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Conjugate addition of nitroalkanes to dimethyl maleate. Regioselective formation of both monoesters of 2-alkylsuccinic acids

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Abstract—Diesters of (*E*)-2-alkylidenesuccinic acids obtained by conjugate addition of nitroalkanes to dimethyl maleate can be selectively monohydrolyzed at the more reactive carboxyl group to the corresponding half-ester. Alternatively, total hydrolysis to the diacid allows a subsequent selective methyl esterification of the alkanoic carboxyl group to give the other regioisomeric half-ester. 2-Alkylsuccinic monoesters can be finally obtained by catalytic hydrogenation of the unsaturated derivatives.

1. Introduction

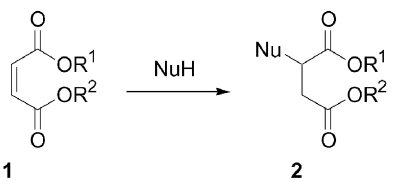
Monoesters of 2-substituted succinic acids are involved in a large number of synthetic processes leading to the preparation of biologically active substances.[1] Deprotonation at the α position of succinic acid esters provides the corresponding carbanions that are associated to the classical Stobbe condensation with aromatic aldehydes.[2] This condensation leads to the synthesis of 2-arylidenesuccinic acid monoesters but it works efficiently only with non-enolisable aldehydes. A Stobbe-like procedure using less basic phosphonate carbanions of *t*-butyl/ethyl succinates greatly improves the process effectiveness especially in the reaction with aliphatic aldehydes.[3] The obtained adducts can be regioselectively hydrolyzed since *t*-butyl esters are easily cleaved in acidic conditions.[4] *t*-Butyl monoesters of succinic acids can also be transformed into the corresponding dianions with LDA and directly alkylated at low temperature giving 2-alkyl derivatives.[5] A complementary approach concerns a conjugate addition of nucleophilic reagents to ester derivatives of maleic acid **1** (Scheme 1).[6]

The presence of two ester groups linked to each side of the double bond increases the reactivity toward conjugate addition but inevitably dictates the utilization of symmetric maleic esters in order to avoid regiochemical problems.[7] 2-Alkylsuccinates **2** obtained in this way can be converted into the corresponding monoesters only by means of a regioselective hydrolysis that is particularly difficult to carry out by conventional methods because of the close reactivity of the two ester functions. This problem can be partially worked out by enzymatic hydrolysis that however, is particularly suitable for the resolution of racemic mixtures since only one stereoisomer is actually hydrolyzed.[8]

In this paper, a new synthetic approach to the regioselective preparation of monoesters of 2-alkylsuccinic acids is presented. Our procedure is based on the lesser reactivity displayed by 2-alkenoic esters compared to their saturated homologs toward hydrolysis.

2. Results and discussion

Some years ago, we reported that methyl maleate **3** reacts with nitroalkanes **4** in the presence of DBU to give Michael adducts **5** that suffer elimination of nitrous acid affording unsaturated derivatives **6** as single *E* stereoisomers in good yield (Scheme 2).[9]



1 2

Scheme 1.

Keywords: addition reactions; esters; hydrolysis; nitro compounds; reduction.

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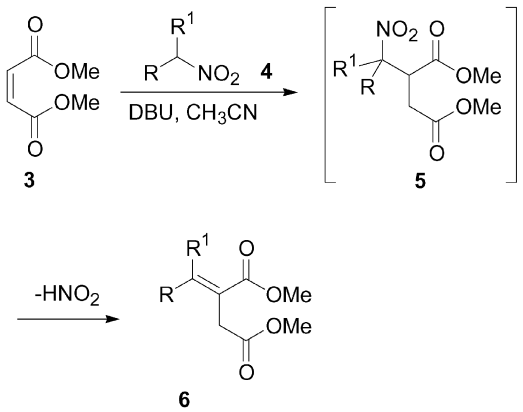
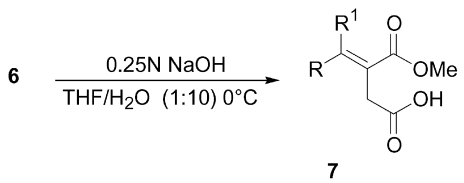


Scheme 2.

This reactivity is peculiar of enedione systems and has been exploited for the synthesis of important intermediates.[10] The ester groups in compounds **6** are well differentiated since one of them is part of an α,β-unsaturated moiety while the other can be considered as a simple alkanoic ester. It is conceivable that using carefully controlled conditions the alkanoic ester group would be hydrolyzed faster than the less reactive unsaturated ester. According to the procedure of Niwayama[11] diesters **6** have been selectively monohydrolyzed using 0.25N NaOH in THF–water (1:10) at 0°C (Scheme 3, Table 1).



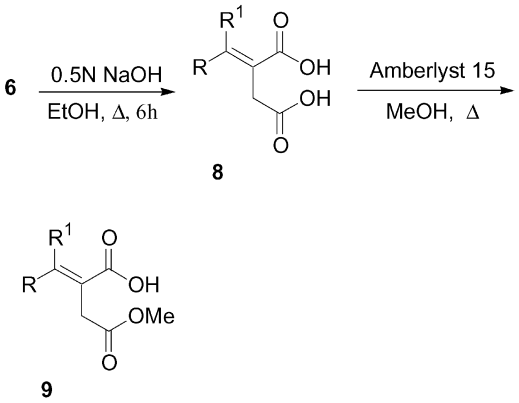
Scheme 3.

Table 1. Regioselective hydrolysis of diester **6**

Entry	Diester **6**			Mono ester **7**	Time (h)	Yield[a] (%)
		R	R^1			
1	**6a**	$CH_3(CH_2)_3$	H	**7a**	16	68
2	**6b**	$-(CH_2)_5-$		**7b**	7.5	85
3	**6c**	CH_3CH_2	H	**7c**	7.5	95
4	**6d**	$CH_3(CH_2)_4$	H	**7d**	17	63
5	**6e**	CH_3	CH_3	**7e**	7	80
6	**6f**	$HO(CH_2)_4CH_2$	H	**7f**	6	74
7	**6g**	$CH_3OCCH_2CH_2$	H	**7g**	5	73
8	**6h**	$(CH_3)_2CH$	H	**7h**	5	68
9	**6i**	$(CH_3)_2CHCH_2$	H	**7i**	6.5	76
10	**6j**	$-(CH_2)_4-$		**7j**	7	80

[a] Yields of pure, isolated products.

Temperature control is mandatory for the regioselectivity of the process since at room temperature variable amounts of the corresponding diacid are also formed. However, when the hydrolysis is carried out at 0°C, a good regioselectivity is usually observed since the yield of diacid derivatives never exceeds 4–5%.The major propensity of the alkanoic portion of diester **6** to undergo a selective hydrolysis makes rather troublesome the reverse process, i.e. monohydrolysis of the α,β-unsaturated ester. This goal is usually attained through a regioselective esterification of the corresponding cyclic anhydrides that privileges the formation of the ester at the more reactive alkanoic side of the molecule.[12] A similar selective esterification can be also conducted on the corresponding diacid **8** that is obtained by total hydrolysis of diester **6** using 0.5N NaOH in EtOH/water at reflux (Scheme 4).[13]



Scheme 4.

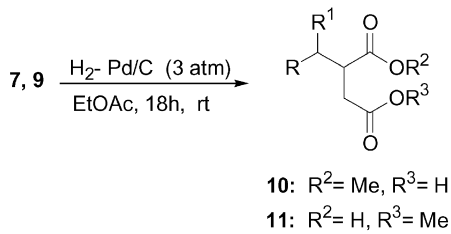
Crude diacid **8** is regioselectively monomethylated at the alkanoic group using the acidic macroreticular resin Amberlyst 15 in methanol at reflux (Scheme 4, Table 2).[14]

Table 2. Regioselective methyl esterification of diacid **8** obtained from complete hydrolysis of diester **6**

Entry	Diester **6**	Diacid **8** (yield %)[a]	Monoester **9**	Time (h)	Yield[b] (%)
1	**6a**	**8a** (95)	**9a**	15	82
2	**6b**	**8b** (92)	**9b**	7	80
3	**6c**	**8c** (98)	**9c**	7	86
4	**6d**	**8d** (90)	**9d**	16	85
5	**6e**	**8e** (95)	**9e**	4	78
6	**6f**	**8f** (89)	**9f**	16	76
7	**6g**	**8g** (91)	**9g**	17	71
8	**6h**	**8h** (97)	**9h**	15	75
9	**6i**	**8i** (90)	**9i**	6.5	86
10	**6j**	**8j** (96)	**9j**	7.5	84

[a] Yields of crude diacid, after complete hydrolysis.
[b] Overall yields of pure, isolated products from diester **6**.

Monoesters **7**,**9** are obtained together with a slight amount of diesters **6** (5–6%) from which can be easily separated by column chromatography. Compounds **7**,**9** can be finally reduced to 2-alkylsuccinic monoesters **10**,**11** by a classical catalytic hydrogenation in the presence of Pd/C (Scheme 5, Table 3).[13]



Scheme 5.

Table 3. Reduction of unsaturated monoesters **7**,**9**

Entry	Alkenyl monoester **7**,**9**	Alkyl monoester **10**,**11**	Yield[a] (%)
1	**7a**	**10a**	95
2	**7b**	**10b**	93
3	**7c**	**10c**	96
4	**7d**	**10d**	97
5	**7e**	**10e**	94
6	**7f**	**10f**	97
7	**7g**	**10g**	93
8	**7h**	**10h**	98
9	**7i**	**10i**	91
10	**7j**	**10j**	95
11	**9a**	**11a**	89
12	**9b**	**11b**	98
13	**9c**	**11c**	97
14	**9d**	**11d**	99
15	**9e**	**11e**	96
16	**9f**	**11f**	94
17	**9g**	**11g**	94
18	**9h**	**11h**	96
19	**9i**	**11i**	96
20	**9j**	**11j**	97

[a] Yields of pure, isolated products.

3. Conclusions

In summary, diesters of (*E*)-2-alkylidenesuccinic acids **6** can be selectively transformed into both regioisomeric monoesters **7**,**9** by operationally simple and straightforward procedures. Monohydrolysis of the more reactive alkanoic ester function in **6** provides the corresponding half-ester **7**. Regioisomeric half-ester **9** is obtained from diester **6** by a total hydrolysis to diacid **8** followed by a selective esterification of the alkanoic acid portion of the molecule. Catalytic hydrogenation of the double bond in compounds **7**,**9** gives the corresponding 2-alkylsuccinic monoesters **10**,**11** in good overall yields.

4. Experimental

4.1. General

^{1}H NMR were recorded at 300 MHz on a Varian VXR300 in $CDCl_3$ as solvent. ^{13}C NMR were recorded at 75 MHz in $CDCl_3$ as solvent. Microanalyses were performed with a CHNS-O analyzer Model EA 1108 from Fisons Instruments. IR spectra were recorded with a Perkin–Elmer Paragon 500 FT-IR. GLC analyses were performed on a Hewlett–Packard 5890 equipped with a capillary column of fused silica (0.32 mm×25 m), stationary phase SE54. Mass spectra were performed on a Hewlett–Packard GC/MS 5970 by means of the EI technique (70 eV). THF was dried by refluxing it over sodium wire then distilled. All chemicals used are available commercially. Diesters **6** as pure *E* stereoisomers were prepared as previously described.[9,10]

4.2. General procedure for the preparation of mono-esters 7

Sodium hydroxide 0.25N (32 mL) was added dropwise at 0°C to a solution of diester **6** (5 mmol) dissolved in THF–H_2O (1:10, 90 mL). The mixture was stirred at 0°C until TLC indicates that no starting material remains, (Table 1) and then was acidified with 1N HCl. The aqueous solution was extracted with ethyl acetate (5×30 mL), washed with brine and dried over $MgSO_4$. After filtration and evaporation of the solvent, crude monoester **7** was purified by column chromatography (1:9 methanol–chloroform)

4.2.1. (*E*)-3-(Methoxycarbonyl)oct-3-enoic acid, 7a. Yield 68%; clear oil; IR (cm^{-1}, neat) 1654, 1717, 3250; ^{1}H NMR δ (ppm) 0.93 (t, 3H, J=6.9 Hz), 1.27–1.50 (m, 4H), 2.17–2.31 (m, 2H), 3.41 (s, 2H), 3.78 (s, 3H), 7.01 (t, 1H, J=7.7 Hz). ^{13}C NMR δ (ppm) 13.8, 22.4, 28.7, 30.5, 32.2, 52.1, 124.7, 146.7, 167.6, 176.2. Anal. calcd for $C_{10}H_{16}O_4$ (200.23) C, 59.99; H, 8.05. Found C, 60.05; H, 8.09.

4.2.2. 3-Cyclohexylidene-4-methoxy-4-oxobutanoic acid, 7b. Yield 85%; waxy solid; IR (cm^{-1}, neat) 1633, 1713, 1748, 3300; ^{1}H NMR δ (ppm) 1.60–1.72 (m, 6H), 2.23–2.30 (m, 2H), 2.62–2.70 (m, 2H), 3.44 (s, 2H), 3.77 (s, 3H). ^{13}C NMR δ (ppm) 26.3, 27.9, 28.2, 32.5, 32.6, 34.9, 51.7, 116.7, 156.4, 169.2, 176.9. Anal. calcd for $C_{11}H_{16}O_4$ (212.24) C, 62.25; H, 7.60. Found C, 62.21; H, 7.63.

4.2.3. (*E*)-3-(Methoxycarbonyl)hex-3-enoic acid, 7c. Yield 95%; waxy solid; IR (cm^{-1}, neat) 1648, 1654, 1718, 3280; ^{1}H NMR δ (ppm) 1.06 (t, 3H, J=7.5 Hz), 2.14–2.28 (m, 2H), 3.34 (s, 2H), 3.74 (s, 3H), 7.11 (t, 1H, J=7.5 Hz). ^{13}C NMR δ (ppm) 12.9, 22.3, 32.1, 51.9, 125.0, 147.3, 167.7, 173.4. Anal. calcd for $C_8H_{12}O_4$ (172.18) C, 55.81; H, 7.02. Found C, 55.86; H, 7.03.

4.2.4. (*E*)-3-(Methoxycarbonyl)non-3-enoic acid, 7d. Yield 63%; yellow oil; IR (cm^{-1}, neat) 1654, 1718, 3350; ^{1}H NMR δ (ppm) 0.90 (t, 3H, J=6.8 Hz), 1.26–1.38 (m, 4H), 1.40–1.56 (m, 2H), 2.17–2.31 (m, 2H), 3.42 (s, 2H), 3.77 (s, 3H), 7.00 (t, 1H, J=7.7 Hz). ^{13}C NMR δ (ppm) 13.9, 22.4, 28.1, 28.9, 31.4, 32.2, 52.1, 124.6, 146.8, 167.7, 175.4. Anal. calcd for $C_{11}H_{18}O_4$ (214.26) C, 61.66; H, 8.47. Found C, 61.70; H, 8.44.

4.2.5. (*E*)-3-(Methoxycarbonyl)-4-methylpent-3-enoic acid, 7e.[15] Yield 80%; white solid, mp 58°C; IR (cm^{-1}, KBr) 1633, 1715, 3300; ^{1}H NMR δ (ppm) 1.91 (s, 3H), 2.17 (s, 3H), 3.43 (s, 2H), 3.76 (s, 3H). ^{13}C NMR δ (ppm) 23.3, 23.4, 35.3, 51.7, 119.7, 144.7, 170.0, 175.6. Anal. calcd for $C_8H_{12}O_4$ (172.18) C, 55.81; H, 7.02. Found C, 55.77; H, 6.99.

4.2.6. (*E*)-9-Hydroxy-3-(methoxycarbonyl)non-3-enoic acid, 7f. Yield 74%; yellow oil; IR (cm^{-1}, neat) 1651, 1714, 3400; ^{1}H NMR δ (ppm) 1.28–1.60 (m, 6H), 2.17–2.31 (m, 2H), 3.37 (s, 2H), 3.61 (t, 2H, J=6.4 Hz), 3.74 (s, 3H), 5.90 (br s, 2H), 6.97 (t, 1H, J=7.7 Hz). ^{13}C NMR δ (ppm) 25.4, 28.2, 28.9, 32.2, 32.3, 52.2, 62.6, 125.3, 146.5, 167.8, 175.5. Anal. calcd for $C_{11}H_{18}O_5$ (230.26) C, 57.38; H, 7.88. Found C, 57.41; H, 7.85.

4.2.7. (*E*)-3-(Methoxycarbonyl)-7-oxooct-3-enoic acid, 7g. Yield 73%; yellow oil; IR (cm^{-1}, neat) 1648, 1654, 1718, 3350; ^{1}H NMR δ (ppm) 2.17 (s, 3H), 2.40–2.53 (m, 2H), 2.60–2.71 (m, 2H), 3.46 (s, 2H), 3.76 (s, 3H), 6.90 (t, 1H, J=7.5 Hz). ^{13}C NMR δ (ppm) 17.7, 24.7, 26.9, 36.4, 46.9, 120.5, 139.1, 162.0, 165.8, 201.7. Anal. calcd for

$C_{10}H_{14}O_5$ (214.22) C, 56.07; H, 6.59. Found C, 56.02; H, 6.63.

4.2.8. (*E*)-3-(Methoxycarbonyl)-5-methylhex-3-enoic acid, 7h. Yield 68%; white solid, mp 75°C; IR (cm^{-1}, KBr) 1708, 3250; ^1H NMR δ (ppm) 1.03 (d, 6H, J=6.6 Hz), 2.54–2.66 (m, 1H), 3.33 (s, 2H), 3.73 (s, 3H), 6.78 (d, 1H, J=10.0 Hz). ^{13}C NMR δ (ppm) 21.9, 28.4, 32.2, 51.9, 123.3, 152.0, 168.2, 173.3. Anal. calcd for $C_9H_{14}O_4$ (186.21) C, 58.05; H, 7.58. Found C, 58.09; H, 7.61.

4.2.9. (*E*)-3-(Methoxycarbonyl)-6-methylhept-3-enoic acid, 7i.[16] Yield 76%; clear oil; IR (cm^{-1}, neat) 1645, 1690, 1747, 3300; ^1H NMR δ (ppm) 0.96 (d, 6H, J=6.6 Hz), 1.71–1.91 (m, 1H), 2.12 (t, 2H, J=7.4 Hz), 3.41 (s, 2H), 3.79 (s, 3H), 7.03 (t, 1H, J=7.4 Hz). ^{13}C NMR δ (ppm) 22.4, 28.2, 32.3, 38.0, 52.1, 125.3, 145.6, 167.6, 175.9. Anal. calcd for $C_{10}H_{16}O_4$ (200.23) C, 59.99; H, 7.58. Found C, 59.95; H, 7.62.

4.2.10. 3-Cyclopentylidene-4-methoxy-4-oxobutanoic acid, 7j. Yield 80%; white solid, mp 107°C; IR (cm^{-1}, KBr) 1693, 1710, 3250; ^1H NMR δ (ppm) 1.61–1.79 (m, 4H), 2.40 (t, 2H, J=6.4 Hz), 2.79 (t, 2H, J=6.4 Hz), 3.36 (s, 2H), 3.72 (s, 3H), 10.53 (bs, 1H). ^{13}C NMR δ (ppm) 25.7, 27.2, 34.5, 34.8, 36.2, 51.8, 116.3, 166.2, 167.9, 177.7. Anal. calcd for $C_{10}H_{14}O_4$ (198.21) C, 60.59; H, 7.12. Found C, 60.64; H, 7.09.

4.3. General procedure for the preparation of mono-esters 9

Diester **6** (2.6 mmol) was dissolved in EtOH (10 mL) and 0.5N NaOH (50 mL) was added at room temperature. The solution was refluxed for 6 h then concentrated to 1/3 of the volume. Water (100 mL) was added and the solution was washed with EtOAc (3×10 mL). The aqueous phase was acidified to pH 1 with 2N HCl, extracted with EtOAc (5×20 mL), washed with brine (20 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent at reduced pressure diacid **8** was obtained enough pure to be used in the next step. To a solution of diacid **8** (2.0 mmol) in MeOH (10 mL), Amberlyst 15 (0.35 g) was added at room temperature and the obtained suspension was refluxed for the appropriate time (Table 2). After cooling at room temperature the resin was filtered off and washed with methanol, the solvent was then evaporated to give product **9** which was purified by column chromatography (1:9 methanol–chloroform).

4.3.1. (*E*)-2-(2-Methoxy-2-oxoethyl)hept-2-enoic acid, 9a. Yield 82%; white solid, mp 48°C; IR (cm^{-1}, KBr) 1644, 1694, 1749, 3300; ^1H NMR δ (ppm) 0.93 (t, 3H, J=6.9 Hz), 1.20–1.60 (m, 4H), 2.16–2.30 (m, 2H), 3.37 (s, 2H), 3.70 (s, 3H), 7.13 (t, 1H, J=7.6 Hz). ^{13}C NMR δ (ppm) 13.8, 22.4, 28.9, 30.4, 31.8, 52.0, 124.7, 148.8, 171.2, 172.0. Anal. calcd for $C_{10}H_{16}O_4$ (200.23) C, 59.99; H, 8.05. Found C, 59.95; H, 8.01.

4.3.2. 2-Cyclohexylidene-4-methoxy-4-oxobutanoic acid, 9b. Yield 80%; waxy solid; IR (cm^{-1}, neat) 1654, 1687, 1740, 3280; ^1H NMR δ (ppm) 1.54–1.70 (m, 6H), 2.21–2.29 (m, 2H), 2.71–2.78 (m, 2H), 3.40 (s, 2H), 3.67 (s, 3H). ^{13}C NMR δ (ppm) 26.3, 28.1, 28.4, 32.6, 33.2, 34.6, 52.1, 116.7, 159.1, 172.2, 173.0. Anal. calcd for $C_{11}H_{16}O_4$ (212.24) C, 62.25; H, 7.60. Found C, 62.29; H, 7.57.

4.3.3. (*E*)-2-(2-Methoxy-2-oxoethyl)pent-2-enoic acid, 9c. Yield 86%; white solid, mp 68°C; IR (cm^{-1}, KBr) 1644, 1693, 1727, 3285; ^1H NMR δ (ppm) 1.10 (t, 3H, J=7.5 Hz), 2.19–2.32 (m, 2H), 3.37 (s, 2H), 3.70 (s, 3H), 7.12 (t, 1H, J=7.5 Hz). ^{13}C NMR δ (ppm) 13.0, 22.7, 31.9, 52.3, 124.5, 150.2, 171.4, 172.3. Anal. calcd for $C_8H_{12}O_4$ (172.18) C, 55.81; H, 7.02. Found C, 55.80; H, 7.05.

4.3.4. (*E*)-2-(2-Methoxy-2-oxoethyl)oct-2-enoic acid, 9d. Yield 85%; white solid, mp 50°C; IR (cm^{-1}, KBr) 1732, 1749, 3300; ^1H NMR δ (ppm) 0.91 (t, 3H, J=6.6 Hz), 1.24–1.39 (m, 4H), 1.41–1.57 (m, 2H), 2.18–2.33 (m, 2H), 3.36 (s, 2H), 3.70 (s, 3H), 7.12 (t, 1H, J=7.6 Hz). ^{13}C NMR δ (ppm) 13.9, 22.4, 28.0, 29.1, 31.5, 31.8, 52.1, 124.7, 148.8, 171.1, 172.0. Anal. calcd for $C_{11}H_{18}O_4$ (214.26) C, 61.66; H, 8.47. Found C, 61.71; H, 8.45.

4.3.5. (*E*)-2-(2-Methoxy-2-oxoethyl)-3-methyl but-2-enoic acid, 9e.[12b] Yield 78%; white solid, mp 97°C; IR (cm^{-1}, KBr) 1659, 1694, 1747, 3300; ^1H NMR δ (ppm) 1.92 (s, 3H), 2.24 (s, 3H), 3.42 (s, 2H), 3.70 (s, 3H), 10.74 (br s, 1H). ^{13}C NMR δ (ppm) 23.7, 24.1, 35.0, 52.0, 119.8, 153.9, 171.9, 173.2. Anal. calcd for $C_8H_{12}O_4$ (172.18) C, 55.81; H, 7.02. Found C, 55.83; H, 7.06.

4.3.6. (*E*)-8-Hydroxy-2-(2-methoxy-2-oxoethyl)oct-2-enoic acid, 9f. Yield 76%; white solid, mp 71°C; IR (cm^{-1}, KBr) 1643, 1681, 1731, 3380 ^1H NMR δ (ppm) 1.30–1.63 (m, 6H), 2.18–2.33 (m, 2H), 3.35 (s, 2H), 3.64 (t, 2H, J=6.3 Hz), 3.69 (s, 3H), 5.48 (br s, 2H), 7.09 (t, 1H, J=7.7 Hz). ^{13}C NMR δ (ppm) 25.4, 28.1, 29.0, 31.8, 32.2, 52.1, 62.4, 125.0, 147.9, 170.9, 171.4. Anal. calcd for $C_{11}H_{18}O_5$ (230.26) C, 57.38; H, 7.88. Found C, 57.43; H, 7.85.

4.3.7. (*E*)-2-(2-Methoxy-2-oxoethyl)-6-oxohept-2-enoic acid, 9g. Yield 71%; yellow oil; IR (cm^{-1}, neat) 1715, 3380; ^1H NMR δ (ppm) 2.20 (s, 3H), 2.41–2.53 (m, 2H), 2.62–2.71 (m, 2H), 3.42 (s, 2H), 3.71 (s, 3H), 7.03 (t, 1H, J=7.5 Hz). ^{13}C NMR δ (ppm) 23.3, 30.1, 31.9, 41.8, 52.3, 125.9, 146.6, 171.3, 172.6, 207.0. Anal. calcd for $C_{10}H_{14}O_5$ (214.22) C, 56.07; H, 6.59. Found C, 56.01; H, 6.63.

4.3.8. (*E*)-2-(2-Methoxy-2-oxoethyl)-3-methylbut-2-enoic acid, 9h.[17] Yield 75%; white solid, mp:61°C; IR (cm^{-1}, KBr) 1643, 1697, 1732, 3250; ^1H NMR δ (ppm) 1.06 (d, 6H, J=6.6 Hz), 2.57–2.70 (m, 1H), 3.37 (s, 2H), 3.70 (s, 3H), 6.90 (d, 1H, J=9.9 Hz). ^{13}C NMR δ (ppm) 22.0, 28.9, 32.1, 52.3, 122.8, 154.7, 171.5, 172.2. Anal. calcd for $C_9H_{14}O_4$ (186.21) C, 58.05; H, 7.58. Found C, 58.01; H, 7.63.

4.3.9. (*E*)-2-(2-Methoxy-2-oxoethyl)-4-methyl pent-2-enoic acid, 9i.[16] Yield 86%; waxy solid; IR (cm^{-1}, neat) 1644, 1687, 1742, 3320; ^1H NMR δ (ppm) 0.96 (d, 6H, J=6.6 Hz), 1.70–1.90 (m, 1H), 2.13 (t, 2H, J=7.4 Hz), 3.39 (s, 2H), 3.70 (s, 3H), 7.15 (t, 1H, J=7.4 Hz), 8.17 (bs, 1H). ^{13}C NMR δ (ppm) 22.4, 28.2, 31.9, 38.1, 52.1, 125.4, 147.7, 171.2, 172.2. Anal. calcd for $C_{10}H_{16}O_4$ (200.23) C, 59.99; H, 7.58. Found C, 60.05; H, 7.60.

4.3.10. 2-Cyclopentylidene-4-methoxy-4-oxobutanoic acid, 9j. Yield 84%; white solid, mp 103°C; IR (cm^{-1}, KBr) 1690, 1711, 1738, 3250; ^1H NMR δ (ppm) 1.62–1.83 (m, 4H), 2.42 (t, 2H, J=6.2 Hz), 2.85 (t, 2H, J=6.2 Hz), 3.34 (s, 2H), 3.68 (s, 3H), 11.81 (s, 1H). ^{13}C NMR δ (ppm) 25.6, 27.1, 34.9, 35.1, 35.8, 52.1, 116.6, 168.9, 172.1, 173.0. Anal. calcd for $C_{10}H_{14}O_4$ (198.21) C, 60.59; H, 7.12. Found C, 60.55; H, 7.10.

4.4. General procedure for catalytic hydrogenation of monoesters 7,9

Monoester **7**,**9** (2 mmol) was dissolved in EtOAc (20 mL) and 10% Pd/C (0.1 g) was added. The suspension was hydrogenated (3 atm) at room temperature for 16 h. The catalyst was removed by filtration through celite pad and washed with EtOAc (3×5 mL). After evaporation of the solvent the crude product **10**,**11** was purified by flash chromatography (5:95 methanol–chloroform).

4.4.1. (*E*)-3-(Methoxycarbonyl)octanoic acid, 10a. Yield 95%; yellow oil; IR (cm^{-1}, neat) 1709, 1733, 3300; ^1H NMR δ (ppm) 0.87 (t, 3H, J=7.0 Hz), 1.21–1.38 (m, 6H), 1.40–1.63 (m, 2H), 2.43–2.50 (m, 1H), 2.69–2.85 (m, 2H), 3.69 (s, 3H), 11.21 (bs, 1H). ^{13}C NMR δ (ppm) 14.1, 22.6, 26.7, 31.7, 32.0, 35.9, 41.0, 52.1, 175.6, 178.4. Anal. calcd for $C_{10}H_{18}O_4$ (202.25) C, 59.39; H, 8.97. Found C, 59.34; H, 9.01.

4.4.2. 3-Cyclohexyl-4-methoxy-4-oxobutanoic acid, 10b. Yield 93%; clear oil; IR (cm^{-1}, neat) 1761, 1790, 3300; ^1H NMR δ (ppm) 0.98–1.36 (m, 5H), 1.54–1.82 (m, 6H), 2.38–2.60 (m, 1H), 2.63–2.83 (m, 2H), 3.71 (s, 3H). ^{13}C NMR δ (ppm) 25.8, 26.1, 29.9, 30.3, 32.8, 39.6, 46.5, 51.4, 174.7, 177.2. Anal. calcd for $C_{11}H_{18}O_4$ (214.26) C, 61.66; H, 8.47. Found C, 61.61; H, 8.51.

4.4.3. (*E*)-3-(Methoxycarbonyl)hexanoic acid, 10c. Yield 96%; yellow oil; IR (cm^{-1}, neat) 1707, 1742, 3290; ^1H NMR δ (ppm) 0.89 (t, 3H, J=7.0 Hz), 1.24–1.42 (m, 2H), 1.44–1.67 (m, 2H), 2.44 (dd, 1H, J=16.1, 4.3 Hz), 2.68–2.86 (m, 2H), 3.68 (s, 3H), 10.57 (bs, 1H). ^{13}C NMR δ (ppm) 14.0, 20.3, 34.2, 35.9, 40.9, 52.1, 175.7, 178.2. Anal. calcd for $C_8H_{14}O_4$ (174.19) C, 55.16; H, 8.10. Found C, 55.18; H, 8.07.

4.4.4. (*E*)-3-(Methoxycarbonyl)nonanoic acid, 10d. Yield 97%; clear oil; IR (cm^{-1}, neat) 1712, 1741, 3300; ^1H NMR δ (ppm) 0.89 (t, 3H, J=6.6 Hz), 1.24–1.38 (m, 8H), 1.48–1.72 (m, 2H), 2.49 (dd, 1H, J=15.4, 1.8 Hz), 2.78–2.92 (m, 2H), 3.72 (s, 3H). ^{13}C NMR δ (ppm) 14.0, 22.5, 26.8, 29.0, 31.6, 31.9, 35.5, 40.9, 51.9, 175.4, 176.7. Anal. calcd for $C_{11}H_{20}O_4$ (216.27) C, 61.09; H, 9.32. Found C, 61.015; H, 9.28.

4.4.5. (*E*)-3-(Methoxycarbonyl)-4-methylpentanoic acid, 10e. Yield 94%; yellow oil; IR (cm^{-1}, neat) 1710, 1736, 3300; ^1H NMR δ (ppm) 0.94 (d, 3H, J=6.7 Hz), 0.97 (d, 3H, J=6.7 Hz), 1.92–2.10 (m, 1H), 2.50 (dd, 1H, J=15.7, 2.9 Hz), 2.64–2.81 (m, 2H), 3.65 (s, 3H), 10.61 (bs, 1H). ^{13}C NMR δ (ppm) 19.7, 20.2, 30.3, 32.9, 47.4, 51.9, 175.0, 178.0. Anal. calcd for $C_8H_{14}O_4$ (174.19) C, 55.16; H, 8.10. Found C, 55.22; H, 8.13.

4.4.6. (*E*)-9-Hydroxy-3-(methoxycarbonyl)nonanoic acid, 10f. Yield 97%; yellow oil; IR (cm^{-1}, neat) 1735, 3400; ^1H NMR δ (ppm) 1.20–1.40 (m, 6H), 1.41–1.69 (m, 4H), 2.40 (dd, 1H, J=15.4, 4.4 Hz), 2.63–2.85 (m, 2H), 3.54 (t, 2H, J=6.6 Hz), 3.64 (s, 3H), 6.21 (bs, 2H). ^{13}C NMR δ (ppm) 25.5, 26.9, 29.2, 31.7, 32.5, 36.2, 41.1, 51.9, 62.6, 175.2, 175.8. Anal. calcd for $C_{11}H_{20}O_5$ (232.27) C, 56.88; H, 8.68. Found C, 56.83; H, 8.70.

4.4.7. (*E*)-3-(Methoxycarbonyl)-7-oxooctanoic acid, 10g. Yield 93%; clear oil; IR (cm^{-1}, neat) 1710, 1735, 3320; ^1H NMR δ (ppm) 1.42–1.78 (m, 4H), 2.12 (s, 3H), 2.41–2.54 (m, 3H), 2.73–2.84 (m, 2H), 3.68 (s, 3H), 9.25 (bs, 1H). ^{13}C NMR δ (ppm) 21.1, 30.1, 31.2, 35.8, 40.8, 43.2, 52.2, 175.2, 177.6, 208.8. Anal. calcd for $C_{10}H_{16}O_5$ (216.23) C, 55.55; H, 7.46. Found C, 55.50; H, 7.49.

4.4.8. (*E*)-3-(Methoxycarbonyl)-5-methylhexanoic acid, 10h. Yield 98%; clear oil; IR (cm^{-1}, neat) 1712, 1740, 3280; ^1H NMR δ (ppm) 0.86–0.94 (m, 6H), 1.22–1.37 (m, 1H), 1.48–1.67 (m, 2H), 2.43 (dd, 1H, J=16.8, 4.9 Hz), 2.62–2.79 (m, 1H), 2.82–2.98 (m, 1H), 3.67 (s, 3H), 11.17 (br s, 1H). 13C NMR δ (ppm) 22.4, 22.7, 25.9, 36.2, 39.4, 41.3, 52.1, 176.0, 178.2. Anal. calcd for $C_9H_{16}O_4$ (188.22) C, 57.43; H, 8.57. Found C, 57.38; H, 8.61.

4.4.9. (*E*)-3-(Methoxycarbonyl)-6-methylheptanoic acid, 10i. Yield 91%; clear oil; IR (cm^{-1}, neat) 1712, 1739, 3308; ^1H NMR δ (ppm) 0.84 (d, 6H, J=6.6 Hz), 1.08–1.34 (m, 2H), 1.40–1.78 (m, 3H), 2.38–2.58 (m, 1H), 2.62–2.91 (m, 2H), 3.68 (s, 3H), 11.03 (bs, 1H). ^{13}C NMR δ (ppm) 22.6, 28.1, 29.9, 35.9, 36.1, 41.2, 52.1, 175.7, 178.3. Anal. calcd for $C_{10}H_{18}O_4$ (202.25) C, 59.39; H, 8.97. Found C, 59.37; H, 9.00.

4.4.10. 3-Cyclopentyl-4-methoxy-4-oxobutanoic acid, 10j. Yield 95%; yellow oil; IR (cm^{-1}, neat) 1711, 1734, 3270; ^1H NMR δ (ppm) 1.10–1.30 (m, 2H), 1.41–1.85 (m, 6H), 1.88–2.05 (m, 1H), 2.38–2.60 (m, 1H), 2.61–2.83 (m, 2H), 3.71 (s, 3H), 10.1 (bs, 1H). ^{13}C NMR δ (ppm) 25.0, 25.1, 30.6, 30.7, 35.6, 42.5, 46.1, 51.9, 175.6, 178.2. Anal. calcd for $C_{10}H_{16}O_4$ (200.23) C, 59.99; H, 7.58. Found C, 59.94; H, 7.60.

4.4.11. (*E*)-2-(2-Methoxy-2-oxoethyl)heptanoic acid, 11a. Yield 89%; yellow oil; IR (cm^{-1}, neat) 1701, 1742, 3300; ^1H NMR δ (ppm) 0.89 (t, 3H, J=7.1 Hz), 1.20–1.67 (m, 8H), 2.44 (dd, 1H, J=16.6, 5.1 Hz), 2.66–2.85 (m, 2H), 3.67 (s, 3H), 10.62 (bs, 1H). ^{13}C NMR δ (ppm) 14.2, 22.6, 26.7, 30.6, 31.7, 35.6, 41.3, 52.1, 172.6, 181.4. Anal. calcd for $C_{10}H_{18}O_4$ (202.25) C, 59.39; H, 8.97. Found C, 59.44; H, 8.93.

4.4.12. 2-Cyclohexyl-4-methoxy-4-oxobutanoic acid, 11b. Yield 98%; yellow oil; IR (cm^{-1}, neat) 1705, 1756, 3270; ^1H NMR δ (ppm) 1.01–1.35 (m, 5H), 1.60–1.84 (m, 6H), 2.42–2.58 (m, 1H), 2.70–2.83 (m, 2H), 3.69 (s, 3H). ^{13}C NMR δ (ppm) 26.3, 26.5, 30.0, 30.8, 33.0, 39.9, 46.9, 52.0, 173.2, 178.9.0. Anal. calcd for $C_{11}H_{18}O_4$ (214.26) C, 61.66; H, 8.47. Found C, 61.72; H, 8.50.

4.4.13. (*E*)-2-(2-Methoxy-2-oxoethyl)-3-methylbutanoic acid, 11c. Yield 97%; yellow oil; IR (cm^{-1}, neat) 1705,

1746, 3290; ^{1}H NMR δ (ppm) 0.90 (t, 3H, J=7.0 Hz), 1.30–1.42 (m, 2H), 1.45–1.69 (m, 2H), 2.42 (dd, 1H, J=16.6, 5.0 Hz), 2.66–2.91 (m, 2H), 3.67 (s, 3H). ^{13}C NMR δ (ppm) 13.8, 20.0, 33.8, 35.4, 40.8, 51.8, 172.4, 180.6. Anal. calcd for $C_8H_{14}O_4$ (174.19) C, 55.16; H, 8.10. Found C, 55.20; H, 8.06.

4.4.14. (*E*)-2-(2-Methoxy-2-oxoethyl)octanoic acid, 11d. Yield 99%; yellow oil; IR (cm^{-1}, neat) 1740, 1763, 3300; ^{1}H NMR δ (ppm) 0.89 (t, 3H, J=6.6 Hz), 1.22–1.42 (m, 8H), 1.50–1.75 (m, 2H), 2.46 (dd, 1H, J=16.3, 5.0 Hz), 2.53–2.98 (m, 2H), 3.70 (s, 3H). ^{13}C NMR δ (ppm) 17.2, 22.7, 27.0, 29.2, 31.8, 31.9, 35.6, 41.2, 52.0, 172.6, 180.6. Anal. calcd for $C_{11}H_{20}O_4$ (216.27) C, 61.09; H, 9.32. Found C, 61.13; H, 9.33.

4.4.15. (*E*)-2-(2-Methoxy-2-oxoethyl)-3-methylbutanoic acid, 11e.[12b] Yield 96%; clear oil; IR (cm^{-1}, neat) 1709, 1740, 3300; ^{1}H NMR δ (ppm) 0.94 (d, 3H, J=7.0 Hz), 0.96 (d, 3H, J=7.0 Hz), 1.92–2.10 (m, 1H), 2.42–2.58 (m, 1H), 2.70–2.90 (m, 2H), 3.71 (s, 3H). ^{13}C NMR δ (ppm) 19.5, 20.3, 30.1, 32.5, 47.4, 52.1, 173.2, 180.6. Anal. calcd for $C_8H_{14}O_4$ (174.19) C, 55.16; H, 8.10. Found C, 55.11; H, 8.07.

4.4.16. (*E*)-8-Hydroxy-2-(2-methoxy-2-oxoethyl)octanoic acid, 11f. Yield 94%; yellow oil; IR (cm^{-1}, neat) 1738, 3307; ^{1}H NMR δ (ppm) 1.11–1.20 (m, 6H), 1.22–1.78 (m, 4H), 2.43 (dd, 1H, J=16.3, 5.0 Hz), 2.63–2.95 (m, 2H), 3.64 (t, 2H, J=6.6 Hz), 3.69 (s, 3H), 6.60 (br s, 2H). ^{13}C NMR δ (ppm) 26.6, 26.9, 29.2, 31.7, 32.5, 35.7, 41.2, 52.0, 62.8, 172.8, 179.9. Anal. calcd for $C_{11}H_{20}O_5$ (232.27) C, 56.88; H, 8.68. Found C, 56.94; H, 8.70.

4.4.17. (*E*)-2-(2-Methoxy-2-oxoethyl)-6-oxoheptanoic acid, 11g. Yield 94%; yellow oil; IR (cm^{-1}, neat) 1712, 1736, 3300; ^{1}H NMR δ (ppm) 1.45–1.77 (m, 4H), 2.13 (s, 3H), 2.38–2.57 (m, 3H), 2.61–2.91 (m, 2H), 3.67 (s, 3H), 10.38 (bs, 1H). ^{13}C NMR δ (ppm) 21.1, 30.1, 31.0, 35.5, 41.0, 43.2, 52.1, 172.5, 180.4, 208.8. Anal. calcd for $C_{10}H_{16}O_5$ (216.23) C, 55.55; H, 7.46. Found C, 55.60; H, 7.49.

4.4.18. (*E*)-2-(2-Methoxy-2-oxoethyl)-3-methylbutanoic acid, 11h. Yield 96%; clear oil; IR (cm^{-1}, neat) 1709, 1741, 3300; ^{1}H NMR δ (ppm) 0.85–0.99 (m, 6H), 1.21–1.36 (m, 1H), 1.53–1.69 (m, 2H), 2.41 (dd, 1H, J=16.5, 4.9 Hz), 2.61–2.72 (m, 1H), 2.83–2.97 (m, 1H), 3.64 (s, 3H), 11.00 (br s, 1H). ^{13}C NMR δ (ppm) 22.5, 22.7, 26.0, 36.3, 39.7, 41.2, 52.0, 172.7, 181.1. Anal. calcd for $C_9H_{16}O_4$ (188.22) C, 57.43; H, 8.57. Found C, 57.49; H, 8.53.

4.4.19. (*E*)-2-(2-Methoxy-2-oxoethyl)-4-methylpentanoic acid, 11i. Yield 96%; clear oil; IR (cm^{-1}, neat) 1708, 1741, 3320; ^{1}H NMR δ (ppm) 0.86 (d, 6H, J=6.6 Hz), 1.14–1.28 (m, 2H), 1.41–1.80 (m, 3H), 2.42 (dd, 1H, J=15.9, 4.6 Hz), 2.62–2.91 (m, 2H), 3.66 (s, 3H), 7.72 (bs, 1H). ^{13}C NMR δ (ppm) 22.6, 28.1, 29.7, 35.6, 36.0, 41.5, 52.0, 172.8, 180.6. Anal. calcd for $C_{10}H_{18}O_4$ (202.25) C, 59.39; H, 8.97. Found C, 59.33; H, 9.03.

4.4.20. 2-Cyclopentyl-4-methoxy-4-oxobutanoic acid, 11j. Yield 97%; yellow oil; IR (cm^{-1}, neat) 1707, 1741, 3280; ^{1}H NMR δ (ppm) 1.10–1.39 (m, 2H), 1.41–1.90 (m, 6H), 1.93–2.05 (m, 1H), 2.35–2.53 (m, 1H), 2.63–2.78 (m, 2H), 3.64 (s, 3H), 10.72 (bs, 1H). ^{13}C NMR δ (ppm) 25.1, 25.2, 30.6, 30.7, 35.3, 42.3, 46.3, 52.0, 172.9, 180.3. Anal. calcd for $C_{10}H_{16}O_4$ (200.23) C, 59.99; H, 7.58. Found C, 59.94; H, 7.60.

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