(7) R. S. Givens and B. Matuszewski, unpublished results.

(8) (a) This probe was chosen over other conventional approaches for several reasons, e.g., (1) changing to more viscous solvents, solvents with extractable hydrogens would be necessary, complicating the reaction product mixture; and (2) trapping agents such as oxygen that would react with the radicals also quench the excited singlet state of **3**.[5] (b) The ***h*** notation indicates unlabeled ester; ***d***, deuterium-labeled ester; ***O***, oxygen-18 labeled ester.

(9) K. Biemann, "Mass Spectrometry", McGraw-Hill, New York, N.Y., 1962, p 224ff. The ^{18}O or D content was determined by directly inserting the labeled sample into the inlet of the Varian-MAT CH5 mass spectrometer. The ionization energy was 70 eV unless otherwise indicated and the inlet temperature, approximated 220 °C. The ^{18}O content was determined from the P/(P + 2) peak heights as measured on the photographic output.

(10) P. Sabatier and M. Murat, *Ann. Chim.* (*Paris*), **4,** 253 (1915).

(11) The extensive studies of White (W. J. le Noble, E. H. White, and P. M. Dzadzic, *J. Am. Chem. Soc.*, **98,** 4020 (1976) and references cited therein) have shown that separated carboxylate–carbonium ion pairs can be generated from *N*-nitrosoamides.

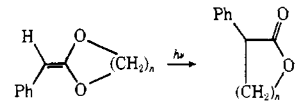
(12) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).

(13) A number of other photodecarboxylations have been reported (for esters, anhydrides, and acids) where radical intermediates are suggested. (See ref 3a,e,f,g, and also A. Zweig, *Pure Appl. Chem.*, **33**, 389 (1973), and references cited therein.)

(14) The decay process may be by way of the triplet manifold. No attempt was made to measure intersystem crossing efficiencies.

(15) (a) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85,** 915 (1963); (b) H. E. Zimmerman and S. Somasekhara, *ibid.*, **85,** 922 (1963). (c) The higher value reflects the material balance for the starting ester disappearance. Although no other products were formed, only 80% of the product was isolated in preparative runs.

(16) This indirectly lends support for a $_{\pi}2_s + {}_{\sigma}2_s$ migration of the benzyl carbon. An interesting parallel is found in the work of J. E. Baldwin and L. E. Walker (*J. Am. Chem. Soc.*, **88,** 3769 (1966)), where the more flexible i photorearranged to a α-phenyl-γ-valerolactone (ii), while iii failed to give any α-phenyl-γ-butyrolactone (iv).



i, $n = 3$
iii, $n = 2$

ii, $n = 3$
iv, $n = 2$

(17) M. Schneider and H. Strohacker, *Tetrahedron*, **32,** 619 (1976).

(18) (a) E. H. White, R. H. McGirk, C. A. Aufdermarsh, Jr., H. P. Tiwari, and M. J. Todd, *J. Am. Chem. Soc.*, **95,** 8107 (1973); (b) E. H. White and C. A. Elliger, *ibid.*, **89,** 165 (1967); (c) E. H. White, *ibid.*, 77, 6014 (1955).

(19) C. S. Marvel, "Organic Syntheses", Collect. Vol. 3, Wiley, New York, N.Y., 1955, p 495.

(20) L. Meites and T. Meites, *Anal. Chem.*, **20,** 984 (1948).

(21) Southern New England Co., Middletown, Connecticut.

(22) The procedure used was patterned after the work of Kice et al. (*J. Am. Chem. Soc.*, **92,** 5608 (1970)).

(23) The alcohol ($[\alpha]^{35}{}_D$ −42°) was resolved as the brucine salt of the phthalate half ester according to the method of Kenyon (E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1939)).

(24) The *N*-(1-phenylethyl)phenylacetamide was synthesized from 1-phenylethylamine (Aldrich Chemical Co., $[\alpha]^{20}{}_D$ +39 (neat)). Specific rotations for the amide were +105.8 (589 nm), +106.3 (573.8), +123.8 (546), +230.4 (436), and +406.0 (365).

(25) The specific rotations were not measured because of the instability of **15.**

Metathesis of Cyclic and Acyclic Olefins[†]

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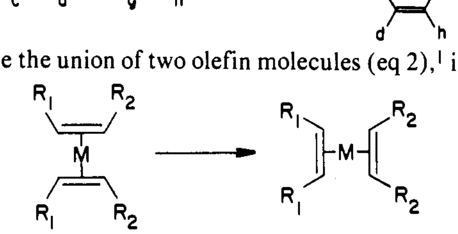
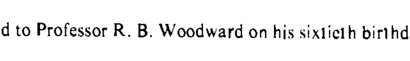
Abstract: Two experimental tests were made to determine whether the mechanism of the olefin metathesis reaction is that indicated in eq 7 or that indicated in eq 3. In one set of experiments, cyclooctene, 2-butene, 4-octene, and a molybdenum-containing catalyst were combined. The distribution of products in equation 4 was analyzed as close to the start of reaction as possible and extrapolated to measure the product ratios at zero time. Calling the ratio at zero time $[C_{14}]/[C_{12}] = r_1$ and $[C_{14}]/[C_{16}] = r_2$, the product $\overline{r_1} \times \overline{r_2}$ was measured as 4.05 ± 0.05 which is in accord with the mechanism in eq 3 and contrary to that in eq 7 no matter whether the first or the second step is rate-determining. The kinetics are analyzed to show how the relative reactivities of two acyclic olefins reacting according to eq 3 can be measured. In the experiments above the ratios of the rate constants for *trans*-2-butene and *trans*-4-octene are 3.08 ± 0.16, for *cis*-2-butene and *cis*-4-octene 6.46 ± 0.87. In another set of experiments, cyclooctene, 2-hexene, and a molybdenum-containing catalyst were combined, and the distribution of the products in eq 5 were analyzed at zero time. It is shown that the ratios of the "triads" of products, like C_{12}, C_{14}, and C_{16}, should be $1{:}r{:}1$, where $r = (k_3/k_4) + (k_4/k_3)$ and k_3 and k_4 are the rate constants for the two possible reactions, according to eq 14, of an olefin with a metal carbene. For the experiment performed here with 2-hexene, r is 3.25, but it is shown that for less symmetrically substituted olefins r should be, and is, much larger. A procedure is developed for measuring the relative reactivities of cyclic and acyclic olefins.

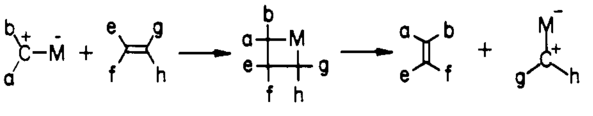
That the mechanism of the olefin metathesis reaction (eq 1), initially thought on the basis of the gross structural change to involve the union of two olefin molecules (eq 2),[1] is instead a chain reaction propagated by the union of an olefin with a metal carbene (eq 3),[2] was first indicated by the distribution of products when both cyclic and acyclic olefins react or form in metathesis. Other evidence has since supported this view.[3]



(1)



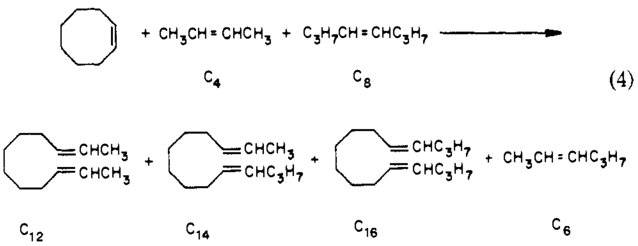
(2)



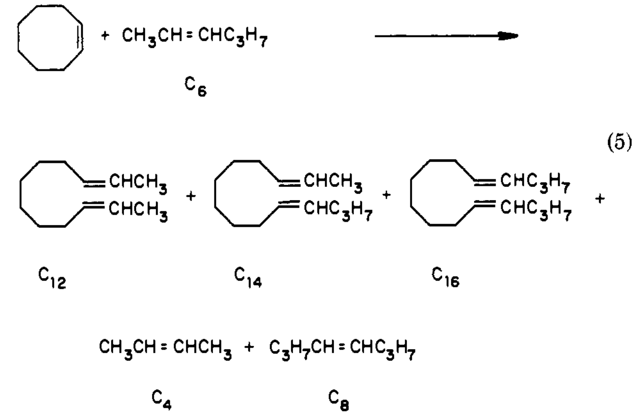
(3)

In this paper we consider two of the original experimental tests of the mechanism, the distribution of products in the reactions summarized in eq 4 and 5. The background of the experiments and a summary of the results were reported previously;[2a] the details both of the measurements and of the IR analysis are reported here.

[†] Dedicated to Professor R. B. Woodward on his sixtieth birthday.



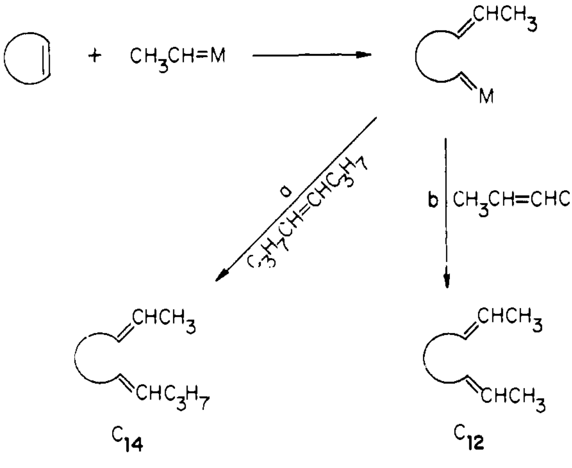
(4)



(5)

Results

Double Cross Experiments. In one series of experiments cyclooctene, 2-butene, and 4-octene were allowed to react simultaneously and the amounts of the hydrocarbons in eq 4 were analyzed to determine the ratios of the concentrations $[C_{14}]/[C_{12}]$ and $[C_{14}]/[C_{16}]$ at the very beginning of reaction. The idea was that if the mechanism of the olefin metathesis were that summarized in eq 2, then at first both ratios would have to be zero, for C_{14} should not form from C_6 as quickly as C_{12} and C_{16} form from C_4 and C_8, since early in the reaction much more C_4 and C_8 would be present than C_6. Similarly C_{14} could not form from C_{12} reacting with C_{16} as neither would yet be present in appreciable quantity. If on the other hand the mechanism were that in eq 3, then C_{14} would have to predominate over C_{12} or C_{16} by at least a factor of 2. If the methyl and propyl groups that differentiate the butene and octene served only as labels and if the amounts of butene and octene were equal, the ratios of C_{12}, C_{14}, and C_{16} products would be 1:2:1 because, as indicated in eq 6, reaction by path *a* would be just as likely as by path *b*.



(6)

Five experiments were carried out, two with cyclooctene mixed with *trans*-2-butene and *trans*-4-octene, and three with cyclooctene mixed with *cis*-2-butene and *cis*-4-octene. $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ plus methylaluminum sesquichloride in chlorobenzene were used to effect the reactions.[7] Measured quantities of the olefins plus an internal standard for GLC analysis were added to the combination, and after incubating the reactions with cis olefins at 0 °C and those with trans olefins at room temperature, samples were withdrawn periodically, quenched with water, and analyzed by GLC. Each sample was analyzed for 2-butene, 2-hexene, 4-octene, cyclooctene, C_{12}, C_{14}, C_{16}, and the internal standard, but cis and trans isomers were not differentiated by the instrument.

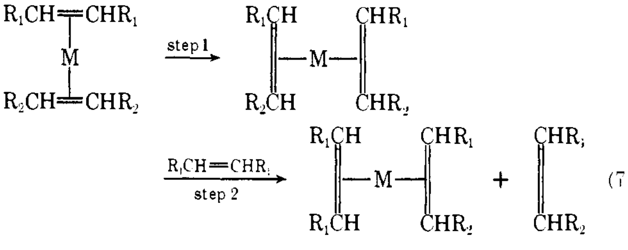
Table I. Initial Product Composition for Reaction of Cyclooctene with 2-Butene and 4-Octene[a]

Experiment No.	$[C_4]/[C_8]$	$[C_{14}]/[C_{12}]$	$[C_{14}]/[C_{16}]$
Trans series			
1	0.97 (±10%)[c]	0.70 ± 0.036	8.35 ± 0.60
2	0.492 ± 0.068[b]	1.34 ± 0.12	3.20 ± 0.21
Cis series			
3	0.752 ± 0.053[b]	0.401 ± 0.046	11.12 ± 0.99
4	0.427 ± 0.010[b]	0.88 ± 0.04	4.87 ± 0.27
5	0.232[b,d]	1.38 ± 0.18	3.45 ± 0.39

[a] Means and standard deviations, except in one case. [b] Determined by GLC. [c] Determined by measurement of the volume of liquefied 2-butene. The estimated error is ±10%. [d] Only one measurement was made. The estimated error is ±5%.

Graphs were plotted of $[C_{14}]/[C_{12}]$ and of $[C_{14}]/[C_{16}]$ as functions of the extent of reaction, measured by $([C_6]/[C_8])/([C_6]/[C_8])_{eq}$, where $([C_6]/[C_8])_{eq}$, the equilibrium ratio of 2-hexene and 4-octene, was taken to be twice the initial molar ratio of 2-butene and 4-octene. One such graph is shown in Figure 1 along with a graph showing the decrease in cyclooctene concentration at each point at which measurements were made. The curves were extrapolated to determine $[C_{14}]/[C_{12}]$ and $[C_{14}]/[C_{16}]$ at "zero time", when $[C_6] = 0$, and these values are summarized in Table I. Since they show that the product (C_{14}), which initially should not form at all according to the conventional mechanism when eq 2 is rate determining, is formed in larger amounts than one or both of the conventional products (C_{12} and C_{16}), they rule out this mechanism.

However, the conventional mechanism would seemingly not be excluded by the data if the rate-determining step were the olefin-displacement reaction, step 2 in eq 7, because, as shown



(7)

in Scheme I, the alkylidene groups would then be scrambled while the initially formed diene was still attached to the metal and not yet released into solution. This possibility, which we call the sticky olefin hypothesis, was first suggested by Calderon to account for the high molecular weights of the polymers formed initially in the metathesis of cycloalkenes.[1d] It is considered and rejected later below.

To see how the metal carbene chain mechanism accounts for the data in Table I, suppose the kinetics to be those indicated in Scheme II. Appendix 1 shows that this scheme has three significant implications about the initial products if

$$(k_2/k_1) \times (k_3/k_4) = k_5/k_6 \tag{8}$$

These are that if $[C_{14+8n}]/[C_{12+8n}]$ is called r_1 and

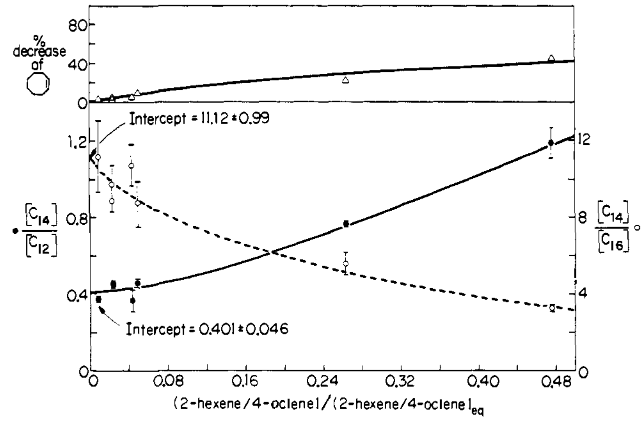
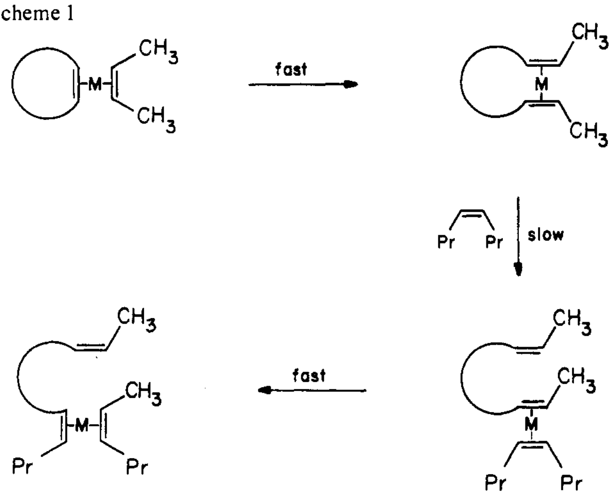


Figure 1. Plot of product composition as a function of the extent of reaction for the reaction of cyclooctene, *cis*-2-butene, and *cis*-4-octene (experiment 3 in Tables I and II). The ordinate is labeled at the left for the solid curve and at the right for the dashed curve.

Scheme I



Scheme II^a

$$
\begin{aligned}
\mathrm{C} + \mathrm{Cy} &\xrightarrow{k_3} \mathrm{A_0}\\
\mathrm{D} + \mathrm{Cy} &\xrightarrow{k_4} \mathrm{B_0}\\
\mathrm{A}_n + \mathrm{Cy} &\xrightarrow{k_7} \mathrm{A}_{n+1}\\
\mathrm{B}_n + \mathrm{Cy} &\xrightarrow{k_7} \mathrm{B}_{n+1}\\
\mathrm{A}_n + \mathrm{Bu} &\xrightarrow{k_1} \mathrm{C}_{12+8n} + \mathrm{C}\\
\mathrm{A}_n + \mathrm{Oc} &\xrightarrow{k_2} \mathrm{C}_{14+8n} + \mathrm{D}\\
\mathrm{B}_n + \mathrm{Bu} &\xrightarrow{k_1} \mathrm{C}_{14+8n} + \mathrm{C}\\
\mathrm{B}_n + \mathrm{Oc} &\xrightarrow{k_2} \mathrm{C}_{16+8n} + \mathrm{D}\\
\mathrm{C} + \mathrm{Oc} &\xrightarrow{k_5} \mathrm{Hex} + \mathrm{D}\\
\mathrm{D} + \mathrm{Bu} &\xrightarrow{k_6} \mathrm{Hex} + \mathrm{C}
\end{aligned}
$$

^{a} Cy is cyclooctene, Bu is butene, Oc is octene, C is $\mathrm{CH_3CH{=}M}$, D is $\mathrm{C_3H_7CH{=}M}$, A_n is $\mathrm{CH_3CH\lbrack{=}CH(CH_2)_6CH\rbrack_{n+1}{=}M}$, and B_n is $\mathrm{C_3H_7CH\lbrack{=}CH(CH_2)_6CH\rbrack_{n+1}{=}M}$. C_{12+8n}, C_{14+8n}, and C_{16+8n} are the homologues of C_{12}, C_{14}, and C_{16} in eq 4 and 5.

$[\mathrm{C}_{14+8n}]/[\mathrm{C}_{16+8n}]$ is called r_2, then

$$r_1 \times r_2 = 4 \tag{9a}$$

$$r_1 = 2k_2[\mathrm{Oc}]/k_1[\mathrm{Bu}] \tag{9b}$$

$$r_2 = 2k_1[\mathrm{Bu}]/k_2[\mathrm{Oc}] \tag{9c}$$

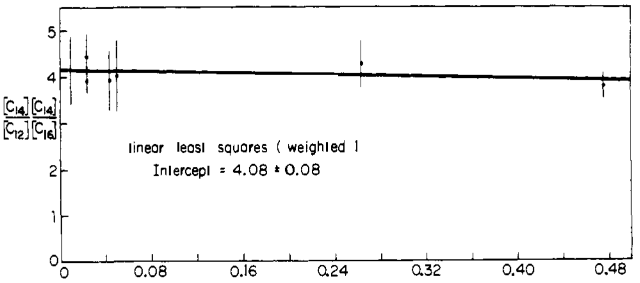


Figure 2. Product $r_1 \times r_2$. The experimental data are the same as in Figure 1.

and

$$\frac{d[\mathrm{C}_{m+8n}]}{d[\mathrm{C}_{m+8(n+1)}]} = 1 + \frac{k_1}{k_7}\frac{[\mathrm{Bu}]}{[\mathrm{Cy}]} + \frac{k_2}{k_7}\frac{[\mathrm{Oc}]}{[\mathrm{Cy}]} \tag{10}$$

where $m = 12$, 14, or 16.

The assumption of eq 8 appears plausible because if k_2/k_1 measures the ratio of the reactivities of octene and butene with a common carbene, and k_3/k_4 measures that of carbenes C and D with a common olefin, their product will measure that of carbene C with octene and D with butene.

That $r_1 \times r_2 = 4$ is analogous to a similar relationship that applies to reactions essentially the reverse of those in eq 4.[2b]

That the experimentally determined values of r_1 and r_2 at zero time in Table I when multiplied equal 4 is indicated in Table II. A more accurate measure is achieved by multiplying r_1 and r_2 at the different times and extrapolating to zero time, as in Figure 2. These products are also summarized in Table II, in the third column.

The ratios of rate constants k_1/k_2 in Scheme II, according to eq 9b and 9c, are recorded in Table III. In both the cis and the trans series 2-butene is more reactive than 4-octene, presumably for steric reasons, which is why, as seen in Table I, C_{12} was always formed in larger amounts than C_{16}, even when the reaction mixture consisted of much less 2-butene than 4-octene. The ratios of C_{12}, C_{14}, and C_{16} at zero time are not the equilibrium ratios, which is why they change with time, as Figure 1 shows. The difference in the reactivities of 2-butene and 4-octene is greater in the cis series than in the trans and presumably in at least small part this is because the experiments in these two series were conducted at different temperatures (0 °C for the cis, room temperature for the trans).

Consider now the sticky olefin hypothesis, that the mechanism of olefin metathesis is that in eq 7 with step 2 rate determining. Suppose the kinetics to be those indicated in Scheme III. Here Me is methyl and Pr is propyl, and substituting methyl for propyl is assumed to increase the rate of attachment and decrease the rate of removal of olefins from the metal, M, by a factor x. These kinetics, as analyzed in Appendix 2 and summarized in the graph in Figure 3, show the product $r_1 \times r_2$ at zero time to be a function of x and of the molar ratio of butene and octene, y. For each experiment y was known, and the factor x was chosen in two ways, one to reproduce the observed ratio $[\mathrm{C}_{12}]/[\mathrm{C}_{16}]$ at zero time ($x = 1.93 \pm 0.16$ in the trans series, 2.69 ± 0.25 in the cis), and two to maximize the value of $r_1 \times r_2$ in the range $0.02 \leq x \leq 50$. The products of r_1 and r_2 expected, together with those determined experimentally, are summarized in Table II. The maximum value of $r_1 \times r_2$ in the range $0.10 \leq y \leq 10$, $0.02 \leq x \leq 50$ is 2.94.

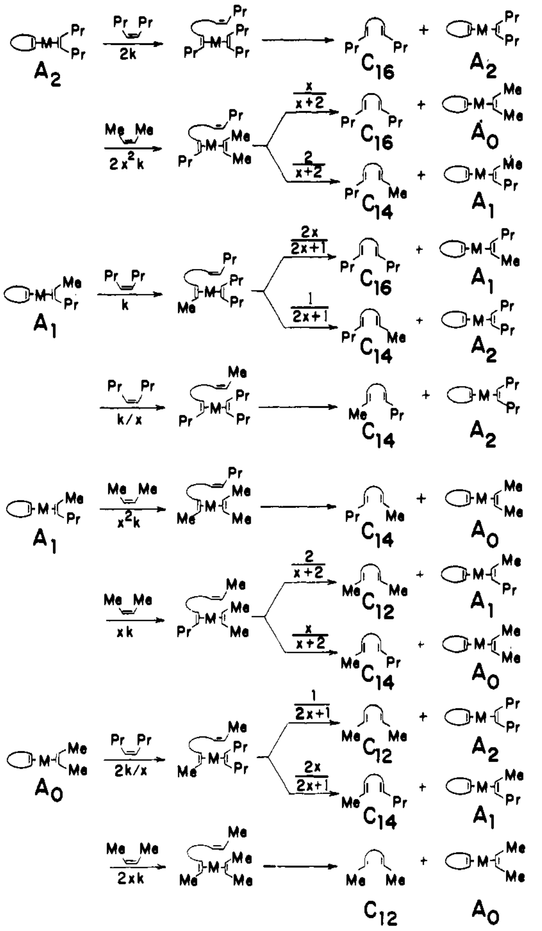
Table II shows the average value (weighted according to the inverse squares of the standard deviations)[9] of $\overline{r_1 \times r_2}$ determined experimentally to be 4.05 ± 0.05, insignificantly different from the value of 4 anticipated according to the metal

Table II. Experimental and Anticipated Values of $r_1 \times r_2$

Experiment No.	Exptl $\bar{r}_1 \times \bar{r}_2$[a]	Exptl $\overline{r_1 \times r_2}$[b]	Anticipated: Metal carbene	Anticipated: Sticky olefin, Based on $[C_{12}]/[C_{16}]$[f]	Anticipated: Sticky olefin, Maximum[g]
Trans series					
1	[5.85 ± 0.52][h]	[5.60 ± 0.80][c,h]	4.0	2.26	2.56
2	4.29 ± 0.48	4.11 ± 0.09[d]	4.0	2.60	2.60
Cis series					
3	4.46 ± 0.65	4.08 ± 0.08[d]	4.0	2.10	2.57
4	4.30 ± 0.31	3.83 ± 0.13[e]	4.0	2.56	2.62
5	4.76 ± 0.82	4.02 ± 0.33[e]	4.0	2.73	2.73
Av[i]	4.35 ± 0.23	4.05 ± 0.05			

[a] Product of r_1 and r_2 each determined separately at zero time. [b] Determined graphically by extrapolating plots of $r_1 \times r_2$ to zero time. [c] This plot is nonlinear. [d] Weighted linear least-squares formula used. [e] Unweighted linear least-squares formula used. [f] Predicted $r_1 \times r_2$ corresponding to the experimental value of $[C_{12}]/[C_{16}]$. [g] Maximum value in range $0.02 \le x \le 50$. [h] Probably incorrect (see note 8). [i] The average excludes experiment 1. Each experiment was weighted according to the inverse square of its standard deviation (see note 9).

Scheme III



carbene chain mechanism, but for each experiment $\overline{r_1 \times r_2}$ is between 4 and 25 standard deviations away from the value anticipated according to Scheme III. Accordingly the latter is rejected in favor of the mechanism in eq 3.

Finally, the conventional mechanism seemingly might account for the product distribution if cyclooctene first polymerized to polyoctenamer[10] and then was cleaved by the acyclic olefins.[11] This possibility has to be rejected for two reasons. One is that since, as Figure 1 illustrates, cyclooctene was largely unconsumed (95% was the average) when the first measurements of $[C_{12}]$, $[C_{14}]$, and $[C_{16}]$ were being made, for this hypothesis to account for the yields of C_{12}, C_{14}, and C_{16}, polyoctenamer would have to be more reactive than cyclooctene toward the acyclic olefins, and that appears unlikely. Two, this hypothesis would not account for the distribution, discussed below, of products formed early in the reactions of cyclic olefins with acyclic olefins that are unsymmetrically substituted.

Single Cross Experiments. In this series of experiments cyclooctene and 2-hexene were allowed to react under conditions similar to those used for the experiments above, and the products in eq 5 were analyzed to determine the ratios of concentrations $[C_{12}]/[C_{14}]$ and $[C_{16}]/[C_{14}]$ at zero time. An experiment like this, using cyclopentene and 2-pentene as the substrates and $WOCl_4 + (n\text{-}C_4H_9)_4Sn$ as the catalyst, had been done earlier by Hérisson and Chauvin.[2g]

In these experiments, according to the conventional mechanism and at zero time, C_{14}, which in the previous experiments was anomalous, would now be the only product. C_{12} and C_{16} would be the anomalies. According to the metal carbene chain mechanism, if the methyl and propyl groups served only as labels, the distribution of C_{12}, C_{14}, and C_{16} products would be 1:2:1. C_{14} would be the major product just as it is according to the conventional mechanism, so the change in product distribution with mechanism is not as striking. However, appreciable amounts of C_{12} and C_{16} would form and should be detectable.

The experiments were similar to those described before. This time $[C_{12}]/[C_{14}]$ and $[C_{16}]/[C_{14}]$ were plotted as functions of $([C_8]/[C_6])/([C_8]/[C_6])_{eq}$, where $([C_8]/[C_6])_{eq}$, the equilibrium ratio of 4-octene and 2-hexene, was taken to be 0.5. One graph is shown in Figure 4. Extrapolation gives $[C_{12}]/[C_{14}]$ and $[C_{16}]/[C_{14}]$ at zero time, when $[C_8] = 0$, and these values for two experiments are summarized in Table IV. Since they should have been zero according to the conventional mechanism, the latter is again excluded. However these values are also not 0.5, the ratio expected for the metal carbene mechanism according to the assumptions made above. This is considered later below.

But consider first how the sticky olefin hypothesis (eq 7, with step 2 rate determining) accounts for the data. Suppose the kinetics to be those indicated in Scheme IV. Here we suppose that RCH=CHPr is displaced from the metal x times as fast as the analogous RCH=CHMe. These kinetics, analyzed in Appendix 3, imply that $d[C_{16}]/d[C_{12}] = 1$, and if we suppose $k_P/k_M = x$, $d[C_{14}]/d[C_{16}]$ is equal to 2.5 if $x = 1$ and is greater than 2.5 if $x \neq 1$. Thus the ratios of $[C_{12}]$, $[C_{14}]$, and

Table III. Ratios of Rate Constants k_1/k_2 in Scheme II[a]

Experiment No.	$\frac{[Bu]^b}{[Oc]}$	$\frac{k_1}{k_2} = \frac{2}{r_1}\frac{[oc]}{[Bu]}$	$\frac{k_1}{k_2} = \frac{r_2}{2}\frac{[Oc]}{[Bu]}$	Av
Trans series				
1	0.97[b]	2.95 ± 0.33	[4.30 ± 0.53]	
2	0.492 ± 0.068	3.03 ± 0.50	3.25 ± 0.50	3.08 ± 0.16[d]
Cis series				
3	0.752 ± 0.053	6.63 ± 0.89	7.39 ± 0.84	
4	0.427 ± 0.010	5.32 ± 0.27	5.70 ± 0.34	
5	0.232[c]	6.25 ± 0.87	7.44 ± 0.92	6.46 ± 0.87[e]

[a] Means and standard deviations. [b] Measured by GLC except for experiment 1, in which it was measured, probably with an error of ±10%, by the weight of 4-octene and the volume of 2-butene. [c] Only one GLC available. Estimated error is ±5%. [d] Average of three numbers, the one in brackets having been excluded (see note 8). [e] Average of six numbers.

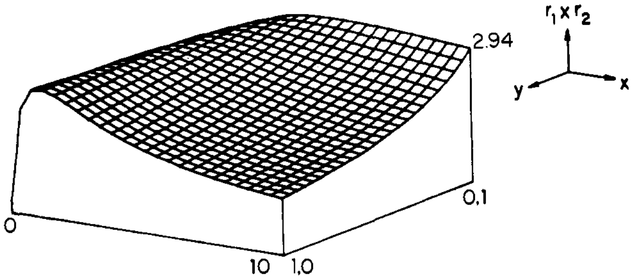


Figure 3. Expected product $r_1 \times r_2$ at zero time according to Scheme III. Here y = [butene]/[octene].

Scheme IV

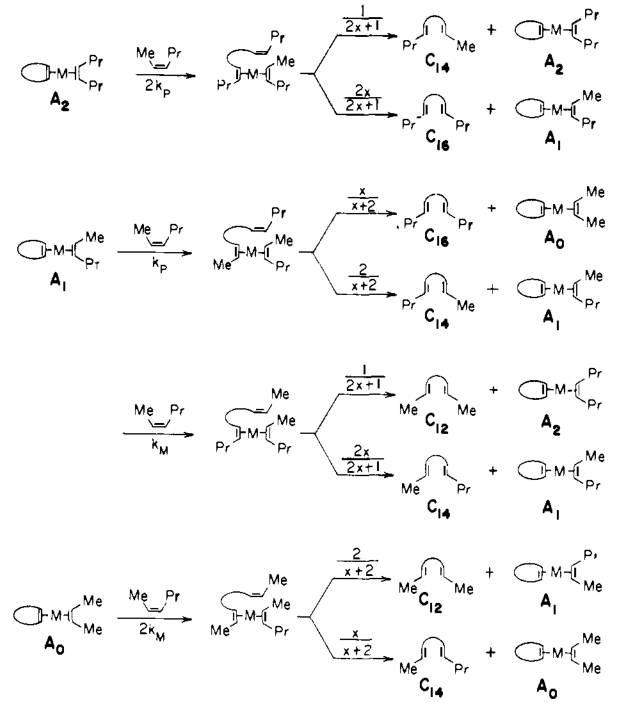


Table IV. Initial Product Composition for Reaction of Cyclooctene with 2-Hexene

Expt	$[C_{12}]/[C_{14}]$	$[C_{16}]/[C_{14}]$
6	0.338 ± 0.053	0.298 ± 0.021
7	0.309 ± 0.036	0.328 ± 0.045
Av[a]	0.318 ± 0.030	0.303 ± 0.019

[a] Averaged with a weighting factor corresponding to the square of the reciprocal of the standard deviation.[9]

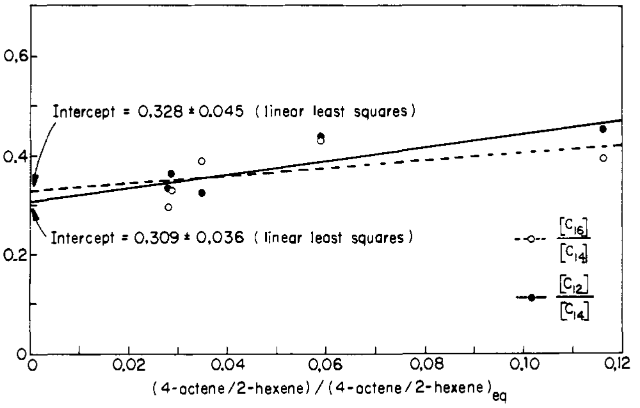


Figure 4. Plot of product composition as a function of extent of reaction for the reaction of cyclooctene with 2-hexene (experiment 7 in Table IV).

$[C_{16}]$ at zero time should be $1{:}r{:}1$, where $r \geq 2.5$. The data in Table IV are in accord with this scheme.

To consider how the metal carbene chain mechanism accounts for these experiments, suppose the kinetics to be those indicated in Scheme V. (See Scheme II for the definition of symbols; Hex is 2-hexene.) Appendix 4 shows that if as above in analyzing Scheme II we again assume, as seems plausible,

$$k_5/k_6 = (k_1/k_2) \times (k_4/k_3) \tag{11}$$

the ratios of products C_{12+8n}, C_{14+8n}, and C_{16+8n}, will be $1{:}r{:}1$, where

$$r = (k_3/k_4) + (k_4/k_3) \tag{12}$$

Moreover,

$$\frac{d[C_{m+8n}]}{d[C_{m+8(n+1)}]} = 1 + \frac{(k_3 + k_4)}{k_7}\frac{[Hex]}{[Cy]} \tag{13}$$

$$(m = 12, 14, 16)$$

Since eq 12 requires that $r = 2$ if $k_3 = k_4$ and that $r > 2$ if $k_3 \neq k_4$, the ratios of the C_{12}, C_{14}, and C_{16} products of the single cross experiments will be $1{:}r{:}1$, where $r \geq 2$.

The ratio r measures whether metal carbenes react with unsymmetrically substituted alkenes preferentially along one or the other of the two paths indicated in eq 14. Since the stability of carbenium ions is sensitive to the substituents attached to the ion center, in any experiment like this there should be some preference for one path over the other, and the three products, like C_{12}, C_{14}, C_{16}, should therefore essentially never form in the 1:2:1 ratio that is likely at thermodynamic equilibrium. The ratio initially should always be $1{:}r{:}1$ with $r > 2$.[12]

Scheme V

$$\mathrm{C + Cy} \xrightarrow{k_1} \mathrm{A_0}$$

$$\mathrm{D + Cy} \xrightarrow{k_2} \mathrm{B_0}$$

$$\mathrm{A}_n + \mathrm{Cy} \xrightarrow{k_7} \mathrm{A}_{n+1}$$

$$\mathrm{B}_n + \mathrm{Cy} \xrightarrow{k_7} \mathrm{B}_{n+1}$$

$$\mathrm{A}_n + \mathrm{Hex} \xrightarrow{k_3} \mathrm{C}_{14+8n} + \mathrm{C}$$

$$\mathrm{A}_n + \mathrm{Hex} \xrightarrow{k_4} \mathrm{C}_{12+8n} + \mathrm{D}$$

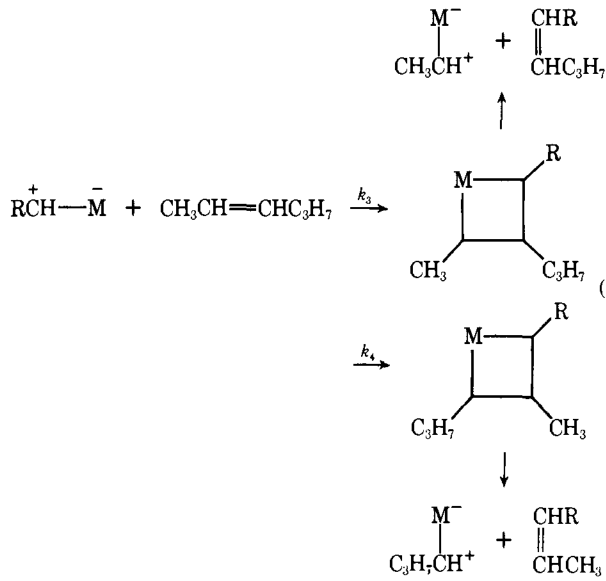
$$\mathrm{B}_n + \mathrm{Hex} \xrightarrow{k_3} \mathrm{C}_{16+8n} + \mathrm{C}$$

$$\mathrm{B}_n + \mathrm{Hex} \xrightarrow{k_4} \mathrm{C}_{14+8n} + \mathrm{D}$$

$$\mathrm{C + Hex} \xrightarrow{k_5} \mathrm{Bu + D}$$

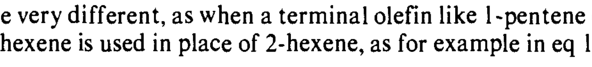
$$\mathrm{D + Hex} \xrightarrow{k_6} \mathrm{Oc + C}$$

The ratio like this measured by Hérisson and Chauvin for the reaction of cyclopentene and 2-pentene was 2,[2g] perhaps because the analysis was performed when the extent of reaction analogous to that in Figure 4 was 0.30, at which point, as the figure indicates, the value of r could have been very different than when the extent of reaction was zero.



(14)

When the substituents at the two ends of the double bond are very different, as when a terminal olefin like 1-pentene or 1-hexene is used in place of 2-hexene, as for example in eq 15,



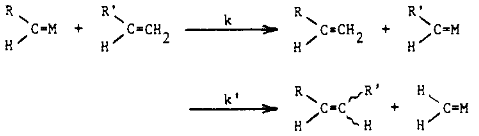
(15)

the preference for one of the paths (presumably the one giving the more highly substituted carbenium ion center)[4] should be large, and in place of triads of products only the conventional products should be, and are, observed.[2g,14,16]

It is this same selectivity that accounts for why terminal olefins upon metathesis rarely give products that are structurally transformed (the starting olefins are recovered)[6a,14,15] and for why unsymmetrically substituted cyclic olefins upon metathesis give polymers that are largely translationally invariant.[6b,c]

This selectivity also means that although for experiments like the single cross (eq 5) to work the substituents at the ends of the acyclic olefin's double bond must be different, for otherwise there would be no cross products like C_{12} or C_{16}, they must not be very different, for then no cross products would be observed either, since one path or the other in eq 14 should be preferred.

Quantitative aspects of the theory are these. Since for 2-hexene the data in Table IV show $r = 3.25 \pm 0.17$, eq 12 indicates that in Scheme V k_3/k_4 or $k_4/k_3 = 2.91 \pm 0.19$. For terminal olefins this figure should be much larger, and in agreement with this expectation other measurements using various tungsten catalysts have shown k/k' in eq 16 to be ca. 100.[6a]



(16)

Equation 12 then requires the ratio r for the triads that form in metatheses of unsubstituted cyclic olefins with terminal olefins also to be ca. 100. Reported ratios, r, in experiments using various tungsten catalysts are: for cyclooctene plus propene, 10;[2g] for cyclooctene plus 1-pentene, 20;[2g] for cyclopentene plus 1-pentene, <38;[14] and for cyclooctene plus 1-hexene, ca. 4.[16] Since in none of these experiments were extrapolations made to zero time, and since with time the measured ratios r will decrease as thermodynamic equilibrium is approached, these figures are in reasonable agreement with expectation.

We have no data to determine $(k_3 + k_4)/k_7$ using eq 13, but published data that have not been extrapolated to zero time indicate that the analogous ratio for cyclopentene plus 2-pentene is approximately 1[2g] and for cyclopentene plus 1-pentene, as seems plausible, larger, ca. 16.[14] For terminal olefins plus cycloolefins the ratio seems smaller for cyclooctene (ca. 2)[2g,16] than for cyclopentene (ca. 16).[14] Since it should be easy to determine for various cycloolefins with p carbon atoms and various acyclic olefins with q_1 and q_2 carbons united by a double bond ratios at zero time of reaction products having $pn + q_r + q_s$ and $p(n + 1) + q_r + q_s$ carbons, where $r = 1, 2$, $s = 1, 2$, and $n = 1, 2, \ldots$, eq 13 will provide a simple way to determine how ratios of rate constants analogous to $(k_3 + k_4)/k_7$ vary with the structure of the cyclic olefin, the acyclic olefin, the initiator, and other experimental variables. Similarly equation 12 provides a way to determine how ratios of rate constants analogous to k_3/k_4 vary.

Experimental Section

The instrument used for analytical GLC was a Varian Aerograph Model 1200 gas chromatograph with a flame ionization detector. The GLC column was 10 ft × ⅛ in. and packed with 20% Apiezon L on 100/120 Chromosorb W. GLC peak areas were measured with a disc integrator, except when the samples were very dilute, then the high amplification resulted in the baseline drifting, and peak areas were measured using a compensating planimeter.

Chlorobenzene was distilled, and a forerun containing benzene was discarded. Just before use it was passed through a 6 cm × 6 mm column of basic alumina onto 5-Å molecular sieves. The *n*-pentane and *n*-heptane internal standards for GLC were shaken repeatedly with concentrated H_2SO_4, washed with water, and distilled from CaH_2. These saturated hydrocarbons, as well as 2-hexene (99+%, from Aldrich Chemical) and *trans*-4-octene (99%, from Aldrich), were all passed through short columns of alumina just before they were weighed. The 2-hexene, analyzed by GLC at 20 °C using a 10 ft ×

Table V. Comparison of Analyses by GLC and by Weight of Reaction Mixtures Used for the Double Cross Experiment

	4-Octene/cyclooctene		4-Octene/internal standard	
Expt	Weight[a]	GLC peak areas[b]	Weight[a]	GLC peak areas[b]
2	0.830	0.874 ± 0.036		
3	0.657	0.687 ± 0.020	1.118	1.144 ± 0.013[c]
4	0.707	0.720 ± 0.011	1.003	1.021 ± 0.023[c]
5	0.744	0.762 ± 0.012	3.36	3.20 ± 0.23[d]

[a] Errors are probably less than 1%. [b] Listed errors are standard deviations of three or four measurements. [c] *n*-Heptane is the internal standard. [d] Pentane is the internal standard.

⅛ in. column prepared by combining one part 17% $AgNO_3$ in ethylene glycol with two parts 60/80 Chromosorb P,[17] was found to be 85.0 ± 0.3% cis and 15.0 ± 0.3% trans. No impurities were detected.

Cyclooctene contained an impurity that was inert to metathesis. The retention time of the impurity was indistinguishable from that of cyclooctane. The cyclooctene for the single cross and trans double cross experiments was distilled from CaH_2 and treated with alumina. It was 90% pure. For the cis double cross experiments it was distilled through a micro spinning band column and stored over 5-Å molecular sieves. This cyclooctene was 96% pure. *cis*- and *trans*-2-butenes were CP grade from Matheson Gas Products. *cis*-4-Octene was prepared from 4-octyne by hydrogenation in methanol containing 5% Pd on $BaSO_4$ and quinoline.[18] The olefin, after aqueous workup, was distilled (micro spinning band), found by GLC to be >99% pure, and identified by proton NMR and IR. It was stored in a refrigerator over 5-Å molecular sieves and used without further purification.

$Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ was prepared[19] and the crude material (mp ca. 190 °C) was purified as needed by chromatographing 0.45 g on 9 g of silica gel, eluting with benzene. The green benzene solution (125 ml) was boiled down to 25 mL, diluted while still hot with 25 mL of pentane, and allowed to cool. Filtration gave 0.21 g of a yellow-green crystalline powder which, after drying over P_2O_5 at 0.03 Torr, melted with decomposition at 205 °C (sealed evacuated capillary). The reported mp is 247 °C.[19] This material was stored in a desiccator and retained its catalytic activity for over 6 months.

General Metathesis Procedure. Metathesis reactions were effected in 150 × 80 mm test tubes sealed with serum caps. The reaction tube contained a magnetic stirring bar and was connected through a sidearm to a source of argon and to a vacuum. After the glassware had been dried overnight at >100 °C, the tube was evacuated three times and filled with argon.

Methylaluminum sesquichloride (MASC, a 20% solution in heptane from Texas Alkyls, Inc.) was transferred as needed by syringe from argon-flushed soda bottles stoppered with punctured crown caps lined with BUNA-N rubber seals. It titrated as 0.80 M. $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$, is only slightly soluble in chlorobenzene, but when MASC solution was added (Al:Mo = 10), a brown solution formed. Because of the reported induction period,[7b] the solution was allowed to stand for at least 1 h before olefins were added. Reaction mixtures were stirred with the magnetic stirring bar. GLC data are collected in the GLC Appendix.

Preparation of 2,10-Dodecadiene, 2,10-Tetradecadiene, and 4,12-Hexadecadiene (C_{12}, C_{14}, and C_{16}). $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (36.3 mg, 0.048 mmol) in 3.5 mL of chlorobenzene under Ar with MASC (0.34 mL, 0.27 mmol) formed a brown solution. After 1 h a solution of cyclooctene (0.36 g, 3.3 mmol) and 2-hexene (0.28 g, 3.3 mmol) in 0.5 mL of chlorobenzene was added by syringe. After standing for 2.5 h the reaction was quenched with water. The organic layer, diluted with pentane, was separated from the water and gelatinous aluminum salts, dried ($MgSO_4$), and distilled, ultimately at 15 Torr and 200 °C.

Analytical GLC on Apiezon L (column temperature, 200 °C; injector, 250 °C; detector, 300 °C) showed a set of three unsymmetrical peaks with retention times of 2.15, 3.9, and 7.4 min that were assigned to C_{12}, C_{14}, and C_{16}.

Samples were collected after GLC on a 12 ft × ⅜ in. column of 20% Apiezon J on 60/80 Chromosorb W. The instrument was a Varian Aerograph A90 gas chromatograph and the GLC conditions were column, 230 °C; injector, 270 °C; detector, 290 °C.

The IR spectra in CCl_4 were virtually identical, each sample showing a trans disubstituted olefin band around 970 cm^{-1} and a cis band at about 690 cm^{-1}. The NMR spectra and the mass spectra were more distinctive.

C_{12}: NMR (CCl_4) τ 4.65 (m, 3.68 H), 8.07 (br s, 4.08 H), 8.37 (m, 6.25 H), 8.70 (br s, 8.09 H); mass spectrum (methane chemical ionization, peaks >10% except parent group) *m/e* (relative intensity), 167 (M + 1, 0.4), 166 (M, 0.7), 165 (M − 1, 1.3), 111 (35), 109 (27), 97 (83), 96 (16), 95 (29), 83 (100), 82 (13), 81 (14), 71 (32), 69 (72), 68 (15), 67 (11), 55 (53), 54 (13); IR (CCl_4) 3023 (m), 2932 (s), 2859 (s), 1654 (w), 1452 (m), 1439 (m), 1403 (w), 1379 (w), 1133 (m), 1119 (m), 972 (m), 720 (w), 695 (w), 620 cm^{-1} (w).

C_{14}: NMR (CCl_4) τ 4.68 (m, 3.83 H), 8.05 (br s, 6.06 H), 8.38 (m, 3.58 H), 8.70 (br s, 8.96 H), 9.10 (br t, J = 7 Hz, 3.52 H); mass spectrum (methane chemical ionization, peaks >20% except parent group) *m/e* (relative intensity), 195 (M + 1, 1.0), 194 (M, 1.3), 193 (M − 1, 1.7), 111 (48), 97 (95), 96 (21), 83 (100), 71 (24), 69 (53); IR (CCl_4) 3018 (m), 2962 (m), 2929 (s), 2856 (m), 1454 (w), 1439 (w), 1403 (vw), 1379 (vw), 1135 (m), 972 (m), 692 (w), 620 cm^{-1} (w).

C_{16}: NMR (CCl_4) τ 4.72 (m, 3.84 H), 8.05 (m, 7.14 H), 8.70 (br s, 12.53 H), 9.10 (t, J = 7 Hz, 6.42 H); mass spectrum (methane chemical ionization, peaks >20% except parent group) *m/e* (relative intensity), 223 (M + 1, 1.9), 222 (M, 1.8), 221 (M − 1, 2.7), 220 (M − 2, 1.1), 125 (28), 111 (49), 97 (85), 96 (20), 83 (100), 71 (32), 69 (43); IR (CCl_4) 3006 (m), 2959 (s), 2928 (s), 2955 (s), 1650 (vw), 1463 (m), 1438 (m), 1379 (m), 1120 (m), 972 (s), 693 (m), 620 cm^{-1} (w).

Accuracy of GLC Measurements. That the GLC peak areas measured by the gas chromatograph's flame-ionization detector were proportional to the masses of the hydrocarbons detected[20] was checked in four ways. (1) In the single cross experiment $[C_{12}]/[C_{14}]$ equals $[C_{16}]/[C_{14}]$ at zero time. (2) In the double cross experiments $r_1 \times r_2$ is not only equal to 4 at zero time, but also at long reaction times. (3) In the samples used for the double cross experiments the weights of the starting materials could be measured with an accuracy of at least ±0.5%, and the weight ratios are similar to the ratios of the GLC areas measured at zero time, as shown in Table V. (4) A mixture of known amounts of *n*-dodecane, *n*-tetradecane, and *n*-hexadecane was analyzed by GLC, and the ratios for each component of its weight and its peak area were themselves in the ratio 0.973 ± 0.005:1:1.059 ± 0.028.

Double Cross Experiment 1. Catalyst solution preformed from $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (40.0 mg, 0.053 mmol) and MASC (0.37 mL, 0.30 mmol) in 1 mL of chlorobenzene was incubated for 3 h at room temperature. During this time *trans*-2-butene was distilled from a lecture bottle through a syringe needle into one side of an H-tube cooled to the temperature of dry ice. The H-tube was attached to a mercury bubbler through a sidearm and was under an argon atmosphere. Each side of the tube had a 1-in. length of 4-mm glass tubing sealed with glass at the bottom and a serum bottle cap at the top. One side of the H-tube was of precalibrated volume and the other was charged with CaH_2. The *trans*-2-butene was initially condensed over the CaH_2, then distilled to the mark of the calibrated side. In this way 0.163 mL (±10% estimated error) of *trans*-2-butene (0.101 g, 1.80 mmol) was measured out. A solution of *trans*-4-octene (0.207 g, 1.85 mmol) and cyclooctene (0.408 g, 3.7 mmol) in 1.2 mL of chlorobenzene was added to it. The resulting olefin mixture was transferred by syringe at salt-ice bath temperature to the catalyst, which was immersed in a salt-ice bath. A stopwatch was started at the moment of mixing, and the stopcock leading to the mercury bubbler was closed to prevent evaporation of 2-butene. A series of samples was withdrawn and quenched with water. GLC analysis of six samples withdrawn at 0 °C revealed no products, and therefore after 2 h at 0 °C the reaction mixture was transferred to a water bath at approximately 20 °C, the stopwatch was restarted, and another series of samples was withdrawn.

Analysis was carried out using linear temperature programming at a rate of 20 °C/min from 70 to 215 °C. The injector was at 250 °C, the detector at 350 °C. Under these conditions the following peaks and retention times were observed: 2-butene (0.7 min), 2-hexene (1.4 min), *n*-heptane (2.1 min), 4-octene (2.9 min), chlorobenzene (3.9 min), cyclooctene (4.6 min), cyclooctane impurity in the cyclooctene (4.85 min), C_{12} (7.1 min), C_{14} (8.7 min), and C_{16} (11.1 min). The *n*-heptane solvent for the MASC was used as the internal standard.

Double Cross Experiment 2. The same procedure was used here as in experiment 1 except that less 2-butene was used. The catalyst consisted of 43.2 mg of $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (0.058 mmol), 0.41 mL of MASC solution in heptane (0.33 mmol), and 1 mL of chlorobenzene. A solution of 0.339 g of *trans*-4-octene (3.03 mmol), 0.454 g of cyclooctene (4.13 mmol), 1.1 mL of chlorobenzene, and a small amount of *trans*-2-butene was prepared at 0 °C as above and added to the magnetically stirred catalyst, which was at 0 °C. The catalyst had been incubated at room temperature for 1.5 h. On mixing the stopwatch was started, and the system was isolated from the mercury bubbler to prevent evaporation of 2-butene. Three samples were withdrawn, quenched, sealed, and stored in a freezer. After 11 min the reaction was warmed at 25 °C, the stopwatch was restarted, and another series of samples was withdrawn and quenched. The analysis procedure was performed as previously, and again no reaction was apparent at 0 °C. The chromatograms of the samples withdrawn at 0 °C measured the amounts of the components, including 2-butene, before any reaction had taken place. The *n*-heptane solvent for the MASC was used as the internal standard.

Double Cross Experiment 3. A solution of MASC in heptane (1.1 mL) was placed in a small round-bottomed flask attached to a mercury bubbler. *n*-Heptane was removed with an aspirator, *n*-pentane was added under argon and stripped, and the residue redissolved in 0.95 mL of pentane forming an approximately 0.72 M solution. This solution (0.32 mL, 0.23 mmol) was added to a mixture of 28.4 mg of $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (0.038 mmol) and 1 mL of chlorobenzene forming a homogeneous brown solution. A mixture of *n*-heptane (GLC standard, 351.9 mg), cyclooctene (599 mg, 5.44 mmol, containing 4% cyclooctane), *cis*-4-octene (393.6 mg, 3.51 mmol), and 1 mL of chlorobenzene was added to about 0.2 mL of liquid *cis*-2-butene that was freshly distilled from CaH_2. A small portion of this solution was stored for analysis in a cold sealed vial, and the remainder was added by syringe at 0 °C to the catalyst, which was stirring rapidly in an ice bath. The experiment, effected at 0 °C, was analyzed much as above.

Double Cross Experiment 4. The procedure was exactly the same as for experiment 3. The catalyst was made from 28.5 mg of $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (0.038 mmol) and MASC (0.3 mL of an approximately 0.75 M solution in pentane, 0.23 mmol) in 1.1 mL of chlorobenzene. The olefin mixture consisted of *cis*-4-octene (0.419 g, 3.74 mmol), *n*-heptane (GLC standard, 0.418 g), cyclooctene (0.593 g, 5.38 mmol), chlorobenzene (1.0 mL), and a smaller amount of liquified *cis*-2-butene than in the previous experiment. The amount of 2-butene was determined by GLC.

Double Cross Experiment 5. The procedure here differs in that *n*-pentane was used as an internal standard. The catalyst consisted of 19.8 mg of $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (0.026 mmol) and MASC (0.16 ml of 0.80 M solution in heptane, 0.13 mmol) in 1.1 mL of chlorobenzene. The hydrocarbon mixture consisted of *cis*-4-octene (0.443 g, 3.95 mmol), cyclooctene (0.596 g, 5.41 mmol), *n*-pentane (0.132 g), *n*-heptane (0.287 g), and *cis*-2-butene (approximately 0.05 mL) in 1.1 mL of chlorobenzene. The amount of 2-butene was determined by GLC. GLC intensities except at zero time were measured relative to *n*-heptane; the zero-time sample was measured relative to *n*-pentane and then converted to the *n*-heptane standard by multiplying by the average *n*-pentane/*n*-heptane ratio of the other samples.

Single Cross Experiment 6. A mixture of $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (14.0 mg, 0.019 mmol) in 2 mL of chlorobenzene with 0.14 mL of MASC in heptane (0.11 mmol) under Ar formed a brown solution, which after 1 h was immersed in an ice bath. A solution of 2-hexene (0.16 g, 1.9 mmol), cyclooctene (0.21 g, 1.9 mmol), and 0.5 mL of chlorobenzene was added by syringe. The experiment was conducted much as those above.

Single Cross Experiment 7. A catalyst solution was made by combining 9.3 mg of $Mo[(C_6H_5)_3P]_2Cl_2(NO)_2$ (0.012 mmol) and MASC (0.10 mL of solution; 0.08 mmol) in 2 mL of chlorobenzene. A solution of 2-hexene (0.15 g, 1.8 mmol), cyclooctene (0.19 g, 1.7 mmol), and chlorobenzene (0.25 mL) was drawn into a 20-mL syringe; the catalyst solution, after standing at room temperature for 1 h, was cooled to about 0 °C in a salt-ice bath and then drawn into the syringe with the olefin mixture and shaken. The stopwatch was started upon mixing, and a series of samples (about 0.2 mL each) were injected into screwcap vials precharged with a drop of water, the time being recorded for each sample. The samples were analyzed as above.

Acknowledgment. The kinetics in Appendices 1-3 were analyzed with the help of David Treatman. Support was provided in part by the National Science Foundation under Grant GP30669X.

Appendix 1. Kinetics of Scheme II

One steady state condition is, for $n > 0$,

$$d[A_n]/dt = 0 = k_7([A_{n-1}] - [A_n])[Cy] - (k_1[Bu] + k_2[Oc])[A_n]$$

implying $[A_n] = k_R[A_{n-1}] = k_R{}^n[A_0]$, where

$$k_R \equiv \frac{k_7[Cy]}{k_7[Cy] + k_1[Bu] + k_2[Oc]}$$

Similarly, for $n > 0$, $[B_n] = k_R{}^n[B_0]$.

The ratio $[A_0]/[B_0]$ at the steady state can be determined from the following three equations:

$$d[A_0]/dt = 0 = k_3[C][Cy] - (k_1[Bu] + k_2[Oc] + k_7[Cy])[A_0]$$

$$d[B_0]/dt = 0 = k_4[D][Cy] - (k_1[Bu] + k_2[Oc] + k_7[Cy])[B_0]$$

$$d[C]/dt = 0 = -k_3[C][Cy] + k_1[Bu]\left(\sum_0^\infty([A_i] + [B_i])\right) - k_5[C][Oc] + k_6[D][Bu]$$

by noting

$$\sum_0^\infty([A_i] + [B_i]) = ([A_0] + [B_0])(1 + k_R + k_R{}^2 + \ldots) = [1/(1 - k_R)]([A_0] + [B_0])$$

and the definition of k_R, above.

If $k_6/k_1k_4 = k_5/k_2k_3$, discussed in the text,

$$[A_0]/[B_0] = k_1[Bu]/k_2[Oc]$$

The rate equations are

$$d[C_{12+8n}]/dt = k_1k_R{}^n[A_0][Bu]$$

$$d[C_{14+8n}]/dt = k_2k_R{}^n[A_0][Oc] + k_1k_R{}^n[B_0][Bu]$$

$$d[C_{16+8n}]/dt = k_2k_R{}^n[B_0][Oc]$$

Equation 10 follows from these and the definition of k_R.

Equation 9 follows from these and the steady state equations, since

$$\frac{d[C_{14+8n}]}{d[C_{12+8n}]} = \frac{k_2[Oc]}{k_1[Bu]} + \frac{[B_0]}{[A_0]} = \frac{2k_2[Oc]}{k_1[Bu]} = r_1$$

$$\frac{d[C_{14+8n}]}{d[C_{16+8n}]} = \frac{[A_0]}{[B_0]} + \frac{k_1[Bu]}{k_2[Oc]} = \frac{2k_1[Bu]}{k_2[Oc]} = r_2$$

$r_1 \times r_2 = 4$ follows.

Appendix 2. Kinetics of Scheme III

We assume that rotations about the olefin-metal bonds are faster than metathesis reactions.

The steady state equations are:

$$\frac{\mathrm{d}[\mathrm{A}_2]}{\mathrm{d}t} = 0 = -[\mathrm{A}_2]2k[\mathrm{Oc}] - [\mathrm{A}_2]2x^2k[\mathrm{Bu}]$$

$$+ [\mathrm{A}_2]2k[\mathrm{Oc}] + \frac{[\mathrm{A}_1]k[\mathrm{Oc}]}{2x+1} + \frac{[\mathrm{A}_1][\mathrm{Oc}]k}{x}$$

$$+ [\mathrm{A}_0][\mathrm{Oc}]\left(\frac{2k}{x}\right)\left(\frac{\ }{2x}\ \frac{\ }{\cdot\,1}\right)$$

$$\frac{\mathrm{d}[\mathrm{A}_0]}{\mathrm{d}t} = 0 = -[\mathrm{A}_0][\mathrm{Oc}]\frac{2k}{x} - [\mathrm{A}_0][\mathrm{Bu}]2xk$$

$$+ [\mathrm{A}_2][\mathrm{Bu}]2x^2k\left(\frac{x}{x+2}\right) + [\mathrm{A}_1][\mathrm{Bu}]kx^2$$

$$+ [\mathrm{A}_1][\mathrm{Bu}]kx\left(\frac{x}{x+2}\right) + [\mathrm{A}_0][\mathrm{Bu}]kx$$

The rate equations are:

$$\frac{\mathrm{d}[\mathrm{C}_{14}]}{\mathrm{d}t} = [\mathrm{A}_2][\mathrm{Bu}]\frac{4x^2}{x+2} + [\mathrm{A}_1][\mathrm{Oc}]\frac{k}{2x+1}$$

$$+ [\mathrm{A}_1][\mathrm{Oc}]\frac{k}{x} + [\mathrm{A}_1][\mathrm{Bu}]kx^2$$

$$+ [\mathrm{A}_1][\mathrm{Bu}]\frac{kx^2}{x+2} + [\mathrm{A}_0][\mathrm{Oc}]\frac{4k}{2x+1}$$

$$\frac{\mathrm{d}[\mathrm{C}_{12}]}{\mathrm{d}t} = [\mathrm{A}_1][\mathrm{Bu}]\frac{2kx}{x+2}$$

$$+ [\mathrm{A}_0][\mathrm{Oc}]\frac{2k}{x(2x+1)} + [\mathrm{A}_0][\mathrm{Bu}]2kx$$

$$\frac{\mathrm{d}[\mathrm{C}_{16}]}{\mathrm{d}t} = [\mathrm{A}_2][\mathrm{Oc}]2k$$

$$+ [\mathrm{A}_2][\mathrm{Bu}]\frac{2x^3k}{x+2} + [\mathrm{A}_1][\mathrm{Oc}]\frac{2kx}{2x+1}$$

For each experiment the equations were solved at the known values of $y = [\mathrm{Bu}]/[\mathrm{Oc}]$ and at numerous values of x. The steady state equations were solved at each point (x,y) for $R_1 = [\mathrm{A}_2]/[\mathrm{A}_1]$ and $R_2 = [\mathrm{A}_0]/[\mathrm{A}_1]$, and the rate equations, written as functions of x, y, R_1, and R_2, then gave the ratios of the initial rates of formation of C_{12}, C_{14}, C_{16} and the product $r_1 \times r_2$. The product $r_1 \times r_2$ as a function of x and y is displayed in Figure 3. Notice that, as for a related scheme,[2b] when $x = y = 1$, $r_1 = r_2 = 1.60$ and $r_1 \times r_2 = 2.56$.

Appendix 3. Kinetics of Scheme IV

We assume rotation about the olefin-metal bond to be faster than metathesis reactions.

The steady state equations are:

$$\frac{\mathrm{d}[\mathrm{A}_2]}{\mathrm{d}t} = 0 = \frac{2k_\mathrm{P}}{2x+1}[\mathrm{Hex}][\mathrm{A}_2]$$

$$+ \frac{k_\mathrm{M}}{2x+1}[\mathrm{A}_1][\mathrm{Hex}] - 2k_\mathrm{P}[\mathrm{A}_2][\mathrm{Hex}]$$

$$\frac{\mathrm{d}[\mathrm{A}_0]}{\mathrm{d}t} = 0 = \frac{k_\mathrm{P}x}{x+2}[\mathrm{A}_1][\mathrm{Hex}]$$

$$+ \frac{2k_\mathrm{M}x}{x+2}[\mathrm{A}_0][\mathrm{Hex}] - 2k_\mathrm{M}[\mathrm{A}_0][\mathrm{Hex}]$$

The rate equations are:

$$\frac{\mathrm{d}[\mathrm{C}_{16}]}{\mathrm{d}t} = \left(\frac{4x}{2x+1}\right)k_\mathrm{P}[\mathrm{A}_2][\mathrm{Hex}] + \left(\frac{x}{x+2}\right)k_\mathrm{P}[\mathrm{A}_1][\mathrm{Hex}]$$

$$\frac{\mathrm{d}[\mathrm{C}_{14}]}{\mathrm{d}t} = \left(\frac{2}{2x+1}\right)k_\mathrm{P}[\mathrm{A}_2][\mathrm{Hex}] + \left(\frac{2}{x+2}\right)k_\mathrm{P}[\mathrm{A}_1][\mathrm{Hex}]$$

$$+ \left(\frac{2x}{2x+1}\right)k_\mathrm{M}[\mathrm{A}_1][\mathrm{Hex}] + \left(\frac{2x}{x+2}\right)k_\mathrm{M}[\mathrm{A}_0][\mathrm{Hex}]$$

$$\frac{\mathrm{d}[\mathrm{C}_{12}]}{\mathrm{d}t} = \left(\frac{1}{2x+1}\right)k_\mathrm{M}[\mathrm{A}_1][\mathrm{Hex}] + \left(\frac{4}{x+2}\right)k_\mathrm{M}[\mathrm{A}_0][\mathrm{Hex}]$$

The solutions of the steady state equations are:

$$[\mathrm{A}_2]/[\mathrm{A}_1] = k_\mathrm{M}/4xk_\mathrm{P} \text{ and } [\mathrm{A}_0]/[\mathrm{A}_1] = xk_\mathrm{P}/4k_\mathrm{M}$$

Substitution into the rate equations shows that $\mathrm{d}[\mathrm{C}_{16}]/\mathrm{d}[\mathrm{C}_{12}] = 1$.

If $k_\mathrm{P}/k_\mathrm{M} = x = 1$, $\mathrm{d}[\mathrm{C}_{14}]/\mathrm{d}[\mathrm{C}_{16}] = 2.5$, but if $k_\mathrm{P}/k_\mathrm{M} = x$ is increased or decreased, $\mathrm{d}[\mathrm{C}_{14}]/\mathrm{d}[\mathrm{C}_{16}] > 2.5$. $\mathrm{d}[\mathrm{C}_{14}]/\mathrm{d}[\mathrm{C}_{16}]$ is unchanged if methyls and propyls are interchanged.

Appendix 4. Kinetics of Scheme V

The analysis is similar to that in Appendix 1. For $n > 0$,

$$\mathrm{d}[\mathrm{A}_n]/\mathrm{d}t = 0 = k_7[\mathrm{A}_{n-1}][\mathrm{Cy}] - [(k_3 + k_4)[\mathrm{Hex}] + k_7[\mathrm{Cy}]][\mathrm{A}_n],$$

implying $[\mathrm{A}_n] = k_\mathrm{R}[\mathrm{A}_{n-1}] = k_\mathrm{R}{}^n[\mathrm{A}_0]$, where

$$k_\mathrm{R} \equiv \frac{k_7[\mathrm{Cy}]}{(k_3 + k_4)[\mathrm{Hex}] + k_7[\mathrm{Cy}]}$$

Similarly, for $n > 0$, $[\mathrm{B}_n] = k_\mathrm{R}{}^n[\mathrm{B}_0]$.

The ratio $[\mathrm{A}_0]/[\mathrm{B}_0]$ at the steady state can be determined from the following three equations:

$$\mathrm{d}[\mathrm{A}_0]/\mathrm{d}t = 0 = k_1[\mathrm{C}][\mathrm{Cy}] - (k_3 + k_4)[\mathrm{A}_0][\mathrm{Hex}] - k_7[\mathrm{A}_0][\mathrm{Cy}]$$

$$\mathrm{d}[\mathrm{B}_0]/\mathrm{d}t = 0 = k_2[\mathrm{D}][\mathrm{Cy}] - (k_3 + k_4)[\mathrm{B}_0][\mathrm{Hex}] - k_7[\mathrm{B}_0][\mathrm{Cy}]$$

$$\mathrm{d}[\mathrm{C}]/\mathrm{d}t = 0 = -k_1[\mathrm{C}][\mathrm{Cy}] + k_3[\mathrm{Hex}]\sum_{i=0}^{\infty}([\mathrm{A}_i] + [\mathrm{B}_i]) - k_5[\mathrm{C}][\mathrm{Hex}] + k_6[\mathrm{D}][\mathrm{Hex}]$$

by noting

$$\sum_0^{\infty}([\mathrm{A}_i] + [\mathrm{B}_i]) = ([\mathrm{A}_0] + [\mathrm{B}_0])(1 + k_\mathrm{R} + k_\mathrm{R}{}^2 + k_\mathrm{R}{}^3 + \ldots) = ([\mathrm{A}_0] + [\mathrm{B}_0])[1/(1 - k_\mathrm{R})]$$

and the definition of k_R above.

If $k_6/k_2k_3 = k_5/k_1k_4$, discussed in the text, $[\mathrm{A}_0]/[\mathrm{B}_0] = k_3/k_4$.

The rate equations are

$$\mathrm{d}[\mathrm{C}_{12+8n}]/\mathrm{d}t = k_4k_\mathrm{R}{}^n[\mathrm{A}_0][\mathrm{Hex}]$$

$$\mathrm{d}[\mathrm{C}_{14+8n}]/\mathrm{d}t = k_3k_\mathrm{R}{}^n[\mathrm{A}_0][\mathrm{Hex}] + k_4k_\mathrm{R}{}^n[\mathrm{B}_0][\mathrm{Hex}]$$

$$\mathrm{d}[\mathrm{C}_{16+8n}]/\mathrm{d}t = k_3k_\mathrm{R}{}^n[\mathrm{B}_0][\mathrm{Hex}]$$

Equation 13 follows from these and the definition of k_R.

That the ratios of products C_{12+8n}, C_{14+8n}, and C_{16+8n} will initially be $1{:}r{:}1$ follows from the rate and steady state equations since

$$\mathrm{d}[\mathrm{C}_{16+8n}]/\mathrm{d}[\mathrm{C}_{12+8n}] = k_3[\mathrm{B}_0]/k_4[\mathrm{A}_0] = 1$$

and

$$\mathrm{d}[\mathrm{C}_{14+8n}]/\mathrm{d}[\mathrm{C}_{12+8n}] = k_3/k_4 + [\mathrm{B}_0]/[\mathrm{A}_0] = (k_3/k_4) + (k_4/k_3)$$

This latter is greater than or equal to 2, since $x + (1/x) = ((x - 1)^2/x) + 2$ and $x > 0$.

Supplementary Material Available: GLC Data Appendix listing summaries of GLC measurements (Tables 6-18) (13 pages). Ordering information is given on any current masthead page.

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Intramolecular Nucleophilic Assistance in the Hydrolysis of Sulfonate Esters: Equilibrium Constant for Sultone Formation

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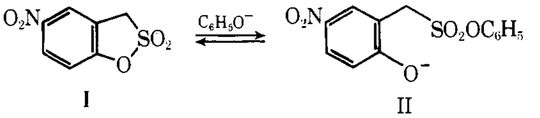
Abstract: The hydrolysis of phenyl 2-hydroxy-5-nitrophenylmethanesulfonate possesses a sigmoid pH dependence with a kinetic pK_a close to the thermodynamic value for the phenolic hydroxyl. This result is consistent with intramolecular nucleophilic participation by the hydroxyl group followed by hydrolysis of the intermediate sultone. Evidence supporting this conclusion is: (a) absence of buffer catalysis; (b) almost complete absence of a solvent deuterium oxide isotope effect; (c) a slightly positive entropy of activation; (d) the fast decomposition of the sultone compared with the observed rate constant for the sulfonate; (e) observation of an intermediate under conditions predicted from the sultone rate constant and that for the sulfonate; (f) the existence of a mass law effect on solvolyses carried out in solutions containing added phenol. The equilibrium constant for formation of the phenyl ester from sultone is 1.4×10^5 M^{-1}, which reflects the strained nature of the five-membered ring sultone. A crude estimate of the effective molarity gives a lower limit of 10^5 M, a relatively small value probably due to ring strain in the transition state of the intramolecular reaction.

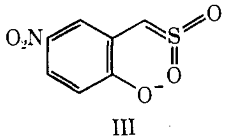
It was argued recently that the observed absence of an E1cB mechanism in the hydrolysis of sultones (I)[1] is consistent with stereoelectronic considerations.[2,3] The demonstration of nucleophilic attack on sultones[3] indicates that, by the principle of microscopic reversibility, the reverse step will also not utilize the sulfene pathway (III), although it is well established that this mechanism predominates in the alkaline hydrolysis of aryl phenylmethanesulfonates (IV).[2,4] Reference to structure III confirms that cyclization will be a difficult process, since it requires a 90° rotation about a C═S double bond.



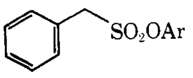
(1)

I

II



III



IV

Studies of the reverse step of eq 1 are likely to be complicated by the hydrolysis of sultone (I), which is a relatively labile species, and by a possible direct and general-base-catalyzed formation of product from II. If it is possible to measure the rate constant for the reverse step then we may estimate the