

# Catalytic C,C-bond forming additions to unsaturated fatty compounds

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A large number of novel fatty compounds have been synthesized by catalytic C,C-bond forming addition reactions to the C,C-double bond of unsaturated fatty compounds. Radical reactions such as the solvent-free addition of  $\alpha$ -halocarboxylic acid esters initiated by electron transfer, e.g., from copper to give fat-derived  $\gamma$ -lactones are described as well as Lewis acid-induced electrophilic addition reactions yielding new oleochemicals such as alkyl-substituted 4-chlorotetrahydropyrans, primary homoallylic alcohols,  $\beta$ -,  $\gamma$ -unsaturated ketocarboxylic acids and Diels–Alder addition products. New catalysts as, e.g., ligand-modified rhodium catalysts for the hydroformylation and heterogeneous boron-modified rhenium catalysts for the olefin metathesis have been developed. The addition of C-nucleophiles such as dimethylmalonate and nitromethane is possible by palladium(0)catalyzed additions to unsaturated fatty compounds after conversion of the electron-rich to an electron-poor double bond. More than fifty literature articles are reviewed.

**KEY WORDS:** renewable raw materials; unsaturated fatty acids; C,C-bond forming reactions; catalysts; Lewis acids.

## 1. Introduction

Recently, modern synthetic methods have been applied extensively to fatty compounds for the selective functionalization of the alkyl chain. Radical, electrophilic, nucleophilic, and pericyclic as well as transition metal-catalyzed additions to the C,C-double bond of, for example, oleic acid as the prototype of a readily accessible, unsaturated fatty acid have led to a large number of novel fatty compounds [1–6]. Great interest has been focused on carbon–carbon bond-forming addition reactions that afford new branched chain or elongated fatty compounds with possibly interesting properties.

We report here how the C,C-double bond of unsaturated fatty compounds (**1–10**, figure 1) can be functionalized by formation of new C,C-bonds by catalytic reactions. Up to now there are only a few reactions known that proceed by catalytic reaction conditions. Many Lewis acid induced addition reactions of unsaturated fatty compounds give interesting modified oleochemicals in good yields but an excess of the Lewis acid is required because the carbonyl group of the fatty acid or acid ester is also complexed. A great challenge should be the development of new and effective catalysts, and of catalytic reactions that allow the selective transformation of fatty compounds to give new products with interesting properties.

## 2. Radical additions

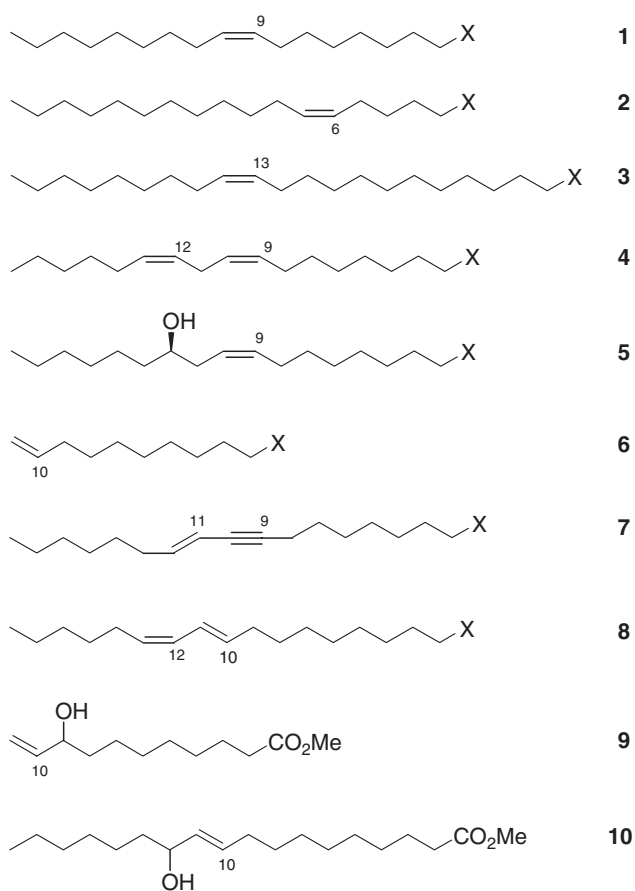
Unsaturated fatty compounds are alkenes having an electron-rich C,C-double bond that can be functionalized by free radical additions with the formation of a new C,C-bond. Free radical addition reactions initiated by different catalysts have been investigated systematically [7].

### 2.1. Manganese(III)acetate initiated additions

Manganese(III)acetate was found to be a good initiator for the addition of enolizable compounds such as acetone, acetic acid, malonic acid, monomethyl malonate and cyanoacetic acid to unsaturated fatty compounds [8,9]. A regioisomeric mixture of 9- and 10-acetyloctadecanoic acid methyl esters **11** was obtained on reaction of methyl oleate **1b** and acetone in the presence of manganese(III)acetate (scheme 1(a)), while addition of copper(II)acetate to the reaction mixture yielded the regioisomeric (*E*)-configured alkenes **12** with high stereoselectivity (scheme 1(b)). Methyl 13-oxotradecanoate **13** was formed in the respective reaction with methyl 10-undecenoate **6b** (scheme 1(c)). Manganese(III)acetate which is usually required in stoichiometric amounts is generated *in situ* from potassium permanganate and a catalytic amount of manganese(II)acetate. In this case, only 20% total manganese(III)salt is required.

The manganese(III)acetate-initiated reaction of methyl oleate **1b** and malonic acid afforded a regioisomeric mixture of  $\gamma$ -lactones **14** (scheme 2). The regeneration of manganese(III)acetate was possible by anodic oxidation [10].

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1 - 8	a	b	c
X	CO <sub>2</sub> H	CO <sub>2</sub> Me	CH <sub>2</sub> OH

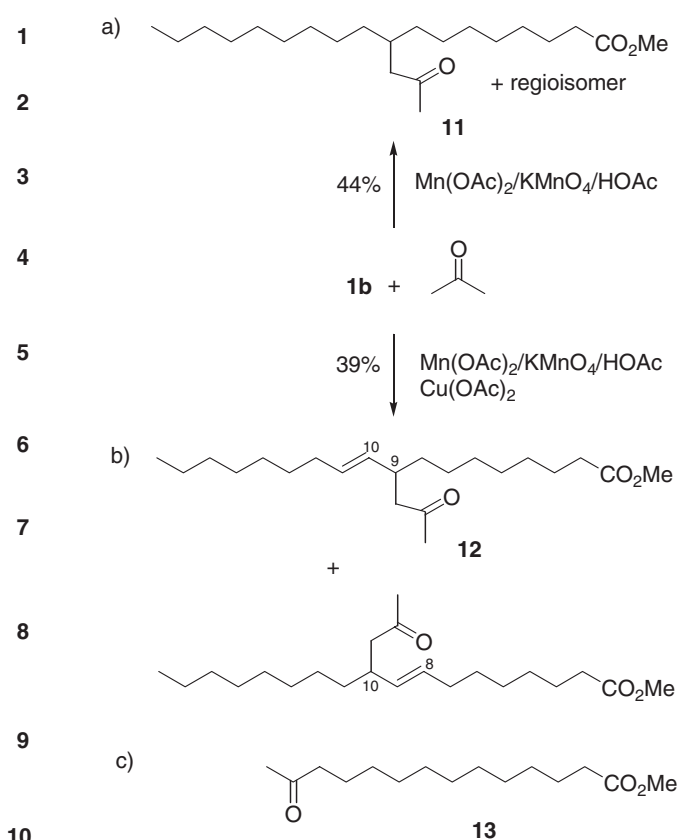
Figure 1. Starting materials for the synthesis of novel fatty compounds: oleic acid **1a**, petroselinic acid **2a**, erucic acid **3a**, linoleic acid **4a**, ricinoleic acid **5a**, 10-undecenoic acid **6a**, santalbic acid **7a**, conjuenoic acid **8a** (regio and stereoisomeric mixture), the respective methyl esters **1b–8b**, and alcohols **1c–8c**, methyl 9-hydroxy-10-undecenoate **9**, methyl 12-hydroxyoctadec-10-enoate **10**.

The reaction was applied to 1-alkenes such as methyl 10-undecenoate **6b** to give the spiro-di- $\gamma$ -lactone **15** as a mixture of diastereomers (figure 2) [9].

## 2.2. Copper-initiated additions

The reaction of higher carboxylic acids and unsaturated fatty compounds can be carried out in a solvent-free reaction by addition of their  $\alpha$ -haloesters initiated by electron transfer from copper [11–13]. The addition of 2-iodocarboxylates, for example, methyl 2-iodopropanoate **16** to **6b** gave the  $\gamma$ -lactone **17** in high yields (scheme 3).

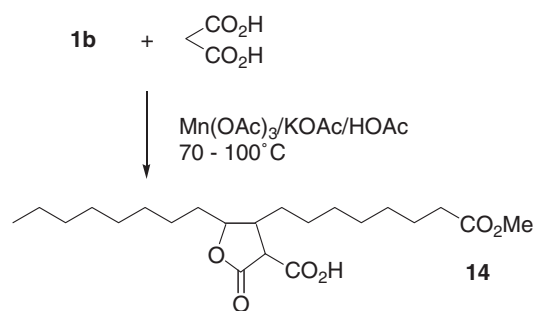
The reaction procedure is very simple: The unsaturated fatty compound, the 2-halocarboxylate and commercial copper powder are mixed without further pretreatment and heated at 100–130 °C under an inert



Scheme 1. Manganese(III)acetate generated *in situ* from KMnO<sub>4</sub>, and catalytic amounts of Mn(OAc)<sub>2</sub>-induced radical addition of acetone to methyl oleate **1b** with formation of (a) methyl 9(10)acetyloctadecanoate **11**; (b) in the presence of copper(II)acetate, the regioisomeric methyl 9(10)-acetyloctadecanoates **12** were obtained; (c) addition of acetone to methyl 10-undecenoate **6b** gave the linear 13-oxotetradecanoic acid methyl ester **13** [8,9].

atmosphere. After a simple workup, analytically pure products are obtained in good yields.

The reaction is initiated by electron transfer from copper to the activated iodoalkane (figure 3). The electrophilic radical formed after cleavage of the halide adds to the electron-rich double bond of the alkene, and subsequent iodo abstraction yields a methyl 4-iodoalkanoate that cyclizes to give a  $\gamma$ -lactone with elimination of iodoalkane.



Scheme 2. Manganese(III)acetate-induced radical addition of malonic acid to methyl oleate **1b** with formation of the regioisomeric  $\gamma$ -lactones **14** [7–9].

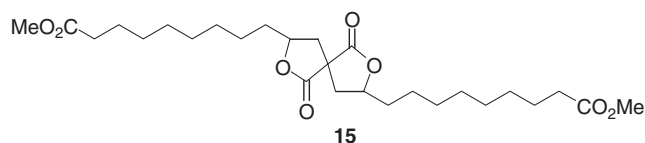
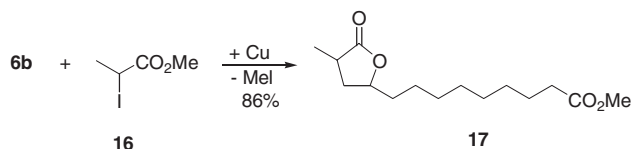


Figure 2. Manganese(III)acetate induced radical addition of malonic acid to methyl 10-undecenoate **6b** with formation of the spiro-di- $\gamma$ -lactone **15** (mixture of diastereomers) [9].



Scheme 3. Copper-initiated addition of methyl 2-iodopropanoate **16** to methyl 10-undecenoate **6b** [12].

2-Iodocarboxylates were generated *in situ* from the readily available bromo compounds by addition of a stoichiometric amount of sodium iodide. The addition of methyl 2-bromopropanoate **18** to methyl oleate **1b** resulted in the formation of the regioisomeric  $\gamma$ -lactones **19** in 58% yield (scheme 4).

Comparable results were obtained with methyl petroselinate **2b** and methyl erucate **3b**.

It is remarkable that the respective reactions of methyl 10-undecenoate **6b** with diethyl bromomalonates could be carried out without addition of sodium iodide. Addition products from **6b** and diethyl 2-bromo-2-methylmalonate (**21**) [10,11] or dimethyl 2-bromo-3-ethylsuccinate **23** [13] were formed in 87 and 50%, respectively (scheme 5).

The addition of 2-iodo- and 2-bromo-alkanenitriles is possible in an analogous manner to the addition of alkyl 2-haloalkanoates. While the copper-initiated reaction, e.g., of iodoacetonitrile **25** and methyl 10-undecenoate **6b** gave 12-cyano-10-iodododecanoic acid methyl ester **26** without problems, the corresponding reaction of 2-bromo-hexanonitrile **27** and **6b** required the addition of sodium iodide to give addition product **28** (scheme 6) [14].

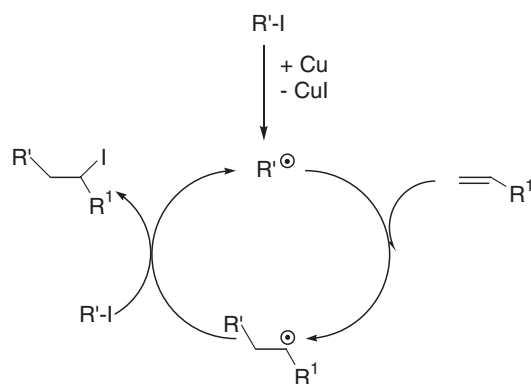
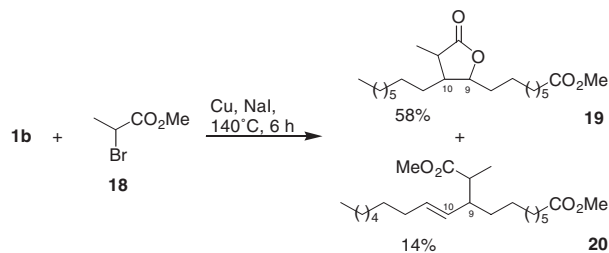
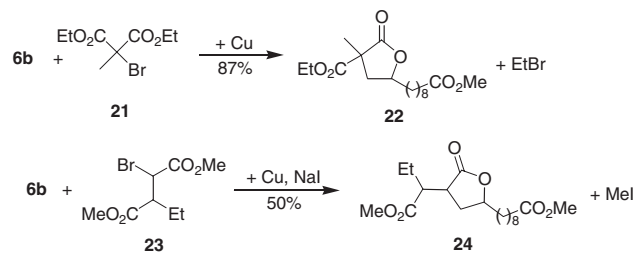


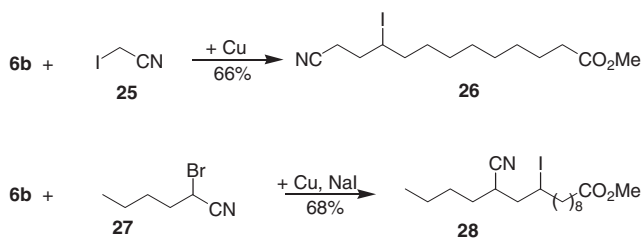
Figure 3. Mechanism for the copper-initiated addition of activated iodoalkanes to alkenes ( $\text{R}'\text{-I}$  = alkyl 2-iodoalkanoate [**16**],  $\text{R}'$  = alkyl,  $(\text{CH}_2)_8\text{COOMe}$ ).



Scheme 4. Copper-initiated addition of methyl 2-bromopropanoate **18** to methyl oleate **1b** in the presence of sodium iodide yields the regioisomeric  $\gamma$ -lactones **19** and the addition-elimination product **20** [11–13].



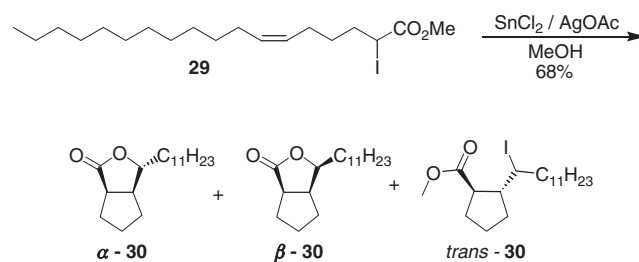
Scheme 5. Copper-initiated addition of diethyl 2-bromo-2-methylmalonate (**21**) [11,12] and ethyl 2-bromo-3-ethylsuccinate **23** [14] to methyl 10-undecenoate **6b** in the presence of sodium iodide.



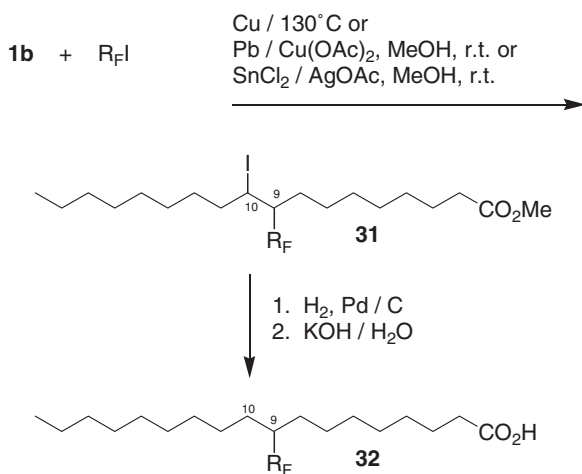
Scheme 6. Copper-initiated addition of iodoacetonitrile **25** and 2-bromohexanonitrile **27** to methyl 10-undecenoate **6b** [14].

Furthermore, the reaction was applied to intramolecular cyclizations [15]. Referring to reaction time, yield and stereoselectivity,  $\text{SnCl}_2/\text{AgOAc}$  (scheme 7) was found to be the most effective initiator system for the cyclization of methyl 2-iodopetroselinate **29** to cyclopentane derivatives **30**.

Perfluoroalkylated oleochemicals, which are of interest because of their surfactant properties [16], can be



Scheme 7. Radical cyclization of methyl 2-iodopetroselinate **29** induced by  $\text{SnCl}_2/\text{AgOAc}$  ( $\alpha$ -**30**: $\beta$ -**30**:*trans*-**30** = 35:31:34) [14].



<b>31, 32</b>	<b>a</b>	<b>b</b>	<b>c</b>
$\text{R}_F$	$\text{C}_4\text{F}_9$	$\text{C}_6\text{F}_{13}$	$\text{C}_8\text{F}_{17}$

Scheme 8. Synthesis of 9- and 10-perfluoroalkyloctadecanoic acids **32** as a regioisomeric mixture: Addition of perfluoroalkyl iodides to **1b** gave the regioisomeric perfluoroalkylated iodoesters **31**, which were then reduced to iodine-free esters and hydrolyzed to free perfluoroalkylated fatty acids **32** [17,18].

synthesized by electron transfer radical reactions initiated by metals such as finely divided silver [17], copper powder [18], or lead with a catalytic amount of copper(II)acetate [18].

The best yields of perfluoroalkylated fatty compounds **31** from reactions of methyl oleate **1b** and perfluoroalkyl iodides were obtained with copper powder or with lead/ $\text{Cu}(\text{OAc})_2$  (scheme 8) [18].

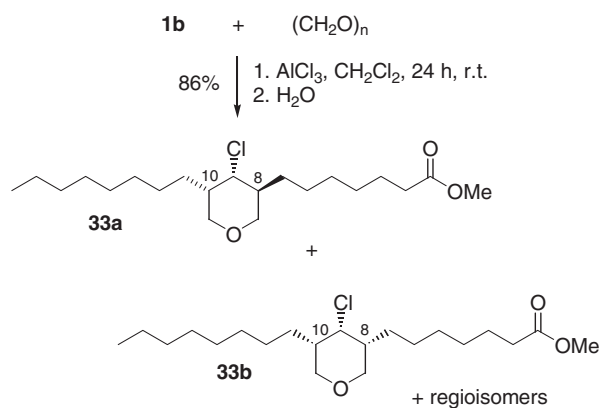
### 3. Lewis acid-induced electrophilic additions

#### 3.1. Additions of aldehydes and ketones

Formaldehyde and higher aldehydes react with unsaturated fatty compounds in the presence of aluminum chloride to form the corresponding alkyl-substituted 4-chlorotetrahydropyrans in good yields and with high selectivity [19]. The reaction of two equivalents of formaldehyde with, for example, methyl oleate **1b**, gave the 3,5-dialkyl-substituted 4-chlorotetrahydropyran **33** as a mixture of regioisomers and diastereomers (scheme 9).

However, the reaction shows a considerable diastereoselectivity. The products were formed in a ratio of **33a**:**33b** = 3:1. The mechanism of this Prins-type cyclization is outlined in scheme 10.

The corresponding reaction of methyl ricinoleate **5b** and formaldehyde proceeded regioselectively to position C9 of the molecule chain yielding a diastereomeric mixture of products **34** (scheme 11) [19]. Using a higher amount of  $\text{AlCl}_3$  compared to the respective reaction of **1b** (scheme 9), the reaction time could be shortened to 3 h.

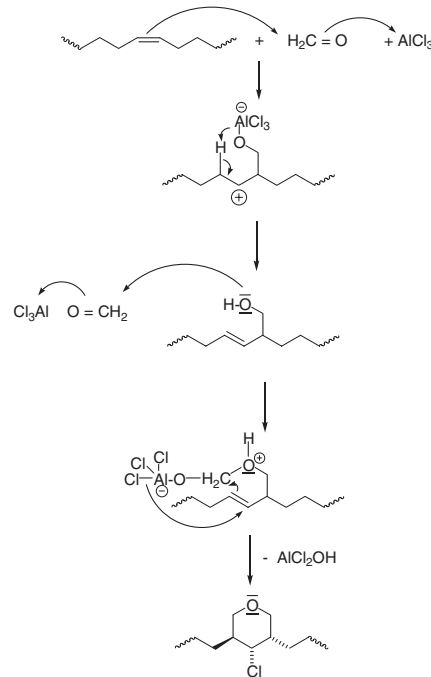


methyl oleate: paraformaldehyde:  $\text{AlCl}_3$  = 2:4:1

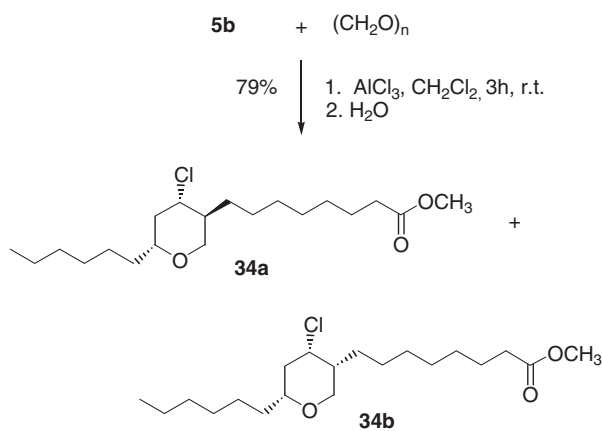
Scheme 9.  $\text{AlCl}_3$ -induced addition of two equivalents of paraformaldehyde to methyl oleate **1b** to give the 4-chlorotetrahydropyrans **33** (**33a**:**33b** = 3:1; mixture of regioisomers) [19].

The synthesis of fat-derived tetrahydropyrans in the presence of montmorillonite clays, which are heterogeneous catalysts with Brønsted- and Lewis acid centers, should be of interest. Heterogeneous catalysts show considerable advantages compared to homogeneous catalysts especially because of their environmental compatibility, reusability, low cost and simple removal by filtration or centrifugation.

The Fe(III)cation-exchanged montmorillonite K10-induced reaction of methyl 10-undecenoate **6b** and formaldehyde gave the dimeric tetrahydropyranol ester **35** as the main product, which was isolated in 45% yield as a diastereomeric mixture (scheme 12) [20].



Scheme 10. Mechanism of the  $\text{AlCl}_3$ -induced Prins-type cyclization to give diastereoselectively tetrahydropyran derivatives (the major diastereomer is given).



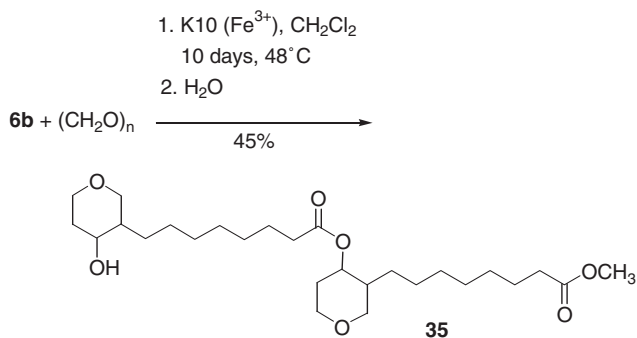
**34a**: m.p. 30 - 31 °C,  $[\alpha]_D^{20} = 27.4$  ( $c=2.82$ ,  $CHCl_3$ )

**5b** : paraformaldehyde :  $AlCl_3 = 1 : 1.7 : 1.7$

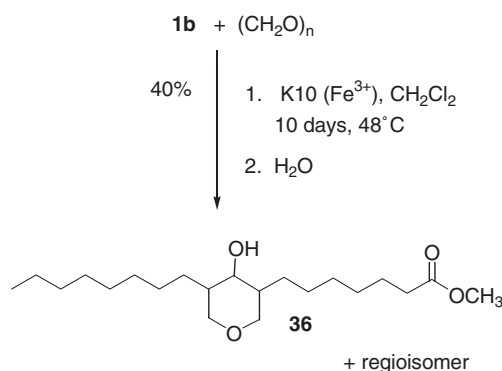
Scheme 11.  $AlCl_3$ -induced addition of one equivalent of paraformaldehyde to methyl ricinoleate **5b** to give 4-chlorotetrahydropyrans **34** (**34a** : **34b** = 3.8 : 1) [19].

In the corresponding reaction of methyl oleate **1b** as main product, 3,5-dialkyl-substituted 4-hydroxytetrahydropyran **36** was obtained as a mixture of regioisomers and diastereomers in 40% yield (scheme 13) [20]. The by-product, a dimeric tetrahydropyranol ester was formed in 18% yield.

It is known from literature that homoallylic alcohols with a terminal C,C-double bond give on reactions with aldehydes the respective 2,6-dialkyl-substituted 4-hydroxytetrahydropyrans in the presence of Amberlyst-15 [21]. This reaction, using montmorillonite KSF as catalyst, was applied to homoallylic alcohols with internal C,C-double bonds such as methyl ricinoleate **5b**. In the respective reaction with heptanal on the surface of KSF in refluxing dichloromethane, the 2,3,6-trialkyl-substituted tetrahydropyranol **37** was obtained remarkably as a mixture of only two diastereomers in 56% yield (scheme 14). The all-*cis*-product **37a** was formed with considerable diastereoselectivity. The ratio of compounds **37a** : **37b** was 2.7 : 1 [20]. Tetrahydropyrans hydroxylated



Scheme 12. Addition of formaldehyde to methyl 10-undecenoate **6b** in the presence of  $Fe^{3+}$ -exchanged montmorillonite K10 to give the dimeric tetrahydropyranol ester **35** [20].



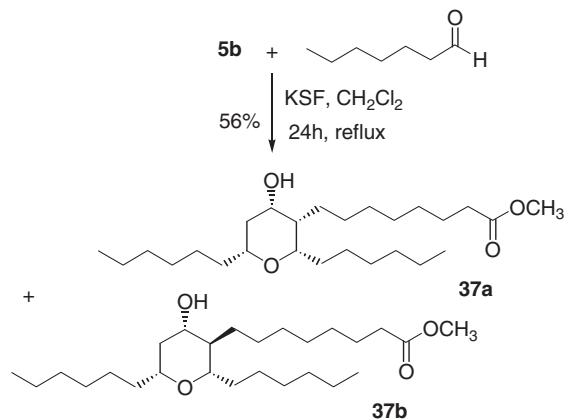
Scheme 13. Addition of formaldehyde to methyl oleate **1b** in the presence of  $Fe^{3+}$ -exchanged montmorillonite K10 to give the 4-hydroxytetrahydropyran **36** [20].

at the 4-position are found in a number of natural products [22].

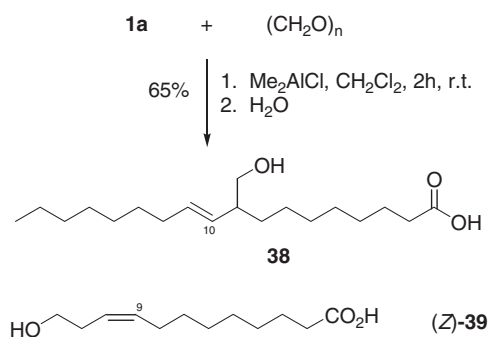
$\omega$ -Hydroxycarboxylic acids, including alkyl-branched acids such as **38**, which are of interest as polyester components, are obtained with high selectivity by the ene addition of formaldehyde to unsaturated fatty acids such as **1a** (scheme 15) [23,24]. However, stoichiometric amounts of dimethylaluminum chloride ( $Me_2AlCl$ ) or ethylaluminum dichloride ( $EtAlCl_2$ ) have to be used as reagents [25,26]. The acid (*Z*)-**39** (scheme 14), obtained by the addition of formaldehyde to 10-undecenoic acid **6a**, induces wound healing of tissue damage in soybeans by stimulation of callus formation at the damaged site [27].

Ene additions of formaldehyde to natural oils proceed with formation of the respective di- and trifunctionalized triglycerides [28], and jojoba oil gives mixtures of 1 : 1 and 1 : 2 adducts [29]. Homoallyl ethers are obtained in an analogous reaction with acetals [30].

Highly regioselective carbon-carbon bond-forming additions take place when santalbic acid **7a**, which is the main fatty acid in the seed oil of sandalwood and which contains a conjugated enyne system, is used as substrate [31]. The  $Me_2AlCl$ -induced addition of formaldehyde to



Scheme 14. Addition of heptanal to methyl ricinoleate **5b** in the presence of montmorillonite KSF to give the 4-hydroxytetrahydropyran **37** (**37a** : **37b** = 2.7 : 1) [19].



Scheme 15.  $\text{Me}_2\text{AlCl}$ -induced addition of paraformaldehyde to oleic acid **1a** to give the homoallyl alcohol **38** and the regioisomer  $(E)$ -10-hydroxymethyl-8-octadecenoic acid. The corresponding addition to 10-undecenoic acid **6a** gives the homoallyl alcohol **39** [ $(E):(Z) = 4:1$ ] [23,24].

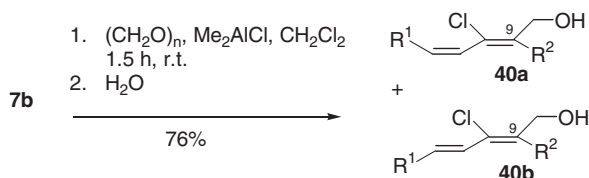
the enyne **7b** afforded the stereoisomeric 10-chloro-9-hydroxymethyl fatty acid esters **40** in 76% yield (scheme 16). Only two of the eight possible regio- and stereoisomers were obtained ([**40a**]:[**40b**] = 1.1:1).

In the presence of ruthenium trichloride, hexachloroplatinum acid, boron trifluoride or tin tetrachloride, formaldehyde was added to methyl oleate **1b** ([**1b**]:[catalyst] = 20:1) to give mixtures of products that consisted mainly of 2:1-adducts such as methyl 8-formyl-10-hydroxyethylstearate and dioxane derivatives [32]. Furthermore, in this reaction, 1:1-adducts such as methyl 9(10)-formylstearate and methyl 9(10)-hydroxymethyl-10(8)-octadecenoate as well as traces of 4:1-adducts were formed.

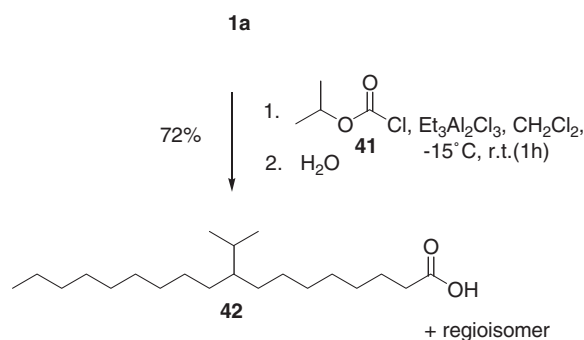
The  $\text{SnCl}_4$ -induced addition of glyoxylic acid ethyl ester to ethyl oleate afforded the regioisomeric ene adducts, while the corresponding reaction with mesoxalic acid diethyl ester [ $\text{EtO}_2\text{CCOCO}_2\text{Et}$ ] gave a product mixture containing the regioisomeric ene adducts and  $\gamma$ -lactones [33].

### 3.2. Ethylaluminum sesquichloride-induced alkylations with alkyl chloroformates

The alkylation of long-chain unsaturated fatty compounds is of great importance because alkyl-branched oleochemicals have interesting properties [34]. They are used for many applications such as lubricants, cosmetics, softeners, defoamers and



Scheme 16. Regioselective and stereoselective reaction of methyl octadec-11-en-9-ynoate **7b** and paraformaldehyde, induced by dimethylaluminum chloride ( $\text{Me}_2\text{AlCl}$ ) [31];  $\text{R}^1 = (\text{CH}_2)_5\text{CH}_3$ ;  $\text{R}^2 = (\text{CH}_2)_7\text{COOCH}_3$ .



Scheme 17. Ethylaluminum sesquichloride-induced reaction of oleic acid **1a** and isopropyl chloroformate **41** to give the alkylation product **42** [35].

wood-protecting agents. Isostearic acid, a commercially available product, which is obtained as a by-product in the montmorillonite-induced dimerization process of oleic acid, is used, e.g., in the cosmetic and lubricant area. However, the commercial isostearic acid is not at all a pure compound—it consists of a mixture of substances with aromatic and cyclic derivatives among others.

The ethylaluminum sesquichloride ( $\text{Et}_3\text{Al}_2\text{Cl}_3$ )-induced Friedel–Crafts alkylation using alkyl chloroformates is a new method for the alkylation of unsaturated fatty compounds [35].

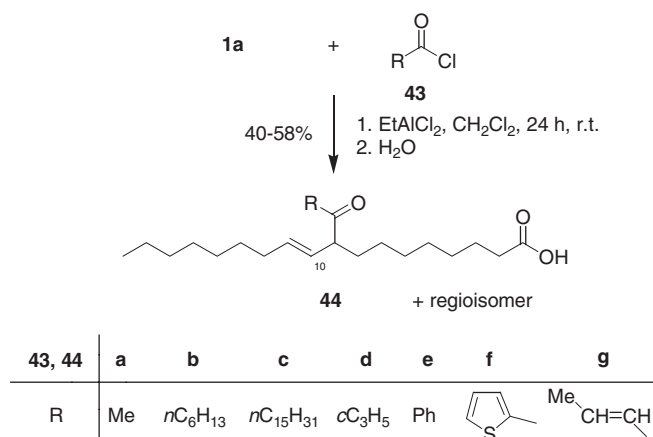
The reaction of oleic acid **1a** with isopropyl chloroformate **41** gave, in the presence of  $\text{Et}_3\text{Al}_2\text{Cl}_3$  after a reaction time of 2 h, an approximately 1:1 mixture of the regioisomers 9- and 10-isopropyloctadecanoic acid **42** in a yield of 72% (scheme 17) [35].

In some cases as, e.g., in alkylations of 10-undecenoic acid **6a**, addition of a hydride donor such as triethylsilane was necessary. With respect to the wide spectrum of applications for alkyl-branched fatty compounds, it should be of interest to find more effective catalysts for this reaction.

### 3.3. Alkylaluminum chloride-induced Friedel–Crafts acylations

The ethylaluminum dichloride ( $\text{EtAlCl}_2$ )-induced Friedel–Crafts acylation is an interesting and versatile method for the functionalization of unsaturated fatty compounds yielding the respective  $\beta,\gamma$ -unsaturated ketones with high selectivity [36–38]. The reaction can be carried out with a great number of different acylating agents such as acyl chlorides, dicarboxylic acid chlorides, cyclic anhydrides, unsaturated acyl chlorides, and aromatic and heteroaromatic acyl chlorides.

The  $\text{EtAlCl}_2$ -induced acylation of oleic acid **1a**, among others, with acyl chlorides **43** gave the  $(E)$ -configured  $\beta,\gamma$ -unsaturated oxocarboxylic acids **44** with high selectivity (scheme 18). The acylation products are substrates for a number of interesting follow-up reactions, for example, for Nazarov cyclizations [39].



Scheme 18. EtAlCl<sub>2</sub>-induced Friedel–Crafts acylations of oleic acid **1a** with the acyl chlorides **43a–g** give the unsaturated regioisomeric oxocarboxylic acids **44a–g** [36–38].

A modified Nazarov cyclization using montmorillonite clay K10 as catalyst is described to give after hydrogenation, the cyclopentanone derivative **48** from the acylation products **46** of methyl oleate **1b** and  $\alpha,\beta$ -unsaturated acyl chlorides **45g** (scheme 19) [39].

EtAlCl<sub>2</sub>-induced acylations of 1-alkenes such as methyl 10-undecenoate **6b** yielded the acylated products with high regioselectivity. The acylation, e.g., with thiophene-2-carboxylic acid chloride took place exclusively to position C11 of the molecule chain to give the 2-thienyl allyl ketone **49** in 59% yield (figure 4).

The acylation of methyl santalbate **7b** with heptanoyl chloride was carried out in the presence of Me<sub>2</sub>AlCl (scheme 20) [31]. A new allenic compound **50** was obtained regioselectively as a diastereomeric mixture in a ratio of approximately 1 : 1.

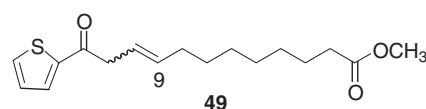
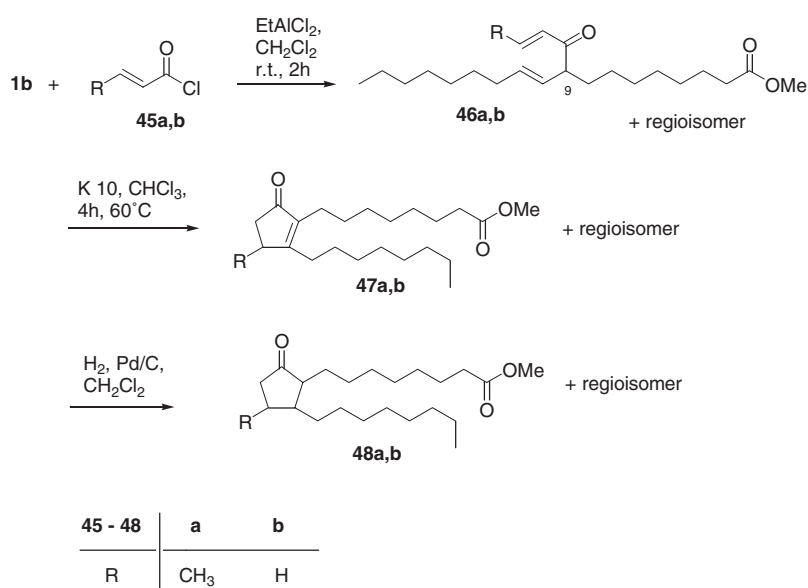


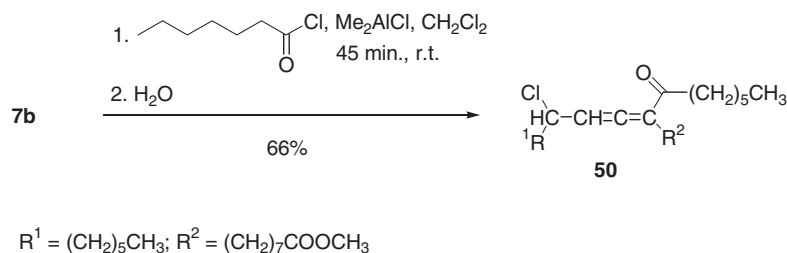
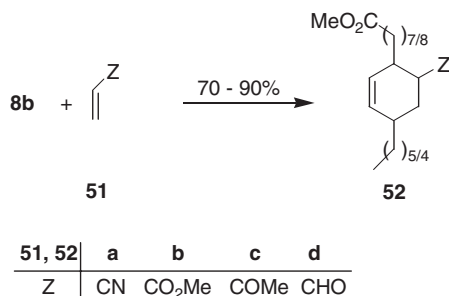
Figure 4. 2-Thienyl allyl ketone **49** obtained from the reaction of methyl 10-undecenoate **6b** and thiophene-2-carboxylic acid chloride [38].

Fatty acid derivatives with an allenic system such as **50** are known to have interesting properties [40], and in special cases, they have been used as substrates in the synthesis of new fatty compounds; one example is as a C<sub>18</sub> keto allenic ester for the synthesis of pyrazole ester derivatives [41].

Intramolecular acylations are also possible. The intramolecular reaction of petroselinic acid chloride



Scheme 19. EtAlCl<sub>2</sub>-induced Friedel–Crafts acylation of methyl oleate **1b** with  $\alpha,\beta$ -unsaturated acyl chlorides **45a** and **45b** followed by Nazarov cyclization of the obtained allyl vinyl ketones **46a,b** to give alkyl-substituted cyclopentenones **47a,b**. Catalytic hydrogenation of **47a,b** affords the saturated cyclopentanone derivatives **48a,b** [39].

Scheme 20. Regioselective acylation of methyl santalbate **7b** with heptanoyl chloride, induced by dimethylaluminum chloride [31].Scheme 21. Diels–Alder reactions of methyl conjugenates **8b** with dienophiles **51a–d** to the regioisomeric addition products **52a–d** [42].

and  $\text{EtAlCl}_2$  gave (*E*)-2-dodecylcyclohexenone in 58% yield [37]. The ring closure took place regioselectively at C-6.

### 3.4. Diels–Alder reactions

The Diels–Alder reaction is one of the most important C,C-bond-forming reactions in organic synthesis. Only few examples of reactions that are carried out at high temperatures are described for unsaturated fatty compounds. Schäfer *et al.*, for the first time, reported Lewis acid induced Diels–Alder reactions, which occur at room temperature [42]. Methyl conjugenate **8b** obtained from methyl linoleate **4b** by base-catalyzed isomerization of the C,C-double bonds with dimethylsulfoxide was reacted with different dienophiles **51** in the presence of boron trichloride or tin tetrachloride, and catalytic amounts of iodine-giving regioisomeric mixtures of Diels–Alder cycloaddition products **52** (scheme 21). Unfortunately, 1–1.8 equivalents of Lewis acid was necessary to accomplish the reaction in an acceptable reaction time while catalytic amounts extended the reaction time dramatically.

Metal triflates, especially  $\text{Sc}(\text{OTf})_3$  and  $\text{Cu}(\text{OTf})_2$  were found to be interesting catalysts for Diels–Alder

cycloadditions of conjugenoic acid esters [43]. The reaction, e.g., of ethyl conjugenate and methyl vinyl ketone gave a regioisomeric mixture of four 1 : 1 adducts in 81% yield. It has to be pointed out that the catalyst concentration is only 10 mol% and can be reused without loss of yield.

## 4. Transition metal-catalyzed reactions

### 4.1. Hydroformylation

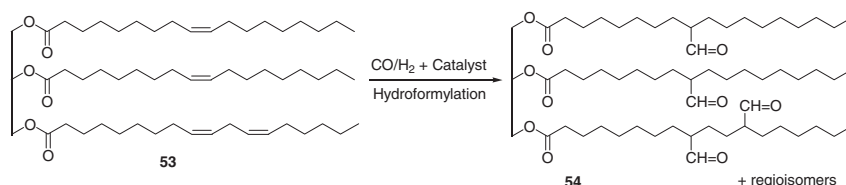
Hydroformylations of unsaturated fatty acid esters and vegetable oils in the presence of rhodium or cobalt catalysts are well known [44–46]. Recently, the hydroformylation of vegetable oils such as soybean, high oleic safflower, safflower and linseed oil using ligand-modified rhodium catalysts was reported. Quantitative yields of hydroformylated oils **54** were obtained with acetylacetonedicyclopentadienylrhodium ( $\text{Rh}(\text{O}_2)\text{Acac}$ ) as catalyst precursor in the presence of triphenylphosphine or  $(\text{PhO})_3\text{P}$  (scheme 22) [47].

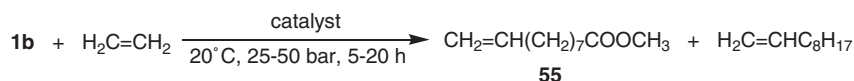
The kinetics and the mechanism of the conversion of soybean oil to polyaldehydes using ligand-modified homogeneous rhodium catalysis under the reaction conditions relevant to industrial processes are reported [48].

The hydroformylation of methyl linoleate **4b** in the presence of a heterogeneous rhodium/*tert*-phosphane-complex afforded diformylstearate with 60% selectivity [49].

### 4.2. Olefin metathesis

Following pioneering work of Boelhouwer *et al.* [50], olefin metathesis was applied by Warwel *et al.* [51,52] to unsaturated fatty compounds and is an important reaction in oleochemistry. Over the past few years,

Scheme 22. Hydroformylation of model triglyceride **53** induced by a ligand-modified rhodium catalyst to give polyaldehyde **54** [47].



catalysts:  $\text{Re}_2\text{O}_7 \cdot \text{B}_2\text{O}_3 / \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{SnBu}_4$   
or  $\text{CH}_3\text{ReO}_3 + \text{B}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$

Scheme 23. Co-metathesis of methyl oleate **1b** and ethylene to methyl 9-decenoate **55** and 1-decene. The ester **1b** used (new sunflower) was 87% pure, the conversions and selectivities each > 90% and the yields of **55** were > 80% [51].

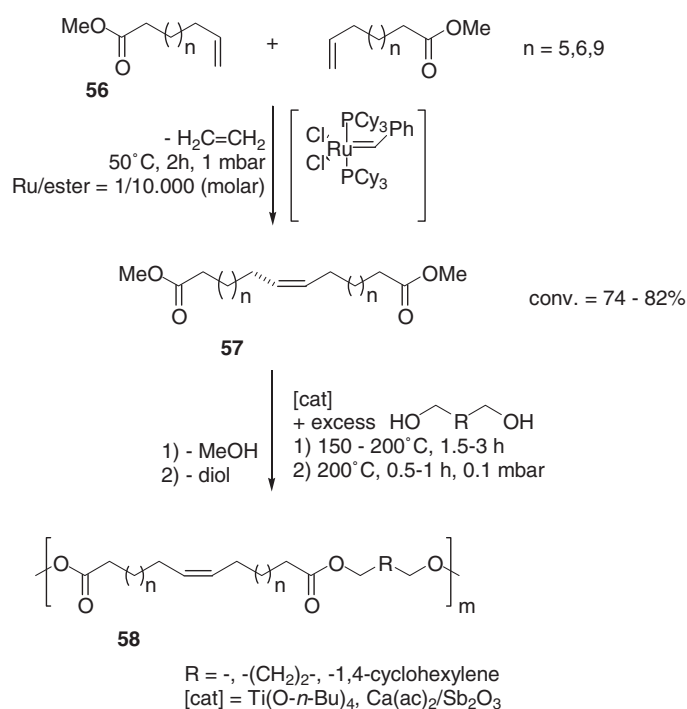
significantly active catalysts such as  $\text{Re}_2\text{O}_7 \cdot \text{B}_2\text{O}_3 / \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{SnBu}_4$  and  $\text{CH}_3\text{ReO}_3 + \text{B}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  have been developed and were successfully tested in a series of metathesis transformations [51]. Scheme 23 illustrates the co-metathesis of methyl oleate **1b** and ethylene to form methyl 9-decenoate **55** and 1-decene. Similarly, methyl 13-tetradecenoate and 1-decene were obtained from methyl erucate **3b** and ethylene [51]. Furthermore, methyltrioxorhenium was found to be a suitable catalyst for the metathesis of unsaturated fatty compounds [53].

Long chain dicarboxylic acid esters **57** were prepared by metathetical dimerization of ( $\omega$ -unsaturated fatty acid methyl esters **56** using highly efficient catalysts such as  $\text{Re}_2\text{O}_7 \cdot \text{B}_2\text{O}_3 / \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{SnBu}_4$  or the homogeneous Ru-carbene complex  $\text{Ru}(=\text{CHPh})\text{Cl}_2(\text{PCy}_3)_3$  (scheme 23) at catalyst concentrations of 0.01 mol% Ru [54]. Transesterification catalyzed by  $\text{Ti}(n\text{-OBu})_4$  or  $\text{Ca}(\text{OAc})_2/\text{Sb}_2\text{O}_3$  was conducted in a two-step process, yielding the linear aliphatic polyester **58** (scheme 24) [53].

#### 4.3. Palladium(0)-catalyzed nucleophilic additions

An interesting method for the functionalization of unsaturated fatty compounds is the nucleophilic addition, which demands a chemical reversal of the polarity of the electron-rich double bond to an electron-poor double bond [55]. If the double bond is conjugated to a carbonyl group, the vinylogous addition of nucleophiles to the double bond becomes possible. Interesting new oleochemicals were synthesized from unsaturated fatty compounds by Michael additions [56,57]. Allylic carbonates were found to be very good substrates for the nucleophilic substitution by palladium(0)-catalysis [58].

The first step in these reactions is the oxidative addition of palladium(0) to the allylic system **A** to form a  $\sigma$ -allylpalladium complex, which quickly decomposes into the more stable  $\pi$ -allylpalladium complex **B**, which then undergoes decarboxylation to **C** (figure 5) [57,58]. The alkoxide is sufficiently basic to deprotonate a number of nucleophiles; in the presence of phosphines, it reacts with complex **D**. To extend this



Scheme 24. Metathetical dimerization of  $\omega$ -unsaturated fatty acid methyl esters **56** to give long chain dicarboxylic acid esters **57** and subsequent transesterification with formation of compound **58** [54].

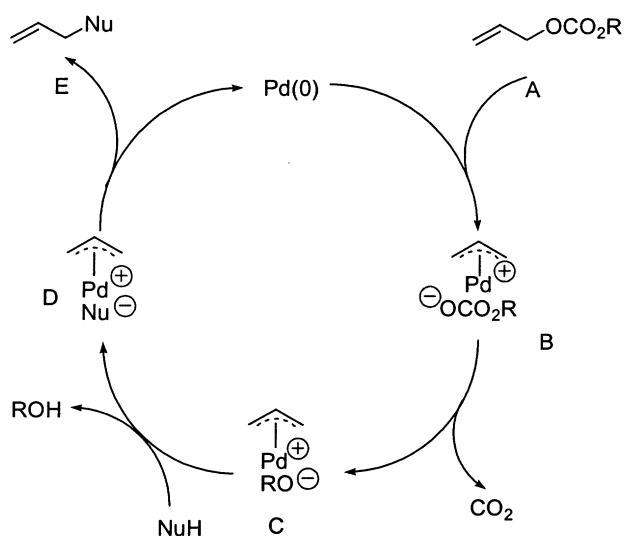
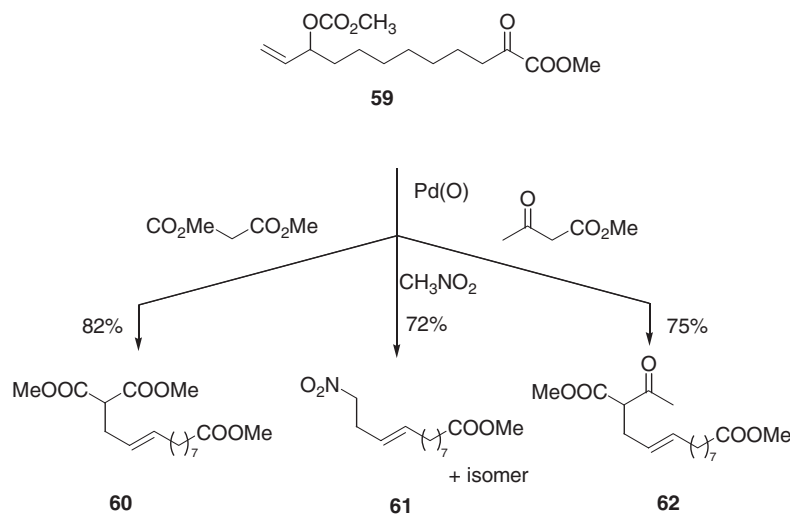


Figure 5. Catalytic cycle for the palladium (0)-catalyzed addition of nucleophiles to allyl carbonates [57,58].

palladium(0)-catalyzed substitution to unsaturated fatty acids, they had to be converted into the respective allyl carbonates.

Michael acceptors derived from fats can be synthesized in different ways, but only the substoichiometric oxidation with selenium dioxide was found to work satisfactorily [56]. The corresponding reactions of methyl 10-undecenoate **6b** and methyl oleate **1b** afforded the allylic alcohols methyl 9-hydroxy-10-undecenoate **9** and methyl 12-hydroxyoctadec-10-enoate **10** (mixture of regioisomers), respectively. After the reaction, selenium dioxide could be precipitated by petroleum ether and recycled.

Allyl carbonates such as **59** were obtained from reaction of, e.g., compound **9** with methyl chloroformate in the presence of pyridine in dichloromethane. **59**



Scheme 25. Pd(0)-catalyzed nucleophilic addition of dimethyl malonate, nitromethane and methyl acetylacacetate to the allyl carbonate **59** to give the substituted methyl undecenoates **60**, **61**, **62** [58].

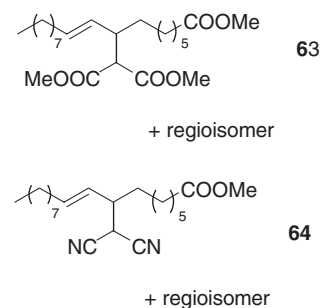


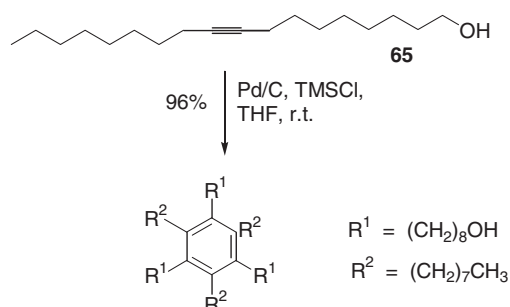
Figure 6. Michael addition products **63** and **64** obtained by reactions of the allyl carbonate of **10** with dimethyl malonate and malononitrile, respectively.

was made to react with different carbon nucleophiles such as dimethyl malonate, nitromethane and methyl acetylacacetate in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, which was generated from Pd<sub>2</sub>(dba)<sub>3</sub>CHCl<sub>3</sub> (1.0–1.5 mol%) and triphenylphosphine (scheme 25) [58].

Addition products **63** and **64** were obtained from reactions of the corresponding allyl carbonate of **10** with dimethyl malonate and malono dinitrile and were formed as mixtures of regioisomers in 79 and 76%, respectively (figure 6).

#### 4.4. Synthesis of aromatic compounds

Aromatic compounds derived from fats can be obtained by transition metal-catalyzed trimerization of the respective alkyne fatty derivatives. The trimerization of, for example, 9-octadecyn-1-ol **65** proceeded by formation of the aromatic compound **66** in a very good yield (scheme 26) [59]. Highly functionalized pyridine derivatives were synthesized by cotrimerization with nitrile moieties induced by a cobalt complex.



Scheme 26. Cyclotrimerization of alkyne **65** to give the aromatic compound **66** (TMS-trimethylsilyl) [59].

## 5. Conclusion

This review discussing more than fifty articles of current literature describes the state of the catalytic C,C-bond forming additions to unsaturated fatty compounds. Radical as well as Lewis acid and transition metal-induced additions have been applied to give “tailor-made” products with possibly new and interesting properties. With respect to the importance of unsaturated fatty compounds as renewable raw materials and their application in numerous areas of the chemical industry such as, e.g., monomers in polymer synthesis, lubricants, surfactants, coatings and cosmetics, great efforts have to be made to extend the spectrum of catalytic addition reactions, which are of interest for the selective synthesis of new oleochemicals in the sense of a sustainable development.

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