Metathesis of Unsaturated Fatty Acids: Synthesis of Long-Chain Unsaturated-α,ω-Dicarboxylic Acids

Helen L. Ngo, Kerby Jones, and Thomas A. Foglia*

USDA, ARS, Eastern Regional Research Center, Wyndmoor, Pennsylvania 19038

ABSTRACT: The self-metathesis of readily available monounsaturated FA has the potential of being an important pathway for the synthesis of symmetrical long-chain unsaturated-α,ω-dicarboxylic acids (C_{18}–C_{26}). Previous studies on the self-metathesis of monounsaturated FA esters using ruthenium catalysts in solution, however, suffered from low conversions as a result of the thermodynamic control of the reaction. We have found that the second-generation Grubbs catalyst can effectively catalyze the solvent-free self-metathesis of monounsaturated FA of varying purity (from 90 to 99%) to afford two important products—monounsaturated dicarboxylic acids and hydrocarbons—in very high molar conversions (>80%). This solvent-free self-metathesis reaction also works for monounsaturated FA containing additional functional groups. Reactions were conducted at catalyst loadings as low as 0.005 mol%, and turnover numbers as high as 10,800 could be obtained. This discovery represents an attractive approach to the large-scale production of useful monounsaturated-α,ω-dicarboxylic acids and long-chain unsaturated hydrocarbons by means of this solvent-free ruthenium-catalyzed self-metathesis of readily available monounsaturated FA.

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KEY WORDS: Dicarboxylic acids, erucic acid, Grubbs catalyst, metathesis, oleic acid, ricinoleic acid.

Aliphatic dicarboxylic acids are important intermediates in the synthesis of biodegradable polymers (1). Short-chain linear α,ω-dicarboxylic acids such as suberic acid (C_8), azelaic acid (C_9), or sebacic acid (C_{10}), which can be derived from fats and oils by chemical oxidation of unsaturated FA, are particularly important building blocks for the synthesis of commercially important materials such as nylon, cosmetics, plasticizers, lubricants, and greases (2,3). The chain length of the dicarboxylic acid in polymers is known to influence not only polymer properties but also the polymer degradation rates (4). Accordingly, the availability of a variety of α,ω-dicarboxylic acids of varying chain length could potentially lead to new polymeric materials that possess better performance and biodegradability. Research in producing aliphatic α,ω-dicarboxylic acids of chain length >10 started in the 1970s. Long-chain α,ω-dicarboxylic acids were produced by either microbial oxidation or microbial fermentation (5). In the 1980s, several research groups reported that microorganisms including *Candida tropicalis* or *C. cloacae* could transform *n*-alkanes and FA to dicarboxylic acids (6,7). Although microbial fermentation processes have been used for commercial production of long-chain α,ω-dicarboxylic acids, there are environmental concerns with these processes.

Alternatively, long-chain dicarboxylic acids can be synthesized by chemical approaches. In 1974, Van Dam *et al.* (8) reported the synthesis of long-chain dicarboxylic acids (C_{18}–C_{26}) by the self-metathesis of monounsaturated carboxylic acid esters in the presence of tungsten hexachloride (WCl_6) and tetramethyltin (Me_4Sn) co-catalyst in chlorobenzene solution. In this manner, monounsaturated fatty esters such as methyl octadec-9-enoate (methyl oleate, **3a**, Scheme 1) were converted to dicarboxylic esters with conversions ranging from 50 to 89%, and the diesters could be saponified and acidified to give the long-chain dicarboxylic acids. In a subsequent study (9), the co-metathesis of methyl oleate with dimethyl-3-hexenedioate was carried out using both homogeneous (WCl_6, Me_4Sn) and heterogeneous (Re_2O_7/Al_2O_3) catalysts. Although these synthetic approaches gave high selectivity and high conversions, the catalyst systems used suffered from low catalyst turnover numbers.

In the 1990s, pioneering work by Grubbs (10) demonstrated that homogeneous ruthenium-based catalysts are effective in catalyzing olefin metathesis. Moreover, these catalysts, in contrast to the tungsten and rhenium catalysts, often tolerate functionally substituted alkenes. These ruthenium-based catalysts have since been used to prepare α,ω-dicarboxylic acids or esters *via* metathetic routes. For example, Warwel *et al.* (11–15) reported a two-step process using Grubbs catalysts to prepare long-chain unsaturated α,ω-dicarboxylic esters. Cross-metathesis of monounsaturated carboxylic acid methyl esters with ethylene in the presence of the first-generation catalyst **1** (Fig. 1) in solution initially gave terminally unsaturated monocarboxylic methyl esters. The resulting terminal monounsaturated esters then underwent self-metathesis in the presence of **1** to give long-chain α,ω-dicarboxylic acid methyl esters with an overall yield between 38 and 40%. Dinger and Mol (16) reported that self-metathesis of methyl oleate in dichloromethane using the second-generation Grubbs catalyst **2** (Fig. 1) gave the long-chain α,ω-dicarboxylic methyl ester **5a** (Scheme 1, Eq. 1) in ~45% conversion. Grubbs and Nguyen (17) reported the self-metathesis of oleic acid in the presence of $Cl_2(PCy_3)_2Ru{=}CH{-}CH{=}CPh_2$ catalyst in dichloromethane solution to give 1,18-octadec-9-enedioic acid (**5b**) and octadec-9-ene (**4**) in 42% yield.

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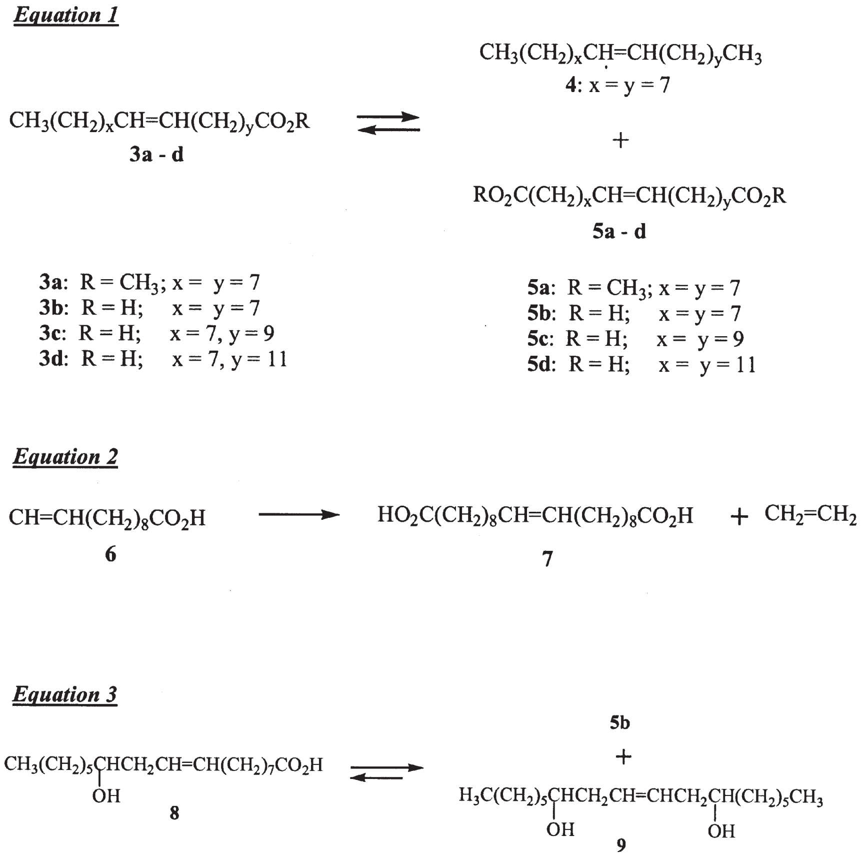
*To whom correspondence should be addressed at Fats, Oils and Animal Coproducts Research Unit, U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, 600 East Mermaid Ln., Wyndmoor, PA 19038. E-mail: tfoglia@arserre.gov



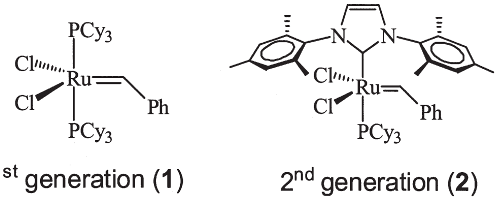
SCHEME 1

Although long-chain α,ω-dicarboxylic acids and esters have been successfully synthesized using ruthenium-catalyzed self-metathesis routes, conversions are low since such reactions are typically subject to thermodynamic control. In this paper, we report the efficient solvent-free self-metathesis of monounsaturated FA catalyzed by second-generation Grubbs catalysts to afford unsaturated α,ω-dicarboxylic acids and hydrocarbons in very high conversions.

MATERIALS AND METHODS

Oleic acid (99%), 11-eicosenoic acid (99%), and ricinoleic acid (99%) were from Nu-Chek-Prep (Elysian, MN). Oleic acid (90%), erucic acid (90%), 10-undecenoic acid (98%), and the Grubbs catalysts (**1** and **2**) were purchased from Aldrich Chemical (Milwaukee, WI). All other reagents used were of the highest purity obtainable from commercial suppliers.

^{1}H and ^{13}C NMR spectra were collected at room temperature in CD_3OD either on a Varian Gemini 200-MHz or Varian Inova 400-MHz (Palo Alto, CA) spectrometer. Operating parameters for ^{1}H NMR were: cycle time (d1) = 1.0 s; acquisition time (at) = 3.744 s; transmitter power (tpwr) = 57 Hz; pulse width (pw) = 90°; operating parameters for ^{13}C NMR were: cycle time (d1) = 2.0 s; acquisition time (at) = 2.399 s; transmitter power (tpwr) = 52 Hz; pulse width (pw) = 45°. GC characterization of products was carried out with a Hewlett-Packard (Agilent, Wilmington, DE) HP 6890 instrument with a capillary inlet (splitless mode). The capillary column used was an HP DB-1 column (30 m × 0.25 mm × 0.25 mm) with carrier gas (N_2) set at a linear velocity of 22 cm/s at 100°C. The oven temperature profile was: initial temperature 50°C; ramp at 15°C /min to 220°C; hold for 10 min; ramp at 15°C/min to 250°C, hold for 5 min. GC/MS characterization of products was carried out with a Hewlett-Packard (Agilent) HP 5890 instrument with a capillary inlet (split-split mode) and an HP Model 5972 mass detector set to scan from 40 to 550 *m/z* at a rate of 1.5 scans/s. The capillary column used was an HP DB-5 column (30 m × 0.25 mm × 0.25 μm) with carrier gas (He) set at a linear velocity of 22 cm/s at 100°C. The injector and detector transfer line temperatures were set at 250 and 280°C, respectively. The oven temperature profile was: initial temperature 100°C; ramp at 10°C/min to 250°C; hold for 5 min; ramp at 10°C/min to 300°C, hold for 5 min.



1st generation (**1**) 2nd generation (**2**)

FIG. 1. First- and second-generation Grubbs catalysts. Cy, cyclohexyl.

*Synthesis of 1,18-octadec-9-enedioic acid (**5b**).* Oleic acid [**3b**; 89 g (90%), 0.315 mol] was transferred into a 250-mL three-necked round-bottomed flask *via* syringe and outgassed with nitrogen gas for 0.5 h. 1,3-Bis-(2,4,6-trimethylphenyl)-2-(imidazolidinylidene)(dichlorophenylmethylene)–(tricyclohexylphosphine)ruthenium (**2**; 267 mg, 0.315 mmol), a second-generation Grubbs catalyst, was then added. The reaction mixture was stirred with a mechanical stirrer and heated at 45°C, and after ~5 min the diacid began to precipitate from the reaction mixture. After 24 h reaction, ~10 mg of crude product was removed from the reaction mixture and transferred to a 2-mL dram vial. The crude diacid product (**5b**, Eq. 1) was added to 1 mL of methanol, and two drops of concentrated sulfuric acid were added. The resulting mixture was heated at 80°C for 0.5 h (18). The reaction mixture was then quenched with 2 mL of 1 M Na_2CO_3 and extracted with diethyl ether (3 × 2 mL); the combined ether layers were then washed with water (3 × 2 mL). The organic layer was dried with $MgSO_4$, filtered, and solvent was removed under reduced pressure. The methylated diacid **5a** was then characterized by GC/MS (retention time = 18 min) and gave an $[M]^+$ of *m/z* 340 (calc. $[M]^+$ for **5a** is *m/z* = 340.26).

The remainder of the crude product was quenched with ethyl vinyl ether (20 mL), and excess ether was removed under reduced pressure. The residue was recrystallized twice from a mixture of hexane (300 mL) and ethyl acetate (50 mL) to give pure 1,18-octadec-9-enedioic acid (**5b**, Eq. 1) as a white solid: m.p. 97.5–98.5° °C [lit. m.p. 88°C (8)]. Isolated yield: 35 g (71%). ^1H NMR of 1,18-octadec-9-enedioic acid (CD_3OD, 400 MHz): δ 5.39 (*m*, –C*H*=C*H*–, 2H), 2.28 (*t*, *J* = 7.2 and 7.6 Hz, $–CH_2CO_2H$, 4H), 1.98 (*m*, 4H), 1.60 (*m*, 4H), 1.32 (*m*, 16H). ^{13}C NMR (CD_3OD, 100 MHz): δ 177.8 (*s*, CO_2H), 131.6 (*s*, *C*H=*C*H), 35.1 (*s*), 33.7 (*s*), 30.8 (*s*), 30.4 (*s*), 30.3 (*s*), 30.2 (*s*), 26.2 (*s*).

*Synthesis of 1,22-docos-11-enedioic acid (**5c**).* 1,22-Docos-11-enedioic acid (**5c**) was synthesized from **3c** as described above in the self-metathesis of oleic acid (**3b**). Pure **5c** was obtained by recrystallization from a mixture of hexane (100 mL) and ethyl acetate (10 mL) to give **5c** in 74% yield (m.p. = 104–106.5°C). The methyl ester of diacid **5c** was analyzed by GC/MS: (retention time *t* = 24 min) and had an $[M]^+$ of *m/z* 396 (calc. $[M]^+$ for **5c** is *m/z* = 396.60). ^1H NMR (CD_3OD, 400 MHz): δ 5.4 (*m*, –C*H*=C*H*–, 2H), 2.28 (*t*, *J* = 7.6 and 7.2 Hz, $–CH_2CO_2H$, 4H), 1.99 (*m*, 4H), 1.58 (*m*, 4H), 1.31 (*m*, 24H). ^{13}C NMR (CD_3OD, 100 MHz): δ 177.9 (*s*, CO_2H), 131.7 (*s*, *C*H=*C*H), 35.2 (*s*, CH_2CO_2H), 33.7 (*s*), 30.9 (*s*), 30.7 (*s*), 30.6 (*s*), 30.5 (*s*), 30.4 (*s*), 30.3 (*s*), 26.2 (*s*).

*Synthesis of 1,26-hexacos-13-enedioic acid (**5d**).* Diacid **5d** was synthesized from **3d** as above. The pure diacid was obtained by recrystallization from acetone in a yield of 70%, m.p. = 105–107.5 °C [lit. m.p. = 96 °C (8)]. The methyl ester of diacid **5d** was analyzed by GC/MS (retention time t = 28.2 min) and had an $[M]^+$ of *m/z* 452 (calc. $[M]^+$ *m/z* 452.38). ^1H NMR (CD_3OD, 200 MHz): δ 5.4 (*m*, C*H*=CH, 2H), 2.28 (*t, J* = 7.4 Hz, CH_2CO_2H, 4H), 1.97 (*m*, $CH_2CH{=}CH$, 4H), 1.6 (*m*, 4H), 1.30 (*m*, 32H). ^{13}C NMR (CD_3OD, 50 MHz): δ 177.9 (*s*, $–CO_2H$), 131.7 (*s*, –*C*H=*C*H–), 35.2 (*s*), 33.7 (*s*), 30.9 (*s*), 30.8 (*s*), 30.78 (*s*), 30.7 (*s*), 30.6 (*s*), 30.4 (*s*), 30.3 (*s*), 26.3 (*s*).

*Synthesis of 1,20-eicos-10-enedioic acid (**7**).* Similar to oleic acid, 10-undecenoic acid [**6**; 10 g (98%), 0.054 mol] underwent self-metathesis in the presence of 46 mg (0.054 mmol) of catalyst **2**. The reaction flask was attached to a mineral oil bubbler, which allowed the gaseous ethylene co-product to escape. The mixture was stirred with a mechanical stirrer and heated at 45°C, and after ~5 min reaction a white precipitate was observed. After 72 h reaction a small amount of the crude product was removed from the reaction mixture and methylated as above for GC/MS analysis.

The remainder of the reaction mixture was quenched with ethyl vinyl ether (~20 mL) and unreacted ether removed under reduced pressure. The residue was recrystallized twice from ~100 mL of acetone to give pure 1,20-eicos-10-enedioic acid (**7**) as a white solid with m.p. = 110–110.5°C [lit. m.p. 108°C (8)]. The isolated yield was 7.5 g (82%). The methyl ester of diacid **7** was analyzed by GC/MS (retention time *t* = 23.9 min) and had an $[M]^+$ of *m/z* 368 (calc. $[M]^+$ *m/z* for 368.30). ^1H NMR (CD_3OD, 400 MHz): δ 5.39 (*m*, –C*H*=C*H*–, 2H), 2.28 (*t*, *J* = 7.2 and 7.6 Hz, $–CH_2CO_2H$, 4H), 1.97 (*m*, 4H), 1.58 (*m*, 4H), 1.31 (*m*, 20H). ^{13}C NMR (CD_3OD, 100 MHz): δ 177.8 (*s*, $–CO_2H$), 131.7 (*s*, –*C*H=*C*H–), 35.1 (*s*), 33.7 (*s*), 30.9 (*s*), 30.6 (*s*), 30.4 (*s*), 30.2 (*s*), 26.2 (*s*).

*Synthesis of 7,12-dihydroxyoctadec-9-ene (**9**).* Ricinoleic acid (**8**, 400 mg 1.34 mmol) was mixed with **2** (11 mg, 0.013 mmol) in a 50-mL Schlenk tube under nitrogen gas flow and the mixture was heated at 50°C. After ~0.5 h, a small amount of white precipitate was observed in the reaction flask. After 3 d of stirring at 50°C, the reaction mixture was quenched with 2 mL of ethyl vinyl ether, and the volatile components were removed under reduced pressure. The crude product contained the diol **9**, ricinoleic acid, and diacid **5b** was methylated using the procedure described above. The methylated product (116 mg) was reacted with 400 µL of N,O-bis(trimethylsilyl)trifluoroacetamide and 120 µL of pyridine at room temperature for 1 h (18). The silylated product was purified by passage through a silica gel column [~20 g; i.d. × length 1.2 × 25 cm (0.5 × 10in.)] using hexane/ethyl acetate (9:1 vol/vol) as eluant to give 34.5 mg of 7,12-bis(trimethylsiloxy)octadec-9-ene (**9a**) as a yellow oil, 28.9 mg of the silylated methyl ester of **8,** and 35.3 mg of the methyl ester of **5b**. Both steps gave quantitative reaction yields. GC/MS of **9a** (retention time *t* = 15.8 min) gave an $[M]^+$ at *m/z* = 427 (calc. $[M]^+$ for **9a** is *m/z* = 428.84). ^1H NMR of **9a** ($CDCl_3$, 200 MHz): δ 5.43 (*m*, $–CH_2CH{=}CH$, 2H), 3.6 (*m*, $–CHOSi(CH_3)_3$, 2H), 2.14 (*m*, $–CH_2CH{=}CH$, 4H), 1.26 (*m*, 20H), 0.878 (*m*, 6H), 0.085 (*s*, $–OSi(CH_3)_3$, 18H). ^{13}C NMR of **9a** ($CDCl_3$, 50 MHz): δ 129.1 (*s*, –*C*H=*C*H–), 72.7 (*s*, $–CHOSi(CH_3)_3$), 41.2 (*s*), 37.1 (*s*), 31.9 (*s*), 29.4 (*s*), 25.7 (*s*), 22.6 (*s*), 14.1 (*s*, $–CH_3$), 0.414 (*s*, $–OSi(CH_3)_3$).

RESULTS AND DISCUSSION

The solvent-free self-metathesis of oleic acid was carried out under a nitrogen atmosphere with 0.1 mol% of Grubbs catalyst

TABLE 1
Ruthenium-Catalyzed Self-Metathesis of Unsaturated FA/Esters[a]

Entry	Fatty ester/FA[b]	% Conv.[c]	% Isolated diester/acid	α,ω-Dicarboxylic ester/acid	Alkene
1	Methyl oleate (**3a**, 99%)	50	39[d]	1,18-Dimethyl octadec-9-enedioate (**5a**)	Octadec-9-ene (**4**)
2	Oleic acid (**3b**, 90%)	79	71[e]	1,18-Octadec-9-enedioic acid (**5b**)	Octadec-9-ene
3	11-Eicosenoic acid (**3c**, 99%)	77	74[e]	1,22-Docos-11-enedioic acid (**5c**)	Octadec-9-ene
4	Erucic acid (**3d**, 90%)	74	70[f]	1,26-Hexacos-13-enedioic acid (**5d**)	Octadec-9-ene
5	10-Undecenoic acid (**6**, 98%)	87	82[e]	1,20-Eicos-10-enedioic acid (**7**)	Ethene
6	Ricinoleic acid (**8**, 99%)	63	40[f,g,h]	1,18-Octadec-9-enedioic acid (**5b**)	7,12-Dihydroxy-octadec-9-ene (**9**)
7	Linoleic acid (**10**, 99%)	56	—	Mixture of diacids[i]	Mixture of alkenes[j]

[a] All the reactions were carried out with 0.1 mol% catalyst **2** (Fig. 1) at 45°C for 3 d.
[b] Starting FA/fatty ester (percent purity) and products shown in Schemes 1 and 2.
[c] Percent conversion determined by GC and expressed as Σ alkene + diacid/Σ alkene + diacid + FA. Dodecane used as the internal reference.
[d] Dimethyl ester isolated by silica gel chromatography.
[e] Isolated by recrystallizing from hexane/ethyl acetate.
[f] Isolated by recrystallizing from acetone.
[g] Product is methyl octadec-9-enedioate.
[h] Reaction carried out at 1.0 mol% catalyst loading.
[i] Diacid product (35%) composed of the following acids: C18:1; C21:5; C26:3 as determined by GC/MS of the reaction product after conversion to methyl esters.
[j] Alkene product (24%) composed of the following alkenes: C12:1; C15:2; C18:3 as determined by GC/MS of reaction mixture.

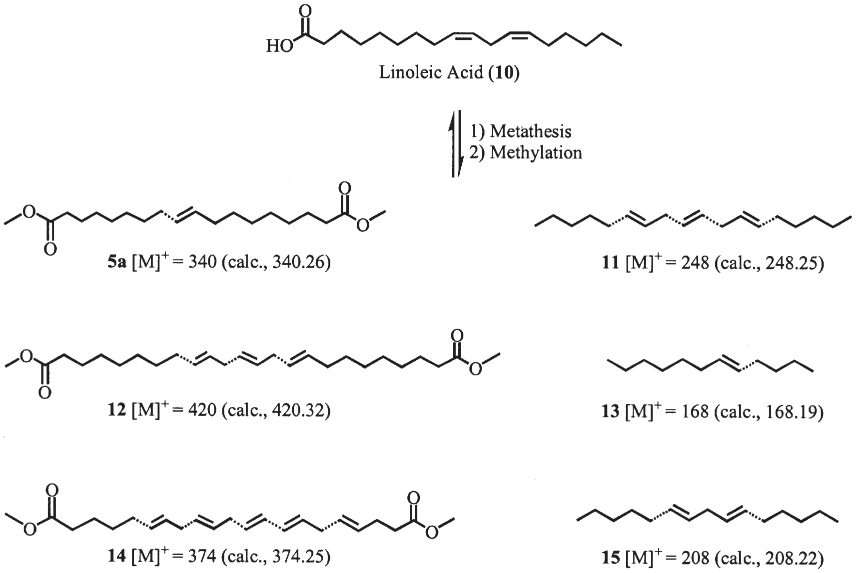
2 (Fig. 1). Catalyst **2** was chosen since, unlike earlier ruthenium-based metathesis catalysts, it was expected to tolerate the presence of functional groups such as the carboxyl group of oleic acid. In general, at a reaction temperature of 45°C, the diacid products started to precipitate from the reaction mixture after ~ 5 min. The reactions are preferably performed between 45 and 55°C. This temperature range is critical since the starting *cis* FA readily isomerize to *trans* isomers in the presence of the catalyst. Thus at reaction temperatures <40°C, the reaction mixtures solidify, which results in low conversion of starting acids to products. On the other hand, at temperatures >55°C the reaction mixtures remain liquid, which result in equilibrium processes and lower conversions. With the reaction conditions used in this work, the starting FA were retained as liquids so that they can further react with the catalyst to generate more diacids. Prolonged stirring of this mixture (48 h) led to the formation of 1,18-octadec-9-enedioic acid (**5b**) and octadec-9-ene (**4**), two potentially important oleochemical intermediates in 79% conversion (Scheme 1, Eq. 1). After quenching the reaction, the mixture was crystallized from hexane/ethyl acetate to give analytically pure **5b** in 71% isolated yield (Table 1, entry 2). The IR spectrum of **5b** indicated that the double bond on the alkyl chain is predominantly *trans* geometry. Octadec-9-ene (**4**) was purified by silica-gel column chromatography of the resulting crystallization mixture (after removal of solvent) using hexane as the eluant. All long-chain, unsaturated-α,ω-dicarboxylic acids and co-product alkenes reported in this study were characterized by ^{1}H and ^{13}C NMR spectroscopy and GC/MS. We also used oleic acid of varying purity (90 and 99%) and found that the self-metathesis reaction works equally well for both oleic acids, indicating the tolerance of **2** to the impurities in the starting oleic acid (primarily saturated FA). The level of conversion achieved here is higher than that previously obtained for ruthenium-catalyzed self-metathesis of FA (typically less than 50%). For comparison, we have carried out a control experiment with methyl oleate under similar conditions (Entry 1 in Table 1). In this instance, the self-metathesis of methyl oleate resulted in an equilibrium distribution of products (50% conversion of **3a**), and an isolated yield of dimethyl-9-octadecenoate (**5a**, 39%) was obtained by silica-gel column chromatography. The significant difference in conversion between oleic acid and methyl oleate is a result of the low solubility of diacid **5b** in the oleic acid and octadec-9-ene reaction mixture. As self-metathesis of **3b** proceeds, diacid **5b** precipitates out of the solution, and the equilibrium is pushed toward the diacid products (Scheme 1, Eq. 1) because of Le Chatelier's Principle.

As shown in Table 1, the solvent-free self-metathesis reaction is general, and other FA were self-metathesized using catalyst **2** under similar conditions to give the unsaturated dicarboxylic acids and hydrocarbons listed in Table 1 in comparatively high conversions. In addition to oleic acid, the self-metatheses of 11-eicosenoic (**3c**) and erucic (**3d**) acids also were investigated, and in both cases a high conversion to diacids **5c** and **5d** (Scheme 1, Eq.1) was obtained. As expected, the self-metathesis of 10-undecenoic acid (**6**) resulted in high yields of diacid **7** (Scheme 1, Eq. 2) because the co-product ethylene readily escapes from the reaction mixture, which further pushes the reaction equilibrium to the diacid products. In this instance, a conversion of 87% was obtained, and analytically pure 10-eicosenedioic acid (**7**) was obtained in 82% isolated yield.

TABLE 2
Effect of Catalyst Loading on the Ruthenium-Catalyzed Metathesis of Unsaturated FA[a]

Entry	FA	Catalyst loading (mol%)	% Conversion[b]	TON[c]
1	Oleic (**3b**, 90%)	0.1	79	790
2	Oleic (**3b**, 90%)	0.01	66	6600
3	Oleic (**3b**, 90%)[d]	0.005	54	10,800
4	10-Undecenoic (**6**, 98%)	0.1	87	870
5	10-Undecenoic (**6**, 98%)[d]	0.01	64	6400

[a] All reactions were carried out with catalyst **2** (Fig. 1) at 45°C for 48 h.
[b] Determined by GC and expressed as Σ alkene + diacid/Σ alkene + diacid + FA.
[c] TON = catalyst turnover number defined as % conversion/mol% catalyst loading.
[d] Acid dried with molecular sieves for 24 h and then vacuum distilled at 180°C before use.



SCHEME 2

Interestingly, the solvent-free self-metathesis reaction also works well with FA containing other functional groups. For example, ricinoleic acid, which has a hydroxyl group on the 12 position of the alkyl chain, underwent self-metathesis to afford 1,18-octadec-9-enedioic acid and 7,12-dihydroxyoctadec-9-ene with high selectivity and conversion up to 63% (Scheme 1, Eq. 3).

We also found that the self-metathesis of monounsaturated FA works well at low catalyst loading (Table 2). For example, self-metathesis of 10-undecenoic acid with catalyst loading of 0.01 mol % gave 1,20-eicos-10-enedioic acid with high selectivity and conversion up to 64%. Self-metathesis of oleic acid with 0.005 mol% catalyst loading gave 1,18-octadec-9-enedioic acid and octadec-9-ene with high selectivity and 54% conversion. A turnover number as high as 10,800 was obtained under these non-optimized conditions.

Self-metathesis of linoleic acid (**10**) in the presence of ruthenium catalyst **2** gave a more complex product mixture (Scheme 2) since both double bonds in linoleic acid are subject to self-metathesis. For example, self-metathesis of both of the 9,10 double bonds between two linoleic acid molecules yields C_{18}-diacid **5b** and C_{18}-triene **11** (Scheme 2) whereas metathesis between both of the 12,13 double bonds gives C_{24}-diacid **12** and the C_{12}-monoene **13** (Scheme 2). Alternatively, self-metathesis can occur between the 9,10 double bond of one linoleic acid molecule and the 12,13 double bond of a second linoleic acid molecule. The complexity of this reaction is further compounded, since each of the newly formed alkenes and unsaturated acids can in turn undergo cross-metathesis to produce compounds **14** and **15** (Scheme 2) so that a very complex product mixture is obtained. Although we have not determined all the hydrocarbons and α,ω-dicarboxylic acid products in this mixture, we were able to identify the compounds shown in Scheme 2 by GC/MS techniques and estimate a conversion of 56% based on the amount of unreacted linoleic acid.

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