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New Oxidation of β-Hydroxy α-Methyl Ketones: A Convenient Synthesis of 3-Methylalkane-2,4-diones

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Abstract:

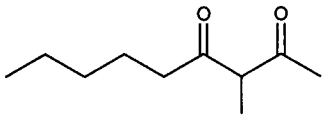
The synthesis of 3-methylalkane-2,4-diones, which are intense strawlike and fruit-flavored compounds, has been performed by the aldol condensation of *n*-alkanal (C2−C7) and methyl ethyl ketone to give 4-hydroxy-3-methyl-2-alkanones in 31−72% yield, followed by oxidation using sodium hypochlorite in the presence of 4-benzoyloxy-2,2,6,6-tetramethyl-piperidine-*N*-oxide in 60−86% yield.

Introduction

Recently, we reported the synthesis of 3-methylnonane-2,4-dione, which is an intense strawlike and fruit-flavored compound (Figure 1), by the aldol condensation of *n*-hexanal and methyl ethyl ketone, followed by oxidation using sodium hypochlorite (NaOCl) in the presence of 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxide (BzOTEMPO, Figure 2)[1].

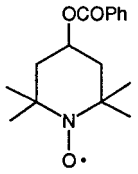
We further investigated the scope and limitations of this method. Although there are a number of approaches to β-diketones, most of these methods afford low yields due in large part to poor conversions.[2]

Previous synthetic methods for the preparation of 3-methylalkane-2,4-diones have been the condensation of *n*-aliphatic anhydride and methyl ethyl ketone with BF_3 gas,[3,4] and the methylation of β-diketone by methyl iodide.[5] However, these reported methods are considered unsuitable for economical and large-scale production. In contrast, the aldol condensation of aliphatic aldehydes and ketones that produces a β-hydroxyketone has been illustrated by many examples.[6] The β-hydroxyketone produced by the aldol condensation can then be oxidized to the corresponding β-diketone with many oxidation reagents. In 1981, Smith et al. reported that the oxidation of an appropriately substituted β-hydroxycarbonyl derivative, which would be readily available via the aldol condensation, would provide β-diketones.[7] Surprisingly, this aldol condensation−oxidation sequence is little known except for their report.



1e

Figure 1. **The structure of 3-methylnonane-2,4-dione (1e).**



BzOTEMPO

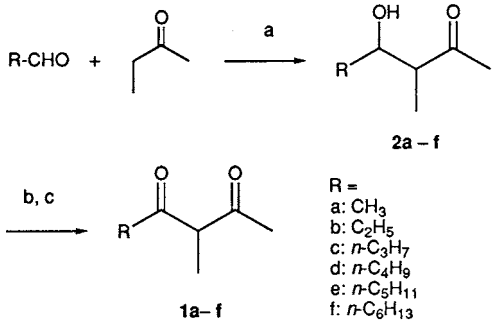
Figure 2. **The structure of 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxide (BzOTEMPO).**

To develop a general synthetic method for 3-methylalkane-2,4-diones (**1**) on the basis of our previous report, we studied in detail the aldol condensation-NaOCl/BzOTEMPO oxidation procedure. We now report a convenient synthetic route of **1**.

Results and Discussion

The 4-hydroxy-3-methyl-2-alkanones (**2**) were synthesized by the route shown in Scheme 1. The aldol condensation of *n*-aliphatic aldehyde (C2 − C7 aldehyde) and methyl ethyl ketone was carried out in aqueous NaOH solution at room temperature for 8 h to give a syn and anti mixture of 4-hydroxy-3-methyl-2-alkanones (**2a**−**2f**) in 31−72% isolated yield (Table 1). For **2a** and **2b**, the reaction was carried

Scheme 1. **Synthetic route to 4-hydroxy-3-methyl-2-alkanones (2) and 3-methylalkane-2,4-diones (1)[a]**



[a] Reagents and conditions: a) 2%NaOH aq rt, 8 h. b) 3 equiv 2 N NaOCl, 15 mol % BzOTEMPO, KBr, $NaHCO_3$, CH_2Cl_2, 5 °C, 2 h. c) 0.6 equiv $Cu(OAc)_2 \cdot H_2O$, MeOH/H_2O, and then 10% H_2SO_4.

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Table 1. **Aldol condensation results of *n*-alkanal and methyl ethyl ketone**

2	R	*syn*/*anti* ratio[a]	yield [%]
a	CH_3	53/47	31
b	C_2H_5	51/49	34
c	*n*-C_3H_7	41/59	64
d	*n*-C_4H_9	45/55	72
e	*n*-C_5H_{11}	47/53	69
f	*n*-C_6H_{13}	44/66	61

[a] The *syn*/*anti* ratio was determined by GC.

Table 2. **The oxidation results of 1**

1	R	keto/enol ratio[a]	yield [%]	odour quality
a	CH_3	71/29	60	strawy (weak)
b	C_2H_5	63/37	65	strawy (weak)
c	*n*-C_3H_7	65/35	83	strawy (weak)
d	*n*-C_4H_9	25/75	86	strawy (middle)
e	*n*-C_5H_{11}	60/40	85	strawy (extremely strong)
f	*n*-C_6H_{13}	60/40	83	strawy (strong)

[a] The keto/enol ratio was determined by NMR (measurement condition; 23 °C, $c = 2-3$ mg in 0.6 mL of $CDCl_3$).

out at 0−5 °C because the 3-methyl-3-alkene-2-ones were predominately obtained at room temperature. On the other hand, the 4-hydroxy-3-methyl-2-alkanone (**2**) using *n*-alkanals over the C8 aldehyde could not be obtained in good yield using this aldol condensation.

In view of investigating the oxidation of **2**, the Collins or Jones oxidation using chromium (VI) oxide was not examined on the basis of environmental concerns. Although the oxidation by NaOCl in the presence of 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) is well-known,[8,9] only a few examples of the oxidation of β-hydroxyketones by this method have been reported. Furthermore, this oxidation system is an efficient, safe, and cost-effective process. The selected oxidation catalyst was BzOTEMPO, which is available from Taoka Chemical (Osaka, Japan) in industrial grades, as with our previous work.[1]

To a mixture of 2% $NaHCO_3$ and 10 mol % of an aqueous KBr solution were added **2** and 15 mol % of BzOTEMPO, and then 2 mol/L NaOCl was added dropwise at 5 °C. The reaction mixture was checked by GC. After treatment by the usual method, the products were distilled under reduced pressure to give **1** in 60−86% yield (Table 2). The odor quality of these 3-methylalkane-2,4-diones shown in Table 2 was "strawy", and the odor intensity of **1e** and **1f** is stronger than that of the others.

To obtain **1** in high purity, the crude **1** was treated with 0.6 mol equiv of copper acetate monohydrate to give a quantitative yield of copper bis(3-methylalkane-2,4-dionate) as a solid. The crystalline solid was treated with 10% sulfuric acid to decompose the complex, and a simple distillation afforded the pure **1**.

We further investigated the scope and limitations of this method for other diketones. Thus, we tried this oxidation

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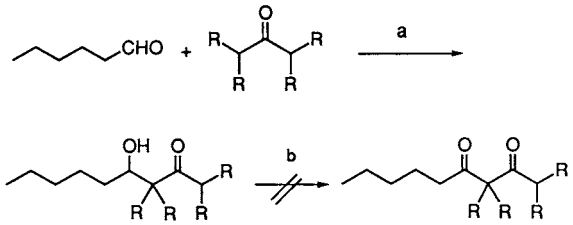
Scheme 2. **Synthetic route to 4-hydroxy-2-nonanone (3a) and 5-hydroxy-2,4,4-trimethyl-3-decanone (3b)[a]**



[a] Reagents and conditions: a) LDA, −78 °C, 1 h. b) 3 equiv 2 N NaOCl, 15 mol % BzOTEMPO, KBr, $NaHCO_3$, CH_2Cl_2, 5 °C, 2 h.

system for 4-hydroxy-2-nonanone (**3a**) without an α-methyl group and 5-hydroxy-2,4,4-trimethyl-3-decanone (**3b**) with an α,α-dimethyl group. **3a** and **3b** were synthesized from *n*-hexanal and acetone/diisopropyl ketone by using lithium diisopropylamide at −78 °C[7] to the corresponding β-diketones in 61 and 70% yield, respectively. However, the oxidation of these β-hydroxyketones did not occur (Scheme 2). The reason for this lack of oxidation cannot be explained at this time.

A compound of commercial value as a flavoring agent is 3-methylnonane-2,4-dione (**1e**), because it is a naturally occurring compound and has an intense odour. From 25.2 kg of *n*-hexanal we have already produced 17.8 kg of **1e** with 99.7% purity in 47.4% total yield by using the above-described method without difficulty.

Experimental Section

All reagents and solvents were obtained from commercial sources and used without further purification. For determination of the melting points, a Yanagimoto micromelting apparatus was used, and the values are uncorrected. NMR spectra were obtained with a Bruker DRX-500. The ^1H and ^{13}C NMR spectra were measured at 500 and 125 MHz, respectively, in $CDCl_3$ with TMS as the internal standard. The chemical shifts are given in δ (ppm). The IR spectra were obtained with a Nicolet Avatar 360 FT-IR. GC−Mass spectra (electronic impact) were obtained with HP5870 and HP5890 II. GC analysis was performed with a Hewlett-Packard HP5890 II with an FID detector (column, Neutrabond-1, df = 0.15 μm, 0.25 mm i.d. × 30 m; carrier gas N_2, 0.1 MPa, oven temperature, 80−200 °C programmed at 5 °C/min; injection temperature, 200 °C, detector temperature, 230 °C).

4-Hydroxy-3-methyl-2-alkanones (2): General Procedure. *n*-Alkanal (0.1 mol) was added dropwise to the mixture of 2% aqueous sodium hydroxide (20 mL, 0.4 mol) and methyl ethyl ketone (0.4 mol) at 5 °C or 20−25 °C for 5−8 h. The reaction mixture was stirred at the same temperature for 15 h, and then the organic layer was separated and washed with 5% NaCl solution. The solvent was removed under vacuum, and the residue was distilled under reduced pressure to give a *syn*/*anti* mixture of 4-hydroxy-3-methyl-2-alkanone (**2**). The purities were 80−93% by GC.

4-Hydroxy-3-methyl-2-pentanone (2a). The product was recovered as an oil (3.6 g, 31%). Bp 56−60 °C/6 Torr (lit.[10] 95−96 °C/35 Torr). ^{1}H NMR (*syn*/*anti* mixture) 1.14 (d, J = 7.3 Hz), 1.15 (d, J = 3.6 Hz), 1.19 (d, J = 7.6 Hz), 2.20 (s), 2.54−2.57 (m), 2.94 (br s), 3.89−3.93 (m), 4.11−4.14 (m); ^{13}C NMR (*syn*/*anti* mixture) 10.03 (CH_3), 13.46 (CH_3), 19.96 (CH_3), 20.62 (CH_3), 29.24 (CH_3), 29.40 (CH_3), 52.16 (CH), 53.98 (CH), 67.13 (CH), 69.24 (CH), 213.55 (C), 213.60 (C); IR (neat) 3439, 2975, 1708, 1457 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 116 (M^+, 2), 101 (6), 98 (21), 83 (8), 72 (51), 57 (38), 56 (59), 43 (100).

4-Hydroxy-3-methyl-2-hexanone (2b). The product was recovered as an oil (4.4 g, 34%). Bp 58−62 °C/5 Torr (lit.[11] 94−96 °C/20 Torr). ^{1}H NMR (*syn*/*anti* mixture) 0.96 (t, J = 7.5 Hz, 3H), 0.98 (t, J = 7.4 Hz), 1.13 (t, J = 7.3 Hz), 1.14 (t, J = 7.2 Hz), 1.38−1.62 (m), 2.20 (s), 2.21 (s), 2.59−2.66 (m), 2.77 (br s), 3.60−3.65 (m), 3.84 (m); ^{13}C NMR (*syn*/*anti* mixture) 9.55 (CH_3), 9.63 (CH_3), 10.30 (CH_3), 13.66 (CH_3), 26.88 (CH_2), 27.21 (CH_2), 29.01 (CH_3), 29.64 (CH_3), 50.54 (CH), 51.77 (CH), 72.44 (CH), 74.55 (CH), 213.68 (C), 213.88 (C); IR (neat) 3450, 2968, 2880, 1705, 1460 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 131 (M^+ + 1, 2), 112 (25), 101 (28), 97 (11), 83 (8), 72 (72), 57 (49), 43 (100).

4-Hydroxy-3-methyl-2-heptanone (2c). The product was recovered as an oil (9.2 g, 64%). Bp 75−80 °C/6 Torr (lit.[10] 112−116 °C/30 Torr). ^{1}H NMR (*syn*/*anti* mixture) 0.93 (t, J = 7.3 Hz), 0.94 (t, J = 7.1 Hz), 1.14 (t, J = 7.2 Hz), 1.29−1.51 (m), 2.19 (s), 2.20 (s), 2.54−2.68 (m), 3.69−3.71 (m), 3.94−3.97 (m); ^{13}C NMR (syn/anti mixture) 9.66 (CH_3), 13.75(CH_3), 13.92 (CH_3), 13.93 (CH_3), 18.63 (CH_2), 19.14 (CH_2), 29.08 (CH_3), 29.74 (CH_3), 36.15 (CH_2), 36.66 (CH_2), 50.93 (CH), 52.19 (CH), 70.66 (CH), 73.11 (CH), 213.81 (C), 213.96 (C); IR (neat) 3443, 2975, 2883, 1709, 1457 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 145 (M^+ + 1, 2), 126 (17), 111 (10), 101 (57), 83 (13), 72 (91), 57 (51), 43 (100).

4-Hydroxy-3-methyl-2-octanone (2d). The product was recovered as an oil (11.2 g, 72%). Bp 70−76 °C/2 Torr (lit.[11] 98 °C/16 Torr). ^{1}H NMR (*syn*/*anti* mixture) 0.93 (t, J = 6.9 Hz), 1.16 (t, J = 7.9 Hz), 1.27−1.52 (m), 2.22 (s), 2.23 (s), 2.48−2.66 (m), 2.80 (br s), 3.70 (br s), 3.94 (br s); ^{13}C NMR (*syn*/*anti* mixture) 9.62 (CH_3), 13.66 (CH_3), 13.88 (CH_3), 22.34 (CH_2), 22.51 (CH_2), 22.52 (CH_2), 27.54 (CH_2), 28.09 (CH_2), 29.02 (CH_3), 29.66 (CH_3), 33.69 (CH_2), 34.12 (CH_2), 50.93 (CH), 52.16 (CH), 70.92 (CH), 73.29 (CH), 213.69 (C), 213.87 (C); IR (neat) 3458, 2958, 2872, 1708, 1460 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 157 (M^+ + 1, 1), 140 (11), 125 (6), 111 (6), 101 (49), 83 (8), 72 (91), 57 (38), 43 (100).

4-Hydroxy-3-methyl-2-nonanone (2e). The product was recovered as an oil (11.9 g, 69%). For the physical and spectra data, see ref 1.

4-Hydroxy-3-methyl-2-decanone (2f). The product was recovered as an oil (11.3 g, 61%). Bp 98−103 °C/3 Torr (lit.[11] 147 °C/23 Torr). ^{1}H NMR (*syn*/*anti* mixture) 0.89 (t, J = 6.8 Hz), 1.06 (t, J = 7.4 Hz), 1.14 (t, J = 7.3 Hz), 1.29−1.51 (m), 2.19 (s), 2.20 (s), 2.46−2.64 (m), 3.67−3.71 (m), 3.92−4.04 (m); ^{13}C NMR (*syn*/*anti* mixture) 9.64 (CH_3), 13.67 (CH_3), 13.93 (CH_3), 22.42 (CH_2), 22.45 (CH_2), 22.48 (CH_2), 25.90 (CH_2), 28.32 (CH_2), 29.16 (CH_3), 29.66 (CH_3), 31.68 (CH_2), 31.70 (CH_2), 34.01 (CH_2), 34.45 (CH_2), 50.93 (CH), 52.17 (CH), 70.96 (CH), 73.32 (CH), 213.67 (C), 213.87 (C); IR (neat) 3459, 2929, 2858, 1709, 1459 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 187 (M^+ + 1, 1), 171 (4), 168 (11), 153 (8), 101 (74), 83 (17), 72 (100), 57 (36), 43 (76).

4-Hydroxy-2-nonanone (3a) and 5-Hydroxy-2,4,4-trimethyl-3-decanone (3b): General Procedure. A solution of lithium diisopropylamide (60 mmol) was prepared in THF (250 mL) from diisopropylamine (7.8 mL) and a 2.4 M solution (21.8 mL) of *n*-butyllithium in *n*-hexane under N_2 at −78 °C. To this reagent solution was added with stirring, under N_2 at −78 °C, a solution of ketone (50 mmol) in THF (25 mL) over 10 min. Stirring at −78 °C was continued for 1 h, and then a solution of *n*-hexanal (55 mmol) in THF (25 mL) was added. The mixture was stirred at −78 °C for a further 30 min, followed by addition of saturated ammonium chloride solution (250 mL). The resultant mixture was poured into diisopropyl ether (800 mL), washed with 10% sodium chloride solution, and dried with magnesium sulfate. The solvent was removed in vacuo, and the residual product was distilled under reduced pressure to give **3**.

4-Hydroxy-2-nonanone (3a). The product was recovered as an oil (5.3 g, 61%). The purity was 96% by GC. Bp 80−84 °C/3 Torr (lit.[12] 147 °C/ 0.4 mbar). ^{1}H NMR 0.89 (t, J = 7 Hz), 1.25−1.52 (m), 2.18 (s), 2.51−2.64 (m), 3.10 (br s), 4.03 (br s); ^{13}C NMR 13.88 (CH_3), 22.47 (CH_2), 25.02 (CH_2), 30.62 (CH_3), 31.62 (CH_2), 36.34 (CH_2), 49.94 (CH_2), 67.46 (CH), 209.82 (C); IR (neat) 3443, 2956, 2931, 2860, 1711, 1418 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 158 (M^+ + 1, 1), 112 (9), 94 (24), 83 (61), 79 (17), 68 (33), 55 (100), 57 (36), 41 (39).

5-Hydroxy-2,4,4-trimethyl-3-decanone (3b). The product was recovered as an oil (8.2 g, 70%). The purity was 95% by GC. Bp 100−102 °C/1.5 Torr. ^{1}H NMR 0.89 (t, J = 6.8 Hz), 1.06 (t, J = 7.4 Hz), 1.14 (t, J = 7.3 Hz), 1.29−1.51 (m), 2.19 (s), 2.20 (s), 2.46−2.64 (m), 3.67−3.71 (m), 3.92−4.04 (m); ^{13}C NMR 9.64 (CH_3), 13.67 (CH_3), 13.93 (CH_3), 22.42 (CH_2), 22.45 (CH_2), 22.48 (CH_2), 25.90 (CH_2), 28.32 (CH_2), 29.16 (CH_3), 29.66 (CH_3), 31.68 (CH_2), 31.70 (CH_2), 34.01 (CH_2), 34.45 (CH_2), 50.93 (CH), 52.17 (CH), 70.96 (CH), 73.32 (CH), 213.67 (C), 213.87 (C); IR (neat) 3501, 2962, 2962, 2973, 1697, 1469 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 215 (M^+ + 1, 1), 196(2), 171 (2), 153 (6), 143 (6), 126(7), 114(63), 99 (30), 81 (17), 71 (61), 56 (367, 43 (100).

3-Methylalkane-2,4-diones (1): General Procedure. Sodium bicarbonate (7 mmol) and potassium bromide (3 mmol) were dissolved in water (10 mL). 4-Hydroxy-3-methyl-2-alkanone (30 mmol) in dichloromethane (25 mL) and 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxide (4.5 mmol) was added to the solution at 5 °C. Sodium hypochlo-

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rite (2 N, 90 mmol) was added dropwise to the mixture at 5 °C for 1.5 h and stirred for an additional 30 min. Sodium sulfite (4.5 mmol) was added to the mixture. The organic layer was separated and then washed with water. The solvent was concentrated under vacuum to give crude 3-methylalkane-2,4-dione **(1)**. The purities were 90−96% by GC. The distillate was dissolved in methanol (5 mL), and copper (II) acetate monohydrate (15.2 mol) dissolved in water (30 mL) was added at 60 °C; the mixture was cooled to room temperature. The gray crystalline solid was filtered and washed with water and then *n*-heptane. The crystalline solid was suspended in toluene (200 mL), and 10% sulfuric acid solution (30 mL) was added dropwise at room temperature. The organic layer was separated and washed with water, and the solvent was removed in a vacuum. The residue was distilled under reduced pressure to give pure 3-methylalkane-2,4-dione **(1)**. The copper content of final product was 0.05−0.07 ppm by atomic absorption spectrophotometry.

3-Methylpentane-2,4-dione (1a). The product was recovered as an oil (2.0 g, 60%). Bp 40−43 °C/5 Torr (lit.[3] 77−79 °C/30 Torr). ^{1}H NMR (keto/enol mixture) 1.38 (t, J = 7.1 Hz), 1.39 (d, J = 1.2 Hz), 1.89 (s), 2.11 (s), 2.17 (s), 2.19 (d, J = 7.1 Hz), 2.24 (s), 3.73 (q, J = 7.1, 14.2 Hz); ^{13}C NMR (keto/enol mixture) 12.34 (CH_3), 12.69 (CH_3), 20.99 (CH_3), 23.15 (CH_3), 28.48 (CH_3), 61.63 (CH), 104.64 (C), 190.23 (C), 204.95 (C); IR (neat) 2988, 2940, 1727, 1702, 1610, 1422 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 114 (M^+, 18), 99 (11), 72 (80), 57 (71), 43 (100).

3-Methylhexane-2,4-dione (1b). The product was recovered as an oil (2.5 g, 65%). Bp 50−53 °C/5 Torr (lit.[3] 88−91 °C/30 Torr). ^{1}H NMR (keto/enol mixture) 1.06 (t, J = 7.2 Hz), 1.14 (t, J = 7.4 Hz), 1.33 (d, J = 7.1 Hz), 1.84 (s), 2.11 (s), 2.18 (s), 2.44 (q, J = 7.5, 15 Hz), 2.52 (q, J = 7.5, 15 Hz), 3.68 (q, J = 7.1, 14.1 Hz); ^{13}C NMR (keto/enol mixture) 7.58 (CH_3), 9.01(CH_3), 12.32 (CH_3), 12.74 (CH_3), 22.66 (CH_3), 22.82 (CH_3), 28.45 (CH_3), 29.54(CH_2), 32.92 (CH_2), 61.16 (CH), 104.10 (C), 188.21 (C), 195.69 (C), 205.19 (C), 207.72 (C); IR (neat) 2980, 2940, 1727, 1703, 1604, 1459 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 128 (M^+, 11), 113 (2), 99 (19), 86 (11), 72 (35), 57 (100), 43 (83).

3-Methylheptane-2,4-dione (1c). The product was recovered as an oil (3.5 g, 83%). Bp 45−46 °C/1 Torr (lit.[3] 93−96 °C/20 Torr). ^{1}H NMR (keto/enol mixture) 0.91 (t, J = 7.4 Hz), 0.97 (t, J = 7.5 Hz), 1.32 (d, J = 7.1 H), 1.57−1.67 (m), 1.84 (s), 2.12 (s), 2.17 (s), 2.38 (t, J = 7.7 Hz), 2.42−2.53 (m), 3.68 (q, J = 7, 14.1 Hz); ^{13}C NMR (keto/enol mixture) 12.45 (CH_3), 12.57 (CH_3), 13.47 (CH_3), 13.81 (CH_3), 16.81 (CH_2), 18.58 (CH_2), 23.38 (CH_3), 28.42 (CH_3), 37.68 (CH_2), 43.48 (CH_2), 61.35 (CH), 104.39 (C), 190.35 (C), 193.09 (C), 205.06 (C), 207.13 (C); IR (neat) 2966, 2938, 1725, 1702, 1604, 1458 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 142 (M^+, 9), 127 (2), 114 (4), 99 (11), 85 (4), 72 (51), 71 (92), 57 (19), 43 (100).

3-Methyloctane-2,4-dione (1d). The product was recovered as an oil (4.0 g, 86%). Bp 56−58 °C/1 Torr. ^{1}H NMR (keto/enol mixture) 0.90 (t, J = 7.4 Hz), 0.93 (t, J = 7.3 Hz), 1.27−1.42 (m), 1.32 (t, J = 7.1 Hz), 1.52−1.62 (m), 1.84 (s), 2.12 (s), 2.17 (s), 2.39 (t, J = 7.6 Hz), 2.42−2.54 (m), 3.68 (q, J = 7.1, 14.2 Hz); ^{13}C NMR (keto/enol mixture) 12.45 (CH_3), 12.61 (CH_3), 13.71 (CH_3), 13.78 (CH_3), 22.11 (CH_2), 22.11 (CH_2), 22.44 (CH_2), 23.34 (CH_3), 25.47 (CH_2), 27.29 (CH_2), 28.39 (CH_3), 35.53 (CH_2), 41.34 (CH_2), 61.36 (CH), 104.30 (C), 190.23 (C), 193.39 (C), 205.05 (C), 207.24 (C); IR (neat) 2960, 2935, 1726, 1702, 1604, 1461 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 156 (M^+, 8), 141 (2), 127 (2), 114 (8), 99 (23), 85 (100), 72 (42), 57 (94), 43 (64).

3-Methylnonane-2,4-dione (1e). The product was recovered as an oil (4.3 g, 85%). The physical and spectra data are shown in ref 1.

3-Methyldecane-2,4-dione (1f). The product was recovered as an oil (4.6 g, 83%). Bp 73−74 °C/0.5 Torr (lit. [12] 103 °C/17 Torr). ^{1}H NMR (keto/enol mixture) 0.88 (t, J = 7.1 Hz), 0.89 (t, J = 6.7 Hz), 1.25−1.38 (m), 1.32 (d, J = 7 Hz), 1.54−1.64 (m), 1.84 (s), 2.12 (s), 2.17 (s), 2.40−2.54 (m), 3.60 (q, J = 7.1, 14.2 Hz); ^{13}C NMR (keto/enol mixture) 12.47 (CH_3), 12.61 (CH_3), 13.91 (CH_3), 13.95 (CH_3), 22.38 (CH_2), 22.41 (CH_2), 22.45 (CH_2), 23.35 (CH_2), 25.15 (CH_2), 28.40 (CH_3), 28.66 (CH_2), 29.02 (CH_2), 31.44 (CH_2), 31.48 (CH_2), 31.55 (CH_2), 41.65 (CH_2), 61.37 (CH), 104.30 (C), 190.21 (C), 193.44 (C), 205.06 (C), 207.27 (C); IR (neat) 2956, 2931, 1725, 1702, 1603, 1458 cm^{-1}; EI-MS (*m*/*e*, relative intensity) 184 (M^+, 6), 166 (4), 155 (38), 127 (15), 114 (57), 99 (100), 85 (49), 57 (81), 43 (94).

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