Metathesis of 1-Hexene and Cyclooctene[1]

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The metathesis reaction between 1-hexene and cyclooctene was examined using several catalysts derived from WCl_6 and an organometallic compound. Using preferred catalysts, $WCl_6 \cdot EtOH/EtAlCl_2$ or $WCl_6 \cdot 2Et_2O/Bu_4Sn$, a high percentage of cyclooctene (>70%) was consumed in a few hours. The reaction product consisted of linear nonconjugated polyenes belonging to three different homologous series. The principal component in the reaction product was $C_{14}H_{26}$ (1,9-tetradecadiene) resulting from the cross-metathesis of 1-hexene and cyclooctene. Ethylene and 5-decene, formed by the self-metathesis of 1-hexene, underwent cross-metathesis with cyclooctene to produce $C_{10}H_{18}$ (1,9-decadiene) and $C_{18}H_{34}$ (5,13-octadecadiene). Further reaction of these primary cross-metathesis products with cyclooctene gave higher members of the homologous series. The influence of the nature of the catalyst, 1-hexene/cyclooctene molar ratio, and cyclooctene conversion on component distribution in the reaction product was determined.

Olefin metathesis is a transition metal catalyzed reaction involving the reorganization of bonds of olefins *via* transalkylidenation.[2,3] It has been investigated primarily for the polymerization of cycloolefins into polyalkenamers. Both heterogeneous[4] and homogeneous[5] catalysts have been found useful in promoting this reaction. Potential applications of the olefin metathesis reaction have been recently reviewed.[5-7]

The cross-metathesis reaction between an α-olefin and a cycloolefin or cyclodiene has been reported in the literature.[8-11] Hérisson and Chauvin[12] and Kelly[13] independently found that the product from the reaction of 1-pentene and cyclopentene consists primarily of linear nonconjugated polyenes having one terminal double bond per molecule. Porri and coworkers[14] have studied the reaction of norbornene with 1-pentene using catalysts derived from iridium. In all these studies, the reaction products were examined after low conversions of reactants (1–15%). In this paper, we have quantitatively characterized the reaction product resulting from the cross-metathesis of 1-hexene and cyclooctene. Experimental conditions were chosen to give cyclooctene conversions of 70% or greater. Several catalysts derived from WCl_6 and an organometallic compound were employed for the study.

Results and Discussion

$WCl_6 \cdot EtOH/EtAlCl_2$ Catalyst.[2] A chromatogram of the reaction product from the cross-metathesis of 1-hexene and cyclooctene using the $WCl_6 \cdot EtOH/EtAlCl_2$ catalyst is shown in Figure 1. In order to characterize the various components in the mixture, seven fractions corresponding to the glc peaks were isolated by the preparative glc unit and analyzed by mass spectrum, nmr, and ir. The results are summarized in Table I.

Fractions 1, 2, and 3 comprising 7, 8.5, and 40 wt % of the product, respectively, were assigned (mass spectral data) the molecular formulas $C_{10}H_{18}$, $C_{10}H_{20}$, and $C_{14}H_{26}$, respectively, and correspond to the following structures:

fraction 1, 1,9-decadiene, $CH_2{=}CH(CH_2)_6CH{=}CH_2$

fraction 2, 5-decene, $C_4H_9CH{=}CHC_4H_9$

fraction 3, 1,9-tetradecadiene, $CH_2{=}CH(CH_2)_6CH{=}CHC_4H_9$

Fraction 4 (12.5 wt % of product) was found to contain primarily two compounds having the molecular formulas $C_{18}H_{32}$ and $C_{18}H_{34}$ (mass spectral data). These compounds were present in molar proportions of 40 and 60% (glc). Based on the chemistry of the metathesis reaction, they were assigned the structures $CH_2{=}[CH(CH_2)_6CH{=}]_2CH_2$ and $C_4H_9CH{=}CH(CH_2)_6CH{=}CHC_4H_9$, respectively.

Fractions 5, 6, and 7 represented 14.5, 7, and 5.5 wt % of the product, respectively. The various compounds present therein belonged to the following three different homologous series of which $C_{10}H_{18}$ in fraction 1, $C_{14}H_{26}$ in fraction 3, and $C_{18}H_{34}$ in fraction 4 were first members.

Series A: the main peaks are assigned to $C_{14}H_{26}$, $C_{22}H_{40}$, and $C_{30}H_{54}$ components of the unsymmetric homologous series $CH_2{=}[CH(CH_2)_6CH{=}]_nCHC_4H_9$ representing about 60 wt % of the total product (primarily $C_{14}H_{26}$).

Series B: composed of $C_{18}H_{34}$, $C_{26}H_{48}$, and $C_{34}H_{62}$ of the symmetric homologous series $C_4H_9CH{=}[CH(CH_2)_6CH{=}]_nCHC_4H_9$ representing about 13% of the product.

Series C: contained $C_{10}H_{18}$, $C_{18}H_{32}$, $C_{26}H_{46}$, and $C_{34}H_{60}$ of the symmetric homologous series $CH_2{=}[CH(CH_2)_6CH{=}]_nCH_2$ representing about 14% of the product.

In the above series, n is an integer and its smallest value is 1. All compounds belonging to the series A, B, and C must contain moieties derived from both the reactants. Consequently, 5-decene (fraction 2) is not included in series B. Likewise, ethylene is not included in series C.

The relative molar ratio of the first components of series A, B, and C, namely, $C_{14}H_{26}$, $C_{18}H_{34}$, and $C_{10}H_{18}$, respectively, containing one cyclooctene-derived octenamer unit and constituting a triad, was approximately 4:1:1. The components of the next triad containing two octenamer units were also present in a similar ratio. However, Hérisson, *et al.*,[12] reported triad ratios of 10:1:1 to 20:1:1 for the reaction of cyclooctene with propylene or 1-pentene in chlorobenzene with a $WOCl_4/(C_4H_9)_4Sn$ catalyst. The relatively high proportion of series A components reported in the latter study is presumably a consequence of the reaction conditions and low cyclooctene conversions (1–15%). Under our experimental conditions, cyclooctene conversion was 70% or greater. Apparently, the cross-metathesis reaction leading to series A components prevails at low cycloolefin conversion but competing reactions leading to series B and C components become important as cyclooctene is depleted. A simplified reaction scheme is given in Scheme I. In addition, series A components may get converted to series B and series C components by subsequent metathesis reaction.[15]

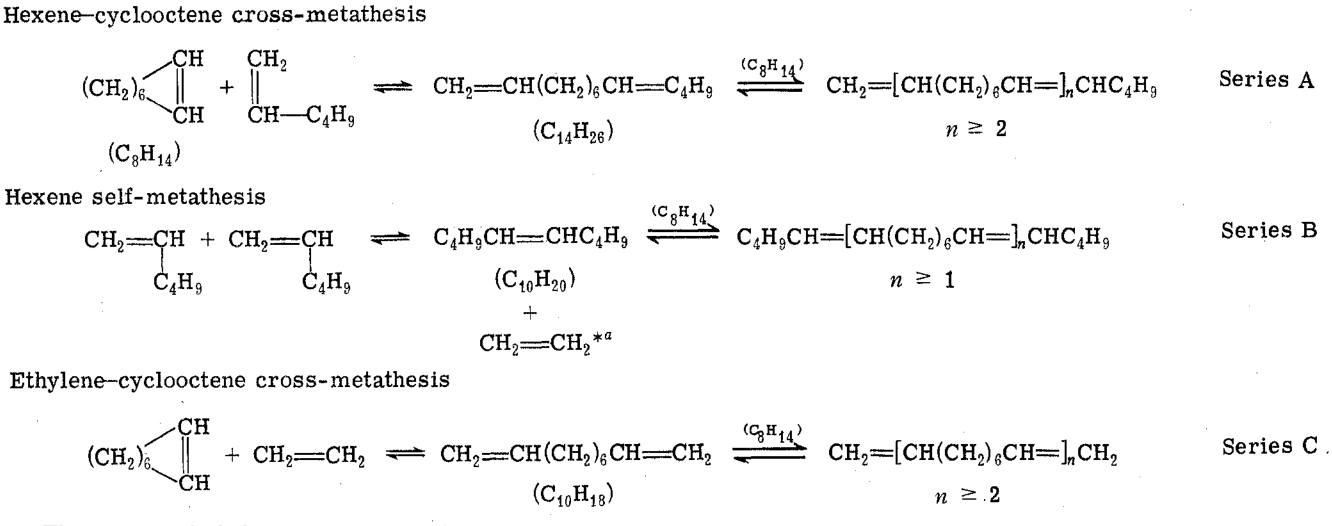
It should be noted that peaks corresponding to macrocyclic oligomers $C_{16}H_{28}$ and $C_{24}H_{42}$, which are reported[16] to be formed during the ring opening polymerization of cyclooctene, are not seen by mass spectrum in the metathesis reaction product. However, $C_{32}H_{56}$ (tetramer) was observed in trace amounts in fraction 6. The absence of $C_{16}H_{28}$ and $C_{24}H_{42}$ does not necessarily preclude their formation in small amounts and subsequent reaction with one of the α-olefins present. The formation of $C_{32}H_{56}$ in trace

Table I
Characterization of the Metathesis Product[a] of 1-Hexene and Cyclooctene ($WCl_6 \cdot EtOH/EtAlCl_2$ Catalyst)

Glc		Mass spectrum			
Fraction no.[b]	Wt % of components	Parent mass obsd (m/e)[c]	Mol formula assigned	Nmr Anal	Series[d]
1	7	138.1393*	$C_{10}H_{18}$	2 terminal double bonds	C
2	8.5	140.1554*	$C_{10}H_{20}$	1 internal double bond	
3	40[e]	194.2029*	$C_{14}H_{26}$	1 terminal and 1 internal double bonds	A
4	12.5[f]	250.2648* 248	$C_{18}H_{34}$ $C_{18}H_{32}$	Consistent with 60 mol % $C_{18}H_{34}$ and 40 mol % $C_{18}H_{32}$	B and C
5	14.5[g]	304.3118*	$C_{22}H_{40}$	1 terminal and 2 internal double bonds	A
6	7	360.3749* 358	$C_{26}H_{48}$ $C_{26}H_{46}$	Consistent with 80 mol % $C_{26}H_{48}$ and 20 mol % $C_{26}H_{46}$	B and C
7	5.5[h]	414.4244* 440 468[i] 470	$C_{30}H_{54}$ $C_{32}H_{56}$ (trace) $C_{34}H_{60}$ $C_{34}H_{62}$		A, B, and C (except $C_{32}H_{56}$)

[a] Reaction conditions were the same as shown for Figure 1. [b] Fraction numbers refer to those in the chromatogram (Figure 1). All fractions were 98–99.5% pure, except fraction 1 (95% pure) and fraction 4 (81% pure). [c] Mass numbers with asterisks represent major peaks by high resolution mass spectrometry. [d] Homologous series refer to those in Scheme I. [e] $n^{30}D$ 1.4430; the internal double bond had 45% cis and 55% trans (ir). [f] $C_{18}H_{34}/C_{18}H_{32}$ molar ratio = 1.50 (glc analysis using a 20-ft, 20% UC-W98 on 60–80 mesh Chromosorb W column). [g] $n^{30}D$ 1.4622; 60% cis and 40% trans double bonds (ir). [h] 93% of C_{30} and 6% of C_{34}. For calculations, 3% each of $C_{34}H_{60}$ and $C_{34}H_{62}$ was assumed to be present (glc analysis using column in footnote *f*). [i] Mass peak was not observed (possibly due to side reactions?).

Scheme I
Schematic Diagram for Metathesis of Cyclooctene and 1-Hexene



[a] The presence of ethylene was ascertained by glc on a 50-ft di-*n*-decyl phthalate column.

amounts might result from the intramolecular cyclization of the diterminal polyene $C_{34}H_{60}$ (series C; $n = 4$) by pinching off ethylene.

The effect of reaction time on the distribution of components in series A, B and C is shown in Figure 2 using the $WCl_6 \cdot C_2H_5OH/EtAlCl_2$ catalyst. Cyclooctene consumption was increased to 86 wt % from 70% as the reaction time was increased to 24 hr from 0.25 hr. Concurrently, there was a slight decrease in the weight percentage of series A components as a consequence of an increase in the weight percentages of both series B and series C components. If the metathesis product were to be utilized for copolymerization with an α-olefin to produce an unsaturated copolymer, it is desirable to terminate the metathesis reaction after 30 min since increase in the relative amount of series C components at longer reaction times will increase gel content of the copolymer.

Catalyst systems based on Et_3Al or $(i\text{-}Bu)_3Al$ with $WCl_6 \cdot EtOH$ exhibited low activity for the metathesis reaction between 1-hexene and cyclooctene. They gave cy-

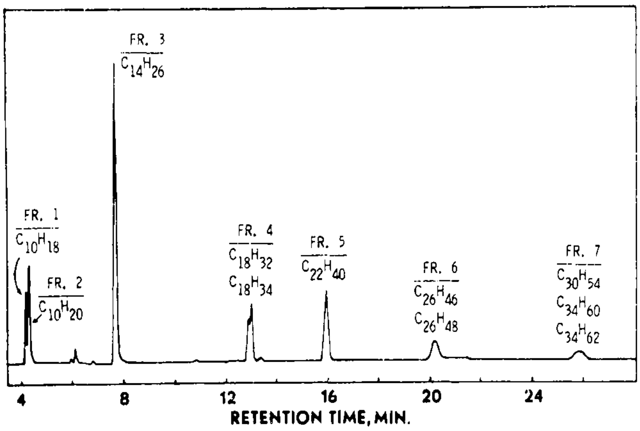


Figure 1. Chromatogram of the reaction product in the metathesis reaction of cyclooctene and 1-hexene. Conditions: catalyst, $WCl_6 \cdot EtOH/EtAlCl_2$; Al/W/O atomic ratio = 4:1:1; 1-hexene/cyclooctene molar ratio = 2; cyclooctene/WCl_6 molar ratio = 1300; reaction for 30 min at 25°.

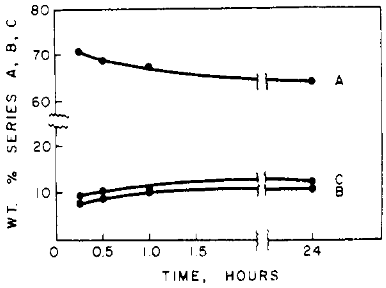


Figure 2. Effect of reaction time on product distribution in the metathesis reaction of cyclooctene and 1-hexene using $WCl_6 \cdot EtOH/EtAlCl_2$ catalyst. Conditions: same as in Figure 1.

clooctene conversion of about 5% in 24 hr, with only one peak ($C_{14}H_{26}$) detectable by glc.

$WCl_6 \cdot CF_3CH_2OH/EtAlCl_2$ Catalyst. The distribution of components in the three series is shown in Figure 3 for the $WCl_6 \cdot CF_3CH_2OH/EtAlCl_2$ catalyst. Cyclooctene conversion of 91 to 96% was obtained, with only slight changes in the product distribution, as the reaction time was increased from 0.25 to 24 hr. In calculating the product distribution here, the relative proportions of components corresponding to fractions 1 and 2 as well as the relative distribution of components in fractions 4, 6, and 7 were assumed to be the same as in Table i. This catalyst gave 44, 13, and 18 wt % of series A, B, and C components, respectively, compared to 60, 13, and 14% resulting from the C_2H_5OH-modified catalyst. Thus, the $WCl_6 \cdot C_2H_5OH/EtAlCl_2$ catalyst gives a higher proportion of the polymerizable components, together with a markedly improved ratio of series A/series C components. The data in Figures 2 and 3 indicate that the two catalyst systems appear to be essentially dead after about 1 hr.

$WCl_6 \cdot 2Et_2O$/Organotin Catalysts.[17] Several catalysts prepared from $WCl_6 \cdot 2Et_2O$ and organotin compounds were examined for the metathesis reaction between 1-hexene and cyclooctene. The reaction conditions were similar to those employed with $WCl_6 \cdot$ alcohol/$EtAlCl_2$ catalysts (Figures 2 and 3). As shown in Table II, only Bu_4Sn and $(C_6H_5)_4Sn$ gave catalysts having fairly high activity. The catalysts based on organotin compounds having one or two chlorine atoms gave less than 5% cyclooctene conversion under these conditions.

Glc of the metathesis product from the tin/tungsten-catalyzed reaction of 1-hexene and cyclooctene indicated that

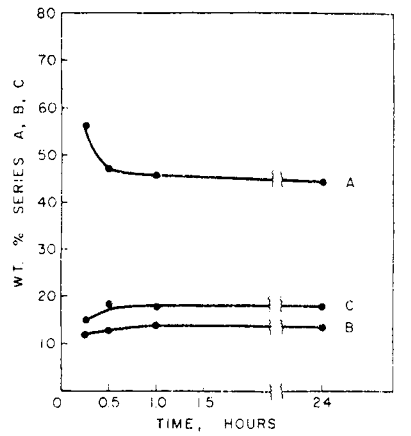


Figure 3. Effect of reaction time on product distribution in the metathesis reaction of cyclooctene and 1-hexene using $WCl_6 \cdot CF_3CH_2OH/EtAlCl_2$ catalyst. Conditions: same as in Figure 1.

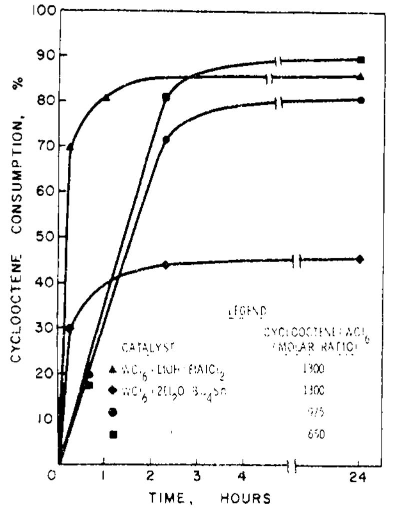


Figure 4. Effect of reaction time on cyclooctene consumption in the metathesis reaction of cyclooctene and 1-hexene. Conditions: for catalyst $WCl_6 \cdot EtOH/EtAlCl_2$, Al/W/O atomic ratio = 4:1:1; for catalyst $WCl_6 \cdot 2Et_2O/Bu_4Sn$, Sn/W/O atomic ratio = 2:1:2; 1-hexene/cyclooctene molar ratio = 2; 25°.

the various compounds present also belonged to the three homologous series described earlier. The $WCl_6 \cdot 2Et_2O/Bu_4Sn$ catalyst was examined at three different catalyst levels for the metathesis of 1-hexene and cyclooctene and the results compared with those obtained by using $WCl_6 \cdot EtOH/EtAlCl_2$ (Figure 4). The rate of cyclooctene consumption with the tin catalyst is seen to be substantially slower (37% in 1 hr and 45% in 3 hr) than that obtained with the aluminum catalyst (~80% in 1 hr) at a cyclooctene/WCl_6 molar ratio of 1300. However, raising the catalyst level by 33 and 100% increased cyclooctene consumption to about 76 and 85%, respectively, in 3 hr.

The compositions of the metathesis products for the aluminum- and tin-catalyzed reactions from Figure 4 are compared in Figure 5. For this purpose, the effect of reaction time on the distribution of polymerizable (series A + C) and nonpolymerizable (series B) components is examined. The weight percentages of the three series were normalized to 100%. Both the tin- and aluminum-based catalysts give essentially identical distribution of components when compared at cyclooctene/WCl_6 molar ratio of 1300. At this catalyst level, the product consists of approximately 86–88% series A + C components and 14–12% series B components at the end of 3 hr. Upon increasing the $WCl_6 \cdot 2Et_2O/$

Table II
Metathesis of 1-Hexene and Cyclooctene using $WCl_6 \cdot 2Et_2O$/Organotin Compound Catalysts[a]

Tin compd	Sn/W (atomic ratio)	Cyclooctene consumption, % 2 hr	 24 hr
Bu_4Sn	2	80–85	90
Bu_3SnCl	2	5	5
Bu_2SnCl_2	2	5	5
$(C_6H_5)_4Sn$	2	5	37[b]
	4	43[b]	47[b]
$(C_6H_5)_3SnCl$	2	5	5

[a] 1-Hexene/Cyclooctene molar ratio 2.0; cyclooctene/WCl_6 molar ratio 650; benzene/cyclooctene vol ratio 3; reaction at 25°; *n*-octane used as the internal standard. [b] These reaction products had essentially the same component distribution as that obtained with the Bu_4Sn catalyst at equivalent conversion of cyclooctene.

Table III
Effect of 1-Hexene/Cyclooctene Molar Ratio on the Composition[a] of Metathesis Product ($WCl_6 \cdot 2Et_2O/Bu_4Sn$ Catalyst[b])

Component of metathesis product	Wt % Hexene/Cyclooctene molar ratio 0.5	 1.0	 2.0
$C_{10}H_{18}$	9.7	10.2	14.2
$C_{10}H_{20}$	10.5	14.3	18.5
$C_{14}H_{26}$	18.7	20.2	29.6
$C_{22}H_{40}$	15.7	14.6	10.2
Cyclooctene consumed, %	95	95	88

[a] Cyclooctene/WCl_6 molar ratio = 1300; benzene/cyclooctene vol ratio = 3; reaction at 25° for 2 hr; *n*-octane used as the internal standard. [b] Sn/W atomic ratio = 2.

Bu_4Sn level 33 to 100%, the percentage of polymerizable components decreased slightly to 79% with a corresponding increase in nonpolymerizable components to 21%. There was essentially no change in the distribution when the reaction was allowed to continue for 24 hr and cyclooctene consumption increased by 10%. It should be noted that at the higher levels of the tin catalyst, the amount of 5-decene based on the total product increased from about 10 to 14% compared to 7% with the aluminum system.

Figures 4 and 5 show that the $WCl_6 \cdot 2Et_2O/Bu_4Sn$ system requires a somewhat higher catalyst level than the aluminum system for obtaining in high conversion a polyene product with a high percentage of polymerizable components. This catalyst system, in marked contrast to the $WCl_6 \cdot EtOH/EtAlCl_2$ system, gives easily reproducible results. Scale-up of the metathesis reaction between 1-hexene and cyclooctene in a 1-gallon container gave a product having essentially the same component distribution as obtainable in a 4-oz bottle.

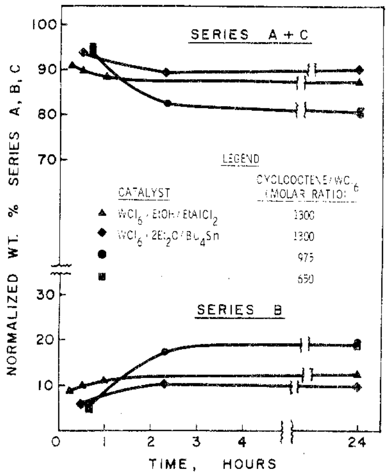


Figure 5. Effect of reaction time on product distribution in the metathesis reaction of cyclooctene and 1-hexene. Conditions: same as in Figure 4.

Effect of 1-Hexene/Cyclooctene Molar Ratio. In the previous discussion, the molar ratio of 1-hexene/cyclooctene for the W/Al and W/Sn catalyst systems was kept at 2 in carrying out the metathesis reactions. This ratio was selected because our preliminary work with the W/Al catalyst system had shown that the relative amount of series A components was highest at this ratio without any sacrifice in the high conversion of cyclooctene to the polyene mixture. The effect of hexene/cyclooctene molar ratio on the distribution of components in the $WCl_6 \cdot 2Et_2O/Bu_4Sn$ catalyzed metathesis product is shown in Table III. To simplify comparison, only the weight percentages of $C_{14}H_{26}$ and $C_{22}H_{40}$ of series A (peaks 3 and 5), $C_{10}H_{20}$ (peak 2) and $C_{10}H_{18}$ (peak 1) of series C were determined from the chromatograms since peaks for these components were well-defined. The overall conversion of cyclooctene to products is reasonably similar for all three ratios. However, the ratio 2 is preferred for the formation of $C_{14}H_{26}$, $C_{10}H_{20}$, and $C_{10}H_{18}$. The enhanced formation of $C_{10}H_{20}$ at this ratio is due to the greater availability of 1-hexene for undergoing self-metathesis. The greater availability of cyclooctene at the lower ratios contributes to enhancement in the formation of $C_{22}H_{40}$ at the expense of $C_{14}H_{26}$ by the cross-metathesis reaction between $C_{14}H_{26}$ and cyclooctene. Similarly, the areas of peaks 4 and 6 increased relative to the combined area of peaks 1 and 2 at the lower ratios (data not shown), consistent with the increased cross-metathesis of cyclooctene with $C_{10}H_{18}$ and $C_{10}H_{20}$.

Experimental Section

Monomers and Solvent. High purity 1-hexene (Gulf) and benzene (Fischer) were dried by passing through an 18-in. activated-silica column and stored over molecular sieves (Linde 4A-XW). Cyclooctene (Cities Service) was distilled over calcium hydride or passed through a silica–alumina column prior to use.

Catalysts. Solutions of $EtAlCl_2$ (1.55 *M*), organometallic tin compounds (0.1–0.2 *M*), and WCl_6 (0.05 *M*) were prepared in benzene under nitrogen. Solutions of WCl_6 were modified by adding appropriate amounts of an alcohol or diethyl ether. In the case of $(C_6H_5)_4Sn$, a 0.20 molar suspension in benzene was used.

Monomers and solvents of high purity and freshly modified WCl_6 solutions were found to be essential for obtaining reproducible results.

Metathesis Reaction. The experimental conditions were organometallic/WCl_6 molar ratio = 2–4; cyclooctene/WCl_6 molar ratio = 650–1300; hexene/cyclooctene molar ratio = 0.5–2; benzene/cyclooctene volume ratio = 3. The order of addition was solution of reactants, organometallic compound, WCl_6 modified with ether or an alcohol. In a typical experiment, the metathesis reaction mixture for characterization studies was prepared in a 1-qt bottle fitted with a metal cap having perforations and backed with a self-sealing gasket and Teflon linear. A solution of 0.50 mol of cyclooctene, 1.0 mol of hexene, 200 ml of benzene, and 10 ml of *n*-octane (glc internal standard) was sparged with nitrogen for three minutes. The catalyst components, 0.75 ml of $EtAlCl_2$ and 8.0 ml of $WCl_6 \cdot EtOH$ solutions, were added by syringe into the reactants solution and the bottle was capped under nitrogen. After agitation on a mechanical shaker for 30 min (ambient temperature, 25°), glc analysis of the homogeneous reaction mixture indicated a 94% consumption of cyclooctene. The reaction was terminated at this point with 1 ml of methanol. The resulting mixture was concentrated on a roto-evaporator under aspirator vacuum to remove benzene, hexene, and cyclooctene prior to fractionation by preparative glc.

Analytical Procedures. Analysis by glc was routinely performed on a Hewlett-Packard 7620A Model gas chromatograph using a 6 ft × ⅛ in. 10% UC-W98 on 80–100 mesh Diatoport S column, programmed from 80 to 270° in 20 min.

As stated earlier, a typical metathesis product was concentrated by the removal of benzene, hexene, and cyclooctene. The concentrate was fractionated by means of a Hewlett-Packard preparative gas chromatograph unit and seven fractions were isolated. They were analyzed by nmr, ir, and mass spectrum.

Nmr analyses were carried out on a Varian A60 spectrometer and ir spectra recorded on a Perkin-Elmer Model 21 spectrophotometer. High resolution mass spectrum measurements were made on a Du Pont Model 21-110C mass spectrometer using perfluorokerosene as the reference compound.

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Registry No.—1-Hexene, 592-41-6; cyclooctene, 931-88-4; WCl_6, 13283-01-7; $EtOH/EtAlCl_2$, 53777-80-3; $CF_3CH_2OH/EtAlCl_2$, 53777-81-4; $2Et_2O/Bu_4Sn$, 53777-82-5; $2Et_2O/Bu_3SnCl$, 53777-83-6; $2Et_2O/Bu_2SnCl_2$, 53777-84-7; $2Et_2O/(C_6H_5)_4Sn$, 53777-85-8; $2Et_2O/(C_6H_5)_3SnCl$, 53777-86-9.

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(15) The formation of series B and series C components from series A components was demonstrated by carrying out the metathesis reaction between 1-hexene and $C_{14}H_{26}$ (fraction 3 from preparative glc). The principal products were $C_{10}H_{20}$ and $C_{18}H_{34}$ of series B and $C_{10}H_{18}$ of series C. In addition, appreciable amounts of $C_{22}H_{40}$ of series A and $C_{26}H_{48}$ of series B were also obtained. Likewise, components of series C can be converted into series B components and vice versa.

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Synthesis of Fatty Acids Using Organocopper(I) Ate Complexes Derived from Grignard Reagents[1]

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Fatty acid esters have been synthesized in good yield by reaction between copper(I) ate complexes formed from methylcopper(I) and primary or secondary Grignard reagents and esters of primary iodoalkylcarboxylic acids. The synthetic method is illustrated with procedures for $CH_2{=}CH(CH_2)_{19}CO_2C_2H_5$, $C_6H_5CH_2O(CH_2)_{16}CO_2C_2H_5$, $CH_3(CH_2)_{25}CO_2C_2H_5$, $CH_3O_2C(CH_2)_{22}CO_2CH_3$, $C_2H_5O_2C(CH_2)_{32}CO_2C_2H_5$, and $CH_3(CH_2)_4CH(CH_3)(CH_2)_{10}CO_2CH_3$. The reaction sequence uses starting Grignard reagent with high efficiency, provides product mixtures that are conveniently worked up, and tolerates a variety of functional groups. It provides the most direct route presently available to a variety of representative classes of simple fatty acids.

A number of procedures for the synthesis of fatty acids are available.[3] Those most commonly used for fatty acids not containing extensive unsaturation include the reaction of carbonyl compounds with alkylidene phosphoranes,[4] the Kolbe anodic coupling of half esters of dicarboxylic acids,[5] and the acylation of enamines with acid chlorides followed by hydrolysis of the resulting β-diketones and Wolff–Kishner reduction of the product keto acid.[6]

The reaction of carbonyl compounds with alkylidene phosphoranes is particularly useful for the preparation of diastereomerically pure unsaturated fatty acids, and has also been used in the preparation of branched-chain fatty acids. Its deficiencies are that it often involves multiple steps of only moderate yields and requires a difficult separation of products from triphenylphosphine oxide. Kolbe electrolysis of half esters of dicarboxylic acids is a useful route to symmetrical long-chain dicarboxylic acid esters, but is not applicable to the preparation of unsymmetrical compounds. The procedure developed by Hünig and coworkers is applicable to the synthesis of asymmetrically disubstituted fatty acids, symmetrically disubstituted fatty acids, and both straight- and branched-chain fatty acids. Although versatile, it is lengthy.

We have developed an efficient alternative to these procedures based on carbon–carbon bond formation by selective coupling between one alkyl group of a "mixed" copper(I) ate complex and primary iodoalkyl carboxylic esters.[7] This procedure is compatible with a number of functional groups, yields products cleanly and in high yield, and is applicable to a number of representative classes of fatty acids.

Results

Both primary and secondary Grignard reagents react with methylcopper(I) and form copper(I) ate complexes that selectively transfer the alkyl group originally bonded to magnesium in high yield in alkylation reactions. By using the readily available methyl or ethyl 11-iodoundecanoate in this reaction, it is possible to synthesize a variety of fatty acids. A typical procedure—that for ethyl 21-do-