2-(Trimethylsilyl)-1,3-dithiane 1-Oxide as a Convenient Reagent for the Transformation of Aldehydes and Ketones into Homologous Carboxylic Acids

Karsten Krohn,* Stephan Cludius-Brandt

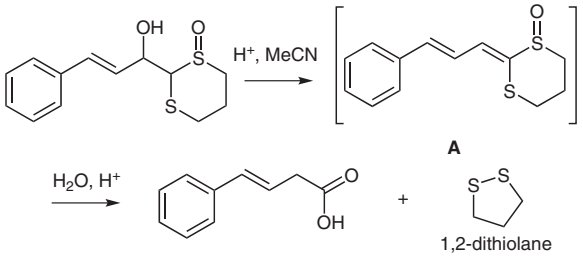
Department Chemie, Universität Paderborn, Warburger Str. 100, 33098 Paderborn, Germany
Fax +49(5251)603245; E-mail: k.krohn@uni-paderborn.de

Received 14 February 2010; revised 9 April 2010

Abstract: Aldehydes and ketones were converted into the corresponding homologous carboxylic acids in two steps by treatment with 2-(trimethylsilyl)-1,3-dithiane 1-oxide. A modified Peterson olefination of the carbonyl compounds gave ketene thioacetal sulfoxides that were readily cleaved in acidic acetonitrile to give the required carboxylic acids.

Key words: aldehydes, ketones, carboxylic acids, homologation

One-carbon homologation reactions of aldehydes, ketones, or carboxylic acids are important transformations in organic synthesis, and many different strategies for these transformations have been developed in recent decades.[1] This one-carbon transfer does not follow mainstream enolate chemistry,[2] and in many cases *umpolung* reagents are used.[3] Aldehyde-to-acid homologation is possible by the addition of an appropriate dithio-substituted nucleophile and subsequent hydrolysis. Indeed, an increase in oxidation state to the corresponding acid was observed during our work on the acid-catalyzed rearrangement reactions of α-hydroxy-1,3-dithianes and α-hydroxy-1,3-dithiane 1-oxides (Scheme 1).[4a] The intermediate ketene dithioacetals, such as **A**, are assumed to act as intermediates.[4b] Depending on the hydrolysis conditions, an ester,[5] thioester,[6] or carboxylic acid[7] can be isolated. Similarly, methyl (methylsulfanyl)methyl sulfoxide can be used in the transformation of substituted benzaldehydes into the corresponding phenylacetic acids.[4b–g] However, the synthesis of this reagent required a somewhat tedious multistep procedure, and its action is restricted to the transformation of aromatic aldehydes.[4b]

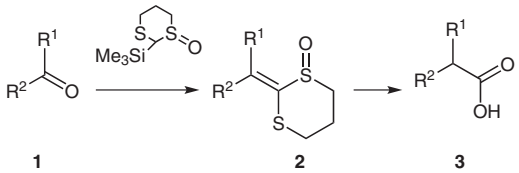


Scheme 1 Formation of a carboxylic acid from an α-hydroxy-1,3-dithiane 1-oxide[4b]

We therefore looked for a more general and more easily obtainable reagent, and preferably one that is available commercially. After some experimentation, we found that 2-(trimethylsilyl)-1,3-dithiane ideally fulfilled our requirements because it is commercially available and it can be oxidized nearly quantitatively in one step by sodium metaperiodate or *tert*-butyl hydroperoxide to give the corresponding 1-oxide. The oxide reagent can also be readily prepared by addition of lithiated 1,3-dithiane to trimethylsilyl chloride[9] and subsequent oxidation by sodium metaperiodate.[10] Oxidation is not required for the addition reaction of the dithiane with carbonyl compounds, but it is needed to facilitate the subsequent cleavage of the dithioacetals to give carboxylic compounds.[8] In addition, the required elimination step to give the intermediate ketene acetal (see Scheme 1) is facilitated when a modified Peterson olefination procedure is used.

We now wish to report on this method, which permits the synthesis of the homologous aromatic or aliphatic carboxylic acids from the corresponding aldehydes or ketones in a simple two-step process.

The general route for the homologation of the carbonyl compound **1** involves the formation of an intermediate ketene acetal (**2**) and its subsequent hydrolysis to the acid **3** (Scheme 2).



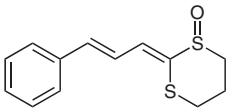
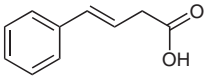
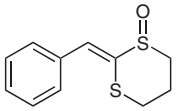
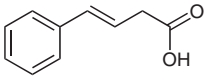
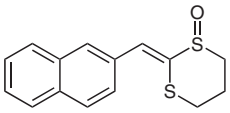
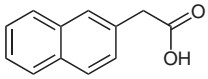
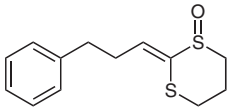
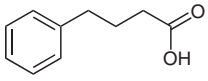
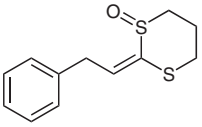
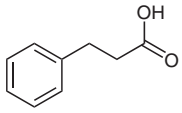
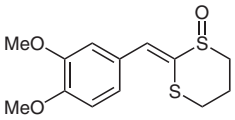
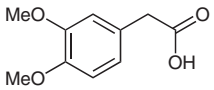
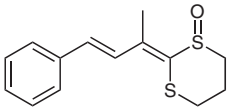
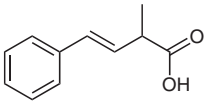
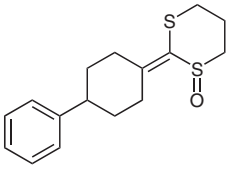
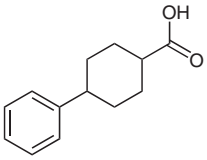
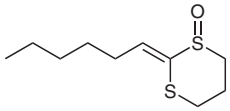
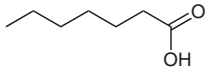
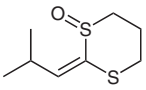
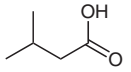
R^1 = H, alkyl
R^2 = alkyl, alkenyl, aryl, aralkyl
R^1–R^2 = cycloalkyl

Scheme 2 Homologation of carbonyl compounds to carboxylic acids

To explore the scope and limitations of the new reagent, we selected a number of aromatic, aliphatic, and unsaturated aldehydes and ketones with various degrees of steric hindrance (**1a–j**). These were readily converted into the required ketene dithioacetals **2a–j** by Peterson olefination with 2-(trimethylsilyl)-1,3-dithiane 1-oxide (Table 1). Subsequently, treatment of the ketene dithioacetals **2a–j** with excess 6 M hydrochloric acid in acetonitrile with warming to 55–65 °C until the starting material was com-

SYNTHESIS 2010, No. 15, pp 2616–2620
Advanced online publication: 17.06.2010
DOI: 10.1055/s-0029-1218820; Art ID: T03610SS

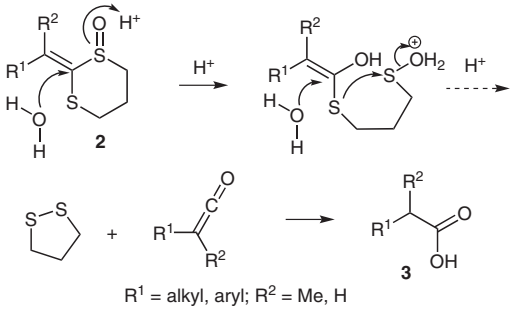
Table 1 Formation of Ketene Dithioacetals **2** and Their Conversion into Carboxylic Acids **3**

Ketene dithioacetal		Yield (%)	Time (h)	Acid		Yield (%)
2a		76	2	**3a**		85
2b		79	7	**3b**		94
2c		70	7	**3c**		88
2d		75	6	**3d**		91
2e		70	2.5	**3e**		92
2f		75	5	**3f**		85
2g		65	2	**3g**		40
2h		69	3	**3h**		71
2i		55	6	**3i**		92
2j		51	11	**3j**		90

pletely consumed (thin-layer chromatography) gave the corresponding carboxylic acids **3a**–**j** in good-to-very good yields, with exception of the olefinic ketene acetal **2g**; in this case, side reactions of the double bond probably occurred in the acidic medium.

Scheme 3 shows the presumed mechanism for the cleavage of the ketene dithioacetals **2a**–**j**.

Addition of a proton to the oxygen atom of the sulfoxide and attack by water led to the formation of the ketene and 1,2-dithiolane, which could be detected in the crude reaction mixture by NMR spectroscopy (see also Ogura and Tsuchihashi[4b]). Because excess water was present in the



Scheme 3 Mechanism for the cleavage of ketene dithioacetals **2a**–**j**

acidic solution, the ketene was transformed directly into the corresponding carboxylic acid.

In summary, we have shown that aromatic or aliphatic aldehydes and ketones can be readily converted into the corresponding homologous carboxylic acids by treatment with 2-(trimethylsilyl)-1,3-dithiane 1-oxide, with subsequent acidic cleavage of the 1,3-dithiane 1-oxide moiety in acetonitrile.

Column chromatography was performed on silica gel 60 (particle size 0.040–0.063 mm). NMR spectra were recorded on a Bruker ARX 200 or ARX 500 instrument at r.t. Chemical shifts are given in ppm relative to TMS. Mass spectra were recorded on Finnegan MAT 8200 and Fison MD 800 instruments. Solvents were purified, if necessary, by standard methods.

Oxidation of 2-(Trimethylsilyl)-1,3-dithiane by Sodium Metaperiodate

A soln of $NaIO_4$ (3.5 g, 16.6 mmol) in H_2O (20 mL) was added to 2-(trimethylsilyl)-1,3-dithiane (3.2 g, 16.6 mmol) in MeOH (150 mL) while the temperature was kept below 10 °C. After 4 h at 0–6 °C, the soln was allowed to warm to r.t. and filtered. The solvent was removed from the filtrate and the residue was partitioned between brine and $CHCl_3$ then dried (Na_2SO_4) and concentrated to give a light yellow oil; yield: 3.1 g (90%).

Ketene Dithioacetals 2a–j; General Procedure

A soln of 2-(trimethylsilyl)-1,3-dithiane 1-oxide (1.04 g, 5 mmol) in THF (20 mL) was cooled to –78 °C and a 2.5 M soln of BuLi in hexane (2.08 mL, 5.2 mmol) was added over 10 min. The soln was allowed to warm to 0 °C during 1.5 h and then cooled to –78 °C. A soln of a carbonyl compound **1a–j** (5 mmol) in THF was added over 10 min, and the soln was warmed to r.t. and left overnight. The soln was poured into sat. aq NH_4Cl (100 mL) and extracted with EtOAc (3×50 mL). The extracts were dried (Na_2SO_4) and concentrated under reduced pressure, and the resulting crude product was purified by column chromatography [silica gel, CH_2Cl_2–MeOH (1%)].

2-[(2*E*)-3-Phenylprop-2-en-1-ylidene]-1,3-dithiane 1-Oxide (2a)

Yield: 76%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.41–3.01 (m, 5 H), 3.35–3.49 (m, 1 H), 6.95 (d, *J* = 14.4 Hz, 1 H), 7.26–7.60 (m, 7 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.1, 31.6, 55.0, 122.2, 127.2, 128.7, 128.8, 135.3, 136.3, 137.0, 138.9.

MS (EI): *m/z* (%) = 250 (40) $[M]^+$, 160 (30), 144 (100), 128 (65), 123 (90), 115 (50), 106 (20), 91 (73).

HRMS: *m/z* calcd for $C_{13}H_{14}OS_2$: 250.04879; found: 250.04485.

2-Benzylidene-1,3-dithiane 1-Oxide (2b)

Yield: 79%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.47–2.67 (m, 3 H), 2.81–2.91 (m, 2 H), 3.39–3.45 (m, 1 H), 7.33–7.45 (m, 3 H), 7.52 (s, 1 H), 7.74–7.78 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.4, 32.2, 55.3, 128.9, 129.6, 130.6, 134.1, 134.7, 137.2.

Anal. Calcd for $C_{11}H_{12}OS_2$: C, 58.91; H, 5.39; S, 28.54. Found: C, 58.66; H, 5.40; S, 28.26.

2-(2-Naphthylmethylene)-1,3-dithiane 1-Oxide (2c)

Yield: 70%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.31–2.92 (m, 5 H), 3.26–3.41 (m, 1 H), 7.40–7.49 (m, 2 H), 7.62 (s, 1 H), 7.71–7.85 (m, 3 H), 7.88–7.97 (m, 1 H), 8.12 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.4, 32.2, 55.4, 126.9, 127.4, 127.5, 128.0, 128.3, 128.9, 130.8, 131.6, 133.4, 133.7, 134.7, 137.5.

MS (EI): *m/z* (%) = 274 (30) $[M]^+$, 171 (57), 141 (16), 106 (20), 90 (23), 57 (20).

HRMS: *m/z* calcd for $C_{15}H_{14}OS_2$: 274.04832; found: 274.05011.

Anal. Calcd for $C_{15}H_{14}OS_2$: C, 65.68; H, 5.14; S, 23.33. Found: C, 63.97; H, 5.11; S, 22.39.

2-(3-Phenylpropylidene)-1,3-dithiane 1-Oxide (2d)

Yield: 75%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.18–3.06 (m, 9 H), 3.14–3.32 (m, 1 H), 6.73 (t, *J* = 7.0 Hz, 1 H), 7.14–7.37 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.3, 30.7, 31.7, 35.2, 55.2, 126.5, 128.7, 129.2, 137.9, 138.0, 141.0.

MS (EI): *m/z* (%) = 252 (19) $[M]^+$, 235 (14), 209 (53), 177 (50), 145 (42), 129 (53), 106 (36), 91 (45), 73 (100), 41 (28).

HRMS: *m/z* calcd for $C_{13}H_{16}OS_2$: 252.06425; found: 252.06074.

Anal. Calcd for $C_{13}H_{16}OS_2$: C, 61.88; H, 6.39; S, 25.36. Found: C, 60.62; H, 6.75; S, 25.46.

2-(2-Phenylethylidene)-1,3-dithiane 1-Oxide (2e)

Yield: 70%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.32–2.88 (m, 5 H), 3.27–3.43 (m, 1 H), 3.84 (d, *J* = 7.5 Hz, 2 H), 6.89 (t, *J* = 7.7 Hz, 1 H), 7.19–7.35 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.3, 31.9, 35.3, 55.2, 126.9, 128.9, 129.1, 137.5, 138.0, 138.7.

MS (EI): *m/z* (%) = 238 (61) $[M]^+$, 221 (71), 147 (69), 115 (74), 106 (69), 91 (85), 84 (88), 49 (100).

HRMS: *m/z* calcd for $C_{12}H_{14}OS_2$: 238.0486; found: 238.04774.

2-(3,4-Dimethoxybenzylidene)-1,3-dithiane 1-Oxide (2f)

Yield: 75%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.46–2.92 (m, 5 H), 3.35–3.40 (m, 1 H), 3.88 (s, 3 H), 3.90 (s, 3 H), 6.87 (d, *J* = 8.3 Hz, 1 H), 7.33 (d, *J* = 8.3 Hz, 1 H), 7.38 (s, 1 H), 7.50 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.0, 31.8, 55.0, 55.9, 110.8, 112.8, 124.2, 126.7, 133.6, 134.2, 148.6, 149.9.

MS (EI): *m/z* (%) = 284 (48) $[M]^+$, 178 (85), 168 (100), 149 (68), 97 (31), 71 (41), 57 (59).

HRMS: *m/z* calcd for $C_{13}H_{16}OS_2$: 284.05387; found: 284.05299.

Anal. Calcd for $C_{13}H_{16}O_3S_2$: C, 54.91; H, 5.67; S, 22.51. Found: C, 53.90; H, 5.55; S, 23.31.

2-[(2*E*)-1-Methyl-3-phenylprop-2-en-1-ylidene]-1,3-dithiane 1-Oxide (2g)

Yield: 65%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 2.61–3.06 (m, 5 H), 3.17–3.37 (m, 1 H), 6.90 (d, *J* = 15.4 Hz, 1 H), 7.33–7.55 (m, 5 H), 7.85 (d, *J* = 15.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.4, 17.9, 31.1, 48.6, 124.1, 127.4, 129.1, 129.2, 134.2, 135.9, 136.8, 146.4.

MS (EI): *m/z* (%) = 264 (12) $[M]^+$, 174 (27), 158 (90), 149 (49), 106 (25), 83 (89), 48 (100).

HRMS: *m/z* calcd for $C_{14}H_{16}OS_2$: 264.06425; found: 264.06234.

2-(4-Phenylcyclohexylidene)-1,3-dithiane 1-Oxide (2h)
Yield: 69%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.49–1.81 (m, 4 H), 1.83–2.19 (m, 4 H), 2.58–2.98 (m, 6 H), 3.08–3.19 (m, 1 H), 7.12–7.34 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.7, 30.7, 31.6, 33.4, 34.8, 35.0, 44.4, 48.6, 126.3, 126.7, 128.5, 129.1, 145.4, 155.1.

MS (EI): *m/z* (%) = 292 (6) $[M]^+$, 275 (77), 209 (38), 177 (36), 106 (30), 91 (30), 73 (100), 41 (30).

HRMS: *m/z* calcd for $C_{16}H_{20}OS_2$: 292.09555; found: 292.09363.

Anal. Calcd for $C_{16}H_{20}OS_2$: C, 65.75; H, 6.90; S, 21.89. Found: C, 64.95; H, 6.82; S, 21.75.

2-Hexylidene-1,3-dithiane 1-Oxide (2i)
Yield: 55%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.5 Hz, 3 H), 1.14–1.51 (m, 6 H), 2.26–3.15 (m, 7 H), 3.19–3.33 (m, 1 H), 6.43 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3, 22.7, 27.2, 28.6, 29.0, 31.6, 31.8, 55.1, 136.7, 145.2.

MS (EI): *m/z* (%) = 218 (10) $[M]^+$, 201 (15), 163 (27), 131 (44), 113 (78), 106 (39), 84 (97), 55 (86), 43 (100).

HRMS: *m/z* calcd for $C_{10}H_{18}OS_2$: 218.0799; found: 218.07815.

2-(2-Methylpropylidene)-1,3-dithiane 1-Oxide (2j)
Yield: 51%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.04 (d, *J* = 6.8 Hz, 3 H), 1.09 (d, *J* = 6.8 Hz, 3 H), 2.28–2.81 (m, 6 H), 3.01–3.22 (m, 1 H), 6.52 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.6, 22.7, 27.4, 28.8, 32.0, 55.2, 134.8, 145.9.

MS (EI): *m/z* (%) = 190 (20) $[M]^+$, 173 (58), 159 (14), 106 (35), 85 (40), 60 (100).

HRMS: *m/z* calcd for $C_8H_{14}OS_2$: 190.0486; found: 190.04716.

Carboxylic Acids 3a–3j; General Procedure
A soln of ketene dithioacetal 1-oxide **2a**–**j** (1 mmol) in MeCN (10 mL) was treated with 6 M aq HCl (1.5 mmol, 0.25 mL), and the soln was warmed to 55–65 °C until the starting material was consumed (TLC). When the reaction was complete, the soln was poured into H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with brine (20 mL), dried (Na_2SO_4), and concentrated to give a crude product that was purified, if necessary, by column chromatography (silica gel, PE–EtOAc).

4-Phenylbut-3-enoic Acid (3a)
Yield: 85%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.35 (d, *J* = 6.9 Hz, 2 H), 6.24–6.44 (m, 1 H), 6.58 (d, *J* = 16 Hz, 1 H), 7.26–7.49 (m, 5 H), 10.57 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 38.4, 121.3, 126.7, 128.2, 129.0, 134.4, 137.1, 178.5.

Phenylacetic Acid (3b)
Yield: 94%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.69 (s, 2 H), 7.21–7.45 (m, 5 H), 11.01 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.5, 127.7, 129.0, 129.8, 133.7, 178.1.

2-Naphthylacetic Acid (3c)
Yield: 88%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.85 (s, 2 H), 7.38–7.92 (m, 7 H), 10.61 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.6, 126.4, 126.7, 127.8, 128.1, 128.6, 128.7, 131.3, 132.9, 133.8, 178.0.

4-Phenylbutanoic Acid (3d)
Yield: 91%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.87–1.94 (m, 2 H), 2.31 (t, *J* = 7.4 Hz, 2 H), 2.61 (t, *J* = 7.7 Hz, 2 H), 7.09–7.23 (m, 5 H), 11.65 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.3, 33.2, 35.1, 126.0, 128.4, 128.5, 141.2, 178.4.

3-Phenylpropanoic Acid (3e)
Yield: 92%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.69 (t, *J* = 8 Hz, 2 H), 2.97 (t, *J* = 8 Hz, 2 H), 7.19–7.33 (m, 5 H), 10.77 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.8, 35.7, 126.4, 128.2, 128.5, 140.2, 178.9.

(3,4-Dimethoxyphenyl)acetic Acid (3f)
Yield: 85%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.69 (s, 2 H), 3.89 (s, 3 H), 3.90 (s, 3 H), 6.85–7.09 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.6, 55.7, 55.9, 111.5, 112.6, 121.6, 125.7, 148.7, 150.3, 177.8.

2-Methyl-4-phenylbut-3-enoic Acid (3g)
Yield: 40%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.42 (d, *J* = 7.1 Hz, 3 H), 3.36 (m, 1 H), 6.28 (dd, *J* = 15.9 Hz, 7.7 Hz, 1 H), 6.52 (d, *J* = 15.9 Hz, 1 H), 7.28–7.42 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.2, 40.1, 126.3, 127.6, 128.0, 128.3, 131.7, 136.7, 181.1.

4-Phenylcyclohexanecarboxylic Acid (3h)
Yield: 71%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.45–1.67 (m, 4 H), 2.07–2.19 (m, 4 H), 2.48–2.57 (m, 1 H), 2.71–2.82 (m, 1 H), 7.15–7.39 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.1, 33.2, 42.7, 43.5, 126.1, 126.7, 128.3, 146.7, 181.0.

Heptanoic Acid (3i)
Yield: 92%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.3 Hz, 3 H), 1.23–1.70 (m, 8 H), 2.37 (m, 2 H), 10.40 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.4, 22.9, 25.0, 29.1, 31.8, 34.5, 180.9.

3-Methylbutanoic Acid (3j)
Yield: 90%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 6.6 Hz, 6 H), 2.08–2.12 (m, 1 H), 2.23 (d, *J* = 7.2 Hz, 2 H), 10.79 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.3, 25.4, 43.0, 178.5.

References

(1) For reviews, see: (a) Badham, N. F. *Tetrahedron* **2004**, *60*, 11. (b) Martin, S. F. *Synthesis* **1979**, 633.

(2) Warren, S.; Wyatt, P. *Organic Synthesis: The Disconnection Approach*, 2nd ed.; Wiley: Chichester, **2008**.

(3) *Umpoled Synthons: A Survey of Sources and Uses in Synthesis*; Hase, T. A., Ed.; Wiley: Chichester, **1987**.

(4) (a) Krohn, K.; Cludius-Brandt, S. *Synthesis* **2010**, 1344. (b) Ogura, K.; Tsuchihashi, G. *Tetrahedron Lett.* **1971**, *34*, 3151. (c) Ogura, K.; Tsuchiashi, T. *Tetrahedron Lett.* **1972**, 1383. (d) Ogura, K.; Tsuchiashi, T. *Tetrahedron Lett.* **1972**, 2681. (e) Seebach, D.; Bürstinghaus, R.; Gröbel, B.-T.; Kolb, M. *Justus Liebigs Ann. Chem.* **1977**, 830. (f) Ogura, K.; Mitamura, S.; Kishi, K.; Tsuchihashi, G. *Synthesis* **1979**, 880. (g) Bonini, B. F.; Franchini, M. C.; Mazzanti, G.; Slief, J.-W.; Margreth, A.; Zwanenburg, B. *Chem. Commun.* **1997**, 1011.

(5) (a) Funk, R. L.; Novak, P. M.; Abelman, M. *Tetrahedron Lett.* **1988**, *29*, 1493. (b) Chamberlin, A. R.; Chung, J. Y. L. *J. Org. Chem.* **1985**, *50*, 4425.

(6) (a) Seebach, D. *Synthesis* **1969**, 17. (b) Seebach, D.; Gröbel, B.-T.; Beck, A. K.; Baruan, M.; Geiss, K. H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 443. (c) Seebach, D.; Bürstinghaus, R. *Synthesis* **1975**, 461. (d) Göbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852.

(7) (a) Semmelhack, M. F.; Bargar, T. *J. Am. Chem. Soc.* **1980**, *102*, 7765. (b) Pang, Y.-P.; Kozikowski, A. P. *J. Org. Chem.* **1991**, *56*, 4499.

(8) Krohn, K.; Cludius-Brandt, S. *Synthesis* **2008**, 2369.

(9) Wedel, T.; Podlech, J. *Org. Lett.* **2005**, *7*, 4013.

(10) Carey, F. A.; Dailey, O. D. Jr.; Hernandez, O.; Tucker, J. R. *J. Org. Chem.* **1976**, *41*, 3975.