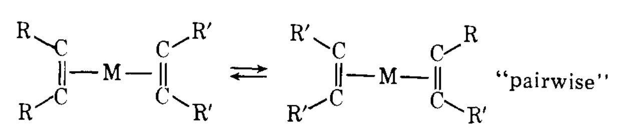
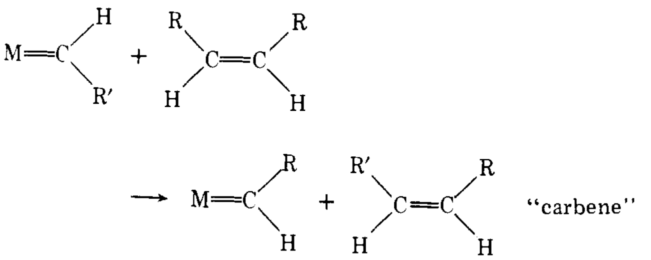




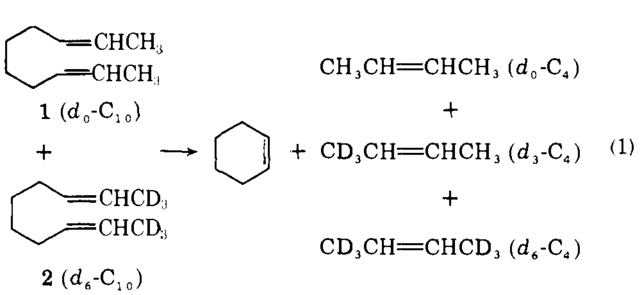
1.6:1 is predicted.[2,4] This analysis required that there was negligible scrambling of the labels in the starting materials or products since all mechanisms result in the equilibrium 1:2:1 mixture if scrambling is allowed. Consequently the reactions were only allowed to proceed to *low conversion* to eliminate possible scrambling. The lack of scrambling of the starting material was determined by mass spectral analysis of the diene mixture before and after reaction.

A second requirement is that the labeled and unlabeled ethylenes produced may scramble via metathesis or other pathways at the metal center before dissociating from the catalyst, again giving ambiguous results. To check for this possibility ethylene-d_0[2] (or ethylene-$1,2$-d_2)[4] was passed through the reaction vessel, and the new ethylene mixture was isolated. If there were a secondary scrambling scheme, the external ethylene would change the equilibrium between the deuterated ethylenes. This was not found since the d_2:d_4 ratio remained the same. However, this is an external probe, and it is not certain whether the ethylene can be properly mixed with the catalyst to achieve realistic results.

In both cases there appeared to be negligible scrambling at the conversions used. However, these studies did not rule out the complete scrambling of the ethylene at the metal center since these probes are external to the reaction system.

The low conversion required for this analysis resulted in a third uncertainty. There is mounting evidence that the initiation steps of metathesis are different than the steps in the propagation mechanism.[5] At the conversions where the products were examined in the earlier studies the majority of the ethylene was the result of the *first* turnover of the catalyst. Consequently the isotopic distributions observed measured that resulting from initiation and not from the desired and *calculated* propagation step. We have now designed a system for study which allows all of these objections to be met. Since the isotopic labels were totally equilibrated, a feature of the metathesis reaction which does not give equilibrium products initially was exploited. Olefin metathesis shows some stereoselectivity during the early stages of the reaction.[6,7] Cis olefins give a predominance of cis products while trans olefins produce twice as much trans as cis product.

A new set of experiments was proposed to more precisely account for the isotopic scrambling in the starting material and products. It was decided to turn to the study of the metathesis of mixtures of unlabeled (**1**) and labeled (**2**) 2,8-decadienes according to eq 1. In a study analogous to the studies of the 1,7-octadiene system the 2-butenes were isolated during the reaction and analyzed for isotopic distribution. At the same time the starting material was also isolated and examined for scrambling. By understanding the isotopic scrambling processes competing with productive metathesis, 2-butene-d_0:d_3:d_6 ratios were obtained which satisfy the restrictions placed on such studies mentioned earlier. In order to follow this scrambling process the metathesis of isomerically pure *cis*-,*cis*-2,8-decadiene was initially studied in some detail. The



(1)

isomeric scrambling, or isomerization, is then compared to the isotopic scrambling over a wide range of conversion. The results allowed a distinction to be made between mechanisms of conversions of starting material as high as 20% (more than 30 turnovers).

Results and Discussion

Synthesis of Olefins. The study of the metathesis of 2,8-decadienes required the synthesis of isomerically and isotopically pure compounds. The synthetic scheme adopted for terminally labeled *cis,cis*-2,8-decadiene-d_6 is outlined in Figure 1. The first step involved the dilithiation of commercially available 1,7-octadiyne and subsequent treatment with fully labeled methyl iodide. The labeled diyne was isolated and characterized and then hydrogenated stereospecifically with Lindlar's catalyst (5% Pd on $BaSO_4$) in pyridine. The material isolated was found to have a high cis content (97 ± 2%) and complete (≥99%) deuterium incorporation.

The corresponding *cis,cis*-2,8-decadiene-d_0 was prepared in the same way except that unlabeled methyl iodide was used. The *trans,trans*-2,8-decadiene-d_0 isomer is commercially available and found to have >99% trans content. Reduction of 2-decyne with Lindlar's catalyst afforded *cis*-2-decene in high yield and specificity.

Catalysts and Metathesis Reactions. The nonsupported catalytic systems used in these studies are typical of those described in the literature. The $Mo(NO)_2Cl_2(PPh_3)_2/Me_3Al_2Cl_3$ system, referred to as catalyst A, was used extensively because of its high selectivity for metathesis and relatively long lifetime.[8a] The mixture produced when Al/Mo = 7 and the concentration of molybdenum is 0.01 M is homogeneous in chlorobenzene, and is light brown. The solution is allowed to "incubate", or stir without any substrate, for 30 min at room temperature before adding the olefin. The catalyst solution must be kept under argon at all times since brief exposure to oxygen will destroy the activity. The catalyst solution may be frozen with dry ice and be stored for several days with only slight loss of activity upon thawing. While incubating, methane and traces of ethylene and HCl are observed in the gas above the solution. The olefin:metal ratio is typically 150–200:1, but may be higher if desired.

The other system studied extensively was the mixture of $WCl_6/SnMe_4$,[8b] referred to as catalyst B. In this case a Sn/W ratio of 2 is used, and the solution in chlorobenzene is mostly homogeneous exhibiting a dark reddish-brown color. Most WCl_6-based systems are believed to be partially heterogeneous in nature.[9] Incubation of this catalyst led to a decrease in activity, and so the olefin was added prior to the addition of the cocatalyst, $SnMe_4$.[10] Methane is detected over the catalyst solution, and in the absence of an olefin ethylene is found in trace amounts. Olefin to tungsten ratios of 100–150 were used.

All of the metathesis reactions were conducted in sealed tubes under argon. The reactions were continuously monitored by withdrawing small liquid and gas samples and analyzing via GLC. Deuterium content of olefins was indicated by mass spectral analysis.

Metathesis of *cis,cis*-2,8-Decadiene. The metathesis of *cis,cis*-2,8-decadiene yields cyclohexene and a thermodynamic

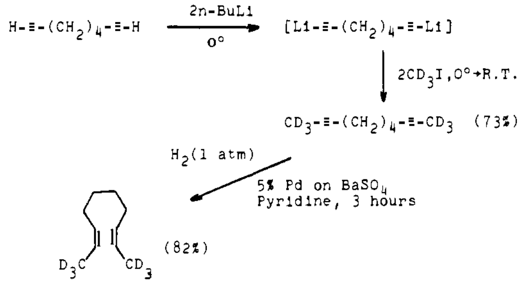
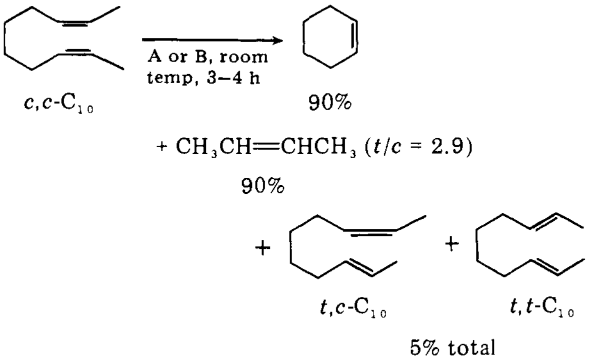


Figure 1. Synthesis of *cis,cis*-2,8-decadiene-d_6 (**2**).

mixture of *cis*- and *trans*-2-butene in high yield and selectivity (eq 2). After only a few hours at room temperature conversions as high as 95% could be obtained with either the molybdenum- (A) or tungsten- (B) based catalysts mentioned before. The yield of cyclohexene is usually about 90% while the remainder of the cis,cis diene is isomerized to the two other possible 2,8-diene isomers. Only a trace of a C_{16} olefin arising from an intermolecular reaction between two dienes was observed, and no other C_{10} isomers were found in the product mixture.



As with the metathesis of other isomerically pure olefins, the metathesis of this cis,cis diene shows moderate stereospecificity at low conversions, giving predominantly *cis*-2-butene. As the reaction proceeds, *trans*-2-butene production increases until the thermodynamic equilibrium is reached, or the *trans*-/*cis*-2-butene ratio (*t*-/*c*-C_4) is about 2.9. During these reactions small gas samples were withdrawn at several time intervals and analyzed for the gaseous *t*-/*c*-C_4 ratio.[10] Other gaseous products observed, such as propylene, are considered elsewhere.[11] The *t*-/*c*-C_4 ratios obtained were plotted against time, and, as in other stereochemical studies, the curve was linear. The curve for the cis,cis diene metathesis using catalyst A is shown in Figure 2. Extrapolation of this curve to $t = 0$ gives the *t*-/*c*-C_4 ratio at 0% conversion. In this case, a value of about 0.25 ± 0.03 is obtained reproducibly. Other olefins were metathesized and extrapolated *t*-/*c*-C_4 values found. These values are given in Table I along with examples of the work of Basset.[7]

It is difficult to compare the results given here with the work of others owing to the complex dependency of the specificity of metathesis reactions on the conditions employed. Nevertheless, it was surprising to discover the relatively high degree of specificity exhibited during the metathesis of *cis,cis*-2,8-decadiene with catalyst A. Initially it was assumed that this phenomenon was due to the intramolecular nature of the reaction. However, the intermolecular metathesis of the corresponding monoolefin, *cis*-2-decene, with the same catalyst exhibited about the same specificity at 0% conversion, which implies that the double bonds in the diene are acting independently.

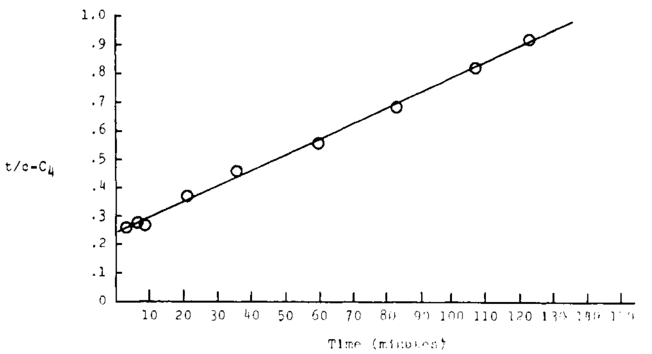


Figure 2. Change in the *trans*-/*cis*-2-butene ratio during the metathesis of *cis,cis*-2,8-decadiene.

Table I. Extrapolated *t*-/*c*-C_4 Values at 0% Conversion

olefin	catalyst	*t*-/*c*-C_4 (0%)
cis,cis-2,8-decadiene	A	0.25 ± 0.03
cis,cis-2,8-decadiene	B	0.61 ± 0.04
cis-2-decene	A	0.21 ± 0.03
cis-2-decene	B	0.62 ± 0.04
cis-2-pentene	B	0.73 ± 0.05[5]
trans,trans-2,8-decadiene	A	2.0 ± 0.2
trans,trans-2,8-decadiene	B	1.9 ± 0.2
trans-2-decene	A	2.1 ± 0.2
trans-2-pentane	B	2.0[5]

Differences in catalyst specificity can also be noted in Table I. Molybdenum catalysts are generally known to be more specific than tungsten-based catalysts,[12] but differences in cocatalysts may also be involved. Basset also used a molybdenum catalyst similar to the one studied here and found a moderate increase in stereospecificity,[5] but this was not as dramatic a difference as shown here between catalysts A and B. The specificity observed with catalyst B is comparable to the results found by Basset using the same catalyst for the metathesis of *cis*-2-pentene. He also studied many other tungsten-based systems, and all exhibited about the same specificity. These results seem to indicate that *cis*-2-pentene, *cis*-2-decene, and *cis,cis*-2,8-decadiene exhibit roughly the same specificity in the early part of the reaction. This further implies that the length of an alkyl group on one side of a methyl olefin does not markedly affect the stereospecificity.[13]

The metathesis of *trans,trans*-2,8-decadiene was also studied. These reactions generally displayed induction periods varying from a few minutes to about 30 min. Conversion to cyclohexene and 2-butene then proceeds at approximately half the rate of the cis,cis isomer. Addition of a trace of 1-hexene eliminated the induction period, but did not increase the rate of conversion. These results confirm other studies that concluded that trans olefins react slower than cis olefins and that trans olefins do not participate in the initiating steps of metathesis.[14] A preference for *trans*-2-butene was found at low conversions, and after about 30% conversion the thermodynamic mixture of 2-butene isomers was observed.

The metathesis of *cis,cis*-2,8-decadiene by using the molybdenum-based catalyst was studied in more detail. Liquid aliquots were withdrawn in addition to the gas samples as the reaction progressed. The liquid samples were analyzed for cyclohexene and for isomerization and conversion of the starting material. The changes in the trans/cis ratios for the 2-butenes (*t*-/*c*-C_4) and the 2,8-decadienes (*t*-/*c*-C_{10}) were plotted against percent conversion of starting material and are shown in Figure 3. The *t*-/*c*-C_{10} ratio was calculated by considering the contribution of the three possible 2,8-decadiene stereoisomers to the total trans and the total cis content of the C_{10} mixture.

It should be noted that these isomerization plots are linear until about 50% conversion. The two processes can be related

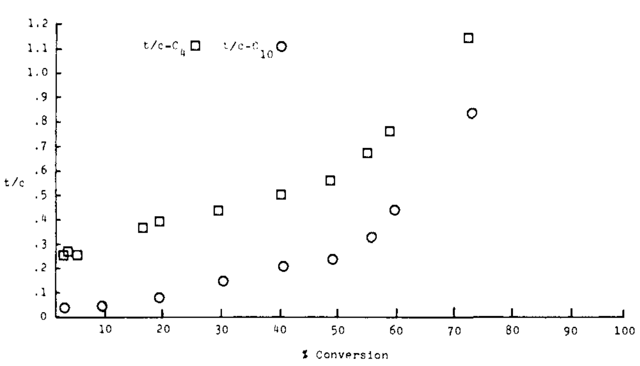


Figure 3. Isomerization of 2-butenes and starting material relative to the amount of conversion of starting material.

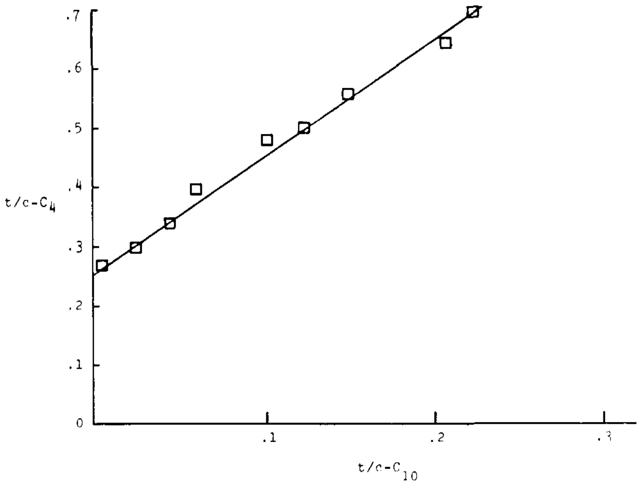


Figure 4. The relationship between *t*-/*c*-C_4 and *t*-/*c*-C_{10}.

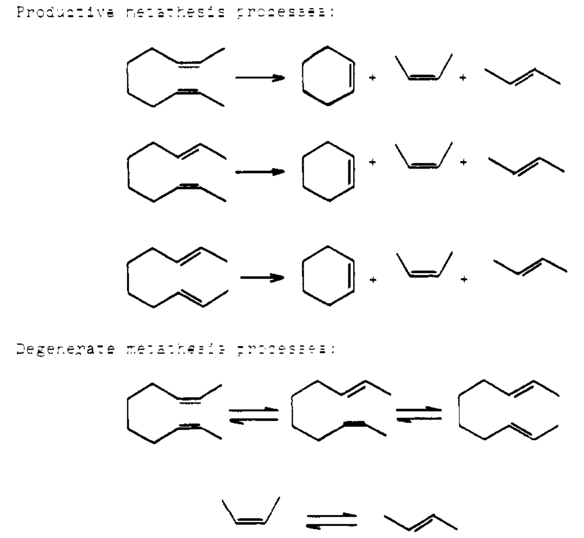


Figure 5. Competing metathesis processes during the metathesis of *cis,cis*-2,8-dedadiene.

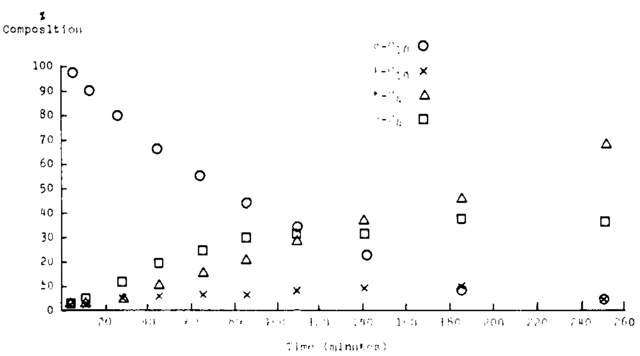


Figure 6. Relative concentrations of acyclic olefins during the metathesis of *cis,cis*-2,8-decadiene with catalyst A.

by plotting *t*-/*c*-C_4 against *t*-/*c*-C_{10} values observed at the same time. This plot is shown in Figure 4. The linearity of this plot implies that the two isomerization processes result from similar reaction pathways and that most of the change in trans/cis ratio is the result of isomerization of starting material.

It has been well established that the isomerizations of olefins observed during metathesis reactions are degenerate metathesis reactions. These are described in Figures 5 and 9. The intramolecular metathesis of *cis,cis*-2,8-decadiene involves several competing metatheses. These reactions are the productive metatheses of the 2,8-decadienes which yield cyclohexene and 2-butenes irreversibly, and the reversible degenerate metatheses which isomerize the double bonds in the diene and 2-butene. Figure 5 illustrates these competing processes.

The measured *t*-/*c*-C_4 values can now be seen to arise from a combination of three processes. Initially, only *cis,cis*-decadiene is present which metathesizes to give a 4:1 preference of *cis*-2-butene over *trans*-2-butene (Table I). As the starting material isomerizes to give an increasing amount of trans double bonds, the ensuing productive metathesis will afford an increasing amount of *trans*-2-butene. Also, once the concentration of the 2-butenes begins to increase they will undergo a reversible degenerate metathesis eventually yielding the thermodynamic mixture. The plots in Figures 3 and 4 reflect *t*-/*c*-C_4 values that are a composite of these three processes. The latter plot will later be accounted for with a kinetics model which considers all of these processes.

The final plot, shown in Figure 6, for the metathesis of *cis,cis*-2,8-decadiene indicates the relative amounts of olefins in the reaction mixture at a particular point in reaction time. It can be seen, for example, that the production of *cis*-2-butene begins to level off late in the reaction reflecting the dominance of the degenerate isomerization to the trans isomer. The amount of trans-C_{10} begins to level off only after most of the cis isomer is converted, which reflects the slower rate of trans olefin metathesis mentioned previously.

The metathesis of *cis*-2-decene with catalyst A exhibits somewhat similar behavior. Figure 7 shows the comparison of the *t*-/*c*-C_4 values obtained from the monoolefin and the diolefin metathesis reactions vs. percent conversion. The curve for the metathesis of *cis*-2-decene is linear only until about 20% conversion, and this linearity matches the plot obtained from the diene metathesis during the same amount of conversion. The difference between the curves at higher conversions results from the inter- or intramolecular nature of the reaction. As with other simple monoolefins, *cis*-2-decene will metathesize to two new products, 2-butene and 7-hexadecene, which can then undergo further metathesis back to the starting material. All of the competing metathesis reactions are reversible during monoolefin metathesis unlike those during diene metathesis (Figure 5). In effect, that means that there are more ways for the olefins to metathesize and thus more ways to isomerize. It should be remembered that *cis*-2-decene is never completely consumed, and the maximum conversion is dictated by the thermodynamic equilibrium between *trans*- and *cis*-2-decene.

By using these stereochemical results it should be possible to devise a kinetics model in a way analogous to that described by Basset[5] which will supply an explanation for the origin of the relationships shown in Figures 4 and 6. The model is based on a nonpairwise metal carbene scheme, the evidence for which

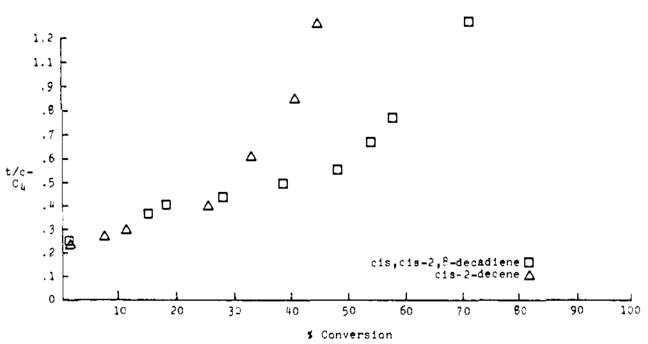


Figure 7. Comparison of *t*-/*c*-C_4 ratios from the metathesis of *cis*-2-decene and *cis,cis*-2,8-decadiene.

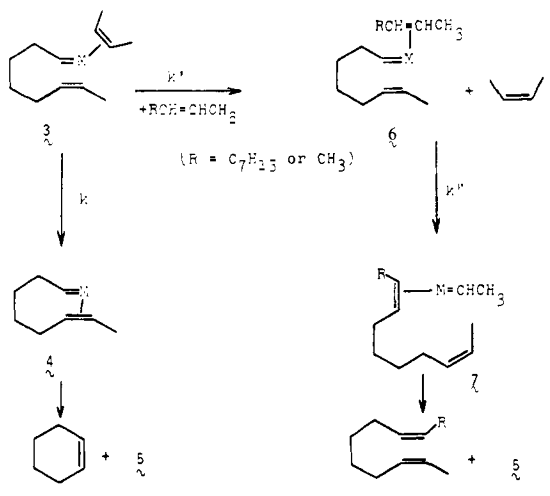
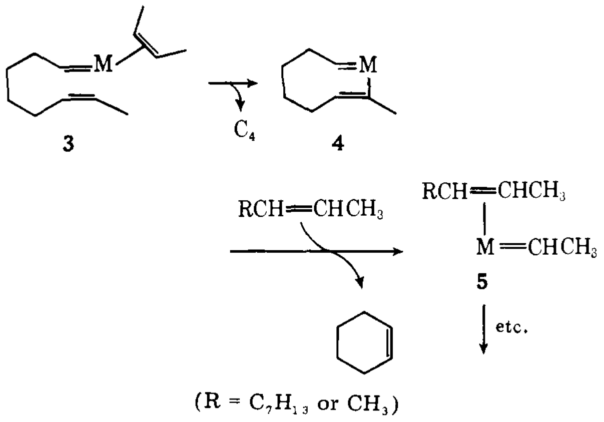


Figure 8. Possible reactions of the C_8 metal carbene **3**.

will be presented in the next section describing the isotopic labeling studies. Only the propagating steps of the olefin metathesis reaction will be considered at this point.

The first assumption to be made is that there is an equal concentration of the two possible metal carbenes formed during the reaction. This is because there seem to be only small differences in steric effects exhibited by most methyl olefins. The C_8 carbene **3** irreversibly cyclizes to form cyclohexene, *cis*- and *trans*-2-butene (C_4), and the C_2 carbene **5** according to eq 3.



(3)

(R = C_7H_{13} or CH_3)

The irreversibility of eq 3 arises from the observation that cyclohexene does not metathesize. It was also observed that no C_{16} olefin was formed from an intermolecular reaction between **3** and a molecule of decadiene. This process is illustrated in Figure 8, where R is equal to the remainder of the decadiene (or C_8), and implies that $k \gg k''$. It is then also reasonable to assume that this relationship is valid when R = CH_3. Another assumption made is that once **3** forms it will preferentially exchange olefins to complex with the readily available intramolecular carbon-carbon double bond to form **4** rather than exchange with an olefin from the bulk solution. This means that $k \gg k'$.

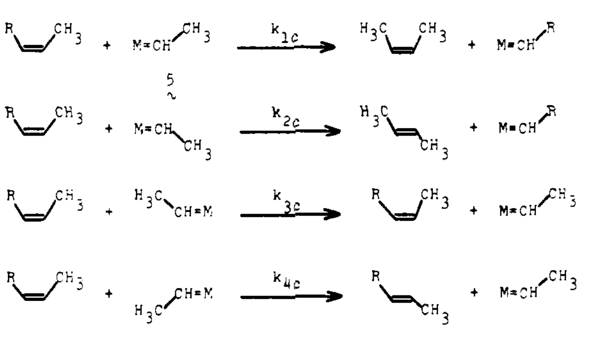


Figure 9. The four primary reactions of **5** with *cis,cis*-2,8-decadiene.

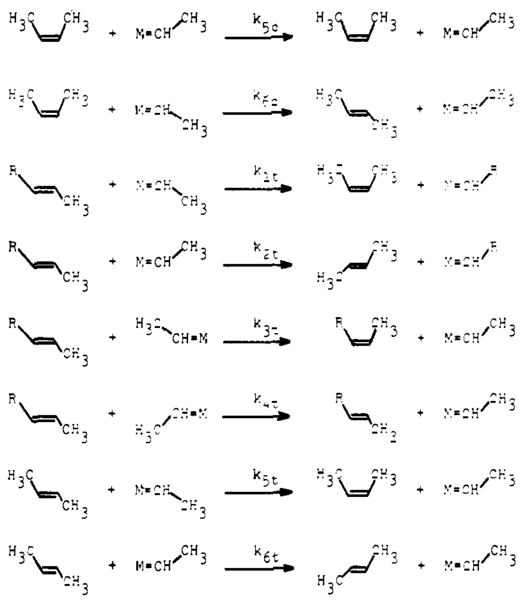


Figure 10. The eight secondary reactions of **5** with *t*-C_{10} and *trans*-2-butene.

With the assumption that $k \gg k'$, one need only consider 12 possible reactions of **5**. Initially, only four primary reactions are possible during the early stages of the reaction, and these are shown in Figure 9.

Since the double bonds in the starting material react independently, the rest of the decadiene is represented as R. The four possibilities shown arise from the different ways the olefin can coordinate with the carbene. This scheme does not reflect on the actual mode of interaction discussed in the Introduction, such as the intermediacy of a puckered cyclobutane, but is simply a kinetic model. The first two reactions are the productive metathesis reactions which yield the 2-butenes and carbene **3** which then cyclizes exclusively to cyclohexene and is not considered further. The latter two reactions are degenerate reactions which can re-form the cis-C_{10} isomer (k_{3c}) or isomerize to the trans isomer (k_{4c}). As the new olefins are produced eight secondary reactions must be considered and are shown in Figure 10.

Rate equations can then be written for the formation of *trans*-2-butene (*t*-C_4), *cis*-2-butene (*c*-C_4), and "*trans*"-decadiene (*t*-C_{10}). The C_2 metal carbene is simply written as [carbene] for simplification. The rate of production of *cis*-2-butene is derived from Figures 9 and 10 and is shown in the equation

$$\frac{\partial[c\text{-C}_4]}{\partial t} = [\text{carbene}](k_{1c}[c\text{-C}_{10}] + k_{1t}[t\text{-C}_{10}] - k_{6c}[c\text{-C}_4] + k_{5t}[t\text{-C}_4]) \tag{4}$$

Similar equations are derived for t-C$_4$ (eq 5) and t-C$_{10}$ (eq 6).

$$\frac{\partial[t\text{-C}_4]}{\partial t} = [\text{carbene}](k_{2c}[c\text{-C}_{10}] + k_{2t}[t\text{-C}_{10}] + k_{6c}[c\text{-C}_4] - k_{5t}[c\text{-C}_4]) \tag{5}$$

$$\frac{\partial[t\text{-C}_{10}]}{\partial t} = [\text{carbene}](k_{4c}[c\text{-C}_{10}] - (k_{1t} + k_{2t} + k_{3t})[t\text{-C}_{10}]) \tag{6}$$

Equation 4 can be rewritten as

$$\frac{\partial[c\text{-C}_4]}{\partial t} = [\text{carbene}][c\text{-C}_{10}]\left(k_{1c} + k_{1t}\frac{[t\text{-C}_{10}]}{[c\text{-C}_{10}]} - k_{6c}\frac{[c\text{-C}_4]}{[c\text{-C}_{10}]} + k_{5t}\frac{[t\text{-C}_4]}{[c\text{-C}_{10}]}\right) \tag{7}$$

Inserting $\alpha = [c\text{-C}_4]/[c\text{-C}_{10}]$ gives the equation

$$\frac{\partial[c\text{-C}_4]}{\partial t} = [\text{carbene}][c\text{-C}_{10}]\left(k_{1c} + \alpha\left(k_{1t}\frac{[t\text{-C}_{10}][t\text{-C}_4]}{[t\text{-C}_4][c\text{-C}_4]} - k_{6c} + k_{5t}\frac{[t\text{-C}_4]}{[c\text{-C}_4]}\right)\right) \tag{8}$$

In a similar way eq 5 can be rewritten as the equation

$$\frac{\partial[t\text{-C}_4]}{\partial t} = [\text{carbene}][c\text{-C}_{10}]\left(k_{2c} + \alpha\left(k_{2t}\frac{[t\text{-C}_{10}][t\text{-C}_4]}{[t\text{-C}_4][c\text{-C}_4]} + k_{6c} - k_{5t}\frac{[t\text{-C}_4]}{[c\text{-C}_4]}\right)\right) \tag{9}$$

Dividing eq 9 by eq 8 gives an equation representing the relative amounts of *trans*- and *cis*-2-butene:

$$\frac{[t\text{-C}_4]}{[c\text{-C}_4]} = \frac{k_{2c} + \alpha\left(k_{2t}\dfrac{[t\text{-C}_{10}][t\text{-C}_4]}{[t\text{-C}_4][c\text{-C}_4]} + k_{6c} - k_{5t}\dfrac{[t\text{-C}_4]}{[c\text{-C}_4]}\right)}{k_{1c} + \alpha\left(k_{1t}\dfrac{[t\text{-C}_{10}][t\text{-C}_4]}{[t\text{-C}_4][c\text{-C}_4]} - k_{6c} + k_{5t}\dfrac{[t\text{-C}_4]}{[c\text{-C}_4]}\right)} \tag{10}$$

In a somewhat analogous way eq 11 is derived for the relative amounts of *trans*- and *cis*-decadiene.

$$\frac{[t\text{-C}_{10}]}{[c\text{-C}_{10}]} = \frac{\alpha k_{4c} - \alpha^2(k_{1t} + k_{2t} + k_{3t})\dfrac{[t\text{-C}_4][t\text{-C}_{10}]}{[c\text{-C}_4][t\text{-C}_4]}}{k_{1c} + \alpha\left(k_{1t}\dfrac{[t\text{-C}_{10}][t\text{-C}_4]}{[t\text{-C}_4][c\text{-C}_4]} - k_{6c} + k_{5t}\dfrac{[t\text{-C}_4]}{[c\text{-C}_4]}\right)} = \frac{[t\text{-C}_{10}]\alpha}{[c\text{-C}_4]} \tag{11}$$

The relative values of the rate constants can be approximated from the experimental data presented earlier. The extrapolated t-/c-C$_4$ value at 0% conversion found for the metathesis of *cis,cis*-2,8-decadiene should correspond to the relative rates of k_{2c} and k_{1c}. This means that $k_{2c}/k_{1c} = 0.25$, and similarly from the studies of the metathesis of the trans,trans diene, $k_{2t}/k_{1t} = 2.0$ (Table I). Since the rate of metathesis of the trans,trans diene is about half that of the cis,cis diene, eq 12 follows.

$$k_{1t} + k_{2t} + k_{3t} + k_{4t} = 0.5(k_{1c} + k_{2c} + k_{3c} + k_{4c}) \tag{12}$$

Table II. Approximated Relative Rate Constants

$k_{1c} = k_{3c} = 1.0$	$k_{1t} = k_{3t} = 0.21$
$k_{2c} = k_{4c} = 0.25$	$k_{2t} = k_{4t} = k_{5t} = 0.42$
$k_{5c} = 2.0$	$k_{6t} = 0.84$
$k_{6c} = 0.50$	

Table III. Calculated t-/c-C$_4$ and t-/c-C$_{10}$ Values

α	t-/c-C$_4$	t-/c-C$_{10}$
0	0.25	0
0.05	0.27	0.012
0.10	0.31	0.024
0.15	0.34	0.034
0.20	0.38	0.045
0.30	0.44	0.062
0.40	0.52	0.077

There is no way to find the values for k_{3c} or k_{4t} from these experiments. However, the size of the alkyl group does not seem to have an effect on the reactivity, and so k_{3c} can be approximated as being equal to k_{1c} and k_{4t} set roughly equal to k_{2t}. At low conversions it was found that the rates of production of *trans*-2-butene and t-C$_{10}$ were about the same.[15] This observation implies that k_{4c} is approximately equal to k_{2c}.

There have only been a few studies conducted concerning the metathesis of trans olefins, but the approximations that $k_{4t}/k_{3t} = 2.0$ and $k_{4t} = k_{2t}$ are not unreasonable. Finally, because 2-butene has an inherent C$_2$ axis, it may coordinate with a metal carbene in two degenerate ways to give the same product. This degeneracy means that the number of possible alignments of **5** with 2-butene to give a particular product must be doubled compared with the alignment of **5** with an unsymmetrical olefin, or one end of 2,8-decadiene, leading to the same product. By using this information the relationships shown in eq 13 are implied.

$$k_{5c} = 2k_{1c},\ k_{6c} = 2k_{2c},\ k_{5t} = 2k_{1t}, \text{ and } k_{6t} = 2k_{2t} \tag{13}$$

The relative rate constants were calculated by using the approximations made above, 12 and 13, and by arbitrarily assigning $k_{1c} = 1.0$. The results are shown in Table II.

At low conversions the concentrations of t-C$_{10}$ and t-C$_4$ are about the same, and the t-/c-C$_4$ ratio is taken to be 0.25. These values along with the values in Table II are put into eq 10 and 11 to yield eq 14 and 15, respectively.

$$\frac{t\text{-C}_4}{c\text{-C}_4} = \frac{0.25 + 0.5\alpha}{1 - 0.34\alpha} \tag{14}$$

$$\frac{t\text{-C}_{10}}{c\text{-C}_{10}} = \frac{0.25\alpha - 0.21\alpha^2}{1 - 0.34\alpha} \tag{15}$$

Recall that $\alpha = c\text{-C}_4/c\text{-C}_{10}$, which is one way of measuring the amount of productive metathesis. These equations predict that the maximum amount of *cis*-2-butene present will occur when $\alpha = 1/0.34 = 3.0$. This value is in rough agreement with the curve in Figure 6. It is also predicted that the amount of t-C$_{10}$ will be maximized when $\alpha = 1/0.21 = 4.76$. The experimental agreement with this value is not as good, probably owing to the high conversion needed to observe this occurrence. Most of the reactions conducted gave inconsistent results after long reaction times owing to the loss of catalytic activity. The equations also predict that the amount of *trans*-2-butene will never level off, a result of the irreversibility of the diene metathesis.

To calculate a curve for t-/c-C$_4$ vs. t-/c-C$_{10}$, various values of α are fed into eq 14 and 15, and the resulting ratios are given in Table III. This curve is plotted and shown in Figure 11. Figure 11 also contains the experimental plot shown earlier in Figure 5 for conversions of less than 50%. The calculated curve

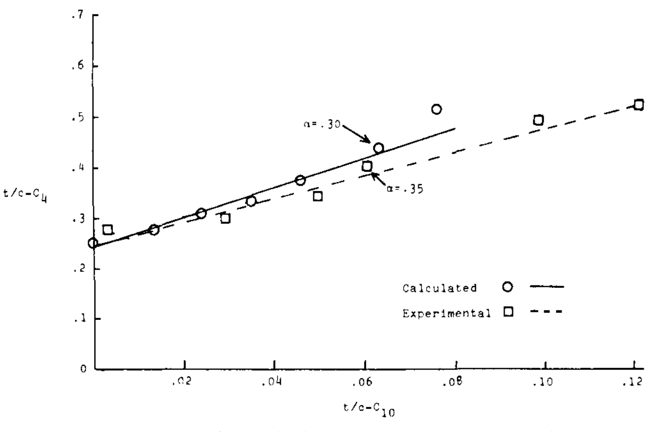


Figure 11. Comparison of the calculated and the experimental relationships between t-/c-C_4 and t-/c-C_{10}.

illustrates a linear relationship as predicted by this model. The slopes of the two curves are in good agreement, especially when one considers the number of assumptions made for this calculation. As a check, the points found experimentally in Figure 11 are related to the amount of conversion, and the corresponding α value is found. These α values are in general agreement with the calculated curve. More accurate curves could perhaps be found by varying the relative rate of trans and cis olefin metathesis, since only a rough approximation was employed in this model.

In summary, a kinetics model was devised, based on a nonpairwise carbene scheme, which successfully accounted for the experimental results obtained from the intramolecular metathesis of *cis,cis*-2,8-decadiene. The number of competing metathesis reactions to be considered was reduced to 12 from the 32 needed in monoolefin studies. The next section describes studies involving the metathesis of isotopically labeled decadienes and uses the results of the "isomerically labeled" decadiene metathesis reactions presented here.

Deuterium Labeling Studies. Mixtures of *cis,cis*-2,8-decadiene-d_6 and -d_0 were metathesized using catalyst A. At several stages of the reaction, gas and liquid samples were withdrawn and analyzed via GLC. The *cis*-2-butene was isolated at several t-/c-C_4 ratios by preparative GLC and submitted for mass spectral analysis. The starting material was analyzed for isomerization, and a portion was isolated and also submitted for mass spectral analysis. In this manner, d_3/d_6 ratios were found for the *cis*-2-butenes and the 2,8-decadienes. Table IV lists the values obtained for the experiment where *cis,cis*-2,8-decadiene-d_0/-d_6 = 1.21 ± 0.02.

Since the t-/c-C_4 ratios change in a linear relationship in the early part of the reaction with respect to conversion (Figure 3), these t/c values can be used as an internal measure of the extent of metathesis, differing from the 1,7-octadiene labeling studies reported earlier in which all probes were external to the system.[2,4] In those studies it was not certain whether the ethylenes isolated were obtained before any of the possible equilibrations of the isotopic labels could take place. Isolation after such an equilibration would give ambiguous results. By plotting the 2-butene-d_3/-d_6 ratios against the t-/c-C_4 ratios it should be possible to extrapolate the -d_3/-d_6 values to 0% conversion, or t-/c-C_4 = 0.25. This extrapolated value should reflect a number obtained during preequilibrium conditions. The graph shown in Figure 12 yields a value for d_3-/d_6-C_4 of 2.4 ± 0.1. The calculated ratio for a carbene scheme is 2.42:1, and the expected value for a pairwise scheme was calculated to be 1.90:1 at 0% conversion, or when there has been no scrambling of labels[2,4] in the starting diene. This value allows for complete scrambling of the labels in the diolefin intermediate.

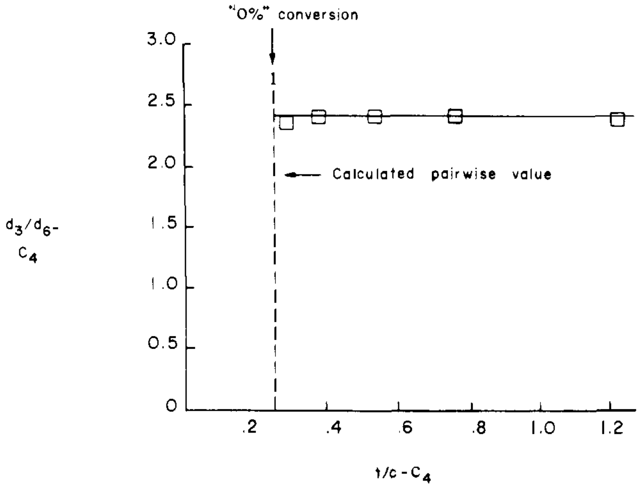
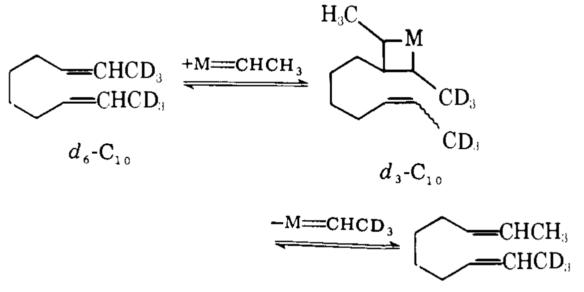


Figure 12. Observed d_3-/d_6-C_4 values during the metathesis of a mixture of 2,8-decadiene-d_0 and -d_6 at particular t-/c-C_4 ratios.

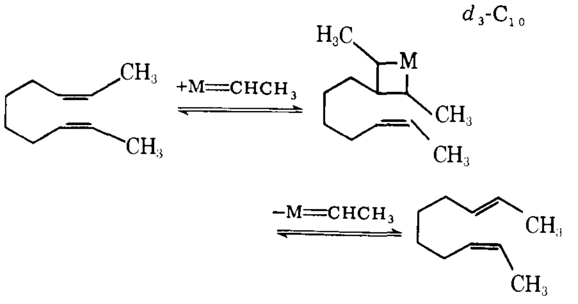
Table IV. Experimental Data from the Metathesis of a 1:1.21 d_6:d_0 Mixture of *cis,cis*-2,8-Decadiene

t-/c-C_4	d_3-/d_6-C_4	d_3-/d_6-C_{10}	% conversion
0.28 ± 0.04	2.35 ± 0.1	0.0 ± 0.02	5 ± 2
0.38 ± 0.04	2.4 ± 0.1	0.12 ± 0.02	15 ± 3
0.54 ± 0.05	2.4 ± 0.1	0.32 ± 0.03	45 ± 3
0.74 ± 0.05	2.4 ± 0.1	0.60 ± 0.05	60 ± 5
1.2 ± 0.10	2.4 ± 0.1		83 ± 4

A more precise study was conducted in order to follow the scrambling of the isotopic labels in the starting material. This process, which is illustrated in eq 16, is very similar to the isomeric scrambling (isomerization) discussed in the previous section and shown in eq 17.



(16)



(17)

Both processes are degenerate metathesis reactions. The increasing d_3-/d_6-C_{10} ratios shown in Table IV result from this scrambling process (eq 16). No other scrambled products were detected which could have arisen from some secondary isomerization process such as a metal-hydride reaction. Theoretically, if the labels in the starting material were completely scrambled, then a d_0-:d_3-:d_6-C_{10} ratio of $(1.21)^2$:2(1.21):1 would be expected from this experiment. As seen in Table IV the fully scrambled d_3-/d_6-C_{10} ratio of 2.42:1 is never ap-

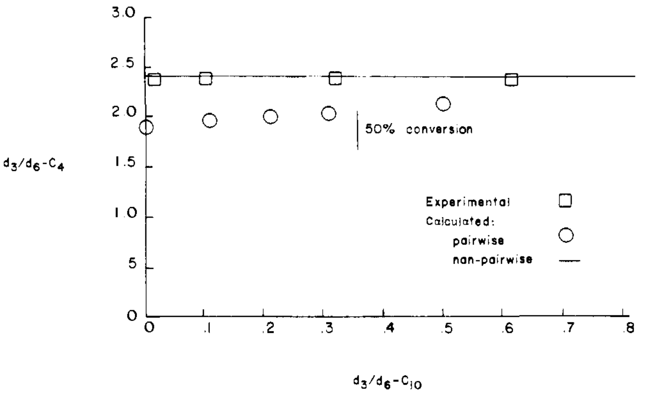


Figure 13. Observed d_3-/d_6-C_4 values compared to the calculated values for the nonpairwise (carbene) and pairwise schemes.

Table V. Calculated d_3-/d_6-C_4 Values by a Pairwise Scheme

d_3-/d_6-C_{10}	calcd d_3-/d_6-C_4
0	1.900
0.116	1.926
0.196	1.933
0.301	1.988
0.519	2.014

proached even at higher conversions. The curve of d_3-/d_6-C_{10} vs. conversion is similar to the t-/c-C_{10} vs. conversion (Figure 3) in that it is linear to about 50% conversion, and then the rate of scrambling increases. At 45% conversion the isotopic scrambling is (0.32/2.42)(100) or 13% complete. This slow rise in isotopic scrambling during the early stages of the reaction is entirely analogous to the behavior exhibited by the isomeric scrambling and is due to the intramolecular nature of the reaction.

It should be recalled from the restrictions presented in the Introduction that if the labels in the starting material are scrambled sufficiently the pairwise scheme and the carbene scheme will predict a random distribution of labels in the products. Calculations were undertaken for the pairwise scheme at several d_3-/d_6-C_{10} ratios from zero to 0.5 and were accomplished by using an iterative scheme similar to ones described in previous reports.[2] In this instance, however, the probability of a metal-butene species interacting with the newly formed decadiene-d_3 is added on in three more terms of each calculation. As the amount of d_3-C_{10} increases, the amount of 2-butene-d_3 increases. When the labels have completely scrambled in the starting material, or d_3-/d_6-C_{10} = 2.42, then d_3-/d_6-C_4 will also be 2.42. The calculated values are shown in Table V. These ratios were derived by only considering the butenes arising from the starting material and should be valid at very low conversions.

To adjust these calculated values to be more realistic the interaction between two butene molecules must also be considered. This means that the total d_3-/d_6-C_4 ratio according to the pairwise scheme will be made up of two processes. The first process is the result of productive metathesis of the scrambled starting material, shown in Table V, and the second process is the degenerate scrambling between the butenes. When the concentration of these butenes increases the latter process will begin to contribute more heavily to the total d_4-/d_6-C_4 ratio which, of course, implies that the values in Table V are too low. Required now is an approximation of the extent of the independent scrambling of the isotopic labels in the 2-butenes at each new value of d_3-/d_6-C_{10}.

The experimental evidence given earlier, and in other reports, indicates that size of the alkyl groups in simple disubstituted olefins does not markedly affect the rate of metathesis. This means that the isotopic scrambling in the starting material (eq 18) can be related to the scrambling in the butenes (eq 19) in a way similar to that presented in the previous section.

Table VI. Adjusted d_3-/d_6-C_4 Values Calculated by a Pairwise Scheme

		% isotopic scrambling		
d_3-/d_6-C_{10}	d_3-/d_6-C_4	C_{10}	C_4	adjusted d_3-/d_6-C_4
0	1.900	0	0	1.900
0.116	1.926	5	10	1.970
0.196	1.933	8	16	1.997
0.301	1.988	12	24	2.070
0.519	2.014	21.5	43	2.145

$$\begin{array}{ccc} C_7CH{=}CHCH_3 & & C_7CH{=}CHCD_3 \\ + & \xrightarrow{k} & + \\ X{=}CHCD_3 & & X{=}CHCH_3 \end{array} \qquad (18)$$

$$\begin{array}{ccc} CH_3CH{=}CHCH_3 & & CH_3CH{=}CHCD_3 \\ + & \xrightarrow{k'} & + \\ X{=}CHCD_3 & & X{=}CHCH_3 \end{array} \qquad (19)$$

The examples shown in these equations illustrate possible interactions required for scrambling. In these cases the X can be a metal for the carbene scheme or an alkylidene for any pairwise scheme. Because of the C_2 axis inherent in the symmetrical 2-butenes it is reasonable to assume that $k' = 2k$ (cf. eq 13). This means that when the labels in the starting material have scrambling to an extent determined by k in eq 18, then the 2-butenes will have undergone twice as much scrambling. For example, when d_3-/d_6-C_{10} is 0.12 (Table IV), then the starting material has undergone (0.12/2.42) (100) = 5% scrambling. The butenes produced will have undergone approximately 10% scrambling independently. The adjusted d_3-/d_6-C_4 calculated values are shown in Table VI. These were calculated by taking the d_3-/d_6-C_4 values derived from the starting material (Table V) and allowing the butenes to partially scramble to the random distribution according to the approximated extent of scrambling. For example, when d_3-/d_6-C_{10} is 0.12, 10% of the corresponding d_3-/d_6-C_4 ratio from Table V (0.193) is allowed to scramble completely and then is added back into the remaining 90% of the d_3-/d_6-C_4 ratio (1.926 − 0.193 = 1.733) that arises directly from the starting material by the productive metathesis.

The adjusted calculated d_3-/d_6-C_4 values from Table VI are plotted against the d_3-/d_6-C_{10} ratios, and the curve is shown in Figure 13 along with the experimental values from Table IV. It was shown earlier that the rate of isomeric scrambling begins to increase after about 50% conversion. It should then be expected that the isotopic scrambling will behave similarly meaning that this calculated pairwise curve will not be as accurate after about 40–50% conversion of starting material, or when d_3-/d_6-C_{10} is about 0.35→0.4. After this point the approach to the random distribution of isotopic labels will change. The calculated carbene curve is, of course, a horizontal line at d_3/d_6 = 2.42.

Figure 13 has important implications. The difference between the two calculated curves clearly indicates that if the butenes are sampled at conversions ≤40% of starting material, the values obtained for the isotopic distribution will, within experimental error, unambiguously distinguish between the two possible schemes. There are two data points well within this limit, and both indicate that a carbene scheme is operative.

Another experiment was undertaken with the initial d_0-:d_6-C_{10} ratio of 2.68:1, and a large sample of 2-butenes was isolated after about 5–6% conversion. In this case, because of the larger 2-butene sample isolated, a d_0-:d_3-:d_6-C_4 ratio was obtained. This ratio is given in the Experimental Section along with the calculated ratios for both schemes. The carbene scheme is again implicated. The previous experiment (Table IV) was continuously monitored and allowed only small samples to be taken, and because of the errant background in the mass spectrometer at the d_0 mass only the d_3-/d_6-C_4 ratio was found.

These isotopic labeling studies have taken advantage of the isomerization studies presented earlier to allow a calculation of a pairwise curve that accounts for the scrambling of the isotopic labels in the products and starting material. These processes must be considered in any such labeling study according to the restrictions discussed in the Introduction. The experimental evidence given here has indicated that a nonpairwise metal carbene mechanism is a more accurate description of the olefin metathesis process rather than any pairwise scheme. The studies presented here most accurately account for all of the competing metathesis processes. Values for the isotopic distribution in the products were obtained that were known to have arisen during preequilibrium conditions. These experiments satisfy the restrictions placed on such labeling studies.

Experimental Section

General. All metathesis reactions were conducted in oven-dried glass tubes sealed with rubber caps and were alternately evacuated and flushed with argon several times on a vacuum line. The solutions of reagents and solvents were stored under argon and were transferred with oven-dried, argon-flushed syringes.

Analytical GLC was conducted with a Varian Series 1400 FID chromatograph with either a 20 ft × 1/8 in. Durapak column (A) at 60 °C or a 32 ft × 1/8 in. 5% Carbowax 20M/Chromosorb W (B) at 100–150 °C. Preparative GLC was conducted with a 10 ft × 1/4 in. 7% paraffin wax/Chromosorb W column at 80 °C for gas samples and a 16 ft × 1/4 in. 5% DC-550/Chromosorb G column at 120 °C for liquid samples, both using a Varian 90-P chromatograph. NMR analyses were obtained using a Varian T-60 spectrometer and δ values were recorded relative to Me_4Si. Infrared spectra were obtained with a Perkin-Elmer 237B and calibrated with a polystyrene standard. Mass spectra were conducted with a Hitachi RMU-6E spectrometer.

The methylaluminum sesquichloride ($Me_3Al_2Cl_3$) was purchased from Ethyl Corp. and used as 1 M solution in chlorobenzene. The light-green $Mo(NO)_2Cl_2(PPh_3)_2$ was prepared according to the procedure of Cotton[16] and was stored in a desiccator. Tetramethyltin was prepared according to the procedure of Edgell and Ward.[17] The tungsten hexachloride was purchased from Ventron and used as a 0.05 M solution in chlorobenzene under argon.

Chlorobenzene was distilled from CaH_2 or P_2O_5 under argon into a flask with a side arm with a two-way stopcock and stored over 4A sieves. A 5% forecut was discarded during the distillation. Commercially available *trans,trans*-2,8-decadiene (Chemical Samples) was stored over sieves and found to be >99% isomerically pure by GLC analysis with column B. All olefins were activated prior to reaction by passing through basic Woelm alumina under an atmosphere of argon.

Preparation of 2,8-Decadiyne-*1,1,1,10,10,10-d*$_6$. In a flame-dried, argon-flushed 250-mL three-neck flask fitted with a gas inlet and a stir bar were placed 3.7 g (35 mmol) of 1,7-octadiyne and 50 mL of distilled hexane (CaH_2). The solution was cooled in an ice bath, and 35 mL of a 2.0 M *n*-BuLi/hexane solution was added dropwise over 30 min with stirring. A white precipitate formed, and after complete addition the slurry was stirred for a few minutes at room temperature. The volatiles were removed in vacuo, and the remaining white solid was dissolved in 100 mL of oxygen-free THF (benzophenone/Na). The flask was fitted with a Friedrichs condenser and an addition funnel, and a solution of 10.0 g (69 mmol) of CD_3I (Aldrich) in 25 mL of oxygen-free THF was added over 15 min at room temperature and then stirred overnight. The contents were poured into ice-water, and the aqueous layer was extracted with three 50-mL portions of *n*-pentane. The combined extracts were washed with 50 mL of dilute aqueous HCl (5%), 50 mL of water, and 50 mL of saturated sodium bicarbonate and were dried over $MgSO_4$. After filtering, the pentane was distilled off and the remaining light yellow liquid distilled (bp 85–87 °C, 10 mm) to give 3.7 g (75%) of GLC-pure product: IR (neat) 2140 ($C{\equiv}C$), no 3300 cm^{-1} ($C{\equiv}CH$); ^1H NMR ($CDCl_3$) δ 1.5 (m, 4, $-CH_2-$), 2.1 (m, 4, $C{\equiv}CCH_2-$), no peak at δ 1.8 for terminal methyl resonances.

Preparation of *cis*-2,8-Decadiene-*1,1,1,10,10,10-d*$_6$. In a dry 250-mL flask with gas inlet and exit were placed 50 mL of freshly distilled pyridine (BaO), 50 mg of 5% Pd on $BaSO_4$ (Ventron), and 3.0 g (21.3 mmol) of 2,8-decadiyne-d_6. Dry hydrogen was then slowly passed through the stirring mixture with a sintered glass frit for several hours at room temperature. The progress of the reaction was easily monitored by periodic GLC analysis of the reaction mixture with the 5% DC-550 column described before. Upon complete conversion of the diyne, the reaction mixture was passed through a short pad of Celite and the filtrate concentrated to about 30 mL by carefully distilling off the pyridine using a short Vigreux column. The concentrate was taken up in 100 mL of ether and washed with 50 mL of 10% aqueous HCl and two 50-mL portions of brine. The ether solution was dried over $MgSO_4$, and after filtering the ether was removed by distillation. The remaining clear liquid was distilled (80–83 °C, 40 mm) to give 2.52 g (82%) of product. Analytical GLC analysis using column B at 105 °C showed that the total trans content was about 2 ± 0.5% or 98% total cis content. ^1H NMR ($CDCl_3$): δ 1.6 (m, 4, $-CH_2-$), 2.2 (m, 4, $=CHCH_2$), 5.5 (m, 4, $=CH$); IR (neat) 1450 cm^{-1} ($C{=}C$), no $C{\equiv}C$ stretch; mass spectrum (70 eV) *m/e* (source) 144 (M^+), 126 ($M^+ - CD_3$), 108 ($M^+ - 2CD_3$) (no significant peaks *m/e* 126 → 144).

Preparation of *cis,cis*-2,8-Decadiene. In the same way described above 5.0 g (37.3 mmol) of 2,8-decadiyne (Chemical Samples), 100 mg of 5% Pd on $BaSO_4$, and 150 mL of freshly distilled pyridine were stirred under a flow of dry hydrogen at room temperature. The product was obtained in the same way as above (bp 78–82°C, 37 mm) to give 3.65 g (71%) of clear product. GLC analysis (column B) indicated 98 ± 1% cis content. ^1H NMR ($CDCl_3$): δ 1.6 (m, 4, $-CH_2-$), 1.8 (d, 6, CH_3), 2.2 (m, 4, $=CHCH_2-$), 5.5 (m, 4, $=CH$); IR (neat) 1450 ($C{=}C$), 725 (cis $C{=}C$), no $C{\equiv}C$, 965 (vw) (trans $C{=}C$) cm^{-1}; mass spectrum (70 eV) *m/e* 138 (M^+), 123 ($M^+ - CH_3$).

Metathesis of *cis,cis*-2,8-Decadiene with Catalyst A. The procedure for the metathesis of *cis,cis*-2,8-decadiene is typical of the procedures used for metathesis reactions.

In an oven-dried 20 × 120 mm glass tube with a magnetic stir bar was placed 10 mg (0.013 mmol) of $Mo(NO)_2Cl_2(PPh_3)_2$. The tube was then fitted with a rubber serum cap and alternately evacuated and flushed with argon on a vacuum line several times. To this were added 3 mL of dry chlorobenzene and 0.1 mL of the 1 M $Me_3Al_2Cl_3$ solution via syringe. The resulting clear brown solution was stirred for 30 min at room temperature. Meanwhile, 0.20 g (1.45 mmol) of *cis,cis*-2,8-decadiene and 50 μL (0.26 nmol) of *n*-decane (internal liquid standard) were passed under argon through 2–3 g of basic alumina (Woelm) with the aid of 2 mL of chlorobenzene into a small vial. This solution was then added to the incubated catalyst solution via syringe. A gas solution of *n*-propane in argon (5 mL 0.026 nmol) was added with a gas syringe. Gas (~0.3 mL) samples were withdrawn at several intervals. The gas samples were analyzed immediately on column A using appropriate calibrations from standard samples. Liquid aliquots were quenched with a few drops of water, passed through Florisil into screw cap vials, and stored at 0°C until GLC analysis with column B.

Reproducible results could also be obtained by running several small reactions simultaneously, quenching each at a specified time with water, and analyzing the gas and liquid from the sealed reaction vessel.

Metathesis of *cis,cis*-2,8-Decadiene with Catalyst B. In a 20 × 120 mm oven-dried, argon-flushed tube fitted with a rubber cap were placed 0.5 mL of the 0.05 M WCl_6 solution, 0.20 g (1.45 mmol) of activated *cis,cis*-2,8-decadiene, 50 μL of *n*-decane, and 70 μL of a 0.75 M $SnMe_4$ in chlorobenzene solution in that order. Analytical GLC analysis was conducted in a similar way as above, except that liquid samples were quenched with a few drops of a dilute aqueous NH_4OH solution.

Metathesis of a (1.21 ± 0.02):1 Mixture of *cis,cis*-2,8-Decadiene-d_0:-d_6. This reaction was conducted by the method described above for catalyst A. To the incubated catalyst was added 0.153 g of a (1.21 ± 0.02):1 mixture of decadiene-d_0 and -d_6 (determined by weight and mass spectral analysis). At four time intervals, 10-mL gas samples were withdrawn and replaced with an equal volume of argon. The gas was injected into the preparative gas column mentioned above and *cis*-2-butenes were isolated with a glass trap cooled in liquid N_2 at the exit port. The trapped butenes were then submitted for mass spectral analysis. The d_3-/d_6-C_4 ratios listed in Table VI were found by comparing the peak heights at *m/e* 59 (d_3-C_4) and 62 (d_6-C_4). Liquid aliquots were withdrawn and the 2,8-decadiene was isolated by preparative GLC with the DC-550 column mentioned above. These samples were analyzed via mass spectroscopy, and the peak heights at *m/e* 138 (d_0-C_{10}), 141 (d_3-C_{10}), and 144 (d_6-C_{10}) were compared. No other peaks in this region were noted. The d_3-/d_6-C_{10} ratios were found and are recorded in Table VI. The *t*-/*c*-C_4 ratio was determined at each gas and liquid sampling and are also listed in Table VI.

Metathesis of a (2.68 ± 0.05):1 Mixture of *cis,cis*-2,8-Decadiene-d_0:-d_6. In the same way as described above, 0.120 g of a (2.68 ± 0.05):1 mixture of *cis,cis*-2,8-decadiene-d_0:-d_6 was added to catalyst A. After 10 min two 20-mL gas samples were withdrawn from the tube and the reaction was immediately quenched with 0.5 mL of H_2O. The 2-butenes were isolated in the same way and the collection tube was submitted for analysis. A d_0:d_3:d_6 ratio of 1:(0.72 ± 0.06):(0.18 ± 0.03) was found. The calculated carbene ratio is 1:(0.75 ± 0.04):(0.14 ± 0.02), and the ratio for the pairwise scheme is 1:(0.64 ± 0.02):(0.17 ± 0.02). The *t*-/*c*-C_4 ratio was 0.31 ± 0.04, which corresponds to about 6-8% conversion of starting material. Using *n*-decane as an internal liquid standard, the yield of cyclohexene was found to be 5 ± 2% based on decadiene.

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Thermal Decomposition of Labeled Cyclohexene. A Complex Reaction Involving a Forbidden 1,2-Hydrogen Elimination

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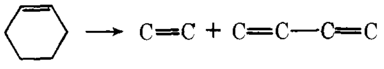
Abstract: The pyrolysis of 3,3,6,6-tetradeuteriocyclohexene is complex and involves four primary unimolecular processes (in a ratio of 20:1:0.1:0.02): retro-Diels-Alder ($\log k_1 = 14.93 \pm 0.79 - (65.2 \pm 2.8)/\theta$), D_2 elimination ($\log k_2 = 12.63 \pm 0.76 - (61.6 \pm 2.7)/\theta$), HD elimination, and H_2 elimination ($\theta = 2.303RT$ kcal/mol). The first two reactions are symmetry allowed. If the last two reactions are concerted, they are symmetry forbidden. The experimental activation energies for processes 3 and 4 are 6 ± 3 kcal/mol larger than that for process 2. Various mechanisms which may account for reactions 3 and 4 are discussed. Secondary reactions producing cyclohexadienes, benzene, H_2, and HD were also observed at low conversion (~2%); any D_2 produced by secondary processes was masked by reaction 2. The secondary reactions were initiated by reaction 9 with an activation energy of approximately 48 kcal/mol followed by reactions 10-16. Since the secondary rate of production of H_2 was much faster than reaction 4, the secondary production rate could be equated to the rate of formation of benzene from 1,3-cyclohexadiene.

Introduction

The gas-phase pyrolysis of cyclohexene[2,3] in the 400-850 °C temperature region produces primarily ethylene and 1,3-butadiene by a retro-Diels-Alder reaction. This reaction has been shown to be homogeneous, first order and is allowed by orbital symmetry; thus, a concerted Woodward-Hoffmann[4] process has been postulated. Along with ethylene and 1,3-butadiene small amounts (~5%) of hydrogen and 1,3-cyclohexadiene are observed.[2d] Presumably, these products, also formed by a homogeneous competitive first-order path,[2d] result from the molecular elimination of hydrogen.



(1′)

The production of molecular hydrogen via primary unimolecular processes could be by one or more of the following paths.

Process 2′ is a simple 1,4-elimination which is allowed by