acid effects isomerization to compound B and refluxing B in xylene effects elimination of a molecule of water to give compound E. Data now at hand do not suffice for unequivocal elucidation of the structures.

Experimental Section

Preparation of the "Wichelhaus Oxide" (2-Hydroxy-3,4′-dinaphthyl-1,4,1′,2′-diquinone, 6). The following modifications in the preparation procedure of Hooker and Fieser[1] improve the yield and quality of the product.

a. The crude yellow product must be washed *absolutely* free of chloride. Mere washing of the filter cake was found to be insufficient, for material so obtained always decomposed to some extent on crystallization. Instead, the filter cake from 10 g of β-naphthoquinone is transferred to a large beaker, stirred mechanically with 300 ml of distilled water, and refiltered. This process is repeated four times, when the filtrate should be colorless. Material thus obtained is stable indefinitely, can be recrystallized almost quantitatively, and is analytically pure.

b. Crystallization is accomplished by dissolving 2 g of the above product in 300 ml of acetone, filtering, and heating the yellow solution of what appears to be a complex with 15 ml of concentrated hydrochloric acid in 250 ml of water. The solution turned orange and crystals soon began to separate. After 1 hr, the product, consisting in orange-red needles, was collected, washed with water, and dried at 110° yield; 1.9 g (95%), mp 251–253°.

Compound A (10). **a.** Hooker's procedure[1] for the air oxidation of the hydroxydiquinone **6** in alkaline solution can be replaced by the following simplified procedure with approximately the same yield. A solution of 10 g of **6** in 300 ml of 6 *N* potassium hydroxide was stirred vigorously in a stream of air until dark red (about 1 hr). The solution was chilled and acidified with 20 ml of concentrated hydrochloric acid, and a flocculent precipitate was filtered and discarded. The filtrate on standing at room temperature for 5 days deposited a first crop of product which was collected, yield 5.5 g (50%).

b. A procedure which is faster and more efficient and which gives a purer product is as follows. A 250-ml erlenmeyer flask containing a suspension of 5 g of **6** in 75 ml of acetic acid was stirred magnetically in a water bath kept at 65° and 6 ml of 30% hydrogen peroxide was added in 1-ml portions over a period of 1 hr. The mixture was stirred for 1 hr longer and then cooled. The product, which separated as a bright yellow solid, was collected, washed with acetic acid, and dried at 100°. As judged by melting point, spectrum, and analysis, it was directly pure, yield 4.5 g.

Compound A Methyl Ester (12). A suspension of 0.5 g of compound A in 50 ml of methanol was treated with 15 drops of concentrated sulfuric acid and refluxed for 1 hr, by which time a clear yellow solution had resulted. The condenser was removed and methanol allowed to distil off until the volume had been reduced to about 5 ml. The product which separated on cooling was recrystallized from methanol and gave 0.4 g of yellow crystals, mp 197° gassing.

Anal. Calcd for $C_{21}H_{14}O_7$ (378.32): C, 66.67; H, 3.73. Found: C, 66.87; H, 3.89.

Compound A Methyl Ester Acetate (13). A 0.3-g sample of the methyl ester was stirred with a solution of ten drops of concentrated sulfuric acid in 19 ml of acetic anhydride until dissolved. After standing for 1 hr at room temperature, water (25 ml) was added with vigorous stirring with cooling when required. A pale yellow crystallizate separated and was collected, washed well with water, and dried at 100°; yield 0.3 g, mp 213–214° (directly pure).

Anal. Calcd for $C_{23}H_{16}O_8$ (420.36): C, 65.71; H, 3.84. Found: C, 65.43; H, 3.37.

Olefin Metathesis. I. Acyclic Vinylenic Hydrocarbons[1]

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Contribution No. 396 from the Research Division, The Goodyear Tire and Rubber Company, Akron, Ohio 44316. Received January 30, 1968

Abstract: Olefin metathesis is a new reaction of olefins and is effected by catalysts derived from WCl_6, C_2H_5OH, and $C_2H_5AlCl_2$. The major product from the metathesis of 2-butene with 2-butene-d_8 was $C_4H_4D_4$ which supports a scheme of interchange of alkylidene groups. The reaction mixture from the metathesis of 2-pentene with 6-dodecene contained all six olefins predicted by the proposed transalkylidenation scheme, and the absence of other olefins indicated that side reactions involving double-bond migration do not occur. The random statistical composition attainable in these reactions indicates that they are essentially thermoneutral, *i.e.*, entropy controlled. *cis–trans* equilibria are attained as a consequence of the transalkylidenation step itself which is relatively nonselective in the formation of geometrical isomers. A three-step sequence is proposed involving bisolefin–metal complex formation, transalkylidenation, and olefin exchange.

Recently, a new catalytic process was disclosed[2,3] whereby vinylenic olefins, when treated with a catalyst combination of WCl_6, C_2H_5OH, and $C_2H_5AlCl_2$, undergo a unique metathetic transformation.

$$2R_1CH{=}CHR_2 \rightleftharpoons R_1CH{=}CHR_1 + R_2CH{=}CHR_2 \qquad (1)$$

It was found that this reaction, designated olefin metathesis, proceeds rapidly under mild conditions and provides a highly effective means of interchanging alkylidene species.

A somewhat related process, designated olefin dismutation or disproportionation, has been reported[4,5] wherein at elevated temperatures the isomerization and disproportionation of olefins over solid bed, mixed metal oxide catalysts leads to a series of homologous products of lower and higher molecular weights. For the particular dismutation of propylene to form ethylene and 2-butene good selectivity was attainable with equilibrium apparently established among the ethylene, propylene, and butene components of the system. When the dismutation of higher olefins was attempted,

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(1) Presented in part before the Division of Organic Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstracts, S172.

(2) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Letters*, 3327 (1967).

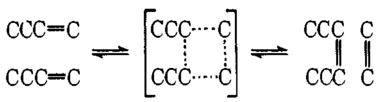
(3) *Chem. Eng. News*, **45**, 51 (Sept 25, 1967).

(4) R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 170 (1964).

(5) C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catalysis*, **7**, 269 (1967).

however, product composition was found to be quite variable, and it was necessary to interpret results in terms of two competing processes: double-bond migration and disproportionation.

For the disproportionation step, Bradshaw and coworkers[5] have conceived a route which involves a "quasicyclobutane" intermediate which they illustrated as shown in eq 2 for 1-butene.



$$\begin{matrix}\text{CCC=C}\\ \text{CCC=C}\end{matrix} \rightleftharpoons \left[\begin{matrix}\text{CCC}\cdots\text{C}\\ \vdots\qquad\vdots\\ \text{CCC}\cdots\text{C}\end{matrix}\right] \rightleftharpoons \begin{matrix}\text{CCC}\ \ \text{C}\\ \|\qquad\|\\ \text{CCC}\ \ \text{C}\end{matrix} \qquad (2)$$

Although metathesis (or exchange) reactions have been classified among redistribution reactions,[6] the term "redistribution reaction" has been more recently applied specifically to reorganization processes involving substituents about a given central atom or moiety,[7,8] frequently with the added criterion that these reactions should approach equilibrium. Such reactions are common in organometallic and inorganic chemistry, and methods of evaluating these systems have been well established. For hydrocarbons, however, thermodynamically controlled redistribution reactions at room temperature are virtually unknown due to the absence of an accessible, low-energy reaction pathway. Therefore, the olefin metathesis reaction is of special interest since it possesses the basic features of a redistribution reaction. Accordingly, redistribution theory appears well suited for describing product mixtures obtained *via* olefin metathesis reactions.

Often when similar substituents are interchanged about a given central atom or moiety, there is no bond energy contribution to the free energy of the process, and the reaction is said to be thermoneutral. The equilibrium distribution of products will then be virtually random as dictated by entropy requirements. However, substantial enthalpy contributions have been observed in the redistribution of polar species such as dialkylamino and halogen groups about trivalent phosphorus,[9] for example, and the deviation of these systems from randomness is a measure of the enthalpy contribution. The results reported previously[2] for the metathesis of 2-pentene suggested the metathesis reaction to be virtually thermoneutral.

It is desired here to demonstrate the following general features of the olefin metathesis reaction as applied to acyclic vinylenic olefins: (1) the reaction proceeds *via* scission of the olefinic bond, *i.e.*, it may be considered to be a transalkylidenation process; (2) redistribution of alkylidene moities leads to a random distribution of products; (3) the transalkylidenation process itself affords mixtures of *cis* and *trans* isomers from pure *cis* or *trans* starting olefins; (4) the *cis–trans* composition is the thermodynamically favored composition at equilibrium. In addition, some views regarding the mechanism will be presented, because the theoretical implications are considered to be quite significant.

Although the present paper is concerned with the fundamental aspects of the metathesis reaction as applied to linear vinylenic olefins, many ramifications of the reaction are of considerable interest. The facile synthesis of higher molecular weight olefins is possible, where the position of the double bond can be readily defined. Of special interest is the application of the metathesis reaction to cycloolefins. The catalyst system comprised of $C_2H_5AlCl_2$ and WCl_6 has been already reported[10] to be highly active in the ring-opening polymerization of a variety of cycloolefins. A detailed analysis of these systems, which lead to the formation of homologous series of macrocyclic species, will be treated separately.[11]

Experimental Section

Materials and Procedures. Benzene (reagent grade), employed as the reaction solvent, was dried over Na and then passed over silica gel desiccant under a N_2 atmosphere prior to use. WCl_6 (Climax Molybdenum Co.) was purified by sublimation of the more volatile contaminant, $WOCl_4$, under a stream of lamp-grade N_2 at about 200°, leaving a residue of quite pure WCl_6. $C_2H_5AlCl_2$ (Texas Alkyls, Inc.) was obtained as a 25% solution in hexane.

The following catalyst solutions were prepared under inert N_2 atmosphere: (I) 0.05 *M* WCl_6 in benzene, to which had been added an equimolar amount of absolute ethanol; and (II) 0.20 *M* $C_2H_5AlCl_2$ in benzene (contains residual hexane from master solution).

Reactions were all carried out under N_2 in 2-oz or 4-oz screw-cap bottles sealed with self-sealing gaskets and Teflon liners. The catalyst components were injected into reaction mixtures by hypodermic syringes, with component I added first, followed immediately by component II. The olefins were commercial reagent grade (unless otherwise specified) and were freshly distilled before use.

Metathesis Reactions with 2-Butene-*d*$_8$. The reaction apparatus is illustrated in Figure 1. Reservoir A contained 1 l. (2.85 g) of 2-butene-*d*$_8$ (isotopic purity 98%, supplied by Merck Sharp and Dohme). The apparatus was attached *via* stopcock a to a vacuum pump and was dried by flaming thoroughly. Stopcock a was then closed and gaseous C_4D_8 was distributed throughout the system by opening stopcocks b and c. Estimation of the amount of C_4D_8 transferred to B was based on the relative volumes of A and B. The reactor was then sealed and sufficient 2-butene (as a dilute solution in benzene) was injected *via* septum d to give an approximately 3:1 ratio of C_4H_8:C_4D_8. Mass spectroscopic analysis of a vapor sample prior to reaction indicated a molar ratio of C_4H_8:C_4D_8 = 74:26. The mixture was treated with 0.25 ml of catalyst component I ($WCl_6 + C_2H_5OH$) followed by 0.5 ml of component II ($C_2H_5AlCl_2$). After several minutes a sample of the vapor was withdrawn for mass analysis.

In a similar fashion, 2-butene-*d*$_8$ was treated with 3-hexene. The product mixture was fractionated by preparative glpc and the fraction corresponding to 2-pentene was analyzed by high-resolution mass spectroscopy.

Metathesis of 2-Pentene with 6-Dodecene. Three series of reactions were conducted at three different 2-pentene:6-dodecene initial charge ratios, with four runs in each series. Two master solutions were prepared and dried by passing over silica gel: 1.0 *M* 6-dodecene in benzene containing 20.0 g l.$^{-1}$ of *n*-decane as the glpc standard, and 0.97 *M* 2-pentene, also containing 20.0 g l.$^{-1}$ of *n*-decane. 6-Dodecene was obtained from the metathesis of 2-octene and was 99% pure by glpc analysis. 2-Pentene was Phillips pure grade, 99 mol % (mixed isomers).

For each series of reactions, appropriate volumes of the two master solutions (5.0, 10.0, or 15.0 ml) were combined to give 20.0 ml of solution, 1.0 *M* in total olefin. Four catalyst levels were employed for each set of olefin charge ratios (see Table II). After 3 min at room temperature, reactions were terminated with 0.25 ml of methanol. Quantitative glpc analyses were obtained using a 20-ft silicone gum rubber column (flame ionization detector). *cis*:*trans* olefin ratios were obtained with a 25-ft tris(2-cyanoethoxy)-propane column. All peaks in the chromatograms of the reaction

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(6) G. Calingaert and H. A. Beatty, "Organic Chemistry. An Advanced Treatise," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1950, p 1806.

(7) J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).

(8) K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 802 (1964).

(9) J. R. Van Wazer and L. Maier, *ibid.*, **86**, 811 (1964).

(10) N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polymer Sci.*, *A1*, **5**, 2209 (1967).

(11) K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, Division of Industrial and Engineering Chemistry, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, L54; Advances in Chemistry Series, in press.

mixtures were identified by comparison of retention times for known materials, with the exception of 3-nonene (its identity was presumed).

cis–trans **Equilibria.** A series of metathesis experiments of each of the following olefins (each 1.0 *M*, in benzene at room temperature) were run over a range of catalyst levels: *cis*-2-butene, *cis*-2-pentene, *trans*-2-pentene, *trans*-2-hexene, 2-heptene (mixed isomers), 3-heptene (mixed isomers), and *trans*-5-decene. The range of catalyst concentrations varied for each olefin, but in all cases it was sufficient to establish that constancy in the *cis*:*trans* composition of reacted mixtures had been attained (generally, $2 \times 10^{-4} \leq WCl_6 \leq 2 \times 10^{-3}$ *M*). Reactions were terminated with methanol after a few minutes at room temperature and were analyzed by glpc.

cis- **and** *trans*-**2-Pentene.** *cis*-2-Pentene (Phillips technical grade) contained 4% *trans*-2-pentene and 1.5% 2-methyl-2-butene. Solutions of either *cis*-2-pentene or *trans*-2-pentene (Phillips pure grade, 99 mol %) in benzene, containing pentane as the glpc internal standard, were dried by passing through a silica gel column. Solutions charged to reaction bottles were sparged briefly with dry N_2. All reactions were carried out at room temperature and terminated with 1 ml of a 5% solution of triisopropanolamine in methanol. Analytical data were obtained by glpc using either a 50-ft Igepal column or a 25-ft tris(2-cyanoethoxy)propane column. The pertinent data are recorded in Table IV.

Results

Catalyst Composition. The catalyst system of $C_2H_5AlCl_2$ and the reaction product from WCl_6 and ethanol is one of the most active combinations for the olefin metathesis reaction. A less active catalyst is obtained in the absence of ethanol. None of the above components was active by itself as a metathesis catalyst or produced double-bond isomerization under the present experimental conditions.

In order to standardize results, the catalyst atomic ratio of 4:1:1 for Al:W:O was adopted (except where otherwise noted). A wide range of Al:W ratios may be tolerated, but the 4:1 ratio was selected as it has been consistently very active. It was necessary to establish the optimum catalyst concentration for each set of experiments separately. As with most processes which are promoted by coordination catalysts, the catalytic activity was quite sensitive to traces of contaminants, and, consequently, variations in the optimum catalyst level among different sets of experiments were observed.

2-Butene with 2-Butene-d_8. Treatment of a mixture of 2-butene and 2-butene-d_8 (C_4H_8:C_4D_8 = 76:24) with the metathesis catalyst afforded only one new species, and that had a mass of 60. The partial mass spectrum of a vapor sample taken from the reaction vessel is given in Table I. The spectra of pure C_4H_8 and C_4D_8 were determined separately in order to eliminate the fragmentation products of these materials from the relative intensity data given in this table.

Table I. Principal Ions in the Mass Spectra of the (C_4H_8 + C_4D_8) Reaction Product

m/e	Assignment	Rel intensity, %[a]	Theory[b]
56	C_4H_8	100	100
58	$C_4H_6D_2$	<1	0
59	$C_4H_5D_3$	<1	0
60	$C_4H_4D_4$	61	63
61	$C_4H_3D_5$	<1	0
62	$C_4H_2D_6$	<1	0
64	C_4D_8	11	10

[a] Values were adjusted by eliminating background spectra of the C_4D_8 and C_4H_8 fragmentation components. [b] Based on a random distribution of CH_3CH= and CD_3CD= moities for C_4H_8:C_4D_8 = 76:24.

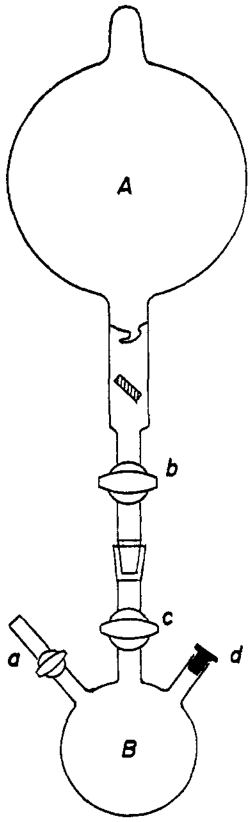


Figure 1. Apparatus for metathesis experiments with C_4D_8.

2-Butene-d_8 with 3-Hexene. When a mixture of 2-butene-d_8 and 3-hexene was treated with the metathesis catalyst, the mass spectrum of the vapor above the reaction mixture indicated the formation of essentially one new product, and this had a mass of 74. Quantitative analysis of the entire vapor sample was not attempted due to the marked differences in volatility of the various components. However, analytical glpc confirmed the presence of *cis*- and *trans*-2-pentenes in the mixture. A sample of this 2-pentene was isolated by preparative glpc, and high-resolution mass spectroscopic analysis indicated a parent mass of 74.1031 (theory for $C_5H_6D_4$ = 74.1033).

2-Pentene with 6-Dodecene. Three series of mixtures of 2-pentene and 6-dodecene (1.0 *M* in total olefin) were treated with the metathesis catalyst. Reaction mixtures were conveniently analyzed by glpc. The chromatograms indicated a very selective reaction for the formation of 2-butene, 2-pentene, 3-hexene, 2-octene, 3-nonene, and 6-dodecene, as seen in a typical chromatogram presented in Figure 2. The experimental conditions and analytical results are summarized in Table II, including the predicted product distributions based on a random distribution of alkylidene fragments (see Discussion).

It was necessary to establish that the equilibrium which was observed in the metathesis reaction was independent of the catalyst concentration. At each of three different initial olefin charge ratios, four separate experiments at different catalyst levels were conducted. The relative constancy of equilibrium constants, K_1 and K_2 in Table II, indicates that an equilibrium was reached in each experiment in which reaction was observed. While the differences between the average

Table II. Metathesis of 2-Pentene with 6-Dodecene

Expt no.	$[WCl_6 + C_2H_5OH]^b \times 10^4$, M	$[C_5]_0$, M	$[C_{12}]_0$, M	Mole fraction after reaction[c] f_4	f_5	f_6	f_8	f_9	f_{12}	Equilibrium constants[d] K_1	K_2	% *cis* C_4	C_5	C_6	C_8	C_9	C_{12}
1	3.75	0.73	0.25	0.123	0.252	0.138	0.177	0.174	0.0665	0.267	1.82	29	20	15	22	17	15
2	5.00	0.73	0.25	0.115	0.230	0.136	0.167	0.182	0.0645	0.296	2.05	29	21	15	21	16	19
3	6.25	0.73	0.25	0.107	0.227	0.133	0.166	0.187	0.0700	0.276	1.95	29	21	15	22	15	19
4	7.50	0.73	0.25	0.084	0.189	0.116	0.143	0.157	0.0620	0.273	1.91	Not determined					
Theory 1-4[a]		...		0.138	0.276	0.138	0.190	0.190	0.0655	0.250	2.00	..	..	..	..	..	..
5	3.75	0.485	0.50	No reaction													
6	5.00	0.485	0.50	0.056	0.115	0.064	0.240	0.244	0.256	0.271	1.99	28	21	14	22	15	17
7	6.25	0.485	0.50	0.047	0.097	0.057	0.198	0.219	0.230	0.285	1.94	28	21	14	21	15	19
8	7.50	0.485	0.50	0.052	0.108	0.061	0.213	0.224	0.247	0.272	1.79	..	24	13	21	17	17
Theory 5-8		...		0.061	0.121	0.061	0.250	0.250	0.258	0.250	2.00	..	..	..	..	..	..
9	3.75	0.24	0.75	No reaction													
10	5.00	0.24	0.75	No reaction													
11	6.25	0.24	0.75	0.015	0.030	0.017	0.171	0.173	0.548	0.283	1.80	28	24	13	21	16	16
12	7.50	0.24	0.75	0.013	0.028	0.016	0.163	0.163	0.531	0.265	1.68	Not determined					
Theory 9-12		...		0.015	0.030	0.015	0.184	0.184	0.571	0.250	2.00	..	..	..	..	..	..

[a] For determination of theoretical values of f_n see Discussion. [b] All reactions conducted at Al:W = 4. [c] Values of f_n were calculated as the fraction of each olefin relative to the total initial molar concentrations, $[C_5]_0 + [C_{12}]_0$ (f_n = mole fraction of C_nH_{2n}). [d] $K_1 = f_4f_6/f_5^2$; $K_2 = f_8f_9/f_5f_{12}$.

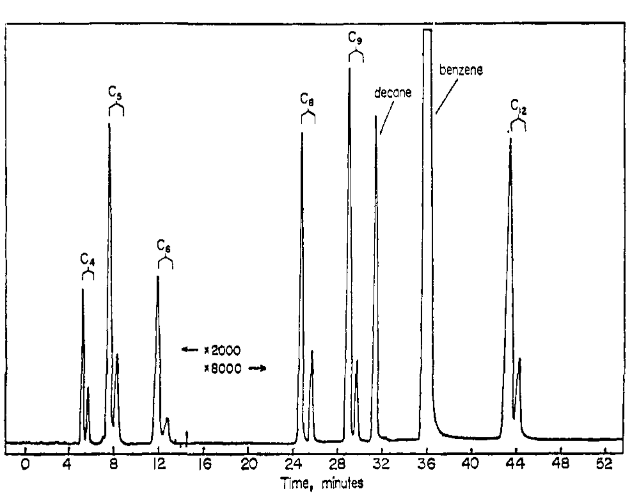


Figure 2. Chromatogram of reaction mixture 6, Table II. Conditions: 25-ft TCEP column, operated for 10 min at 20°, then programmed at 4°/min heating rate. *trans* peak precedes *cis* for each olefin.

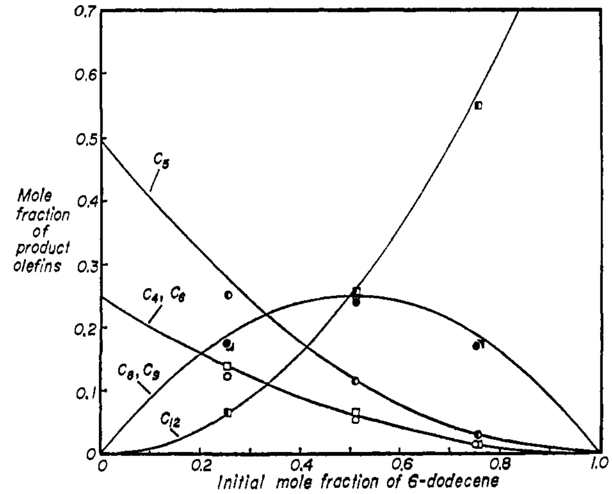


Figure 3. Metathesis of 2-pentene with 6-dodecene. Solid lines represent theory for ideal random composition: (○) C_4, 2-butene; (◐) C_5, 2-pentene; (□) C_6, 3-hexene; (●) C_8, 2-octene; (■) C_9, 3-nonene; (◧) C_{12}, 6-dodecene. Data taken from experiments 1, 6, and 11, Table II.

values of $K_1 = 0.276$ and $K_2 = 1.88$ and their theoretical (thermoneutral) values of 0.25 and 2.00, respectively, are real at a 99% confidence level, K_1 and K_2 are nevertheless sufficiently close to their theoretical values to conclude that these reactions closely approach thermoneutral conditions required for an ideal random distribution of reactants. The constants K_1 and K_2 have been calculated assuming the components were present at their equilibrium *cis–trans* compositions. The data also allow calculating equilibrium constants for either the all-*cis* or the all-*trans* components with the following resultant average values: $K_{1,cis} = 0.270$, $K_{1,trans} = 0.271$, and $K_{2,cis} = 1.76$, $K_{2,trans} = 1.97$. These values also indicate that these reactions approach thermoneutrality.

It was observed that the concentration of each olefin decreased slightly with increasing catalyst level. This has been associated with relatively slow side reactions which lead to some oligomerization of the olefins and alkylation of the benzene solvent. The relative rate of loss of the various olefins due to side reactions was dependent on the location of the double bond, and the relative loss decreased in the order: 2-butene > 2-alkene > 3-alkene > 6-alkene. The formation of olefinic products which might result from double-bond migration in the various components of the system was not observed.

A comparison of the observed product distributions with the theoretical values given in Table II suggests that, in each series of reactions, the lowest catalyst level which was sufficient to cause a reaction was, at the same time, sufficient to afford equilibrium in the metathesis process. The *cis* content of each olefin in the system further indicated that equilibrium had been attained. In fact, it was observed in a detailed study of the metathesis of 2-pentene that the redistribution process apparently proceeds at a slightly faster rate than the isomerization (see below). Therefore, the results from experiments 1, 6, and 11 (which were the most selective and gave the highest recovery of olefins) were compared in Figure 3 with curves which represent the product distribution for the case of an ideal random distribution. The coincidence of the experimental points with theory is excellent.

Table III. Equilibrium Isomer Content from Metathesis Reactions

Starting olefin[a]	% *cis* content of olefin in equilibrated mixture[b] 2-Butene	2-Pentene	2-Hexene	3-Hexene	2-Heptene	3-Heptene	4-Octene	5-Decene
cis-2-Butene	28	..	..	..	..	..	..	..
cis-2-Pentene	29	18	..	13	..	..	..	..
trans-2-Pentene	28	20	..	15	..	..	..	..
trans-2-Hexene	25	..	19	..	..	..	16	..
2-Heptene[c]	27	..	..	..	21	..	..	18
3-Heptene[c]	..	..	..	14	..	15	17	..
trans-5-Decene	..	..	..	..	..	..	..	17

[a] 1 *M*, in benzene at ~25°. [b] Estimated accuracy ±2%. [c] Mixed isomers.

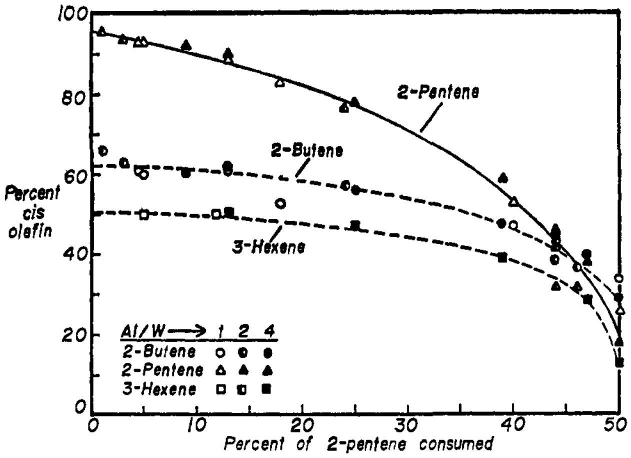


Figure 4. Metathesis of *cis*-2-pentene. Data from Table IV.

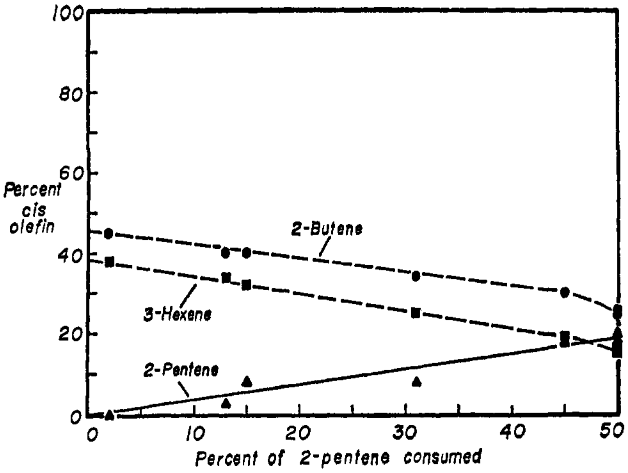


Figure 5. Metathesis of *trans*-2-pentene. Data from Table IV.

cis–trans **Equilibria.** The per cent *cis* contents observed for several vinylenic olefins in the presence of an olefin metathesis catalyst are recorded in Table III.

Steric Course of the Reaction. The steric course of the metathesis reaction for pure *trans*- and *cis*-2-pentenes was investigated. The isomer composition of the initially formed 2-butene and 3-hexene is of particular interest. A kinetic approach to the reaction was not used, since the present catalyst system exhibits a tendency for loss of activity with time. It was found more practical to vary the catalyst level incrementally for a series of reactions, keeping reaction time constant, in order to obtain reaction product mixtures which covered the entire range of conversion of starting olefin. In addition, the effect of different Al:W ratios was examined. The pertinent data and results from metathesis reactions starting with *cis*- or *trans*-2-pentene are included in Table IV. The changes in composition of each component *vs.* conversion for the *cis*- and *trans*-2-pentenes are plotted in Figures 4 and 5, respectively.

It was evident that substantial amounts of both *cis* and *trans* isomers of 2-butene and 3-hexene are formed at the outset, whereas the composition of the residual 2-pentene very gradually approached its equilibrium *cis* content. It was also observed that the initially formed butene and hexene were somewhat higher in *cis* content than the equilibrium values for these olefins, regardless of the structure of the initial pentene. In addition, the *cis*:*trans* isomer ratio of the 2-butene was always different from that of 3-hexene over the entire range of conversions. Finally, the steric course of the reaction was independent of the Al:W ratio for 1 ≤ Al:W ≤ 4.

Table IV. Metathesis of *cis*- and *trans*-2-Pentenes[a]

Expt no.[b]	[WCl_6 + C_2H_5OH] × 10^4, *M*	Al:W	Olefin yield, % C_4	C_5	C_6	% *cis* C_4	C_5	C_6
I-1	0.36	2	0.5	100	0.4	66	96	..
I-2	0.36	2	1.4	97	1.3	63	94	..
I-3	0.72	1	2.9	95	3.0	61	93	..
I-4	0.36	4	4.5	91	4.4	61	91	..
I-5	0.45	2	12.5	76	12.6	57	77	..
I-6	0.90	2	22.1	57	22.3	43	42	..
I-7	0.45	2	23.4	54	23.2	37	32	..
I-8	0.90	1	23.9	47	24.1	34	26	..
II-1	0.80	1	1.6	95	1.4	60	93	50
II-2	0.41	4	6.2	87	6.0	62	90	50
II-3	0.94	1	6.3	87	6.0	62	89	50
II-4	0.94	1	8.8	82	8.7	53	83	..
II-5	0.54	4	12.2	75	12.1	56	78	47
II-6	0.67	4	18.6	61	19.0	48	59	39
II-7	1.07	1	19.6	60	19.7	47	53	..
II-8	0.94	4	21.8	53	22.0	40	38	28
II-9	0.94	4	24.9	50	25.0	29	18	13
III-1	1.70	4	1.4	98	1.5	45	0.1	38
III-2	1.86	4	2.3	87	2.9	40	8.5	34
III-3	2.02	4	8.0	85	8.8	40	3.2	32
III-4	2.54	4	17.4	69	18.2	34	8.3	25
III-5	3.40	4	20.8	55	21.9	30	18	19
III-6[a]	3.40	4	21.6	50	23.9	29	18	16
III-7[a]	4.25	4	21.1	45	24.3	28	20	15

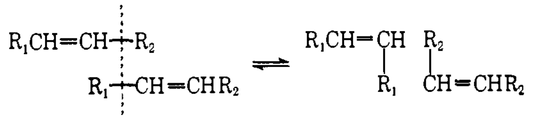
[a] All reactions run for 20 sec at room temperature except III-6 (60 sec) and III-7 (120 sec). [b] Reagent: series I, [*cis*-2-pentene]$_0$ = 1.04 *M*; series II, [*cis*-2-pentene]$_0$ = 1.08 *M*; series III, [*trans*-2-pentene]$_0$ = 1.06 *M*. Series I and II also contained some *trans*-2-pentene (~0.04 *M*) initially.

Discussion

The olefin metathesis reaction is capable of a high degree of selectivity for certain products.[2] The only new products observed in the metathesis of 2-pentene were 2-butene and 3-hexene, and the molar ratio of the olefins in the reaction mixture was found to be essentially 1:2:1 for butene:pentene:hexene.[2]

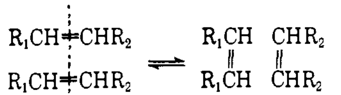
Two simple exchange processes are visualized which could restrict the product mixture to the observed one. The first, a transalkylation scheme (eq 3), formally involves the interchange of alkyl groups *via* scission α to the double bond. The second scheme (eq 4), involving cleavage of the double bond itself as a means of redistributing alkylidene species, would also yield the observed product mixture.

Transalkylation[12]



(3)

Transalkylidenation



(4)

Experiments with deuterated olefins were designed to distinguish between the relative contributions of transalkylation and transalkylidenation mechanisms to the olefin metathesis reaction. Anticipated products for the transalkylation and transalkylidenation schemes are presented in Table V for the metathesis reaction of 2-butene with 2-butene-d_8. The only new product formed in this reaction had a mass of 60, corresponding to $C_4H_4D_4$ (Table I). This result positively eliminates a simple transalkylation mechanism as depicted in eq 3 as being a significant contributor to the olefin metathesis reaction. The observed product is entirely consistent with a transalkylidenation mechanism. A similar conclusion was drawn from the results of the metathesis reaction of 2-butene-d_8 with 3-hexene, since the new product of mass 74 ($C_5H_6D_4$) is readily accounted for by a transalkylidenation process but not by a transalkylation route.

Table V. Anticipated Products from 2-Butene with 2-Butene-d_8

Mechanism	Anticipated products	Mass
Transalkylation (eq 3)	$CH_3CH{=}CHCH_3$	56
	$CH_3CD{=}CDCH_3$	58
	$CH_3CH{=}CHCD_3$	59
	$CH_3CD{=}CDCD_3$	61
	$CD_3CH{=}CHCD_3$	62
	$CD_3CD{=}CDCD_3$	64
Transalkylidenation (eq 4)	$CH_3CH{=}CHCH_3$	56
	$CH_3CH{=}CDCD_3$	60
	$CD_3CD{=}CDCD_3$	64

An alternative, albeit remote, accounting of the observations in these deuterium tracer experiments could be based on a combination transalkylation–transprotonation mechanism, *i.e.*, each time two alkyl groups interchange, two hydrogens must also interchange. Tagged carbon experiments would allow distinguishing between this more complicated mechanism and the simpler transalkylidenation one suggested here.

Metathesis reactions have usually been described as $AB + CD \rightleftharpoons AD + CB$ processes. However, a much wider variety of products is conceivable, including AA, AC, BB, BD, CC, and DD, but these are seldom observed in redistribution processes as a consequence of the bond polarity usually found between the interchangeable constituents. However, in the olefin metathesis reaction, where no such element of bond polarity exists, a general redistribution process does indeed occur. Furthermore, bond energy values do not differ substantially between the various components in the system; thus entropy considerations should dominate the reaction.[7] Thus, it was to be expected that a redistribution process such as the present one would be essentially thermoneutral and afford a statistical distribution of products, and indeed this appears to be the case.

In the particular case of the metathesis of 2-pentene, the product mixture corresponded to a random distribution of ethylidene and propylidene moieties.[2] Likewise, the composition of the 2-butene mixture from the reaction of C_4H_8 with C_4D_8 also conformed to a random distribution of alkylidene moieties (Table I). However, to establish the general nature of this redistribution process under conditions where the relative amounts of each alkylidene constituent were varied, the metathesis of 2-pentene with 6-dodecene was carried out. A general method of predicting equilibrium product mixtures which arise from a random interchanging of parts has been described by Calingaert and Beatty.[13] Their method was employed in the determination of the theoretical curves of Figure 3 and the theoretical values which are listed in Tables I and II.

Three types of alkylidene species are available for redistribution in the metathesis of 2-pentene with 6-dodecene; thus six different combinations are possible. The anticipated components are: 2-butene, 2-pentene, 3-hexene, 2-octene, 3-nonene, and 6-dodecene. The pertinent data are presented in Table II. Figure 3 demonstrates the agreement of the experimental results with theory assuming a general random redistribution process. The selectivity of the reaction for the six anticipated components is well above 90% for reactions conducted at the proper catalyst level, and the relative amount of each component at equilibrium agrees well with the predicted values based on a random redistribution process. Thus, it is demonstrated that the transalkylidenation step is primarily an entropy-controlled process and may be regarded essentially as a thermoneutral reaction. Obviously, there must be some enthalpy contributions which originate in the differences in energy content of the *cis* and *trans* configurations of the olefins to the over-all reaction thermodynamics, and this is expressed in the nonrandom *cis–trans* distributions of the various olefins. Metathesis mixtures derived from olefins containing bulkier alkyl groups, where steric effects are possible, or aromatic groups where conjugation effects are present, may exhibit measurable deviations from randomness, and future work will deal with this aspect of the reaction.

To characterize the metathesis reaction more fully, the effect of catalyst on the *cis* and *trans* isomer content of reaction mixtures was studied. Three conclusions were drawn from the results of Table III and Figures 4 and 5: (a) the isomer content of reaction mixtures can

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(12) A four-centered mechanism is not necessarily implied here.

(13) G. Calingaert and H. A. Beatty, *J. Am. Chem. Soc.*, 61, 2748 (1939).

attain thermodynamic equilibrium, (b) the metathesis reaction is not highly selective in the formation of geometrical isomers, and (c) the metathesis reaction is the principal means of geometrical isomerization.

Equilibrium values of the *cis* and *trans* contents were determined for several different olefins, as well as for the olefins which were formed in a given system as a consequence of the metathesis reaction. The results in Tables II and III indicate that the equilibrium *cis* content for a given olefin is independent of the structure of the initial olefin, catalyst concentration, and the presence of other olefins in the system. Comparable equilibrium values were observed above for the *cis* content of each olefin which was formed in the metathesis of 2-pentene and 6-dodecene, and it appears that the catalyst's capability of promoting the attainment of *cis–trans* equilibria in vinylenic olefins is general.

Table VI lists the average per cent *cis* content and free energy change for the *trans*-to-*cis* transformation for the olefins of Tables II and III. These values have a distinct correlation with steric factors in the structure of the olefins as might be expected. 2-Butene, which has only two methyl groups as substituents on the vinylenic double bond, has the highest *cis* content and hence lowest free energy difference between *trans* and *cis* forms. The 2-alkenes, which have one methyl group and one higher *n*-alkyl group as substituents on the vinylenic double bond, have a *cis* content of about 21% which corresponds to the *trans* isomer being more stable by about 800 cal/mol. The 3-, 4-, 5-, or 6-alkenes, in which both substituents on the vinylenic double bond are higher *n*-alkyl groups, have a *cis* content of about 16% which corresponds to a free energy difference between *trans* and *cis* forms of about 1 kcal/mol.

Table VI. Equilibrium *cis* Content of Vinylenic Olefins

Olefin	% *cis*[a]	ΔF, cal/mol[b]
2-Butene	28	560
2-Pentene	21	790
2-Hexene	19	870
2-Heptene	21	790
2-Octene	21	780
3-Hexene	14	1090
3-Heptene	15	1040
3-Nonene	16	1000
4-Octene	17	970
5-Decene	18	930
6-Dodecene	17	940

[a] Average value to the nearest per cent. [b] Free energy change at 25° for *trans* $\rightleftharpoons$ *cis* reaction in benzene. Average value to the nearest 10 cal/mol.

A detailed examination was made of the isomeric composition of the components present throughout the course of the metathesis of pure *cis*- or *trans*-2-pentene, with a view to determining the steric course of the reaction. The occurrence of considerable amounts of both geometrical isomers of 2-butene and 3-hexene during the initial stages of the reaction, in the absence of extensive isomerization of residual 2-pentene (Figures 4 and 5), demonstrates that the metathesis reaction is not highly selective in the formation of geometrical isomers and also that the metathesis reaction itself is the principal means of geometrical isomerization.

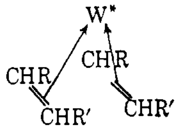
Since olefin isomerization processes are promoted by a variety of catalysts, it was desirable to determine whether any secondary reaction initiated by a catalyst component was involved. Preliminary tests appeared to rule out this possibility. The individual components of the catalyst, and the combinations, WCl_6 + ethanol and $C_2H_5AlCl_2$ + ethanol, were found to be essentially inactive under the usual metathesis reaction conditions. In addition, the steric course of the reaction was independent of the molar ratio of the catalyst components (Figure 4).

Although the present metathesis catalyst is not highly stereoselective, it does exhibit a moderate degree of selectivity during the early stages of the reaction. Regardless of the structure of the starting 2-pentene, the initially formed butenes and hexenes are somewhat higher in *cis* content than the equilibrium values for these olefins. Also, the *cis* isomer content of the 2-butene was always higher than that of the 3-hexene. This last result probably reflects slight differences in steric effects in the transition state due to the difference in the steric requirements of the methyl and ethyl groups.

Mechanism. The mode of bond scission which was observed in the metathesis of 2-butene-d_8 with the other olefins is very suggestive of a four-center transition state. In fact, for the possibly related process called olefin dismutation (or disproportionation), Bradshaw and coworkers[5] proposed a "quasicyclobutane" intermediate (eq 2), although they admitted the lack of detailed knowledge to support such an intermediate. We also recognize a need to characterize more fully the structure of the active species of the metathesis catalyst described herein. However, the results of the present work, when taken in conjunction with several recent observations by others regarding the properties of olefin–metal complexes, make plausible the following interpretation of the essential details of the metathesis reaction. The three processes which are proposed as essential are depicted in eq 5–7.

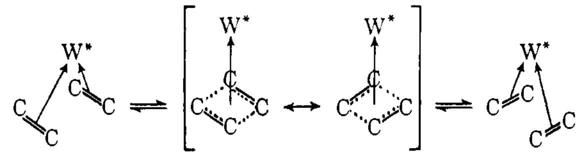
Bisolefin–Metal Complex Formation[14]

$WCl_6 + C_2H_5OH + C_2H_5AlCl_2 + 2RCH{=}CHR' \longrightarrow$



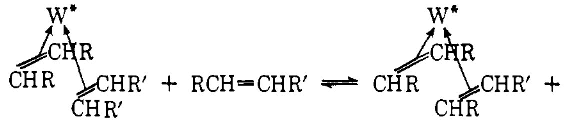
(5)

Transalkylidenation



(6)

Olefin Exchange



$R'CH{=}CHR'$ (7)

To account for the high catalytic activity of the system, alternating transalkylidenation and olefin exchange steps must occur at a very rapid rate.

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(14) The notation W* is used here because the composition of the remaining ligands about the coordination sphere is not elucidated as yet. For example, the ultimate fate of the ethanol is unknown. In addition, the participation of Al in the complex in strongly suspected, and this could occur through a μ-chloride bridge to the W.

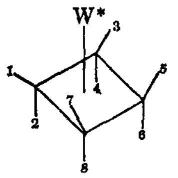

Figure 6.

The properties of olefin–transition metal complexes have been the focus of considerable attention. The nature of the olefin–metal bond is generally accepted as comprising a σ-bond element and a π-type "back bond."[15] The formation of such a complex is thought to be involved here in the initial step which results from the interaction of W^{VI} with $C_2H_5AlCl_2$ in the presence of free olefin. The known capability of organoaluminum compounds to reduce transition metal halides is expected to lead to a lower valence state of W. It is proposed that W acquires two olefinic ligands in a *cis* configuration about the tungsten (eq 5). Stable hexacoordinate diolefin complexes of zerovalent group VIB metals are well known,[16] although similar complexes possessing higher oxidation states of the metals are generally much less stable because they do not possess the rare gas electronic configuration present in the zerovalent complexes.

The olefinic bonds of bisolefin complexes do not normally exhibit mutual bonding interactions, although this possibility has been considered[17] in special cases such as the metal complexes of bicyclo[2.2.1]heptadiene. Nevertheless, the actual step of the metathesis reaction, the extensive bond delocalization which allows reorientation of the σ bonds in the four-center transition state, has a distinct analogy in the previously reported dimerization reactions of bicyclo[2.2.1]heptadiene to cyclobutane derivatives,[18] catalyzed by transition metal complexes, and also in the valence isomerization of quadricyclene to bicyclo[2.2.1]heptadiene.[19]

Based on the concept of molecular orbital symmetry conservation employed successfully by Woodward and Hoffmann[20] in relation to several electrocyclic reactions, Mango and Schachtschneider[21] demonstrated that a reaction pathway does exist for the conversion of two olefinic ligands coordinated to a transition metal into a four-membered ring. Evidently, the particular tungsten complex present in the metathesis reaction leads to an electronically excited four-membered ring (eq 6) which does not convert to a ground-state cyclobutane. Rather, it transforms back to a bisolefin–metal complex and in so doing provides the transalkylidenation step.

In order to account for the high rates of reaction which are observed at very low catalyst levels, a very rapid olefin exchange step is required (eq 7) which alternates with the transalkylidenation step. Such rapid olefin exchange reactions are well known for several olefin–metal complexes. Thus, displacement of ethylene in Zeise's salt, $K[(CH_2{=}CH_2)PtCl_3]\cdot H_2O$, by other olefins occurs readily (eq 8).[22] The half-life of coordinated ethylene in bis(ethylene)acetylacetonatorhodium(I) in the presence of free ethylene was estimated to be less than 10^{-4} sec at 25°.[23]

$$[(CH_2{=}CH_2)PtCl_3]^- + \text{olefin} \rightleftharpoons [(\text{olefin})PtCl_3]^- + CH_2{=}CH_2 \quad (8)$$

Such displacement reactions of coordinated ligands may be considered as nucleophilic reactions,[24] and these may occur readily if the reacting complex can accommodate an entering ligand without exceeding the rare gas electronic configuration in the transition state of the displacement step. Therefore, the occurrence of the rapid exchange process (eq 7) in the metathesis reaction does have several precedents, and is considered quite plausible for intermediate valent tungsten complexes.

The stereochemical course of the reaction and the ease with which equilibrium is attained in the *cis–trans* compositions of reacting mixtures are not surprising when one considers the very great number of configurations for the transition state which are possible according to the above scheme. The eight different available positions for alkyl substituents in the transition state are indicated in Figure 6. For the present discussion which is limited to the metathesis of vinylenic olefins, there will be only one alkyl substituent on each carbon atom. Considering the metathesis of 2-pentenes for example, although there are only two types of alkyl groups in this system, CH_3^- and $C_2H_5^-$, there are 55 possible configurations from various combinations of these groups, not including optical isomers! Furthermore, there are six different entering olefins (*cis-* and *trans-*2-butene, -2-pentene, and -3-hexene) which may participate in the olefin-exchange step, and many configurations of approach for each olefin are possible. Finally, relative to the transition state, four modes of elimination in each exchange step are also possible. Granted that many of the above steps are redundant, the very large number of possible routes which can lead to each of the six components in this metathesis system results in a nonselective process. It does not appear possible from the present data regarding isomer distributions at low conversions to assign preferences to certain configurations.

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