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Comparison of Reactivity in the Cross Metathesis of Allyl Acetate-Derivatives with Oleochemical Compounds

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Abstract The metathesis of unsaturated oleochemicals is an excellent tool for generating α,ω-difunctional substrates, which are useful intermediates for polymer synthesis. This article describes the cross metathesis of allyl acetate and *cis*-1,4-diacetoxy-2-butene with methyl 10-undecenoate and methyl oleate, which are oleochemical key substrates. Detailed optimizations led to high conversion rates and yields of the desired products under mild reaction conditions by using a low concentration of commercially available homogeneous ruthenium catalysts.

Keywords Oleochemistry · Metathesis · Homogeneous catalysis · Allyl acetate · *cis*-1,4-Diacetoxy-2-butene · Methyl oleate · Methyl 10-undecenoate

Introduction

Recently, the industrial relevance of renewable resources as alternative raw material has increased significantly. Especially the chemical utilization of natural fats and oils has great potential, but also represents a challenge in its industrial application [1]. Oleochemical metathesis reactions in particular are of great importance in oleochemical research due to their role in obtaining value-added intermediates for polymer synthesis. Metathesis is an atom-efficient reaction that usually works under very mild reaction conditions [2]. Over the years, the homogenous ruthenium metathesis catalysts have been developed to such an extent that they even tolerate functional groups such as carboxylic and ester groups. Therefore, these catalysts can also be used for applications in oleochemistry [1].

The fatty acid methyl esters examined in this paper are among the most important agents in oleochemical metathesis: Methyl 10-undecenoate **1** (Fig. 1) is a terminal C_{11}-ester, which can easily be generated by the pyrolysis of castor oil [2]. Methyl oleate **6** (Fig. 2)—an ester with a C_{18}-chain length and a *cis*-9-double bond—can for instance be obtained from high oleic sunflower oil via transesterification with methanol. In recent years, some cross metathesis (CM) reactions with oleochemical substrates have already been studied which resulted in bifunctional products with a number of potentially interesting uses [3–16].

This article describes the reaction optimization of oleochemical cross metathesis reactions in detail. First, the cross metathesis with methyl 10-undecenoate **1** and methyl oleate **6** with allyl acetate **2** will be illustrated. Then the cross metathesis of these fatty esters with *cis*-1,4-diacetoxy-2-butene **5** will be presented. The latter co-substrate constitutes the symmetrical analogue of allyl acetate **2**. Allyl acetate is the only by-product of the corresponding cross metathesis, which in turn can build the same range of products. The reaction products of the investigated oleochemical cross metathesis are the difunctional C12-compound **3** based on methyl 10-undecenoate **1** and the C11-compound **7** based on methyl oleate **6**. Products within this range of chain length are especially convenient materials for the technical preparation of surfactants [17, 18]. Furthermore, the coproducts undec-2-enyl acetate **8** and methyl dec-9-enoate **10** are formed which can be used as platform chemicals, and could be processed further into polyesters, polyethers or polyamides. Another possible application is the synthesis of fine chemicals, such as fragrances or lubricants [3, 19]. Dec-1-ene **9** is generated in the ethylene cross metathesis

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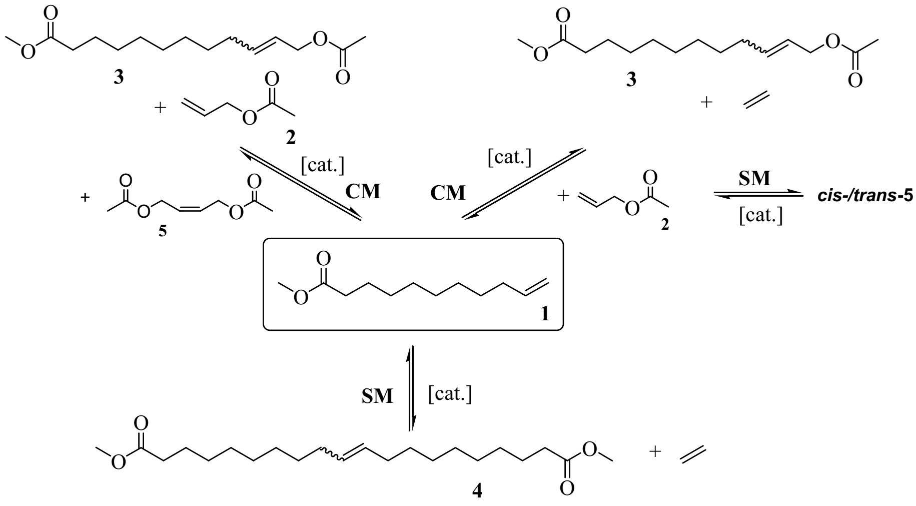

Fig. 1 Self metathesis (SM) and cross metathesis (CM) of methyl 10-undecenoate **1** with allyl acetate **2** and *cis*-1,4-diacetoxy-2-butene **5**

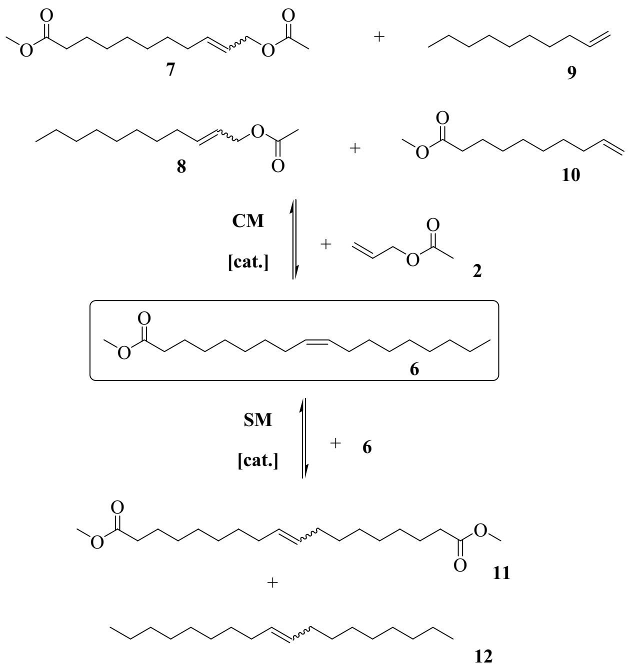

Fig. 2 Self metathesis (SM) and cross metathesis (CM) of methyl oleate **6** with allyl acetate **2**

of methyl oleate **6**. Dec-1-ene is an important intermediate for organic synthesis which can be used for a wide range of applications, for example, for the synthesis of polyolefins, lubricants and surfactants [20]. By linking oleochemical raw materials with commercial petrochemicals value-added products arise. A partial substitution of petrochemicals with renewable resources may be a prospective step in the direction of sustainable chemistry.

Until recently, allyl acetate **2** was only rarely used in cross metathesis, predominantly in investigations of catalyst activities in the cross-metathesis with terminal olefins [21] or as an intermediate in natural substance synthesis [22]. Allyl acetate **2** is a very interesting substrate for cross metathesis because of its easy commercial availability. The traditional procedure of producing allyl acetate is the reaction of propene with acetic acid and oxygen in the gas phase [23]. Its production is also possible by using Pd-catalyzed oxidation reactions [24]. By contrast, *cis*-1,4-diacetoxy-2-butene **5** is a classic subject of metathesis substrate investigations. Several procedures for oleochemical cross metathesis reactions have already been published [13, 25–27].

Experimental Procedures

The reactions were carried out at least twice to ensure the accurate reproducibility of the achieved results. They were first conducted under argon to check whether this was necessary. All reactions can be handled in the air without a loss of activity.

Materials

High oleic sunflower oil (HOSO, ca. 91.2 % oleic acid) was obtained from Emery Oleochemicals GmbH; allyl acetate (99 %), undecenoic acid (99 %) and the solvents were purchased from Acros in analytical quality (>98 %), the *cis*-2-butene-1,4-diol (97 %) was purchased from ABCR. The benzylidene ruthenium catalysts (see Fig. 3) (**[Ru]-1** and **[Ru]-2**) were obtained from Sigma-Aldrich, the thioether-catalysts (**[Ru]-12** and **[Ru]-13**) were provided by Evonik Industries, and the remaining indenylidene catalysts (**[Ru]-3** up to **[Ru]-11**) were provided by Umicore AG & Co. KG and were used as received.

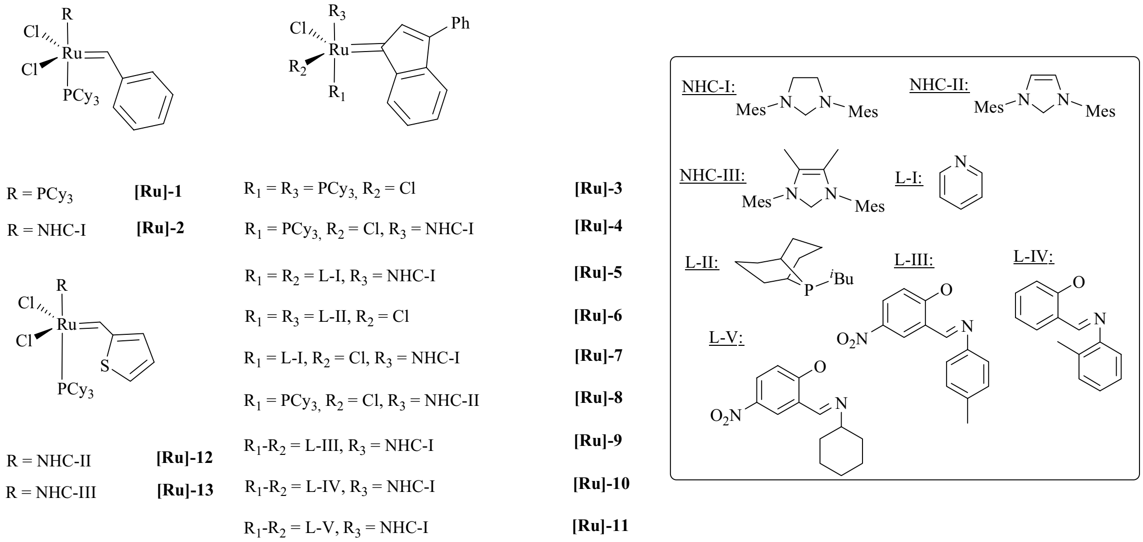

Fig. 3 Ruthenium catalysts

Analytical Equipment and Methods

Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$-d6 on a Bruker AVANCE DRX spectrometer operating at 400 MHz and 500 MHz at 298 K. Chemical shifts (δ) were indicated in parts per million relative to TMS as internal standard (TMS, $\delta = 0.0$ ppm). Gas chromatography (GC) analyses of the reaction solutions were carried out on a Hewlett-Packard gas chromatograph Series 6,890 equipped with a HP5 capillary column (coating 5 % diphenyl-95 % dimethoxy-polysiloxane, length 30 m, diameter 0.25 mm, thickness 0.25 μm) and an autosampler. A flame ionization detector (FID) was used for the detection of the components. The oven temperature program was as follows: initial temperature 130 °C, hold for 6 min, increased by 25 °C min^{-1} up to 320 °C, hold for 4 min. Measurements were performed in split–split mode (70:1) with nitrogen as a carrier gas. The qualitative assignment of the chromatographically determined retention times of the individual components was carried out by comparing them to the respective pure substances. The quantitative determinations were made by the method of an internal standard.

The mass spectra were recorded by GC–MS. The mass spectrometer was a Hewlett-Packard 5,973 with electron energy of 70 eV and a scan range (*m*/*z*) of 50–700. The oven temperature program, the split–split mode and the specification of the carrier gas were identical to those in the GC-FID mode.

Cross Metathesis with Allyl Acetate 2

When using 0.20 g (1.0 mmol) of methyl 10-undecenoate **1** [or 0.30 g (1.0 mmol) methyl oleate **6**], 0.50 g (5.0 mmol) allyl acetate **2**, 6.34 g toluene (7.20 g) and an appropriate amount of catalyst was added (1.0 mol%, e.g. **[Ru]-4** = 0.009 g/0.01 mmol). The reaction was heated to the desired temperature (range 20–90 °C). After a defined reaction time (range 30 min–24 h), the closed reaction tube was placed directly into an ice bath to stop the reaction. Quenching the reaction by addition of ethyl vinyl ether led to the same results, so this procedure was not necessary for the examined reaction. After cooling, the GC samples were weighed (0.1 g reaction solution, 0.4 g isopropanol and 0.5 g *n*-pentadecane as internal standard) and analyzed accordingly. The reaction mixture was separated with flash chromatography on silica gel 60 (40–60 μm, Acros Organics), with the solvents cyclohexane and ethyl acetate having a gradient of 100:1 up to 10:1. The products were isolated and characterized via NMR and MS.

Cross Metathesis with *cis*-1,4-Diacetoxy-2-Butene 5

When using 0.20 g (1.0 mmol) of methyl 10-undecenoate **1** [or 0.30 g (1.0 mmol) methyl oleate **6**], 0.87 g (5.0 mmol) *cis*-1,4-diacetoxy-2-butene **5**, 9.63 g toluene (10.53 g) and an appropriate amount of catalyst was added (1.0 mol%, e.g.**[Ru]-4** = 0.009 g/0.01 mmol). The reaction, the sample preparation and the product isolation occurred analogous to the cross metathesis described above.

Characterization of the Substrates

Methyl 10-Undecenoate 1

Initially, 184.28 g (1.00 mol) methyl undec-10-enoic acid, 82 mL (2.00 mol) methanol und 4.52 g (26 mmol) *p*-toluenesulfonic acid were dissolved in 200 mL dichloromethane and heated under reflux for 48 h. After cooling to room temperature, the organic phase was washed with 100 mL distilled water, 100 mL of a 5 % solution of sodium bicarbonate, and with another 100 mL of distilled water consecutively. The solvent was removed under reduced pressure after drying with sodium sulfate. Finally, a fractional distillation (83 °C, 10^{-3} mbar)was carried out to isolate 178.87 g of methyl 10-undecenoate **1** (0.90 mol, 90 %) with a purity of about 99 % in the form of a clear, colorless liquid.

Methyl Oleate 6

First, 300.00 g (0.34 mol) high oleic sunflower oil was dried at 10^{-3} mbar at 120 °C for 1 h. After cooling, 35.97 g (1.12 mol, 3 eq) methanol and 5.59 g (0.10 mol) 30 % sodium methoxide solution were added, and the reaction was stirred at 70 °C for 2 h in an inert atmosphere. The glycerol phase was separated and another 5.42 g (0.12 mol) methanol was added. After 1 h at 70 °C, the excess of methanol was evaporated. After separation of the glycerol phase, the fatty phase was washed twice with 150 mL distilled water to remove the catalyst and remaining glycerol. Finally, 88.49 g of methyl oleate **6** (0.30 mol, 88 %) was isolated as a colorless oil via fractionized distillation at 160 °C and 10^{-3} mbar with a purity of about 98.5 %.

cis-1,4-Diacetoxy-2-Butene 5

The entire synthesis was performed in an inert atmosphere. First, 79.63 g (0.78 mol) fresh distilled acetic acid anhydride was added dropwise to a solution of 20.26 g (0.23 mol) *cis*-2-butene-1,4-diol in 20 mL abs. dichloromethane at 0 °C. Afterwards, 55.37 g (0.7 mol) pyridine was added dropwise and the solution was stirred for 30 min at 0 °C. After being stirred for 18 h at room temperature, the reaction solution was washed three times with 30 mL 2 M HCl and with 25 mL brine. The organic product phase was dried with $MgSO_4$. After that, the solvent of the reaction was removed. A 35.10-g amount of*cis*-1,4-diacetoxy-2-butene **5** (0.20 mol, 89 %) were isolated as a colorless liquid with a purity of about 98.5 %.

Methyl 12-Acetoxy Dodec-9-Enoate 3

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 1.25 (m, 10H, –CH_2–), 1.52 (dd, 2H, J = 6.9 and 14.0 Hz, –C(O)–CH_2–CH_2–), 1.99 (m, 5H, –CH–CH_2–, –C(O)–CH_3), 2.21 (t, 2H, J = 7.5 Hz, –C(O)–CH_2–), 3.57 (s, 3H, –O–CH_3), 4.47 (dd, 2H, J = 6.6 and 44.5, –C(O)–O–CH_2), 5.55 (m, 2H, –CH–). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 20.8 (–C(O)–$C$$H_3$), 24.7, 27.3, 28.6, 28.8, 28.8, 28.9, 29.0, 32.0, 33.8, 51.2 (–O–$C$$H_3$), 65.0 (–O–$C$$H_2$), 123.5 (–$C$H–), 136.3 (–$C$H–), 170.5 (–$C$(O)–$CH_3$), 173.9 (–$C$(O)–O–). MS electron ionization (EI): *m/z* (%) 271 (1, M^+), 227 (10), 210 (8), 196 (27), 178 (25), 168 (9), 161 (3), 149 (13), 136 (12), 129 (6), 121 (9), 112 (10), 95 (21), 81 (28), 67 (27), 55 (37), 43 (100), 28 (67).

Dimethyl Icos-10-Enedioate 4

^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) = 1.21 (m, 20H, –CH_2–), 1.58 (dd, 4H, J = 7.1 and 14.2 Hz, –C(O)–CH_2–CH_2–), 1.96 (m, 4H, –CH_2–CH_2–), 2.27 (t, 4H, J = 7.6 Hz, –C(O)–CH_2–), 3.64 (s, 6H, –O–CH_3), 5.33 (s, 2H, –CH–). ^{13}C NMR (125 MHz, $CDCl_3$):δ(ppm) = 24.9 (–$C$$H_2$–), 29.0, 29.1, 29.2, 29.3, 29.5, 32.5, 34.0, 51.4 (–O–$C$$H_3$), 130.2 (–$C$H–), 174.2 (–$C$(O)–). MS electron ionization (EI): *m/z* (%) 369 (1, M^+), 336 (9), 318 (2), 304 (4), 194 (1), 180 (2), 165 (2), 151 (3), 135 (4), 123 (5), 109 (9), 95 (20), 81 (27), 74 (25), 67 (28), 55 (64), 41 (39), 28 (100).

Methyl 11-Acetoxy Undec-9-Enoate 7

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 1.23 (bs, 8H, –CH_2–), 1.53 (dd, 2H, J = 7.0 and 14.2 Hz, –C(O)–CH_2–CH_2–), 1.98 (m, 5H, –CH–CH_2–, –C(O)–CH_3), 2.23 (t, 2H, J = 7.5 Hz,–C(O)–CH_2–), 3.59 (s, 3H, –O–CH_3), 4.43 (d, 2H, J = 6.5 Hz, –C(O)–O–CH_2–), 5.49 (m, 1H, –CH–), 5.70 (m, 1H, –CH–). ^{13}C NMR (100 MHz, $CDCl_3$):δ(ppm) = 20.8 (–C(O)–$C$$H_3$), 24.7, 27.3, 28.7, 28.8, 28.9, 29.1, 32.0, 33.8, 51.2 (–O–$C$$H_3$), 65.1 (–O–$C$$H_2$–), 135.1 (–$C$H–), 136.3, 170.6 (–$C$(O)–), 174.0 (–$C$(O)–O–). MS electron ionization (EI): *m/z* (%) 252 (0, M^+), 230 (1), 208 (4), 196 (16), 182 (12), 164 (24), 154 (6), 147 (4), 135 (17), 129 (9), 117 (55), 107 (18), 91 (36), 87 (22), 81 (95), 74 (36), 67 (100), 55 (68).

Undec-2-Enyl Acetate 8

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.86 (t, 3H, J = 6.8 Hz, –CH_3), 1.27 (m, 12H, –CH_2–), 2.04 (m, 5H, –C(O)–CH_3, –CH–CH_2–), 4.49 (d, 2H, J = 6.5 Hz, –O–CH_2–), 5.67 (m, 2H,–CH–CH–). ^{13}C NMR (100 MHz, $CDCl_3$):δ(ppm) = 13.9 (–$C$$H_3$), 20.9 (–C(O)–$C$$H_3$), 22.5, 24.8, 28.7, 29.0, 29.1, 29.3, 31.1, 65.2 (–O–$C$$H_2$), 136.6 (–$C$H–), 138.9 (–$C$H–), 170.7 (–$C$(O)–). MS electron ionization (EI): *m/z* (%)212 (0, M^+), 170 (6), 152 (13), 141 (6), 124 (18), 110 (14), 96 (36), 91 (3), 82 (63), 79 (14), 67 (75), 54 (100).

Dec-1-Ene 9

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.91 (t, 3H, J = 6.8 Hz, –CH_3–), 1.39 (m, 12H, –CH_2–), 2.07 (dt, 2H,

$J = 6.9$ and 14.3 Hz, –CH–CH_2–), 4.98 (dd, 1H, $J = 4.0$ and 8.0 Hz, –CH_2–), 5.00 (dd, 1H, $J = 4.0$ and 16.0 Hz, –CH_2–), 5.83 (tdd, 1H, $J = 6.7$, 10.1 and 16.7 Hz, –CH$_2$–C*H*). ^{13}C NMR (100 MHz, CDCl$_3$): δ(ppm) = 13.8 (–*C*H$_3$), 22.4, 28.7, 28.9, 29.1, 29.3, 31.7, 33.6, 113.8 (–*C*H$_2$–CH–), 138.8 (–CH$_2$–*C*H–). MS electron ionization (EI): *m/z* (%)141 (5, M$^+$), 111 (16), 97 (34), 83 (43), 70 (84), 56 (96), 41 (100), 29 (43).

Methyl-Dec-9-Enoate 10

^{1}H NMR (400 MHz, CDCl$_3$): δ(ppm) = 1.26 (m, 8H, –CH_2–), 1.57 (m, 2H, –CH_2–CH$_2$–C(O)–), 2.00 (m, 2H, –CH–CH_2–), 2.26 (t, 2H, $J = 7.2$ Hz, –CH_2–C(O)–),3.64 (s, 3H, –CH_2–C(O)–), 4.88 (dd, 1H, $J = 4.0$ and 8.0 Hz, –CH–CH_2–(*cis*)), 4.95 (dd, 1H, $J = 4.0$ and 16.0 Hz, –CH–CH_2–(*trans*)), 5.72 (ddt, 1H, $J = 8.0$, 12.0 and 16.0 Hz, –CH$_2$–C*H*–). ^{13}C NMR (100 MHz, CDCl$_3$): δ(ppm) = 24.9, 28.9, 29.0, 29.5, 29.6, 32.5, 34.0, 51.4 (–O–*C*H$_3$), 116.3 (–*C*H$_2$–CH–), 130.2 (–CH$_2$–*C*H–), 174.3 (–*C*(O)–). MS electron ionization (EI): *m/z* (%)186 (0,M$^+$), 152 (19), 141 (3), 135 (19), 123 (16), 110 (42), 96 (27), 93 (4), 87 (52), 84 (32), 81 (14), 74 (100), 69 (43), 65 (2), 59 (31), 55 (71), 51 (2), 41 (63), 29 (20), 26 (2).

Dimethyl-Octadec-9-Enedioate 11

^{1}H NMR (400 MHz, CDCl$_3$): δ(ppm) = 1.27 (m, 16H, –CH_2–), 1.58 (m, 4H, –CH_2–CH$_2$–C(O)–), 1.93 (m, 4H, –CH–CH_2–), 2.26 (m, 4H, –CH_2–C(O)–), 3.63 (s, 6H, –CH_3), 5.34 (m, 2H, –C*H*–). ^{13}C NMR (100 MHz, CDCl$_3$): δ(ppm) = 26.4 (–CH$_2$–CH$_2$–C(O)–), 28.6, 30.9, 35.5, 52.8 (–*C*H$_3$), 131.3 (–*C*H–), 175.7 (–*C*(O)–). MS electron ionization (EI): *m/z* (%)340 (1, M$^+$), 308 (7), 290 (3), 276 (16), 265 (1), 207 (1), 165 (7), 151 (11), 133 (12), 121 (13), 109 (18), 95 (38), 81 (59), 74 (44), 67 (58), 55 (100).

Octadec-9-Ene 12

^{1}H NMR (400 MHz, CDCl$_3$): δ(ppm) = 0.86 (m, 6H, –CH_3–), 1.28 (bs, 24H, –CH_2–), 1.97 (m, 4H, –CH_2–CH–), 5.37 (m, 2H, –C*H*–). ^{13}C NMR (100 MHz, CDCl$_3$): δ(ppm) = 13.8 (–*C*H$_3$), 22.5, 27.0, 28.4, 29.3, 30.7, 31.0, 33.4, 131.3 (–*C*H–). MS electron ionization (EI): *m/z* (%)252 (17, M$^+$), 224 (19), 182 (1), 168 (2), 154 (3), 139 (6), 125 (22), 111 (50), 97 (90), 83 (100), 69 (86), 55 (87), 41 (78), 29 (36).

Results and Discussion

Cross Metathesis (CM) of Methyl 10-Undecenoate 1 and Allyl Acetate 2

In the cross metathesis of methyl 10-undecenoate **1** and allyl acetate **2** (Fig. 1) a detailed catalyst screening was performed and a broad number of homogeneous ruthenium complexes **[Ru]-1** to **[Ru]-13** was tested (Fig. 3) under the following standard conditions: A catalyst concentration of 1.0 mol% (based on **1**), a reaction temperature of 50 °C, a reaction time of 5 h and a ratio of substrate **1**/co-substrate **2** of 1:5 in the solvent toluene. Due to the bidentate Schiff base ligands the catalysts [**Ru**]-**9** to **[Ru]-11** required activation by the addition of 100 equivalents of phenyltrichlorosilane [28, 29].

The silane-activated catalysts **[Ru]-9-[Ru]-11** lead to the highest yields of the desired product **3** and resulted in conversion rates (*X*) and yields (*Y*) of about 60 %. However, the use of a catalyst without silane activator has the benefit not to use the toxic PhSiCl$_3$, meaning the synthesis of the product is more environmentally friendly. Therefore, further investigations were carried out with the non-activated catalyst **[Ru]-4** which has only a slightly lower activity and conversions of *X* (**1**) = 53 % and yields of *Y* (**3**) = 44 %.

Different ratios of the substrate **1** and the co-substrate **2** were investigated: At an excess of 1/5 (of **1/2**), the yield of **3** increased to 44 %. The conversion of methyl 10-undecenoate **1** decreased by further increasing the amount of co-substrate **2**. Therefore, a ratio of 1:5 was chosen as the starting point for all further investigations. Because of the high difference in substrate boiling points, the excess co-substrate can easily be distilled off after the reaction.

The ratio of substrate to solvent, i.e. the concentration of substrate, was varied in order to achieve comparable yields by using a less amount of solvent. The yields of **3** and **4** were highest at a substrate concentration of 10 wt%. The conversion rate of **1** and the yield of **3** decreased when the amount of solvent was reduced which maybe caused by the increased substrate viscosity.

When increasing the reaction temperature up to 80 °C product yields rise slightly to 46 % which may be caused again by substrate viscosity. At a temperature of 90°C isomerization of the C,C-double bond location of the oleochemical compounds **1** and **3** was observed. Therefore, higher temperatures than 80 °C are not reasonable. The effect of reaction time was investigated, to determine how the increased temperature of 80 °C influences the course of the reaction. The highest yield [*Y* (**3**) = 46 %] was detected after a reaction time of 2 h. By sampling hourly for up to 24 h, it was observed that increased reaction times had no further effect on the yields of the desired product **3**. Longer reaction times only increased the percentage of the isomerization of the substrates. The reaction time of 2 h proved to be very beneficial because only a 2 % yield of the oleochemical self-metathesis product **4** was observed.

Under the previously mentioned optimized reaction conditions the investigation of the catalyst concentration was performed within the range of 0.05 mol% to 2.0 mol% (Table 1). In the entire concentration range only a 2 % yield

Table 1 Variation of catalyst concentration in the cross metathesis of **1** and **2**

Conc. (mol%)	*X* (1) (%)	*Y* (3) (%)	*Y* (4) (%)
0.05	26	15	2
0.1	30	19	2
0.25	34	25	2
0.5	44	35	2
0.75	49	42	2
1.0	52	46	2
1.25	52	45	2
1.5	53	43	2
2.0	54	43	2

Reaction conditions: $T = 80$ °C, $t = 2$ h, solvent: toluene, catalyst: **[Ru]-4**, **1/2**: 1/5, 10 wt% substrates (**1** + **2**)

Table 2 Variation of the catalyst concentration in the cross metathesis of **1** and **5**

Conc. (mol%)	*X* (1) (%)	*Y* (3) (%)	*Y* (4) (%)
0.05	12	0	0
0.1	39	29	0
0.25	78	73	1
0.5	87	84	1
1.0	89	87	1
1.25	91	87	2
1.5	91	89	2
2.0	92	88	2

Reaction conditions: $T = 80$ °C, $t = 2$ h, solvent: toluene, catalyst: **[Ru]-4**, 10 wt% substrates (**1** + **5**), **1/5** = 1/3

of the by-product **4** was observed. At a catalyst concentration of 1.0 mol%, a maximum yield of product **3** of 46 % was achieved, rendering a further increase of the amount of catalyst unnecessary.

Various classes of solvents were investigated to determine their influence on the reaction. Using cyclohexane, heptane, dichloromethane and ethyl acetate led to nearly the same results. When using oxygen containing solvents, such as 1,4-dioxane or tetrahydrofurane, the yields of the desired product **3** are halved compared to toluene.

After the optimization, the excess of **2** could be significantly reduced to 1:2.5 (of **1/2**), which led to a yield of **3** of 49 %.Under these conditions, the catalyst screening was reassessed. Comparable results to catalyst **[Ru]-4** were found with the catalysts **[Ru]-2**, **[Ru]-8**, **[Ru]-12** and **[Ru]-13** which all do not require an activating agent. They contain a phenylindenylidene ligand with a greater functional group tolerance than its benzylidene counterpart [30]. Furthermore, they all contain an NHC-ligand, which increases the electron density of the ruthenium and thereby accelerates the catalysis [31, 32].

In further investigations, *cis*-1,4-diacetoxy-2-butene **5**, the symmetric analogue to allyl acetate **2**, was used in the cross-metathesis with methyl 10-undecenoate **1** with the aim to increase the product yields.

Cross Metathesis of Methyl 10-Undecenoate 1 and *cis*-1,4-Diacetoxy-2-Butene 5

Also in the cross metathesis of methyl 10-undecenoate **1** with the symmetric co-substrate *cis*-1,4-diacetoxy-2-butene **5** (Fig. 1) the reaction conditions described above were chosen as the starting point of the investigations (1.0 mol% **[Ru]-4**, $T = 80$ °C, $t = 2$ h, 10 wt% substrates, solvent: toluene). The benefit of this cross metathesis is that no self-metathesis of **5** is possible. The only “by-product” is allyl acetate **2**, which, however, yields the same products as using the symmetric co-substrate **5**. When investigating the ratio of the substrates **1** and **5**, the best ratio proved to be 1:3 with a yield of **3** of 87 %. The oleochemical self-metathesis to product **4** only occurred in traces.

By varying the catalyst concentration (Table 2) the concentration of 1.0 mol% was seen as a favorable compromise as less of the expensive catalyst was required [*X* (**1**) = 89 %, *Y* (**3**) = 87 %].

In the cross metathesis of **1** and **5** the investigation of the reaction time showed a result similar to in the reaction with allyl acetate **2**. However, a great benefit of the cross metathesis of **1** with **5** is that the highest yield [*Y* (**3**) = 87 %] is reached within 30 min. Longer reaction times led only to an increased isomerization of the substrates. Hence, the reaction of methyl 10-undecenoate with the symmetrical substrate **5** is four times faster than the cross metathesis with the unsymmetrical substrate **2**.

However, in the reaction of **1** with **5** also a high dilution of the reaction mixture was necessary in comparison to the metathesis with allyl acetate **2**. A substrate concentration of 10 wt% has to be used. As in the case of allyl acetate **2** only a negligible yield of 1 % of the oleochemical self-metathesis was observed.

The same trends were observed even when examining the reaction temperature (Table 3). An increased product yield of 87 % of **3** was detected at a temperature of 80 °C. At a reaction temperature of 90 °C, isomerization of the substrates and products were determined. In the solvent tests the same results were found as observed in the cross metathesis with allyl acetate **2**. Also the analogue catalysts proved to be the most active.

It can be concluded that in cross metathesis of methyl 10-undecenoate **1** with both symmetric and unsymmetric substrates the highest product yields are achieved using the same catalysts under nearly the same reaction conditions.

Table 3 Variation of the reaction temperature in the cross metathesis of **1** and **5**

T (°C)	*X* (1) (%)	*Y* (3) (%)	*Y* (4) (%)
r.t.	89	77	5
30	88	76	6
40	87	75	6
50	96	80	9
60	91	84	4
70	86	85	1
80	89	87	1
90	90	87	1
100	90	85	1

Reaction conditions: $t = 30$ min, solvent: toluene, catalyst: 1.0 mol% **[Ru]-4**, 10 wt% substrates (**1** + **5**), **1/5** = 1/3

Further testing is necessary to determine whether this is transferable to other cross metathesis reactions. Meier *et al*. [27] reported a yield of product **3** of 98 % under nearly similar conditions (50 °C, 3 h, and 0.5 mol% of Grubbs-Hoveyda-catalyst) using a very low excess of *cis*-1,4-diacetoxy-2-butene **5** of only 1:2. However, this procedure has to use 3 mol% 1,4-benzoquinone to suppress any isomerization. The catalysts described in the present article do not require any auxiliary.

Further investigations were conducted to determine whether the cross metathesis of allyl acetate **2** showed similar effects in optimization studies with methyl oleate **6**, i.e., a substrate with an internal double bond.

Cross Metathesis of Methyl Oleate 6 and Allyl Acetate 2

In contrast to the cross metathesis of the 1-alkene methyl 10-undecenoate **1**, an alkene with internal CC-double bond as methyl oleate **6** yielded a completely different product spectrum (Fig. 2). Depending on the catalyst system, very different product ratios were generated. A high ratio of substrate **6** to co-substrate **2** of 1:7 resulted in the highest product yields, so this ratio was used in all further investigations. Figures 4 and 5 show the variation in substrate concentration with catalyst **[Ru]-4** and catalyst **[Ru]-10**, whereas the latter required 100 equivalents of PhSiCl$_3$ as activation agent.

With both catalysts a relatively similar product distribution was achieved up to a concentration of substrates of 30 wt%. Using **[Ru]-4** the yields of the products **7** to **10** were nearly constant in the range investigated. Using **[Ru]-10** the functionalized substrates **7** and **8** achieved values of about 70 %, whereas the products **9** and **10** only reached yields of about 20 %.

Subsequent studies of the cross metathesis were carried out with **[Ru]-10** to determine whether a more effective

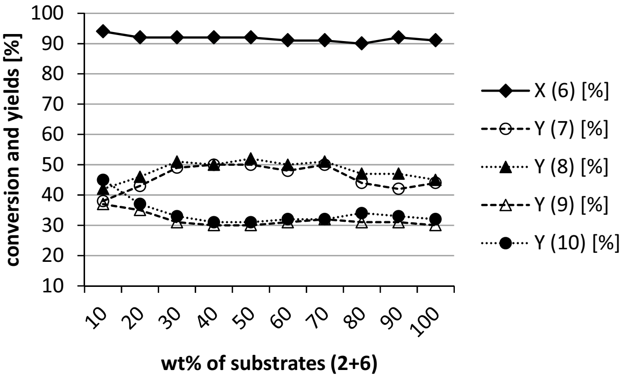

Fig. 4 Cross metathesis of methyl oleate **6** with allyl acetate **2**; Variation of the concentration of the substrates (**2** and **6**) using catalyst **[Ru]-4**. Reaction conditions: T = 80 °C, t = 90 min, solvent: toluene, 2 mol% **[Ru]-4**, **6/2** = 1/7

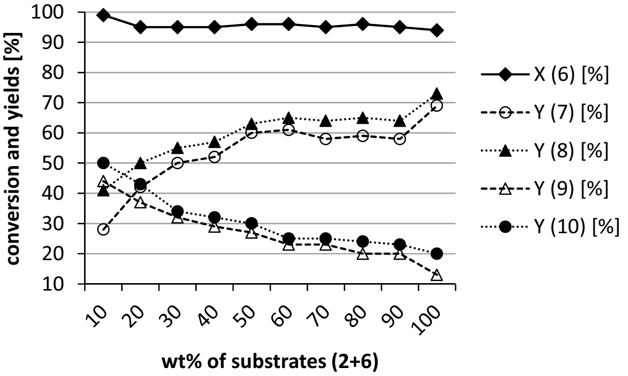

Fig. 5 Cross metathesis of methyl oleate **6** with allyl acetate **2**; Variation of the concentration of the substrates (**2** and **6**) using catalyst **[Ru]-10**. Reaction conditions: T = 80 °C, t = 90 min, solvent: toluene, 2 mol% **[Ru]-10**, 100 eq PhSiCl3, **6/2** = 1/7

product distribution to the inner standing products **7** and **8** could be achieved. When varying the catalyst concentration it was found that with up to 0.25 mol% of **[Ru]-10** all products were generated to approximately 30 %. A maximum yield of products **7** and **8** was detected at a catalyst concentration of 0.75 mol%. The use of a higher catalyst concentration hinders the reaction, an effect which was also observed in oleochemical ethenolysis [33].

By varying the ratio of the substrate **6** to co-substrate **2** maximum values of about 75 % of products **7** and **8** were observed at ratios from 1:5 to 1:6. Investigating the reaction time showed that the reaction equilibrium is given as early as after 30 min. After a reaction time of 6 h, again isomerization of the C,C-double bond location of the substrates was detected.

The distribution of the products can be explained by secondary reactions: For example, the self-metathesis of **9** yields product **12** and the self-metathesis of **10** yields product **11**. Both reactions are reversible. The self-metathesis of compound **7** produces **11** and **5** and the self-metathesis of compound **8** yields **12** and **5**. In addition all these substrates can react in further cross metathesis reactions.

Thus, the reaction network is very complex as allyl acetate **2** is an unsymmetrical, terminal co-substrate. Further kinetic investigations are necessary to acquire a deeper understanding of the product distributions.

In the cross metathesis of methyl oleate **6** with *cis*-1,4-diacetoxy-2-butene **5,** a 78 % yield of the desired difunctional product **7** was achieved using **[Ru]-10** as catalyst in a concentration of 1.5 mol% [13]. Again, the experiments demonstrated that the same catalysts had a very similar activity with both unsymmetric and symmetric co-substrates. However, using the unsymmetric co-substrate **2** only a lower catalyst loading was necessary.

Conclusions

The cross metathesis reactions of methyl 10-undecenoate **1** and methyl oleate **6** with allyl acetate **2** and *cis*-1,4-diacetoxy-2-butene **5** were carried out using relatively low concentrations of commercially available homogeneous ruthenium catalysts. The resulting products are interesting intermediates for polymer production. In all reactions very mild conditions were sufficient to achieve high conversions and yields.

In the cross metathesis of methyl 10-undecenoate **1**, higher yields of the bifunctional product **3** were reached with the symmetric substrate *cis*-1,4-diacetoxy-2-butene **5**. Furthermore, this reaction was faster and a substrate to co-substrate ratio of only 1:3 was required. The other conditions are similar to the reaction of methyl 10-undecenoate with allyl acetate **2**.

In the cross metathesis of methyl oleate **6** with allyl acetate **2** a valuable product distribution was only possible when the reaction conditions were altered. The reaction of methyl oleate **6** with both allyl acetate **2** and *cis*-1,4-diacetoxy-2-butene **5** requires very similar reaction conditions. These findings may eliminate the need for detailed optimizations when using symmetrical or unsymmetrical substrates in comparable metathesis reactions.

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