

CH₂=CHCH₂CH₂Br, 5162-44-7; 4-(2'-hydroxyphenyl)-1-methyl-4-piperidinol dipropionate, 59043-58-2; 3-(2'-hydroxyphenyl)-2-tropene, 59043-59-3.

References and Notes

- (1) The authors gratefully acknowledge assistance from the Eli Lilly Research Foundation for support of part of this work.
- (2) Taken in part from the undergraduate independent study theses of (a) R. W. Thrakill, Duke University, 1974; (b) G. E. Keyser, Duke University, 1975.
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Metathesis of 1-Alkene

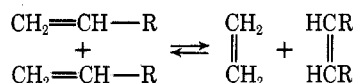
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In the WCl₆/Bu₄Sn catalyzed metathesis of 1-alkene, the addition of esters, acetonitrile, phenylacetylene, dicyclopentadiene, and ethers raised the selectivity to the metathesis by depressing side reactions including double bond migration, and the products of the metathesis reaction were obtained in high yield. This is a very easy and effective process for the direct synthesis of the symmetric internal alkenes. In the metathesis of 1-octene catalyzed by the WCl₆-CH₃COO-*n*-Pr/Bu₄Sn system at 80 °C, the optimum range of the Bu₄Sn/WCl₆ ratio was 2-8 and that of the 1-octene/WCl₆ ratio 20-400. The *cis*:*trans* isomer ratio of the product olefin approached its equilibrium value at the end of the reaction.

The metathesis of 1-alkene gives an ethylene and a symmetric internal alkene as follows:



It has been reported that this reaction is often accompanied by side reactions such as double bond migration and polymerization of alkenes¹⁻³ and that the yield of the metathesis products is low, except in a few cases.^{4,5}

In this paper, we report that the WCl₆-CH₃COOR (R = Et, *n*-Pr, *n*-Bu, and *sec*-Bu)/Bu₄Sn and the WCl₆-CH₃CN/Bu₄Sn systems catalyzed the metathesis of 1-alkenes with high activity and high selectivity. This result appears to increase the merit of the metathesis reaction in synthetic chemistry.

Results and Discussion

Effects of Additives in the Metathesis of 1-Octene. In this study, tetrabutyltin⁶ was employed as a cocatalyst because of the stability and the easiness to treat of the compound. Trichloroethylene⁷ was used as a solvent, for it gave a good yield of the metathesis products without the formation of the undesirable Friedel-Crafts products in the metathesis of 2-heptene.

The WCl₆/Bu₄Sn catalyst system in combination with 1-octene afforded a mixture of alkenes ranging from C₂ to C₁₄ in trichloroethylene at room temperature. At 80 °C, the amount of consumed 1-octene greatly increased, and the increase in the yield of alkenes ranging from C₉ to C₁₄ was recognized. A polymerization reaction probably took place at the same time, since the amount of product alkenes was much less than that of the consumed 1-octene. The addition of *n*-propyl acetate to the reaction system suppressed the formation of alkenes ranging from C₉ to C₁₃ and from C₃ to C₇, and the polymerization, but 7-tetradecene and ethylene were formed in high yield and in high selectivity. The addition of ethyl

acetate, *n*-butyl acetate, and *sec*-butyl acetate also provided high yield of 7-tetradecene and high selectivity, respectively. The distribution of the alkenes ranging from C₃ to C₁₄ was not influenced by the presence of air. In the WCl₆/Bu₄Sn catalyzed 1-octene metathesis, *cis*- and *trans*-2-octene, which are produced by the double bond migration of 1-octene, were detected by a capillary squalane column. Presumably alkenes ranging from C₂ to C₁₄ were formed not only by the self-metathesis of 1- and 2-octene and by the cross-metathesis of 2-octene with 1-octene but also by the successive reactions of product alkenes such as the isomerization of 1-heptene into 2-heptene and the self- and the cross-metathesis of 2-heptene. The WCl₆-CH₃COO-*n*-Pr/Bu₄Sn system reduced the amounts of *cis*- and *trans*-2-octene and the product alkenes ranging from C₉ to C₁₃. This fact indicates that the addition of *n*-propyl acetate suppresses the isomerization of 1-octene to 2-octene. These results are shown in Table I. Acetonitrile showed an excellent effect at the CH₃CN/WCl₆ ratio of 2, though the yield of 7-tetradecene decreased at the CH₃CN/WCl₆ ratio of 4. Phenylacetylene, dicyclopentadiene, ethyl ether, *n*-propyl ether, and tetrahydrofuran were also found to be comparatively effective additives. Water, hydrochloric acid, benzoic acid, tri-*n*-butylamine, tri-*n*-butylphosphine, and tetrahydrothiophene were not effective ones. In the presence of such compounds, the catalytic activity was hardly recognized at the additive/WCl₆ ratio of 1 and 4. Water, hydrochloric acid, and benzoic acid might destroy the catalyst. However, the addition of 1-propanol gave 11% 7-tetradecene at the equimolar amount to tungsten. Tri-*n*-butylamine, tri-*n*-butylphosphine, and tetrahydrothiophene induced yellow precipitations with a solution of tungsten hexachloride. Probably the stable acid-base tungsten complexes were formed.

Effects of Temperature and of the Amount of *n*-Propyl Acetate. The effects of temperature and of the CH₃COO-*n*-Pr/WCl₆ ratio on the yield and the selectivity were inves-

Table I. Effects of Additives in the Metathesis of 1-Octene^a

Additive	Additive/ WCl ₆	Distribution of alkenes, mol % ^b						Selectivity, ^c %
		C ₈	C ₉	C ₁₀	C ₁₂	C ₁₃	C ₁₄	
None ^{d,e}	0	87.8	1.4	0	0.2	0.5	1.4	23.0
None ^e	0	6.7	5.1	1.8	2.3	2.6	2.8	6.0
None ^f	0	14.7	7.2	2.0	4.0	4.7	5.1	12.1
<i>n</i> -Propyl acetate	4 ^e	64.3	1.0	0.8	0.4	0.6	14.8	82.9
	4 ^g	57.5	1.1	0.9	0.2	0.9	16.9	79.5
Ethyl acetate	4	68.2	0.4	0.8	0.2	0.3	14.1	88.7
<i>n</i> -Butyl acetate	4	69.2	0.5	0.7	0.2	0.3	13.7	89.0
<i>sec</i> -Butyl acetate	4	74.5	0.6	0.4	0.2	0.3	11.3	88.6
Acetonitrile	2	60.2	0.1	0	0.2	0.1	19.4	97.5
	4	73.5	0	0	0	0	13.2	100
Phenylacetylene	4	44.1	3.2	1.4	0.9	2.6	17.0	60.8
	8	44.8	2.3	1.5	0.7	1.7	16.1	58.5
Dicyclopentadiene	4	37.5	4.0	1.1	1.6	3.1	15.4	49.3
	8	51.7	1.6	0.5	1.6	1.2	15.4	64.0
Ethyl ether	4	30.8	6.3	1.6	1.6	3.9	12.1	34.8
	8	38.5	5.1	1.7	1.5	3.6	15.3	49.9
<i>n</i> -Propyl ether	4	22.1	7.5	1.5	2.0	4.7	9.9	25.4
	8	36.9	5.6	1.5	1.5	3.3	13.7	43.4
Tetrahydrofuran	4	73.4	0.8	0.5	0	2.7	9.4	70.4
	8	84.9	0	0	0	0	4.5	59.6
1-Propanol	1	43.7	8.2	2.1	1.2	3.8	10.6	37.7
	4	100	0	0	0	0	0	

^a The mixture of 1-octene (1.2 M), WCl₆ (0.024 M), Bu₄Sn (0.048 M), and an additive was heated in trichloroethylene in the absence of air at 80 °C for 3 h. ^b Mole % of each alkene based on the amount of 1-octene used. The product alkenes lower than C₃ were not determined. ^c % selectivity = (moles of 7-tetradecene × 2) × 100/moles of 1-octene consumed. ^d The reaction was carried out at room temperature. ^e The reaction was carried out in the presence of air. ^f Detected octenes were composed of 1-octene (0.11 M), *trans*-2-octene (0.04 M), and *cis*-2-octene (0.02 M). Detected C₁₄ components contained *cis*- and *trans*-7-tetradecene mainly, with several other components. 7-Tetradecene contained 21% *cis* isomer. ^g Detected octenes were composed of 1-octene (0.67 M), *trans*-2-octene (0.02 M), and trace of *cis*-2-octene. No other C₁₄ component except 20% *cis*- and 80% *trans*-7-tetradecene was detected.

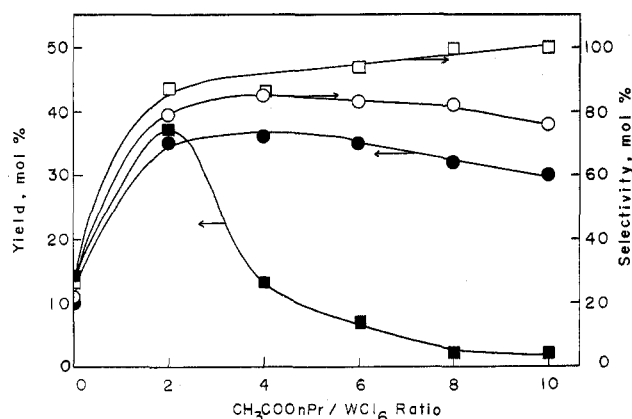


Figure 1. Effects of temperature and of the amount of *n*-propyl acetate: 60 °C, ■ yield, □ selectivity; 80 °C, ● yield, ○ selectivity. % yield = (moles of 7-tetradecene × 2) × 100/moles of 1-octene used. % selectivity = (moles of 7-tetradecene × 2) × 100/moles of 1-octene consumed. The mixture of 1-octene (1.2 M), WCl₆ (0.024 M), Bu₄Sn (0.048 M), and *n*-propyl acetate was heated in trichloroethylene in the absence of air for 3 h.

tigated in the metathesis of 1-octene catalyzed by the WCl₆-CH₃COO-*n*-Pr/Bu₄Sn system (Figure 1). At room temperature, *n*-propyl acetate hindered the reaction at the CH₃COO-*n*-Pr/WCl₆ ratio of 2. At 60 °C, 37% yield and 87% selectivity were obtained at the same CH₃COO-*n*-Pr/WCl₆ ratio, though the yield decreased sharply with the increase in the CH₃COO-*n*-Pr/WCl₆ ratio. At 80 °C, the yield of 36–32% and the selectivity of 85–79% were obtained at the CH₃COO-*n*-Pr/WCl₆ ratio of 2–8. The yield gradually decreased with increasing the amount of *n*-propyl acetate when the CH₃COO-*n*-Pr/WCl₆ ratio was higher than 4. However, 27% yield and 74% selectivity were obtained even at the

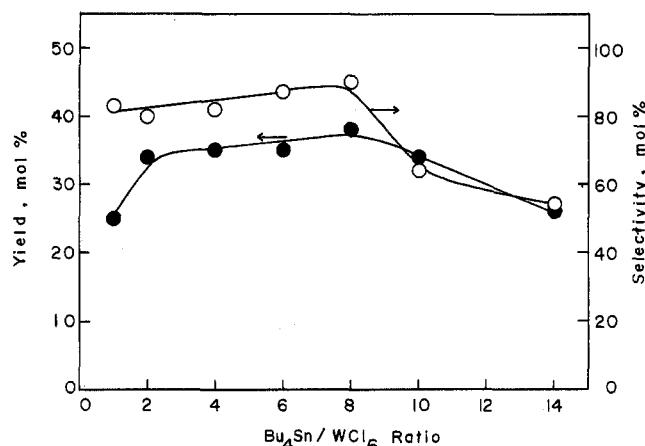


Figure 2. Effect of Bu₄Sn/WCl₆ ratio: ● yield; ○ selectivity. The mixture of 1-octene (1.2 M), WCl₆ (0.024 M), Bu₄Sn, and *n*-propyl acetate (0.096 M) was heated in trichloroethylene in the absence of air at 80 °C for 3 h.

CH₃COO-*n*-Pr/WCl₆ ratio of 20. This result means that an excess amount of *n*-propyl acetate inhibits the metathesis and that heating promotes the metathesis and extremely widens the optimum range of the CH₃COO-*n*-Pr/WCl₆ ratio.

Effect of the Bu₄Sn/WCl₆ Ratio. In the metathesis of 1-octene catalyzed by the WCl₆-CH₃COO-*n*-Pr/Bu₄Sn system at 80 °C, the yield of 38–34% and the selectivity of 90–80% were obtained at the Bu₄Sn/WCl₆ ratio of 2–8 (Figure 2). The optimum range was extremely wider than those of the cocatalyst/WCl₆ ratio in the metathesis of 2-heptene in benzene at room temperature.^{6,8} This result shows that the catalyst effective for the metathesis of 1-alkene is easily prepared from WCl₆, Bu₄Sn, and *n*-propyl acetate in trichloroethylene.

Table II. Metathesis of Various 1-Alkenes^a

Registry no.	Reactant	Product	Additive	Yield, mol %	Cis isomer content, %
109-67-1	1-Pentene	4-Octene	(A)	38	22
			(B)	28	34
592-41-6	1-Hexene	5-Decene	(A)	41	20
			(B)	40	21
592-76-7	1-Heptene	6-Dodecene	(A)	32	33
			(B)	24	32
111-66-0	1-Octene	7-Tetradecene	(A)	43	19
			(B)	43	20
872-05-9	1-Decene	9-Octadecene	(A)	45	
			(B)	44	

^a The mixture of 1-alkene (1.5 M), WCl_6 (0.024 M), Bu_4Sn (0.048 M), and *n*-propyl acetate (0.096 M) (A) or acetonitrile (0.048 M) (B) was heated in trichloroethylene in the absence of air at 80 °C for 3 h.

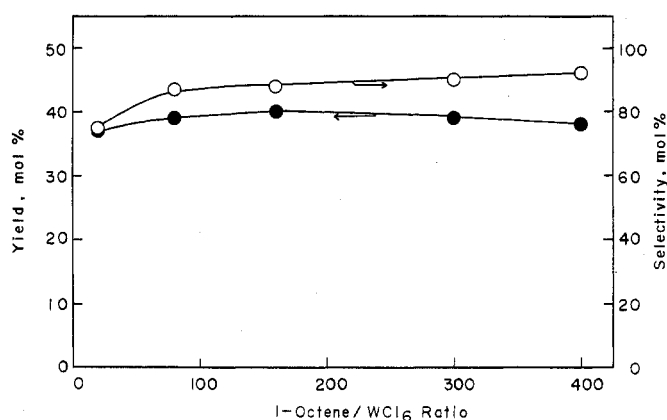


Figure 3. Effect of 1-octene/ WCl_6 ratio: ● yield; ○ selectivity. The mixture of 1-octene, WCl_6 (0.024 M), Bu_4Sn (0.048 M), and *n*-propyl acetate (0.096 M) was heated in trichloroethylene in the absence of air at 80 °C for 3 h.

Effect of the 1-Octene/ WCl_6 Ratio. In the metathesis of 1-octene catalyzed by the WCl_6 - CH_3COO -*n*-Pr/ Bu_4Sn system at 80 °C, the yield of 40–37% and the selectivity of 92–75% were obtained at the 1-octene/ WCl_6 ratio of 20–400 (Figure 3). The selectivity increased with an increase in the 1-octene/ WCl_6 ratio. The maximum yield was obtained at the 1-octene/ WCl_6 ratio of 160. When the 1-octene/ WCl_6 ratio was higher than 160, the increase in the amount of 1-octene led to the slight decrease in the yield. Also, the yield decreased from 38 to 14% when the concentration of WCl_6 was changed from 0.024 M to 0.008 M at the 1-octene/ WCl_6 ratio of 400. At 0.008 M of the WCl_6 concentration, the yield of 14–9% and the selectivity of 99–93% were obtained at the 1-octene/ WCl_6 ratio of 400–800. In the reaction of 2-heptene catalyzed by the WCl_6 / Bu_4Sn system in benzene at room temperature, the yield of 5-decene considerably changed with the variation of the 2-heptene/ WCl_6 ratio, where the optimum range was ~50–200. However, heating and the addition of *n*-propyl acetate gave the markedly wide optimum range in the reaction in trichloroethylene. This result also means that this reaction does not require certain strict reaction conditions.

Metathesis of Various 1-Alkenes. The yield and the cis-isomer content of the reaction product from the metathesis of 1-alkene using the WCl_6 - CH_3COO -*n*-Pr/ Bu_4Sn or the WCl_6 - CH_3CN / Bu_4Sn catalyst system are shown in Table II. Symmetric internal alkenes were obtained in good yield. The additives prevented the double bond migration but permitted

the geometric isomerization, for the ratio of cis isomer in the product alkene approached its equilibrium value⁹ at the end of the reaction.

When the ethylene formed was removed from the reaction system by liquefaction with liquid nitrogen in the metathesis of 1-octene catalyzed by the WCl_6 - CH_3COO -*n*-Pr/ Bu_4Sn system in trichloroethylene at 80 °C for 5 h, 59% yield and 94% selectivity were obtained. The reaction also proceeded without solvent.

Experimental Section

Materials. 1-Alkenes were purified by distillation under nitrogen. Trichloroethylene was dried over anhydrous $CaSO_4$ (Drierite) and distilled under nitrogen. Tungsten hexachloride was purified by preferential sublimation of the more volatile contaminants, WO_2Cl_2 and WCl_4 , under nitrogen at ca. 200 °C, leaving a residue of pure WCl_6 . Tetrabutyltin was purchased and used without further purification.

An Example of Metathesis Reaction. To a dried glass tube sealed with a neoprene rubber cap, 1-octene (0.18 ml, 1.2 mmol), a trichloroethylene solution of WCl_6 (0.024 mmol), *n*-propyl acetate (11 μ l, 0.096 mmol), and a trichloroethylene solution of Bu_4Sn (0.048 mmol) were injected, in this order, by means of hypodermic syringes. The total volume of the reaction mixture was 1 ml. After air was evacuated, the glass tube was sealed. The reaction mixture was heated at 80 °C for 3 h, and then analyzed by gas-liquid chromatography.

Analytical Procedures. Quantitative GLC analyses were routinely performed on a JEOL GC-1100 chromatograph, or a Shimadzu GC-4APF chromatograph, using a 1 m \times 3 mm column or a 1.5 m \times 3 mm column packed with 10% SE-30 on 80–100 mesh Chromosorb W and a 2 m \times 3 mm column packed with 20% FFAP on 60–70 mesh Anakrom ABS. *n*-Undecane was used as an internal standard. Isomer content of olefin was obtained with a 90 m \times 0.25 mm capillary column coated with squalane. Products were identified by gas-liquid chromatography using authentic samples.

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