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Oxidation of cycloalkanones with hydrogen peroxide: an alternative route to the Baeyer–Villiger reaction. Synthesis of dicarboxylic acid esters

Alexander O. Terent'ev *, Maxim M. Platonov, Alexey S. Kashin, Gennady I. Nikishin

N.D. Zelinsky Institute of Organic Chemistry, Leninsky Prospect 47, Moscow 119991, Russian Federation

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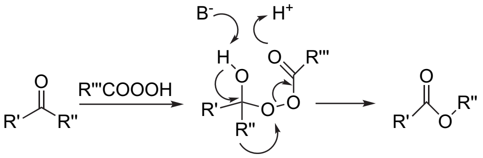
ABSTRACT

The acid-catalyzed oxidation of cycloalkanones C_5–C_8 and C_{12} with hydrogen peroxide in alcohols was performed, and dicarboxylic acid esters were obtained as the major products in 53–70% yields. In the first step, geminal bishydroperoxides are generated from five-to-seven-membered cyclic ketones. The Baeyer–Villiger reaction is a side process accompanied by the formation of ω-hydroxycarboxylic acid esters.

1. Introduction

The Baeyer–Villiger reaction has been used for more than 100 years[1] as an efficient procedure for the synthesis of lactones and ω-hydroxy acids from cyclic ketones. This reaction can be performed using numerous oxidants, such as H_2SO_5, $H_2S_2O_8$, perbenzoic acid, *m*-chloroperbenzoic acid, hydrogen peroxide, performic acid, peracetic acid, and trifluoroacetic acid.[2] The asymmetric Baeyer–Villiger oxidation proceeds under catalytic conditions in the presence of transition metals[3] or monooxygenases.[4] The commonly accepted mechanism of acid- or base-catalyzed oxidation of ketones suggested by Criegee[5] (Scheme 1) involves the addition of peracids to carbonyl compounds and the rearrangement of the resulting adducts accompanied by the migration of the alkyl group.



Scheme 1. Mechanism of acid- or base-catalyzed oxidation of ketones suggested by Criegee.

In almost all studies on the Baeyer–Villiger reaction, the latter was reported to produce hydroxy acids and lactones. The fact that treatment of cyclic ketones with peracetic acid affords dicarboxylic acids (containing the same number of carbon atoms) as by-products was documented in only one study.[6] The oxidation of cyclohexanone gave adipic acid in trace amounts (~1%). The oxidation of cycloheptanone and cyclooctanone afforded pimelic and suberic acids in 33 and 59% yields, respectively.

The problem of the development of efficient methods for the synthesis of dicarboxylic acids and their derivatives has attracted considerable attention for more than half a century, because these compounds are building blocks in the production of polyamide, polyurethane, and polyester polymers, plasticizing agents, lubricants, and anticorrosive systems.

The oxidation reactions of cyclic ketones to dicarboxylic acids with nitric acid,[7] potassium permanganate,[8] and other oxidants in the presence of catalysts containing W,[9] Ce,[10] Re,[11] Mn,[12] Cu,[10a] Co,[12d,e] Pt,[13] V,[14] or Mo[9b,14] were studied in detail. However, simple methods of oxidation (without the use of additional reagents) of cyclic ketones to dicarboxylic acids with hydrogen peroxide are lacking.

2. Results and discussion

In the present study, we report the oxidative transformation of ketones **1a**–**g** in the reaction with hydrogen peroxide in an alcoholic solution, which does not require the use of percarboxylic acids and metal-containing catalysts. This reaction affords dicarboxylic

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* Corresponding author. Tel.: +7 499 135 64 28; fax: +7 499 135 53 28.
E-mail address: terentev@ioc.ac.ru (A.O. Terent'ev).

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acids **3a**–**g** as the major products, which are then transformed into the corresponding esters **4a**–**g** (Scheme 2). The reaction gives also ω-hydroxycarboxylic acid esters as by-products generated by the Baeyer–Villiger oxidation of cycloalkanones. The design of the oxidative reaction differs from that of the Baeyer–Villiger reaction by the order of mixing of the reagents, the temperature conditions, and the concentration of the catalyst (strong acid).

Earlier, we have developed a facile procedure for the synthesis of geminal bishydroperoxides from cyclic ketones and hydrogen peroxide in THF at 15–20 °C.[15] Under more severe temperature conditions, these bishydroperoxides were demonstrated to be oxidized in alcohols (solvents) with hydrogen peroxide to form dicarboxylic acid esters.[16] These results led us to the idea to use a new procedure for the oxidation of cyclic ketones to dicarboxylic acids, that is, to perform these two reactions in one pot. The essence of this reaction is that the conditions favorable for the formation of geminal bishydroperoxides and for the oxidation of the latter to dicarboxylic acids are created in the first and second steps, respectively.

For this purpose, the reaction was performed in two steps. Initially, ketone was added with stirring to a mixture of alcohol, excess hydrogen peroxide, and sulfuric acid at 20–25 °C. The reaction mixture was allowed to stand for 5–10 min and then heated at the boiling point for 20–120 min. The oxidation products, dicarboxylic acids, were isolated from the reaction mixture as esters.

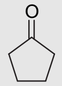
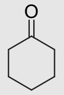
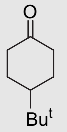
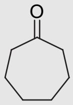
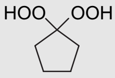
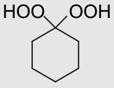
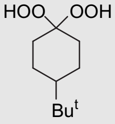
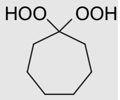
To confirm the formation of geminal bishydroperoxides in the first step of the oxidative reaction, a series of reactions with hydrogen peroxide were carried out in ethanol and propanol using medium-size ring ketones, such as cyclopentanone **1a**, cyclohexanone **1b**, 4-*tert*-butylcyclohexanone **1d**, and cycloheptanone **1e**. At 20–25 °C, the reactions of the above-mentioned ketones afforded geminal bishydroperoxides as the major products in 75–91% yields (Table 1). Under the same conditions, the reactions of hydrogen peroxide with cyclooctanone **1f** and cyclododecanone **1g** produced the corresponding geminal bishydroperoxides **2f**,**g** in low yields (26 and 17%, respectively). It should be emphasized that geminal bishydroperoxides have attracted considerable attention of chemists and pharmacologists because of the high antimalarial activity discovered in these compounds and their derivatives.[17]

The mechanism of the oxidation reaction is not quite clear. However, the following sequence of transformations of cyclic ketones into dicarboxylic acids can be suggested.

The first step involves the peroxidation of ketones **1**. At heating of the reaction mixture the acid-catalyzed transformations of bishydroperoxides **2** occur, which include oxidation using hydrogen peroxide. As a result dicarboxylic acids **3** are formed, which are then transformed into the corresponding esters **4**. Attempts to isolate intermediates failed because of the very high rate of oxidation.

Table 1

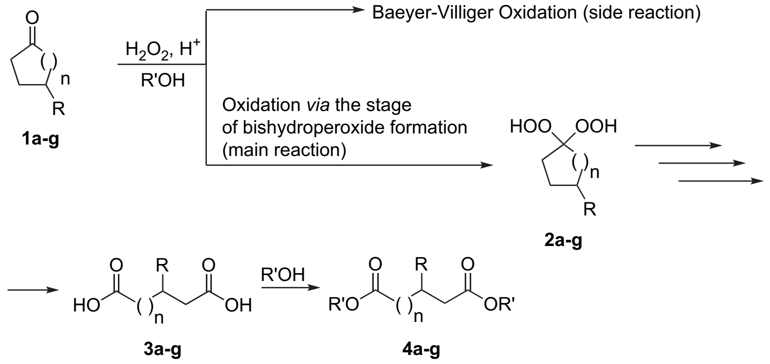
Synthesis of *gem*-bishydroperoxides **2a**,**b**,**d**,**e** by the reaction of ketones **1a**,**b**,**d**,**e** with hydrogen peroxide catalyzed by sulfuric acid in ethanol and propanol[a]

Ketones **1a**,**b**,**d**,**e**	 **1a**	 **1b**	 **1d**	 **1e**
gem-Bishydroperoxides **2a**,**b**,**d**,**e**	 **2a**	 **2b**	 **2d**	 **2e**
Yield,[b] %	75–82	78–84	88–91	81–85

[a] The reaction conditions: H_2O_2 (5 mol per mole of ketone), the H_2SO_4 concentration was 0.5 mol/L, the reaction time was 30 min, and the temperature was 20–25 °C. The conversion of ketones was 95–100%.

[b] The yields of *gem*-bishydroperoxides **2a**,**b**,**d**,**e** were determined based on the isolated reaction product.

The influence of the reaction temperature and the sulfuric acid concentration on the yield of dibutyl adipate **4b** was exemplified by the oxidation of cyclohexanone bishydroperoxide **2b** with the use of butanol as the co-solvent and an esterification reagent (Tables 2 and 3). At 50 °C, a long period of time (48 h) was required to achieve the complete conversion of peroxide **2b**. At 98–100 °C (boiling point of the reaction mixture), the reaction rate increases by more than two orders of magnitude, and the yield of dibutyl adipate **4b** increases from 38 to 68%. These characteristics were achieved at an H_2SO_4 concentration of 0.5 mol/L. An increase in the concentration to 1 mol/L leads to an increase in the rate of conversion of peroxide **2b** and a simultaneous decrease in the yield of **4b**. A decrease in the concentration to 0.1–0.2 mol/L results in a decrease in both the reaction rate and the yield of the ester. The choice of butanol was dictated by the necessity to maintain the temperature at ~100 °C; the use of ethanol or propanol instead of butanol leads to a decrease in the boiling point of the reaction mixture and, as a consequence, to a decrease in the yields of the target diethyl and dipropyl adipates.



a: n = 1, R = H; **b:** n = 2, R = H; **c:** n = 2, R = Me;
d: n = 2, R = Bu^t; **e:** n =3, R = H; **f:** n = 4, R = H; **g:** n = 8, R = H
R' = Et, Pr, Bu

Scheme 2. Proposed scheme of oxidation of ketones.

Table 2
Influence of the temperature on the time of complete conversion of bishydroperoxide **2b** and the yield of dibutyl adipate **4b**[a]

Temperature, °C	50	70	98–100[c]
Time of complete conversion of **2b**, h	48	3	0.15
Yield of dibutyl adipate **4b**,[b] %	38	56	68

[a] The reaction conditions: BuOH (20 mL), H_2SO_4 (1.2 g, 0.5 mol/L), bishydroperoxide **2b** (1.48 g, 10 mmol), and H_2O_2 (50 mmol, 37% aqueous solution).
[b] The yield based on the isolated reaction product.
[c] The boiling point of the reaction mixture.

Therefore, the best results in the key step of oxidation of cyclohexanone **1b**, which involves the transformation of geminal bishydroperoxide of cyclohexanone **2b** into adipic acid **3b** accompanied by its esterification to give dibutyl adipate **4b**, were obtained at an H_2SO_4 concentration of 0.4–0.6 mol/L and at ~98 °C. Under these conditions, the virtually complete conversion of **2b** was achieved within 8–10 min. The yield of **4b** was 68%.

To examine the possibility of the use of low-boiling alcohols for the oxidation of ketones, several reactions were carried out in ethanol and propanol. The influence of an excess of hydrogen peroxide on the yield of diethyl adipate and the diethyl adipate to ethyl 6-hydroxyhexanoate ratio was studied for the oxidation of cyclohexanone **1b** in ethanol (the solvent, which has the lowest boiling point in the series of alcohols under study and is, consequently, least favorable for the formation of diesters). It was found that the reaction with the use of the 3-, 5-, or 10-fold molar excess of hydrogen peroxide at the boiling point of the reaction mixture (78–82 °C) for 3 h afforded diethyl adipate in 32, 51, and 47% yields, respectively; the ratio of the yields of diethyl adipate and ethyl 6-hydroxyhexanoate was 1.3, 1.5, and 1.6, respectively. Therefore, the oxidative reaction alternative to the Baeyer–Villiger reaction is the major process even in low-boiling ethanol.

The oxidation of cyclic ketones can be performed in a virtually anhydrous medium. The reaction of cyclohexanone with hydrogen peroxide (the fivefold molar excess; a 6% ethereal solution) in ethanol in the presence of sulfuric acid afforded diethyl adipate in 54% yield; under analogous conditions in an aqueous alcoholic solution, the yield was 51%.

The catalytic effect of HBF_4 and $BF_3 \cdot Et_2O$ in the oxidation of ketones was exemplified by the synthesis of dipropyl adipate; the yield of the diester was 57 and 65%, respectively. The reaction with $BF_3 \cdot Et_2O$ was carried out with anhydrous hydrogen peroxide, which allowed us to perform the oxidation of ketones under mild conditions.

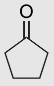
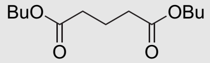
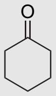
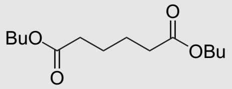
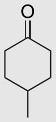
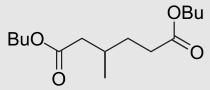
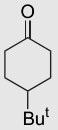
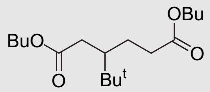
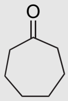
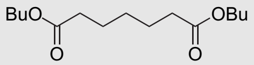
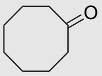
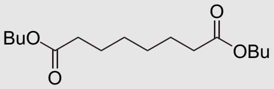
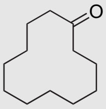
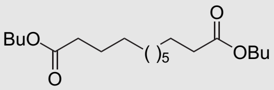
The oxidation of ketones with the ring size of C_5–C_8 and C_{12} was performed taking into account the results of oxidation of cyclohexanone **1b** and its bishydroperoxide **2b** (Table 4).

Table 3
Influence of the H_2SO_4 concentration on the time of complete conversion of bishydroperoxide **2b** and the yield of dibutyl adipate **4b**[a]

Concentration of H_2SO_4, mol/L	0.1	0.2	0.5[b]	1
Time of complete conversion of bishydroperoxide **2b**, min	40–50	30–35	8–10	5–7
Yield of dibutyl adipate **4b**,[c] %	50	55	68	60

[a] The reaction conditions: BuOH (20 mL), bishydroperoxide **2b** (1.48 g, 10 mmol), H_2O_2 (50 mmol, 37% aqueous solution), and temperature 98–100 °C.
[b] In experiments with the use of H_2SO_4 at a concentration of 0.4 or 0.6 mol/L, the results remain virtually unchanged.
[c] The yield based on the isolated reaction product.

Table 4
Oxidation of ketones **1a–g** under optimized conditions in butanol[a]

Ketones **1a–g**	Diesters **4a–g**	Yield of diester,[b] % in oxidation	
		With aqueous H_2O_2	With ethereal H_2O_2
 **1a**	 **4a**	53	57
 **1b**	 **4b**	61	65
 **1c**	 **4c**	59	64
 **1d**	 **4d**	57	63
 **1e**	 **4e**	62	67
 **1f**	 **4f**	61	65
 **1g**	 **4g**	64	70

[a] General reaction conditions: BuOH (20 mL), H_2SO_4 (1.2 or 1.1 g, 0.5 mol/L), ketones **1a–g** (10 mmol), H_2O_2 (60 mmol, 37% aqueous or 6% ethereal), 102–106 °C (oxidation with ethereal H_2O_2) and 98–100 °C (oxidation with aqueous H_2O_2), and the oxidation time was 20 (**1a–e**) and 40 (**1f,g**) min.
[b] The yield based on the isolated reaction product.

3. Conclusion

It was found that the oxidation of C_5–C_8 and C_{12} cyclic ketones with hydrogen peroxide in alcohols in the presence of sulfuric acid can proceed not as the Baeyer–Villiger reaction but as the formation of geminal bishydroperoxides followed by their oxidation to dicarboxylic acids, which were isolated as the corresponding esters. The key conditions for this transformation are as follows: the temperature higher than 80 °C, the H_2SO_4 concentration of 0.2–1 mol/L, and the molar ketone to hydrogen peroxide ratio of 5–10. Under these conditions, the oxidation in butanol, which provides the maintenance of the reaction temperature within 98–106 °C, affords the corresponding dibutyl esters in 53–70% yields.

4. Experimental section

4.1. General

The NMR spectra were recorded on Bruker AC-200 (200.13 MHz for ^1H), Bruker WM-250 (250.13 MHz for ^1H and 62.9 MHz for ^{13}C), and Bruker AM-300 (75.4 MHz for ^{13}C) spectrometers in $CDCl_3$. The TLC analysis was carried out on Silufol UV-254 chromatographic plates. Flash chromatography was performed on silica gel L 40/100 μm. The melting points were determined on a Kofler hot-stage apparatus. Mass spectra were obtained at an ionization potential of 70 eV with a Finnigan MAT ITD-700.

Ketones were purchased from Acros. Ethanol, propanol, butanol, $CHCl_3$, petroleum ether (PE) (bp 40–70 °C), Et_2O, $BF_3\cdot Et_2O$, H_2O_2 (37% aqueous solution), H_2SO_4 (98%), HBF_4 (48%), $NaHCO_3$, and K_2CO_3 of high-purity grade were domestically produced. A solution of H_2O_2 in Et_2O (6 wt %) was prepared by extraction from a 37% aqueous H_2O_2 solution followed by drying over $MgSO_4$.[18]

4.2. General procedure for the synthesis of *gem*-bishydroperoxides 2a,b,d–g by the reaction of ketones 1a,b,d–g with hydrogen peroxide in ethanol or propanol catalyzed by sulfuric acid (Table 1)

Hydrogen peroxide (4.6 g, 50 mmol, aqueous solution) and H_2SO_4 (1.2 g, 12 mmol) were added to EtOH or PrOH (20 mL). Then ketones **1a**,**b**,**d**–**g** (10 mmol) were added with stirring at 20–25 °C for 5 min. The reaction mixture was stirred for 30 min. The conversion of ketone was monitored by TLC. Then CH_2Cl_2 (100 mL) and a saturated aqueous $NaHCO_3$ solution were added to pH 7–8. The organic layer was separated, washed with water (4×5 mL), dried over $MgSO_4$, and filtered. Dichloromethane was evaporated at 7–10 mmHg, residues of alcohol and H_2O_2 were removed in vacuo (0.2–1 mmHg) at room temperature for 2–3 h, and bishydroperoxides **2a**,**b**,**d**–**g** were isolated. Analytically pure samples of bishydroperoxides were isolated by flash chromatography using PE/Et_2O=80/20 as the eluent.

The spectral data of bishydroperoxides **2a**,**b**,**d**–**g** are identical to that reported in the literature.[15,17c,d,19]

4.3. Influence of the temperature on the time of complete conversion of bishydroperoxide 2b and the yield of dibutyl adipate 4b (Table 2)

Hydrogen peroxide (4.6 g, 50 mmol) and H_2SO_4 (1.2 g, 12 mmol, the concentration in the reaction mixture was ~0.5 mol/L) were added to butanol (20 mL). Then bishydroperoxide **2b** (1.48 g, 10 mmol) was added at room temperature. The reaction mixture was heated at 50, 70, and 98–100 °C (boiling point) until the complete conversion of **2b** was achieved (TLC monitoring). Then $CHCl_3$ (100 mL) was added to the reaction mixture, and the mixture was refluxed using a Dean–Stark trap until water was completely removed. The reaction solution was washed with saturated aqueous $NaHCO_3$ to pH 7–8. The organic layer was separated, washed with water (4×30 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated, and dibutyl adipate **6b** was isolated by silica gel column chromatography.

4.4. Influence of the H_2SO_4 concentration on the time of complete conversion of bishydroperoxide 2b and the yield of dibutyl adipate 4b (Table 3)

Under analogous conditions, the influence of the H_2SO_4 concentration on the time of complete conversion of bishydroperoxide **2b** and the yield of dibutyl adipate **4b** was studied. The experiments were carried out at the boiling point (98–100 °C) by varying the amount of H_2SO_4 (0.24 g, 2.4 mmol; 0.48 g, 4.8 mmol; and 2.4 g, 24 mmol). Dibutyl adipate **4b** was isolated as described above.

4.5. Influence of an excess of H_2O_2 on the ratio of the yields of diethyl adipate and ethyl 6-hydroxyhexanoate in the oxidation of cyclohexanone

The experiment was carried out by adding cyclohexanone **1b** (0.98 g, 10 mmol) with stirring to an H_2O_2 solution (2.76 g, 30 mmol; 4.6 g, 50 mmol; or 9.2 g, 100 mmol; aqueous solution) and, correspondingly, to H_2SO_4 (1.1 g, 1.2 g, or 1.4 g, the concentration in the reaction mixture was ~0.5 mol/L) in ethanol (20 mL) at 20–25 °C for 5 min. The reaction mixture was kept for 5–10 min and then heated at 78–82 °C for 120 min. Then $CHCl_3$ (100 mL) was added, and the reaction mixture was refluxed using a Dean–Stark trap until water was completely removed. Dry K_2CO_3 (5 g) was added, and the suspension was stirred until sulfuric acid was neutralized. The reaction products were isolated by silica gel column chromatography. The reactions with the use of the 3-, 5-, or 10-fold excess of H_2O_2 afforded diethyl adipate in 32, 51, and 47% yields, respectively; the ratio of the yields of diethyl adipate and ethyl 6-hydroxyhexanoate was 1.3, 1.5, and 1.6, respectively.

4.6. Oxidation of cyclohexanone 1b with H_2SO_4 and anhydrous H_2O_2

Hydrogen peroxide (28.3 g, 50 mmol, ethereal solution) and H_2SO_4 (1.1 g, 11 mmol, the concentration in the reaction mixture after the removal of diethyl ether was ~0.5 mol/L) were added to EtOH (20 mL). Diethyl ether was distilled off from the reaction mixture under reduced pressure (~100 Torr) at room temperature. Then cyclohexanone **1b** (0.98 g, 10 mmol) was added with stirring at 20–25 °C for 5 min. The reaction mixture was heated at the boiling point (77–80 °C) until the complete conversion of **1b** was achieved (TLC monitoring, ~120 min). Diethyl adipate was isolated as described in the experiment under Table 2. The yield was 54%.

4.7. Oxidation of cyclohexanone 1b with HBF_4

The oxidation of cyclohexanone **1b** with HBF_4 was carried out analogously at the boiling point in PrOH (20 mL) for 60 min with the use of cyclohexanone **1b** (0.98 g, 10 mmol), H_2O_2 (4.6 g, 50 mmol, aqueous solution), and HBF_4 (2.36 g, 13 mmol, 48% aqueous solution, the concentration in the reaction mixture was ~0.5 mol/L). Dipropyl adipate was isolated as described in the experiment under Table 2. The yield was 57%.

4.8. Oxidation of cyclohexanone 1b with $BF_3\cdot Et_2O$ and anhydrous H_2O_2

Hydrogen peroxide (28.3 g, 50 mmol, ethereal solution) and $BF_3\cdot Et_2O$ (2.1 g, 15 mmol) were added to PrOH (20 mL). Diethyl ether was distilled off from the reaction mixture under reduced pressure (~100 Torr) at room temperature. Then cyclohexanone **1b** (0.98 g, 10 mmol) was added with stirring at 15–25 °C for 5 min. The reaction mixture was heated at the boiling point (92–94 °C) until the complete conversion of **1b** was achieved (TLC monitoring, ~60 min). Dipropyl adipate was isolated as described in the experiment under Table 2. The yield was 65%.

4.9. Oxidation of ketones 1a–g in the optimized conditions: synthesis of ethers 4a–g (Table 4)

Hydrogen peroxide (5.5 g, 60 mmol, aqueous solution) and H_2SO_4 (1.2 g, 12 mmol) or H_2O_2 (34 g, 60 mmol, ethereal solution) and H_2SO_4 (1.1 g, 11 mmol) were added to BuOH (20 mL). In the reaction with the use of an ethereal solution, diethyl ether was distilled off from the reaction mixture under reduced pressure (~100 Torr) at room temperature. Then ketones **1a**–**g** (10 mmol) were added with stirring at 15–25 °C for 5 min. The reaction mixture was heated at the boiling point (102–106 °C (anhydrous reaction mixture) and 98–100 °C (aqueous reaction mixture)) for 20 (**1a**–**e**) or 40 (**1f**,**g**) min and cooled, $CHCl_3$ (100 mL) was added, and the mixture was refluxed using a Dean–Stark trap until water was completely removed. The reaction solution was washed with saturated aqueous $NaHCO_3$ to pH 7–8. The organic layer was separated, washed with water (4×50 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated. Esters **4a**–**g** were isolated by silica gel chromatography.

The preparation and data for diethyl hexanedioate,[20] ethyl 6-hydroxyhexanoate,[21] dipropyl hexanedioate,[22] dibutyl pentanedioate (**4a**),[23] dibutyl hexanedioate (**4b**),[23] dibutyl heptanedioate (**4e**),[23] dibutyl octanedioate (**4f**),[24] and dibutyl dodecanedioate (**4g**)[25] have been previously reported.

4.9.1. *Dibutyl 3-metylhexanedioate, **4c***

^1H NMR (250.13 MHz, $CDCl_3$), δ: 0.83–0.96 (m, 9H, CH_3), 1.23–1.70 (m, 11H, CH_2), 2.20–2.35 (m, 4H, CH_2COOBu), 4.03 (t, 4H, $COOCH_2$, J=6.7 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ: 13.6 (CH_3), 17.0 (CH_3), 19.1, 19.3, 28.6, 29.9, 30.5, 30.6, 31.5 (CH_2), 31.9, 41.4 (CH_2COOBu), 64.1, 64.2 (OCH_2Pr), 172.8, 173.5 (C=O). MS (EI), m/z (I_{rel} (%)): 273 $[M+H]^+$ (15), 199 $[M-BuO]^+$ (71), 143 $[M-BuO-Bu]^+$ (44), 125 $[M-2BuO-H]^+$ (53), 41 (100). Anal. Calcd for $C_{15}H_{28}O_4$: C, 66.14; H, 10.36. Found: C, 66.20; H, 10.68.

4.9.2. *Dibutyl 3-tert-butylhexanedioate, **4d***

^1H NMR (250.13 MHz, $CDCl_3$), δ: 0.79–0.97 (m, 15H, CH_3), 1.21–1.73 (m, 11H, CH_2), 2.18–2.44 (m, 4H, CH_2COOBu), 4.02 (t, 4H, $COOCH_2$, J=6.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ: 13.6 (CH_3), 19.07, 19.1, 26.3, 27.2, 30.5, 30.6 (CH_2), 33.4 (C), 33.6, 35.7 (CH_2COOBu), 44.4 (CH), 64.1, 64.2 (OCH_2Pr), 173.6, 174.1 (C=O). MS (EI), m/z (I_{rel} (%)): 315 $[M+H]^+$ (11), 241 $[M-BuO]^+$ (19), 167 $[M-2BuO-H]^+$ (20), 41 (100). Anal. Calcd for $C_{18}H_{34}O_4$: C, 68.75; H, 10.90. Found: C, 68.51; H, 10.87.

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