Ethyldiphenylphosphine.—The phosphine (1 mol equiv) was added to the quinone in CH_2Cl_2 at 20°. After 2 hr at 20°, the solvent was removed *in vacuo* and the residue, **32**, was recrystallized from benzene–hexane.

Triphenylphosphine.—Equimolar amounts of the reagents were mixed at 20°. There was no evidence of reaction. The mixture was kept 4 hr at 120°, cooled, and triturated with hexane. The insoluble product, **33**, was recrystallized from benzene. Elemental analyses and spectral data are given in Table I and II.

Registry No.—Hexafluoroacetone, 684-16-2; **1**, 17224-68-7; **2**, 1708-77-6; **3**, 6509-88-2; **4**, 15607-05-3; **5**, 6509-81-5; **6**, 4903-06-4; **17**, 17244-55-2; **18**, 17244-56-3.

Metathesis of 2-Pentene by a Binary Catalyst System of Tungsten Hexachloride and *n*-Butyllithium

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Nearly pure *cis* (94%), pure *trans*, and a mixture of 46% *trans*- and 54% *cis*-2-pentene were metathesized by a catalyst system of tungsten hexachloride and *n*-butyllithium. The reaction with *cis*-2-pentene or mixed 2-pentene reached redistribution equilibrium in 4 hr, where scrambling of the alkylidene groups attained the theoretical maximum, at which 50% of the original olefin was converted. However, conversion of *trans*-2-pentene was only 40% under the same conditions. Regardless of the extent of conversion of 2-pentene, the selectivity to 2-butene and 3-hexene was 100 mol % in experiments at room temperature with ratios of olefin/W = 50, and *n*-BuLi/W = 2. Good results were not obtained at other ratios. A possible mechanism of this metathesis reaction with the *n*-butyllithium catalyst system is proposed. This use of alkyllithium and tungsten hexachloride has not been reported previously.

Recently, a new reaction in olefin chemistry, called "olefin metathesis," has been reported.[1,2] It was found that a ternary catalyst system containing tungsten hexachloride, ethylaluminum dichloride, and ethanol breaks carbon–carbon double bonds in internal olefins and randomly rejoins the fragments.

$$\underset{(50\%)}{2RCH{=}CHR'} \rightleftharpoons \underset{(25\%)}{RCH{=}CHR} + \underset{(25\%)}{R'CH{=}CHR'}$$

A similar reaction, labeled "olefin dismutation" or "olefin disproportionation" by the authors,[3,4] has been described for internal and terminal olefins, which are passed over a solid catalyst of molybdenum or tungsten oxides on alumina. Isomerization and oligomerization were also observed under certain conditions.

To minimize possible cationic reactions due to aluminum compounds, we chose *n*-butyllithium as the reducing agent for tungsten hexachloride, in the absence of ethanol. To the best of our knowledge, alkyllithium and tungsten hexachloride have not been reported previously in this application, although claimed in a patent.[5]

Experimental Section

Materials.—Mixed 2-pentene (*trans/cis* = 0.85), 96% *cis*- and 100% *trans*-2-pentene, and *n*-pentane, from Chemical Samples Co., Columbus, Ohio, were all dried over sodium wire and distilled from sodium bisulfite under nitrogen. The distillates were tested by potassium iodide in acetic acid and found to be free of peroxides. Benzene was distilled and dried with sodium wire. Tungsten hexachloride was purified by sublimation of the more volatile reddish orange tungsten(VI) oxychlorides (WO_2Cl_2 and $WOCl_4$) and nitrogen at about 200°, leaving a residue of pure tungsten hexachloride.

Procedure.—All the reactions were carried out in 4-oz glass bottles at room temperature. Before sealing with rubber and Teflon gaskets, a 4-oz bottle was oven-dried for several hours at 110° and then cooled with nitrogen for about 5 min.

Injections of chemical reagents were done by means of hypodermic syringes from which air and moisture were carefully excluded. The injection order of reactants used in all the experiments was (1) 5 ml of 0.04 M WCl_6 in benzene (2×10^{-4} mol), (2) 2.25 ml of 4.5 M 2-pentene in *n*-pentane (1×10^{-2} mol), (3) 10 ml of 0.04 M *n*-BuLi in benzene (4×10^{-4} mol), and (4) 1 ml of isopropyl alcohol.

Reaction time shown in the tables began from the time of injection of *n*-butyllithium, whereupon the reaction mixture was agitated on a Burrell shaker. It was found that vigorous mixing was necessary for good reproducibility. After a chosen reaction time was reached, reaction was stopped by injecting 1 ml of isopropyl alcohol into the reaction mixture. Then the reaction mixture was cooled in Dry Ice before analysis by vapor phase chromatography (vpc).

Vpc Analysis.—All the analyses were done on a 42 ft × 0.125 in. Tergitol column at a column temperature of 60° and 40 cc/min of helium flow rate. The Aerograph 202 T/C instrument was programmed to 180° after elution of 3-hexene. *n*-Pentane was used as an internal standard to estimate percentage of conversion and selectivity to the products, *trans*- or *cis*-2-butene and 3-hexene. (The isomers of 3-hexene were not resolved by the Tergitol column.) The olefins 2-pentene, 2-butene, and 3-hexene all have the same ratio of vpc area response to *n*-pentane as the weight ratio of each component to *n*-pentane.

Results and Discussion

The terms "conversion" and "selectivity" used here are defined as follows: % conversion = % of initial 2-pentene reacted; mol % selectivity = (moles of 2-butenes or moles of 3-hexenes) × 100/moles of 2-pentene reacted.

The conversion of mixed 2-pentene increased rapidly during the first 60 min and then very slowly until redistribution equilibrium (50% conversion) was reached at 240 min (Figure 1). After that, per cent conversion remained independent of time. *cis*-2-Pentene also attained 50% conversion at 240 min, whereas *trans*-2-pentene reached only 40% conversion after 240 min. The failure of the latter to attain equilibrium

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[1] (a) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, **34**, 3327 (1967); (b) *Chem. Eng. News*, **45** (41), 51 (1967).

[2] N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, in press.

[3] C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, **7**, 269 (1967).

[4] R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 170 (1963).

[5] N. Calderon, Belgian Patent 698,075 (May 5, 1967).

TABLE I

COMPARISON OF STARTING 2-PENTENES

	120 min[a]			240 min[a]			1025 min[a]		
	Starting 2-pentene								
	96% *cis*–4% *trans*	100% *trans*	54% *cis*–46% *trans*	96% *cis*–4% *trans*	100% *trans*	54% *cis*–46% *trans*	96% *cis*–4% *trans*	100% *trans*	54% *cis*–46% *trans*
Conversion, %	40	38	43	50	40	51	50	40	51
Selectivity to 3-hexene, mol %	48	46	48	49	48	48	48	48	49
Selectivity to 2-butene, mol %	52	50	50	51	49	51	51	51	51
Total selectivity, mol %	100	96	98	100	97	99	99	99	99
2-Pentene, *trans/cis*	0.8	7.4	3.0	2.9	6.8	4.2	2.9	7.2	4.2
2-Butene, *trans/cis*	0.8	3.3	1.6	1.8	3.1	2.5	1.8	3.1	2.6

[a] Reaction time.

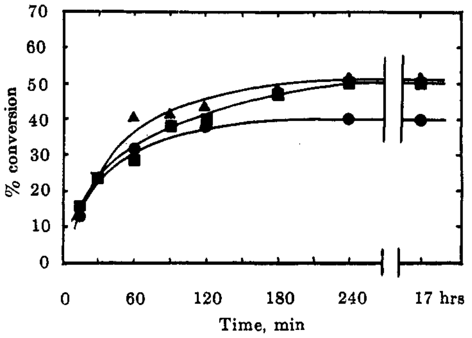


Figure 1.—A plot of % conversion *vs.* time: ▲, mixed 2-pentene ●, *trans*-2-pentene; ■, *cis*-2-pentene.

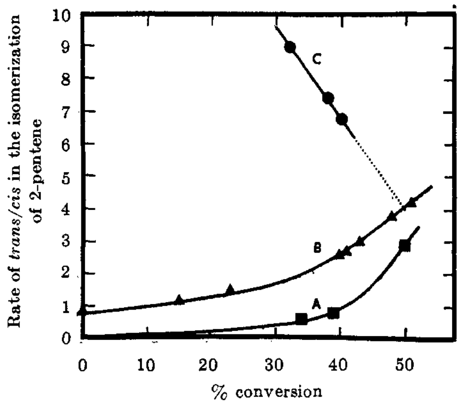


Figure 2.—A plot of isomerization of 2-pentene *vs.* % conversion: ■, for *cis*-2-pentene; ▲, for mixed 2-pentenes; ●, for *trans*-2-pentene.

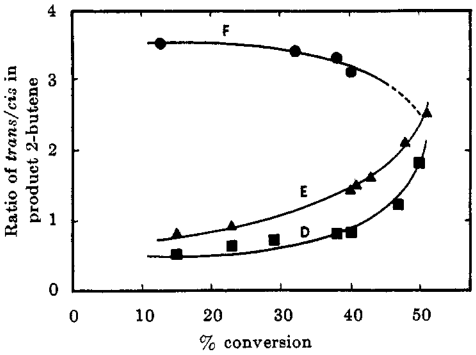


Figure 3.—A plot of isomerization in product 2-butene *vs.* % conversion: ■, for product from *cis*-2-pentene; ▲, for product from mixed 2-pentenes; ●, for product from *trans*-2-pentene.

may result from catalyst deactivation, although rigorous precautions to prevent this were taken.

The *trans/cis* ratio of mixed 2-pentene increased nonlinearly as per cent conversion increased (Figure 2, curve B). The *trans/cis* ratio reached a maximum of 4.2, or 81% *trans*, at 50% conversion, and remained there after 1025 min reaction time. Per cent *trans* in product 2-butene was 72% (Figure 3, curve E).

For *cis*-2-pentene, at 50% conversion, the ratio of *trans/cis* 2-pentene was 2.9, or 75% *trans* (curve A). However, this is lower than the 81% described above for the mixed 2-pentenes. While the Al catalyst system (olefin/W = 10,000) produces 82% *trans*-2-pentene and 71% *trans*-2-butene, the corresponding values for the Li catalyst (olefin/W = 50) are 75 and 64%.

Conversion of pure *trans*-2-pentene leveled out at only 40%; at this point the *trans/cis* ratio was 6.8 (87% *trans*) (curve C).

With WCl_6–EtOH–$EtAlCl_2$, the final *trans/cis* ratios for the internal olefins 2-pentene, 2-hexene, 2-heptene, and 3-heptene were nearly the same, *i.e.*, the thermodynamic ratio.[1] The reactions had proceeded to thermodynamic equilibrium, and the final ratios were independent of the *trans/cis* distribution of the initial olefins.

Present results (Table I) indicate stereochemistry somewhat different from that reported previously above. The *trans/cis* ratios at redistribution equilibrium were not the same, *i.e.*, *trans/cis* ratios during the methathesis was partially dependent on the *trans/cis* distribution of the starting olefins used. Further, Figure 1 shows that the mixed 2-pentenes and pure *cis* attain 50% conversion faster than pure *trans* under the same conditions.

While the catalyst WCl_6–EtOH–$EtAlCl_2$ is quite selective at very low levels of catalyst,[1,2] WCl_6–*n*-butyllithium is ineffective at olefin/WCl_6 > 100. However, with a WCl_6–Et_3Al catalyst system, 100% conversion to unknown oligomers was obtained at the ratio of mixed 2-pentene/WCl_6 = 50, whereas with WCl_6–*n*-butyllithium, 50% conversion and 100 mol % selectivity to 3-hexene and 2-butene were observed.

A surprising observation was the sharp dependence of metathesis on the ratio Li/W. At olefin/WCl_6 = 100, where the olefin was a 46:54 *trans/cis* mixture of 2-pentenes, Li/W was varied from 0.5 to 15 with little or no reaction. At pentene/WCl_6 = 50, Li/W was varied at 1, 2, and 3, and only at Li/W = 2 were good results obtained. Why these relatively high levels of catalyst are necessary is unknown, but optimization at Li/W = 2 strongly suggests a W^{IV} catalytic intermediate.

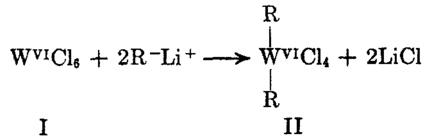
Neither *n*-butyllithium nor tungsten hexachloride alone caused any reaction of 2-pentene. This rules out anionic reactions due to alkyllithium and possible cationic reactions due to tungsten hexachloride.

With respect to efficiency in metathesis, several alkyllithiums were tried and were ranked *n*-butyl >

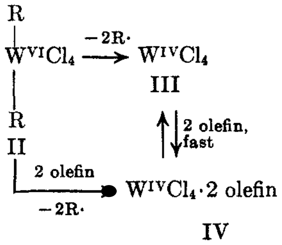
sec-butyl > *t*-butyl. Conversions by these reagents at the end of 15 min were 15, 4, and 0%, respectively.

Mechanism.—Catalyst systems containing aluminum and tungsten have been shown to exhibit some cationic character, as previously mentioned in the comparison of aluminum *vs.* lithium. It is likely that these catalysts react either cationically or by a metal–olefin coordination, or both, depending on the substrate and experimental conditions. It was our purpose to ascertain if metathesis can proceed only by metal–olefin coordination. This work with 2-pentene, tungsten hexachloride, and *n*-butyllithium indicates that it can, and thus confirms previously reported results with butene-2-d_8, which can be explained by such coordination.[1,2]

From items already discussed above, especially isomerization, effect of Li/W ratio, and lack of reaction by either alkyllithium or tungsten hexachloride alone, the following rationales are proposed: (1) the displacement of $2Cl^-$ by $2R^-$, probably occurring in rapid succession, as in eq 1, where the observed order of efficiency, *n*-butyl > *sec*-butyl > *t*-butyl, roughly parallels the order of nucleophilicity for these anions; (2) unimolecular or bimolecular reduction of W, and coordination with 2-pentene as in eq 2; and (3) formation of products and regeneration of catalyst, as in eq 3. The detailed formation of products from $W^{IV}Cl_4\cdot$2 olefin may be explained[6] by Scheme I.



$$\underset{\text{I}}{W^{VI}Cl_6} + 2R^-Li^+ \longrightarrow \underset{\text{II}}{\overset{\displaystyle R}{\underset{\displaystyle R}{W^{VI}Cl_4}}} + 2LiCl \qquad (1)$$

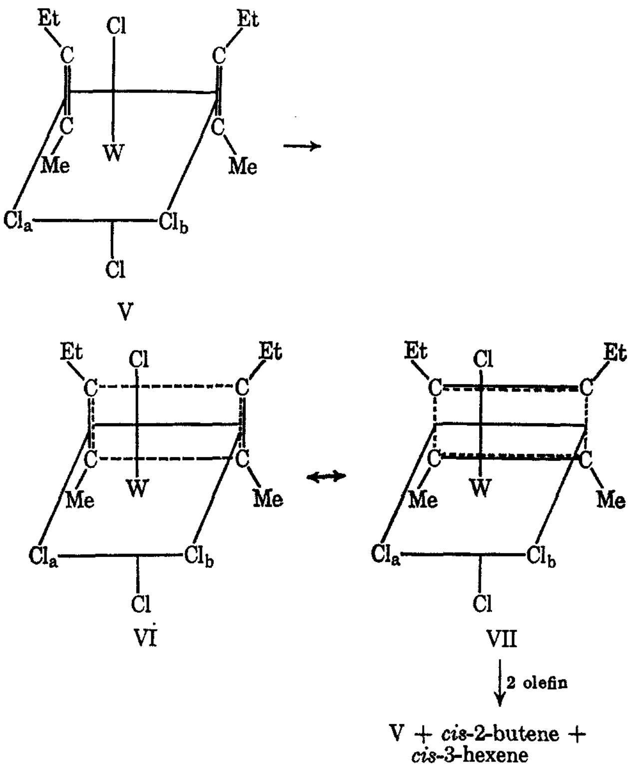


$$\begin{tikzcd} \underset{\text{II}}{\overset{\displaystyle R}{\underset{\displaystyle R}{W^{VI}Cl_4}}} \arrow[r, "-2R\cdot"] \arrow[dr, bend right, "2\text{ olefin}", "-2R\cdot"'] & \underset{\text{III}}{W^{IV}Cl_4} \arrow[d, shift left, "2\text{ olefin, fast}"] \\ & \underset{\text{IV}}{W^{IV}Cl_4\cdot 2\text{ olefin}} \arrow[u, shift left] \end{tikzcd} \qquad (2)$$

$$\begin{tikzcd} W^{IV}Cl_4\cdot 2\text{ olefin} \arrow[r, shift left] & W^{IV}Cl_4 + \text{products} \arrow[l, shift left] \arrow[l, bend left=60, "\text{two new olefins}"] \end{tikzcd} \qquad (3)$$

Figures 1, 2, and 3 and Table I further support a path like Scheme I. Initially 100% *trans*-2-pentene does not reach redistribution equilibrium even after 17 hr, reflecting the steric problems in coordinating *trans* olefin to W; initially 96% *cis*-2-pentene yields a mixture of 2-butenes retaining 36% *cis*-2-butene (*trans*/*cis* = 1.8). These differences from aluminum catalysts may be due to more extensive isomerization by cationic aluminum species. Isomerization could also occur in Scheme I during VI → VII.

SCHEME I[a]



[a] Cl_a, Cl_b, and W define a plane perpendicular to C=C and the paper.

In conclusion, metathesis of 2-pentene can be executed to redistribution equilibrium (50% conversion), with 100 mol % selectivity, by tungsten hexachloride and *n*-butyllithium at room temperature. Aluminum is not necessary for this reaction to proceed. Stereochemistry and other aspects of the tungsten–lithium system can be explained best by a metal–olefin coordination mechanism, involving, most likely, tungsten(IV).

Registry No.—*cis*-2-Pentene, 627-20-3; *trans*-2-pentene, 646-04-8; tungsten hexachlororide, 13283-01-7; *n*-butyllithium, 109-72-8.

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(6) V. M. Kothari, The Goodyear Tire & Rubber Co., personal communication, 1967.