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Metathesis of Fatty Acid Esters

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ABSTRACT

In metathesis reactions, unsaturated compounds are converted into new compounds via an exchange of alkylidene groups:

$$2\ RCH = CHR' \rightleftharpoons RCH = CHR + R'CH = CHR'$$

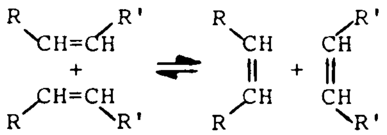
Since its discovery in 1964, this catalytic reaction has found several large-scale applications in petrochemistry. One of the most promising synthetic applications of metathesis is to functionalized olefins such as unsaturated esters, ethers, amines, etc., because this allows single-step syntheses of a variety of mono- and difunctional hydrocarbon derivatives. Unfortunately, however, most metathesis catalysts are easily poisoned by polar groups. In 1972 in our institute, the WCl_6-$(CH_3)_4Sn$ system was found to be effective as a catalyst for homogeneous metathesis of fatty acid esters. Thus methyl oleate was converted into 9-octadecene and dimethyl 9-octadecene dioate, starting materials for the synthesis of valuable chemical products. In 1977 we developed a heterogeneous catalyst system: Re_2O_7 on Al_2O_3, activated with a small amount of $(CH_3)_4Sn$. Systematic research has led to interesting applications of metathesis and cometathesis reactions with these catalysts. An example is the cometathesis of methyl oleate with ethene, to produce shorter-chain compounds with terminal double bonds:

$$CH_3(CH_2)_7CH = CH(CH_2)_7COOCH_3 + CH_2 = CH_2 \rightleftharpoons$$
$$CH_2 = CH(CH_2)_7CH_3 + CH_2 = CH(CH_2)_7COOCH_3$$

Cometathesis of olive oil (mainly triolein) with ethene opens the possibility of producing both α-olefins in the C_{10} range and fatty oils with lower molecular weight (palm oil type). Until now, metathesis of fatty esters has been restricted mainly to synthetic purposes. Large-scale applications depend mainly on the development of more active and cheaper catalyst systems.

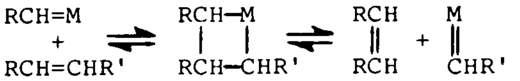
INTRODUCTION

The catalytic metathesis of olefins, a reaction discovered by Banks and Bailey in 1964 (1), can be described as an exchange of alkylidene groups in the participating molecules to form new unsaturated molecules:



[1]

The reaction in all probability proceeds via a chain reaction, involving metal-carbenes that react reversibly with the olefins via a metallacyclobutane intermediate:



$$\begin{array}{c}\mathrm{RCH{=}M}\\ +\\ \mathrm{RCH{=}CHR'}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{RCH{-}M}\\ |\qquad|\\ \mathrm{RCH{-}CHR'}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{RCH}\\ \|\\ \mathrm{RCH}\end{array} + \begin{array}{c}\mathrm{M}\\ \|\\ \mathrm{CHR'}\end{array} \qquad [2]$$

Both homogeneous and heterogeneous catalysts have been developed (2-5).

For the metathesis of simple olefins (a reaction which has found several large-scale industrial applications), the most active of these catalysts are based on the transition metals tungsten, molybdenum and rhenium. One of the most promising applications of the metathesis reaction, both from a synthetic as well as a technological point of view, is to functionalized olefins, because such reactions would allow single-step syntheses of a variety of mono- and difunctional derivatives of hydrocarbons. Unfortunately, however, most metathesis catalysts are easily poisoned by polar groups and thus not suited for conversion of functionally substituted olefins, such as unsaturated acids, esters, alcohols, ethers, nitriles, etc.

In 1972, Van Dam et al. (6-8) reported an effective and selective catalyst system, consisting of equimolar amounts of WCl_6 and $Sn(CH_3)_4$ for the homogeneously catalyzed metathesis of unsaturated fatty acid esters of different type. A few years later, Verkuijlen et al. (9) found that Re_2O_7/Al_2O_3, a highly efficient catalyst for the metathesis of simple olefins, can be transformed to an active catalyst system for the metathesis of unsaturated esters by the addition of a small amount of $Sn(CH_3)_4$. This development is of particular importance for practical applications, the more so as this heterogeneous catalyst systems is already active at room temperature. In this review, the most relevant applications in this field are discussed.

MONOUNSATURATED CARBOXYLIC ESTERS

Van Dam et al. (6-8) reported the conversion of methyl oleate into equimolar amounts of 9-octadecene and the dimethyl ester of 9-octadecene dioic acid:

$$[3]$$

$$2\ \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3} \rightleftharpoons$$
$$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3} +$$
$$\mathrm{H_3COOC(CH_2)_7CH{=}CH(CH_2)_7COOCH_3}$$

Equilibrium conversion (50 mol%) was reached within 2 hr at 110 C. Analysis of the reaction mixture showed that the *cis-trans* ratio of the reaction products was ca. 1:3, corresponding to thermodynamic equilibrium.

Other examples of conversions of commercially available fatty esters are the metathesis of methyl erucate:

$$[4]$$

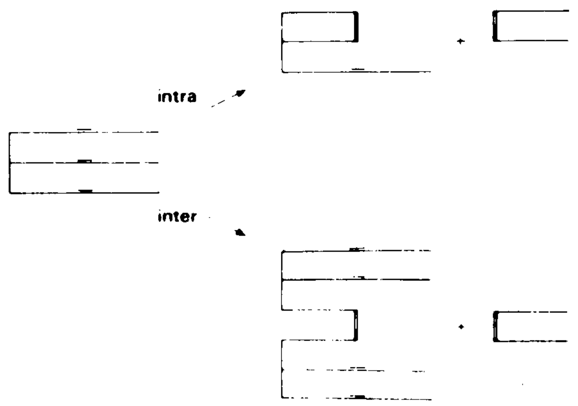
$$2\ \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOCH_3} \rightleftharpoons$$
$$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3} +$$
$$\mathrm{H_3COOC(CH_2)_{11}CH{=}CH(CH_2)_{11}COOCH_3}$$

and methyl 9-undecenoate:

$$2\ \mathrm{CH_2{=}CH(CH_2)_8COOCH_3} \rightleftharpoons \mathrm{CH_2{=}CH_2} + \qquad [5]$$
$$\mathrm{H_3COOC(CH_2)_8CH{=}CH(CH_2)_8COOCH_3}$$

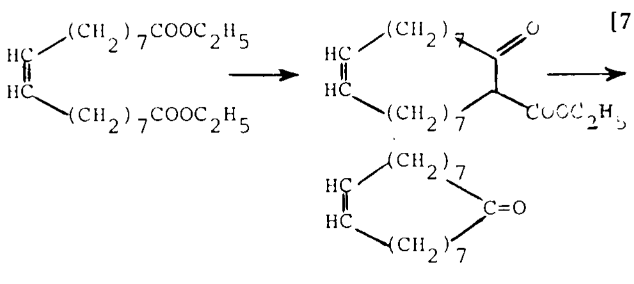
The latter equilibrium can be shifted to the right by continually removing the volatile ethene.

Metathesis of esters of glycerol, i.e., the direct conversion of unsaturated fatty oils, is also possible. Thus, olive oil (consisting mainly of glycerol trioleate) yields 9-octadecene as the main distillable product, besides dicarboxylic acid glycerol esters, formed by intra- or intermolecular metathesis:



The latter reaction strongly predominates. Note that this process of molecule enlargement does not involve the consumption of double bonds. Comparable metathesis experiments with drying and semidrying oils, like linseed and soybean, have shown that viscous, high molecular oils with outstanding drying properties can be obtained along this route.

Dicarboxylic esters, obtained by metathesis of unsaturated fatty acid esters, are promising starting materials for the synthesis of valuable chemical products. Van Thiel et al. (10) reported the preparation of vulcanizable polyesters and polyamides. Tsjui and Hashiguchi (11) described the synthesis of civetone, an important base material in the perfume industry, from diethyl-9 octadecene dioate by cyclocondensation and dicarboxylation:



civetone

Experiments with a variety of unsaturated esters of different chain lengths have shown that metathesis is possible when the ester group and the carbon-carbon double bond are separated by at least one methylene group (Table I) (12,13).

Apparently, conjugation of the carbon-carbon double bond and the ester group prohibits metathesis; in the case of methacrylic and 2-methylcrotonic esters, the steric effect may also have a negative influence on reactivity.

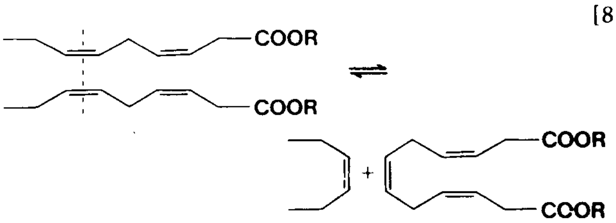
TABLE I

Metathesis of Unsaturated Carboxylic Esters by Re_2O_7/Al_2O_3-$Sn(CH_3)_4$ (Conversion After 24 hr at Room Temperature (13)

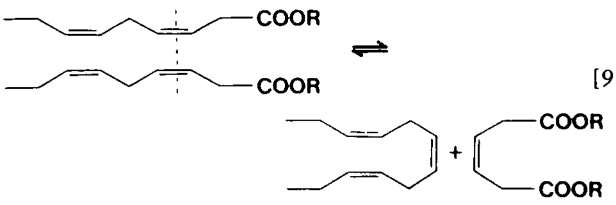
Ester	Conversion (mol %)	Selectivity (%)	Reaction products
C_8-C=C-C_7-COOC (oleic)	50	95	C_8-C=C-C_8 + COCC-C_7-C=C_7-COOC
C=C-C-C-COOC (allyl acetic)	70	95	C=C + COOC-C-C-C=C-C-C-COOC
C=C-C-COOC (vinyl acetic)	70	95	C=C + COOC-C-C=C-C-COOC
C=C-COOC (acrylic)	0	–	–
C-C=C-COOC (crotonic)	0	–	–
$\mathrm{C\text{-}C{=}\underset{\substack{\vert\\ C}}{C}\text{-}COOC}$ (2-methylcrotonic)	0	–	–
$\mathrm{C{=}\underset{\substack{\vert\\ C}}{C}\text{-}COOC}$ (methacrylic)	0	–	–

POLYUNSATURATED CARBOXYLIC ESTERS

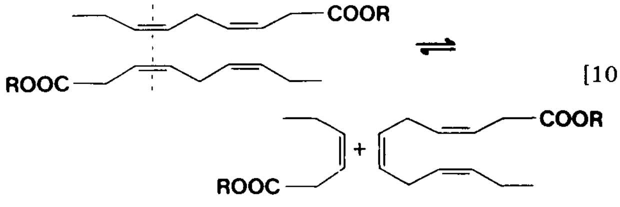
Metathesis of esters of polyunsaturated fatty acids, such as linoleic and linolenic, leads to a very large number of reaction products. The conversion results in the formation of polyenes, unsaturated monocarboxylic esters and unsaturated dicarboxylic esters, e.g., for linoleic esters:



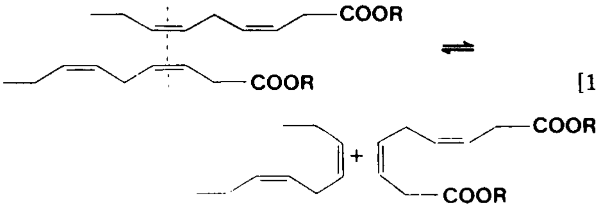
[8]



[9]

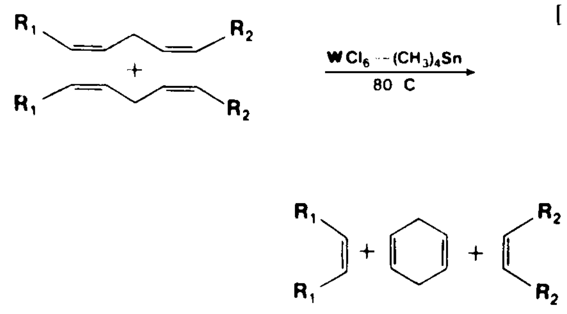


[10]



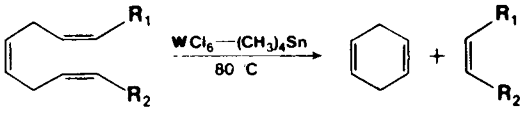
[11]

Because each of the reaction products in its turn can react with every other unsaturated compound present in the reaction mixture, the product distribution at equilibrium corresponds to a statistical scrambling of alkylidene and carboxy-alkylidene moieties, resulting in a 1:2:1 molar ratio of polyolefins, monocarboxylic esters and dicarboxylic esters (14-18). In addition to these products, 1,4 cyclohexadiene and higher cyclopolyenes are formed, either as a consequence of an intermolecular process (in the case of methyl linoleate):



[12]

or by an intramolecular reaction (methyl linolenate):



[13]

The amounts of 1,4 cyclohexadiene obtained from methyl linoleate and methyl linolenate were 6 mol% and 30 mol%, respectively (18); from linseed oil, 1,4-cyclohexadiene was obtained in amounts up to 56 mol% by metathesis (19).

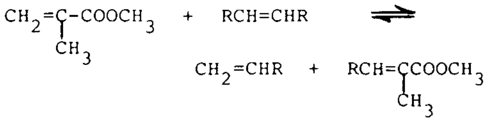
COMETATHESIS REACTIONS

Cometathesis reactions of unsaturated esters with olefins are very promising, particularly from a synthetic point of view, because they offer new routes to a variety of fatty acid derivatives which are often difficult to obtain by other methods.

An example is the reaction of methyl oleate with 3-hexene:

$$\begin{array}{l} CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 \; + \\ CH_3CH_2CH{=}CHCH_2CH_3 \; \rightleftharpoons \\ CH_3(CH_2)_7CH{=}CHCH_2CH_3 \; + \\ CH_3CH_2CH{=}CH(CH_2)_7COOCH_3 \end{array} \qquad [14]$$

In addition to the products of self-metathesis of methyl oleate, equimolar amounts of 3-dodecene and methyl 9-dodecenoate are formed. In the same way, other homologs of methyl oleate and other monounsaturated fatty esters can be easily obtained (12,13). It is interesting that even methyl methacrylate, which is inactive in self-metathesis, effectively reacts with a symmetric olefin:

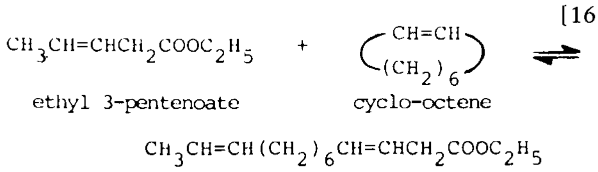


$$CH_2{=}C(CH_3){-}COOCH_3 + RCH{=}CHR \rightleftharpoons CH_2{=}CHR + RCH{=}C(CH_3)COOCH_3 \qquad [15]$$

Thus, cometathesis of methacrylic esters with proper olefins offers a suitable method for the synthesis of α-methyl β-unsaturated esters.

Cometathesis of unsaturated esters with cyclic olefins results in the formation of long-chain linear diunsaturated esters (20), e.g.,

[16]



In this example, a 25% conversion was observed after 20 hr at 70 C, using WCl_6-$Sn(CH_3)_4$ as a catalyst; the selectivity with respect to the C_{13}-monoester amounted to 46%.

Highly interesting are cometathesis reactions of unsaturated fatty acid esters with ethene (ethene cleavage), to produce shorter chain molecules with terminal double bonds:

$$\begin{array}{l} CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 \; + \; CH_2{=}CH_2 \; \rightleftharpoons \\ CH_2{=}CH(CH_2)_7CH_3 \; + \; CH_2{=}CH(CH_2)_7COOCH_3 \end{array} \qquad [17]$$

methyl 9-decenoate

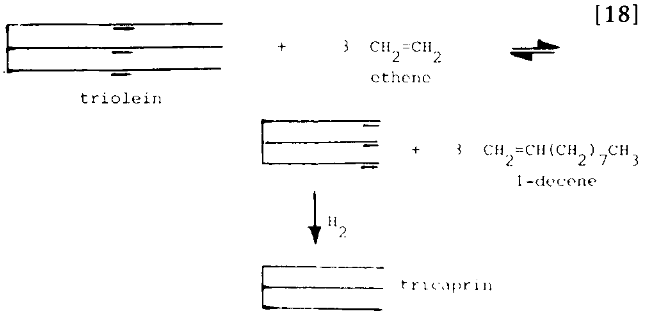
Bosma and coworkers (21) investigated this reaction both with the homogeneous WCl_6-$Sn(CH_3)_4$ catalyst and the heterogeneous Re_2O_7/Al_2O_3-$Sn(CH_3)_4$ system (Table II). Note that the tendency of methyl oleate to self-metathesis can be almost completely suppressed by using an excess of ethene. Table II also demonstrates the more pronounced activity of the heterogeneous rhenium catalyst.

The product methyl 9-decenoate is the key intermediate in the synthesis of 9-oxo-*trans*-2-decenoic acid, a honeybee pheromone (the "queen substance"), and in the synthesis of 9-oxodecanoic acid, a prostaglandin intermediate.

Also, methyl 9-decenoate can be converted to the epoxide or to hydroxy compounds for use in polymer production, whereas on hydrolysis and hydrogenation it yields decanoic acid or decanol, which are used in lubricants and plasticizers.

Of practical importance is the ethene cleavage of distinct fatty oils, which allows the transformation of long-chain glycerides into glycerides of lower molecular weight. Examples are the production of tricaprin from olive oil (mainly triolein) by metathesis and subsequent hydrogenation:

[18]



and the conversion of erucic (C_{22}) glycerides into myristic (C_{14}) glycerides via a similar route.

Because C_{10}-C_{14} fatty acids are in short supply on the world market and monounsaturated C_{18} acids predominate in natural fatty oils (22,23), cometathesis of distinct fatty oils (olive, cotton, sesame, rape) with ethene might offer an attractive, selective and nondestructive route to these lower molecular weight oils. The terminal olefins, formed as by-products in these reactions, are themselves valuable intermediates for a variety of synthetic applications.

Cometathesis of polyunsaturated esters with an excess of ethene might be useful as a simple tool in determining location of the double bonds and can also be applied for the synthesis of distinct unsaturated hydrocarbons. Thus, from linoleic and linolenic esters,

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOCH_3$$

methyl linoleate

$$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOCH_3$$

methyl linolenate

1,4 pentadiene is obtained in good yields besides 1-heptene (in the case of linoleic) or 1-butene (in the case of linolenic

TABLE II

Cometathesis of Methyl Oleate and Ethene (Conversion in mol% of Methyl Oleate after 5 hr; Molar Ratio of Methyl Oleate/catalyst 20:1)

Pressure (MPa)	Re_2O_7/Al_2O_3-$Sn(CH_3)_4$		WCl_6-$Sn(CH_3)_4$	
	Cometathesis	Self-metathesis	Cometathesis	Self-metathesis
0.2	73	11	47	15
5.0	90	1	64	2

esters (24). Distinct unsaturated fatty oils (soybean, linseed, tung, herring, menhaden, etc.) may serve as easily obtainable raw materials for the synthesis of these hydrocarbons.

ALKENYL ESTERS

Interesting possibilities can also be found in the metathesis of esters with the double bond present in the alcohol fragment (alkenyl esters). Levisalles and Villemin (25) showed that, in the presence of the homogeneous catalyst system WCl_6-$Sn(CH_3)_4$, metathesis of ω-unsaturated alkenyl esters only occurs when the double bond and ester group are separated by at least two methylene groups:

$$2\ CH_2{=}CH(CH_2)_nOCOCH_3 \rightleftharpoons CH_2{=}CH_2 + H_3COCO(CH_2)_nCH{=}CH(CH_2)_nOCOCH_3 \quad [19]$$

Thus, for n = 2,3 of 8, under proper reaction conditions conversions of 40-45% were obtained (selectivity 88-95%). Verkuijlen (18) observed that in the case of allyl acetate (n = 1) allyl chloride was formed, and concluded that the applied WCl_6-$Sn(CH_3)_4$ catalyst was completely deactivated, due to the decomposition of the allyl acetate.

In contrast with these results, the heterogeneous metathesis of allyl acetate could be performed quite easily and with a high selectivity using the Re_2O_7/Al_2O_3-$Sn(CH_3)_4$ system. At room temperature, 17% of the starting material was converted with 96% selectivity into the expected products:

$$2\ CH_2{=}CHCH_2OCOCH_3 \rightleftharpoons CH_2{=}CH_2 + H_3COCOCH_2CH{=}CHCH_2OCOCH_3 \quad [20]$$

Cometathesis of ω-unsaturated alkenyl esters with suitable olefins offers single-step routes to highly interesting biologically active compounds. For instance, cometathesis of 9-decenyl acetate and 3-hexene yields 9-dodecenyl acetate, the *cis*-component of which is the sex pheromone of the grapeberry moth (a leaf roller):

$$[21]\quad CH_2{=}CH(CH_2)_8OCOCH_3 + C_2H_5CH{=}CHC_2H_5 \rightleftharpoons C_2H_5CH{=}CH(CH_2)_8OCOCH_3 + CH_2{=}CHC_2H_5$$

The use of such pheromones offers an effective and selective method of pest control.

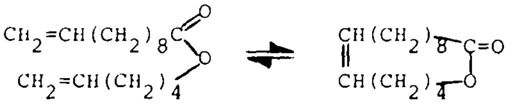
Another example of the application of cometathesis is the synthesis of macrocyclic lactones (macrolides). Villemin (26) described two synthetic routes:

- cometathesis of an unsaturated alkenyl ester with an unsaturated carboxylic ester:

$$[22]\quad CH_2{=}CH(CH_2)_8COOCH_3 + CH_2{=}CH(CH_2)_4OCOCH_3 \rightleftharpoons H_3COCO(CH_2)_4CH{=}CH(CH_2)_8COOCH_3 + CH_2{=}CH_2$$

followed by hydrolysis of the diester and cyclization of the ω-hydroxy acid thus obtained.

- intramolecular metathesis of an ester which is unsaturated both in the acid as well as in the alcohol fragment:



[23]

The lactone, obtained in this way, can be reduced to exaltolide (1, 15-pentadecanolide), which is identical to the naturally occurring product.

PERSPECTIVES

It is remarkable that, from the many metathesis catalysts described in the literature (1-4), only a few are effective in the conversion of unsaturated esters and other functionalized olefins. For instance, for the homogeneous metathesis of unsaturated esters, practically none besides WCl_6-based catalyst systems have been reported, of which the WCl_6-$Sn(CH_3)_4$ system is the most active and selective, at reaction temperatures of 70-100 C.

Recent research showed that the catalyst system $WOCl_4$-$(CH_3)_4Sn$ exhibits about the same activity for the metathesis of methyl oleate as the WCl_6-$(CH_3)_4Sn$ system, which suggests that the ester converts WCl_6 to $WOCl_4$, the precursor of the active intermediate (18,27).

Tsuji and Hashiguchi (28) recommended the system $WOCl_4$-(cyclopentyl)2Ti$(CH_3)_2$ (ref. 11). Banks et al. (29) developed a number of homogeneous catalysts, based on heteroatom-substituted carbene complexes, e.g., (phenyl methoxycarbene) pentacarbonyl tungsten, with $SnCl_4$, WCl_6 or $WOCl_4$ as cocatalysts, but these systems are as yet less effective than WCl_6-$Sn(CH_3)_4$.

However, the activity of these homogeneous catalyst systems is not so high, due to the interaction of the polar group with the catalyst, which hinders the coordination of double bonds. This fact and the technical problems related to the recovery of the rather precious catalyst components have so far restricted their use mainly to small-scale syntheses. The main barrier to larger scale applications of ester metathesis is, therefore, the development of more active, stable and—if possible—cheap catalysts. In this respect, heterogeneous catalyst systems are preferred. The modification of the solid Re_2O_7/Al_2O_3 catalyst with alkyl tin compounds is certainly an important step forward. These heterogeneous catalysts are already active at room temperature and highly selective for the primary metathesis products; moreover, they allow the metathesis of certain substrates—the conversion of allyl acetate was discussed as an example—that do not react in the presence of homogeneous catalysts.

In this review, we have shown that the catalytic metathesis of unsaturated esters opens new routes not only to distinct nondestructive transformation processes of fatty oils (which might increase their interchangeability and applicability), but also to many valuable chemical products.

It is not surprising that research interest in this field has grown so rapidly in recent years. Further developments, particularly in the field of heterogeneous catalysis, will undoubtedly make these new routes of increasing importance for the fat industry.

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Hydrozirconation of Unsaturated Fatty Acid Derivatives

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ABSTRACT

In the hydrozirconation reaction, developed by Schwartz and coworkers, *bis*(π-cyclopentadienyl)zirconium hydridochloride $Cp_2Zr(H)Cl$, is added to the double bond of an olefin. The organozirconium intermediate can be functionalized by reaction with a variety of electrophiles such as oxygen, halogens, acetyl chloride and carbon monoxide. Furthermore, the double bond can be reformed by treatment with a hydride acceptor such as triphenylmethyl tetrafluoroborate. When a short-chain internal olefin is hydrozirconated, the initially formed alkylzirconium intermediate is rapidly isomerized to a compound in which the zirconium moiety is bound to the sterically least hindered position, which most often is the terminal position. The isomerization occurs rapidly at room temperature in contrast to the corresponding organoboron or aluminum compounds, which slowly positionally rearrange only at elevated temperatures. Because of the facile isomerization of internal alkylzirconium compounds to the terminal ones, we investigated application of the reaction to unsaturated fatty acids such as oleic and erucic acids. However, reactions on long-chain alkenes (such as oleic acid) are frequently much slower than those conducted on shorter-chain alkenes, and attention must be given to optimizing the reaction conditions if good yields are to be obtained. It would also be necessary to find an easily removable protecting group for the carboxylic function, as $Cp_2Zr(H)Cl$ reduces carboxylic acids to alcohols. We found that the 4,4-dimethyl-2oxazoline function is a suitable protecting. group, and therefore synthesized the oxazolines from oleic acid and erucic acid. Hydrozirconation of the 4,4-dimethyl-2-oxazoline of oleic acid followed by oxidation with *t*-butyl hydroperoxide and conversion to methyl esters, gave methyl 3-hydroxy and methyl 18-hydroxy stearate in 13% and 17% yield, respectively. The relatively low yield is due to competing hydrogenation, the mechanism of which is discussed. Recent results indicate that the carboxyl group can be protected as *t*-butyl esters in the hydrozirconation and that oleyl alcohol derivatives can also be used. To understand the isomerization pattern in hydrozirconation, the reaction with α,β- and β,γ-unsaturated fatty acid oxazolines is discussed. Possibilities of making the hydrozirconation reaction catalytic by binding of the hydrozirconation reagent to a solid support as well as the synthetic potential in combining hydrozirconation with the olefin metathesis reaction are briefly reviewed.

INTRODUCTION

In 1970, Wailes and Weigold prepared *bis*(π-cyclopentadienyl) zirconium hydridochloride, $Cp_2Zr(H)Cl$, by reaction of certain aluminum hydrides with cyclopentadienylzirconium dichloride (1) (Fig. 1). They also found that olefins reacted with $Cp_2Zr(H)Cl$ to give alkylzirconium(IV) complexes, $Cp_2Zr(R)Cl$ (2). This hydrozirconation reaction was extensively studied in the 1979s by J. Schwartz and coworkers, who mostly used short-chain olefins (3). The reaction is similar to hydroboration but, in contrast to hydroboration, a rapid isomerization to the terminal zirconium derivatives was observed at room temperature. Thus, all three isomeric octenes (Fig. 2) gave the same alkylzirconium derivative. Two other cases are shown in Figure 3. Note that 2-methyl-2-butene gives the 3-methylbutylzirconium derivative. It was found that the order of reactivity of olefins was α-olefins > *cis*-olefins ≈ *trans*-olefins > oxocyclic olefins > cyclic olefins. Branching at the double bond also decreased the reactivity and trisub-

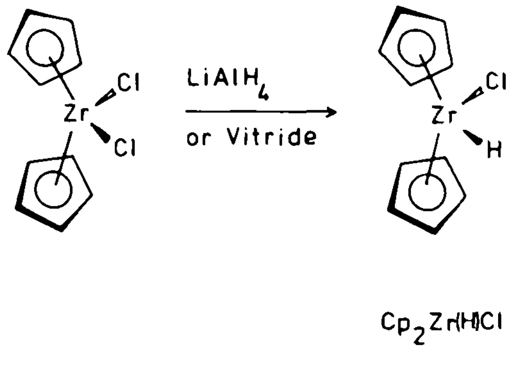

FIG. 1. Preparation of $Cp_2Zr(H)Cl$.