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Solvent-free oxidation of aliphatic alcohols with ceric ammonium nitrate—lithium bromide system*

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Esters are formed during the solvent-free oxidation of primary aliphatic C_5—C_9 alcohols with $Ce(NH_4)_2(NO_3)_6$—LiBr, whereas secondary octan-2-ol gives a mixture of isomeric 1- and 3-bromooctan-2-ones.

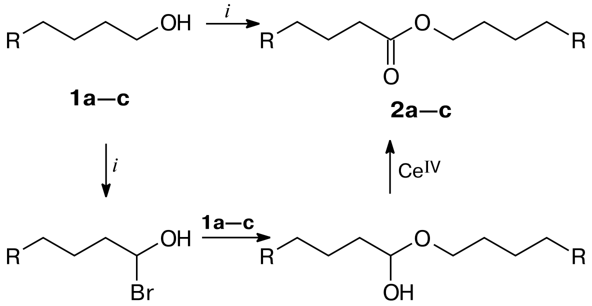
Key words: alkanols, ceric ammonium nitrate, lithium bromide, oxidation, solvent-free reactions, esters, ketones.

Ceric ammonium nitrate (CAN) is one of the widely used oxidizing agents. Recent years showed a noticeable growth of interest to CAN due to a numerous literature examples of functionalization and transformation of organic compounds with its participation.[1] Chemical behavior of hydrocarbons, oxygen-containing aliphatic and alicyclic compounds,[2] and nitrogen-containing structures[3,4] was studied in oxidation reactions with CAN as well as with CAN—I_2 and CAN—MX (M = Li, Na, K, NH_4; X = Br, N_3, SCN, NO_2) systems. Like manganese triacetate, CAN is used as initiator of radical addition of carbonyl compounds to the functionally substituted olefins.[5,6] Also CAN revealed unusual catalytic properties in a number of various reactions, such as esterification of carboxylic acids with primary and secondary alcohols,[7] addition of alcohols to tetrahydropyrane,[8] synthesis of β-aminoenones by condensation of amines with β-dicarbonyl compounds,[9] the Michael addition of amines to α,β-unsaturated electrophiles,[10] protection of carbonyl function in form of 1,3-dithianes,[11] and removal of acetal and ketal protections.[12]

Information on oxidation of alcohols with Ce^{IV} salts goes back to the sixties and seventies. It was found that primary aliphatic alcohols of $\geq C_5$ composition upon treatment with CAN were transformed to 2-alkyltetrahydrofurans,[13] whereas 4-phenylbutan-1-ol and 5-phenylpentan-1-ol, to 2-phenyl- and 2-benzyltetrahydrofurans,[14] respectively. Secondary alcohols were oxidized to ketones or underwent cleavage at C—C(OH) bond, giving rise to aldehydes.[15] All the reactions with participation of CAN and other Ce^{IV} salts were carried out in solutions of acetonitrile, water, methanol, or acetic acid.

In the present work within the framework of the "green chemistry" conception, we investigated the solvent-free reactions of CAN. It was found that primary alcohols, *viz.*, pentan-1-ol (**1a**), heptan-1-ol (**1b**), and nonan-1-ol (**1c**), being in contact with CAN in a closed reactor at room temperature for 48 h, do not undergo any noticeable changes, whereas upon contact with CAN—LiBr system for 20 h, they are converted to esters (Scheme 1, Tables 1 and 2).

Scheme 1



R = Me (**a**), Pr (**b**), *n*-C_5H_{11} (**c**)

i. CAN—LiBr, 20 °C, solvent-free.

When the ratio **1a—c** : CAN : LiBr is equal to 1 : 3 : 1, the conversion of alcohol is ~94—96% and the yield of esters **2a—c** is ~88—91% (see Table 2). A decrease of relative to **1a—c** amounts of CAN or LiBr leads to a decrease in conversion and, therefore, in the yields of

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Table 1. Oxidation of heptan-1-ol (**1b**) with CAN—LiBr system[a]

Entry	Molar ratio **1b** : CAN : LiBr	Reaction conditions		Conversion of **1b** (%)	Yield[b] (%)	
		Solvent	t/h		**2b**	**3b**[c]
1	1 : 3 : 0	—[d]	48	3	Traces	—
2	1 : 3 : 0.5	—[d]	20	78	69/88	—
3	1 : 3 : 1	—[d]	20	95	90/95	—
4	1 : 2 : 1	—[d]	20	60	54/90	—
5	1 : 3 : 3	—[d]	20	96	88/92	—
6[e]	1 : 3 : 1	$CH_3CN—H_2O$	3.5	87	38/44	41/47
7	1 : 3 : 1	H_2O	4	73	40/48	25/34
8[f]	1 : 3 : 1	$CH_3CN—H_2O$	0.5	81	59/73	19/23
9[g]	1 : 3 : 3	—	20	10	3/3	—
10[g]	1 : 3 : 1	$CH_3CN—H_2O$	3.5	89	73/82	12/13
11[g]	1 : 3 : 1	H_2O	4	65	50/77	10/15

[a] **1b**, 0.5 mmol; reaction temperature, 20 °C.
[b] From starting/converted heptanol **1b**.
[c] 2-Propyltetrahydrofuran
[d] Solvent-free.
[e] 70% aq. CH_3CN.
[f] Reaction temperature, 65 °C.
[g] $Ce(SO_4)_2 \cdot 4H_2O$ was used.

Table 2. Solvent-free oxidation of alcohols **1a—d** with CAN—LiBr system[a]

Entry	Alcohols **1a—d**	Conversion of **1a—d** (%)	Product	Yield[b] (%)
1	$C_5H_{11}OH$ (**1a**)	96	$C_4H_9COOC_5H_{11}$ (**2a**)	88/92
2	$C_7H_{15}OH$ (**1b**)	96	$C_6H_{13}COOC_7H_{15}$ (**2b**)	89/93
3[c]	**1b**	3	$C_6H_{13}COOC_7H_{15}$ (**2b**)	+
4	$C_9H_{19}OH$ (**1c**)	94	$C_8H_{17}COOC_9H_{19}$ (**2c**)	91/97
5[c]	$C_6H_{13}CH(OH)CH_3$ (**1d**)	80	$C_6H_{13}COCH_3$ (**4**)	77/96
6[d]	**1d**	97	$C_6H_{13}COCH_3$ (**4**)	3/3
			$C_5H_{11}CH(Br)COCH_3$ (**5**)	75/77
			$C_6H_{13}COCH_2Br$ (**6**)	15/15

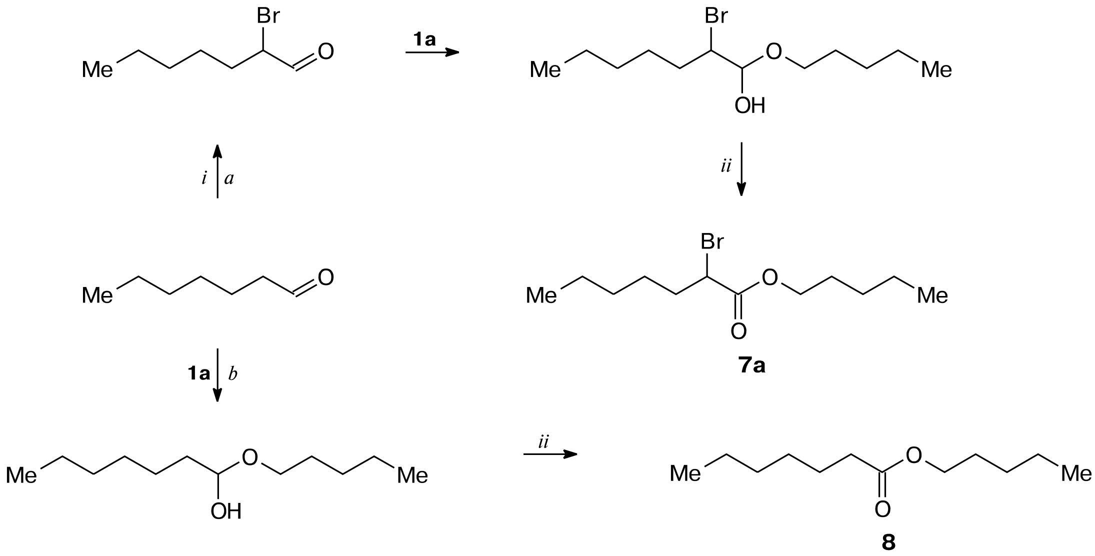
[a] Molar ratio **1** : CAN : LiBr = 1 : 3 : 1; **1**, 0.5 mmol; reaction temperature, 20 °C; reaction time, 20 h.
[b] From starting/converted alcohol **1**.
[c] Molar ratio **1d** : CAN = 1 : 3; reaction time, 48 h.
[d] Molar ratio **1d** : CAN : LiBr = 1 : 4 : 1; when ratio is 1 : 3 : 1, the conversion of **1d** and the yields of compounds **5** and **6** decrease.

esters **2a—c** (see Table 1). These data suggest that in the reaction of alcohols with CAN—LiBr system, the generated from LiBr bromine is the active reagent (the characteristic color can be seen). Most likely, hemi-acetals are formed from alcohols upon treatment with bromine and are further oxidized to esters (see Scheme 1).

Another plausible pathway for transformation of alcohols to esters through the formation of alkanals and their subsequent oxidation seems to contribute little to the total balance of the obtained products. This conclusion follows from the results of the combined solvent-free oxidation of aldehydes and alcohols with CAN—LiBr system at 20 °C. The oxidation of equimolar amounts of pentan-1-ol and heptanal proceeds simultaneously in three directions to form three esters, *viz.*, pentyl 2-bromoheptanoate (**7a**), pentyl heptanoate (**8**), and pentyl pentanoate (**2a**) in the ratio 5.5 : 0.7 : 1.0. Consequently, the oxidant is mainly consumed in bromination of heptanal. The hemi-acetal, obtained from the thus formed 2-bromoheptanal by reaction with pentan-1-ol, is oxidized to bromo ester **7a** (Scheme 2, pathway *a*; Table 3). The smaller part of heptanal along the pathway *b* is converted to hemi-acetal and then to the unsymmetrical ester **8**. Pentan-1-ol in the presence of heptanal is oxidized slower than heptanal, resulting in the low yield of symmetrical esters **2a**.

We assume that oxidation of aldehyde through the formation of Ce^{IV}-oxallylic complex[16] with its subse-

Scheme 2



i. CAN—LiBr; *ii.* CAN.

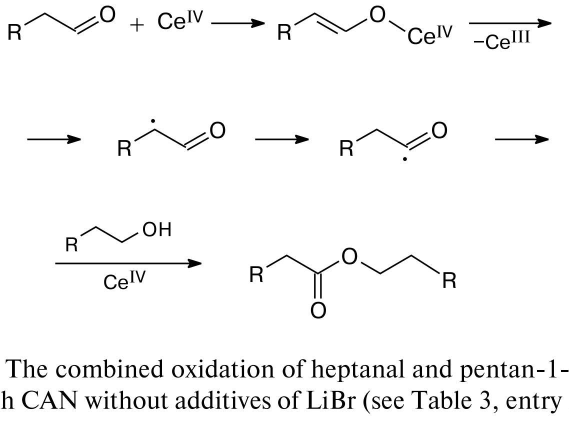
Table 3. Solvent-free combined oxidation of alcohols **1a, b** and heptanal with CAN—LiBr system[a]

Entry	Alcohols	Conversion of (%)		Yield of products[b] (%)		
		alcohol	heptanal	**2**	**7**	**8**
1	**1a**	96	93	**2a**, 13	$C_5H_{11}CH(Br)COOC_5H_{11}$ (**7a**), 72	$C_6H_{13}COOC_5H_{11}$ (**8**), 9
2[c]	**1a**	95	98	**2a**, 8	—	**8**, 80
3	**1b**	90	91	**2b**, 18	$C_5H_{11}CH(Br)COOC_7H_{15}$ (**7b**), 74	—

[a] Molar ratio **1** : heptanal : CAN : LiBr = 1 : 1 : 3 : 1; **1**, 1 mmol; reaction temperature, 20 °C; reaction time, 20 h.
[b] From starting alcohol **1**.
[c] Molar ratio **1a** : heptanal : CAN = 1 : 1 : 3.

quent decomposition in the presence of alcohol to the esters also can not be excluded (Scheme 3).

Scheme 3



The combined oxidation of heptanal and pentan-1-ol with CAN without additives of LiBr (see Table 3, entry *2*) leads mainly to unsymmetrical ester **8**, while the symmetrical esters **2a** is obtained in insignificant amount, and ester of 2-bromoheptanoic acid **7a** does not virtually form (see Table 1).

In another similar example of the combined oxidation of heptan-1-ol and heptanal with CAN—LiBr system (see Table 3, entry *3*), heptyl 2-bromoheptanoate (**7b**) and heptyl heptanoate (**2b**) are formed in the ratio 4 : 1 (see Table 3). Taking into account that symmetrical ester **2b** is formed both by oxidation of alcohol and by oxidation of aldehyde, it can be considered that this ratio is close to the ratio of esters, formed by oxidation of heptanal—pentan-1-ol pair.

These data on the combined oxidation of alkan-1-ol/alkanal pair with CAN—LiBr system serve as a decisive argument in favor of the shown in Scheme 1 mechanism. This Scheme excludes the participation of alkanal as the main intermediate product in the oxidation process. Otherwise, α-bromo esters would have been presented among the reaction products, however, they were not detected.

This result is interesting for the comparison of CAN—LiBr system with $Pb(OAc)_4$—LiBr (NaCl)[17] and Oxone—NaCl[18] oxidation systems, which also convert alkan-1-ols to esters, only, as the authors suggested, through the formation of aldehydes.

In contrast to primary alcohols, secondary octan-2-ol (**1d**) is easily oxidized to octan-2-one (**4**) upon the solvent-free contact with CAN. In the CAN—LiBr system, the oxidation proceeds in two steps: the formed in the first step ketone **4** is further brominated by the generated from LiBr bromine. According to ^1H NMR and chromato-mass spectrometry data, if ratio of reagents is 1 : 4 : 1, then 3-bromooctan-2-one (**5**), 1-bromooctan-2-one (**6**), and a small amount of octan-2-one are obtained (Scheme 4, see Table 2).

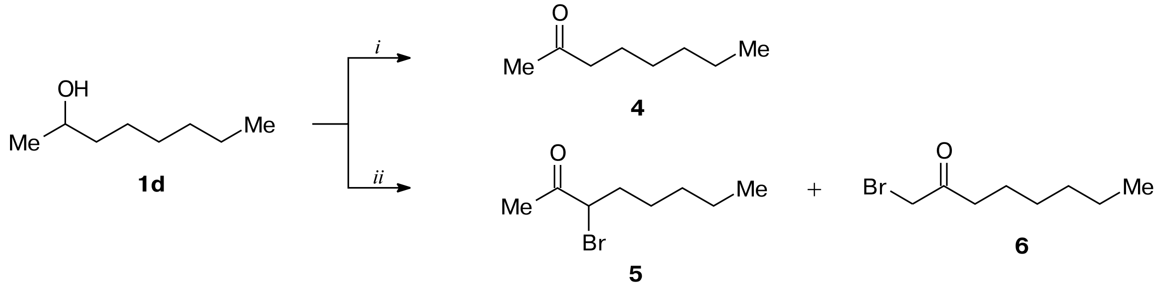
As one can see, the participation of LiBr in oxidation process again increases the conversion of **1d** and the total yield of products **4**, **5**, and **6**.

To compare the solvent-free reaction and reaction in solution of alcohols with CAN—LiBr, the oxidation of alcohol **1b** in $CH_3CN—H_2O$ or in H_2O at 20 °C was carried out. The conversion of **1b** for 4 h was 83—87%, the yield of ester **2b** was ~40%. At the same time, 2-propyltetrahydrofuran (**3b**) was formed in about the same yield (see Table 1). Thus, there are two parallel processes in solution: along with the oxidation of alcohols to esters with CAN—LiBr system, their oxidation to 2-alkyltetrahydrofurans by CAN without LiBr participation takes place (Scheme 5).

The free-radical pathway of oxidation of alkanols, given in Scheme 5, has been postulated earlier,[15] but till now it was not experimentally confirmed. We were able to register the formation of radicals during oxidation of **1b** with ceric sulfate (CS) in the presence of the spin trapping agent, *C*-phenyl-*N*-*tert*-butylnitrone (PBN). In the ESR spectrum, there were two triplets of doublets: one with $\alpha_N = 13.7$, $\alpha_{\beta\text{-H}} = 2.1$ Gs, $g = 2.0060$, corresponding to the spin-adduct of alkoxyl radicals with PBN, and another one with $\alpha_N = 14.4$, $\alpha_{\beta\text{-H}} = 3.4$ Gs, $g = 2.0062$, characteristic of the spin-adduct of carbon-centered radicals with PBN.[19] In this case, the carbon-centered radicals, obviously, have the $^{\bullet}C(Pr)H(CH_2)_3OH$ structure, since exactly these radicals are the precursors of 2-propyltetrahydrofuran (**3b**), formed according to Scheme 5.

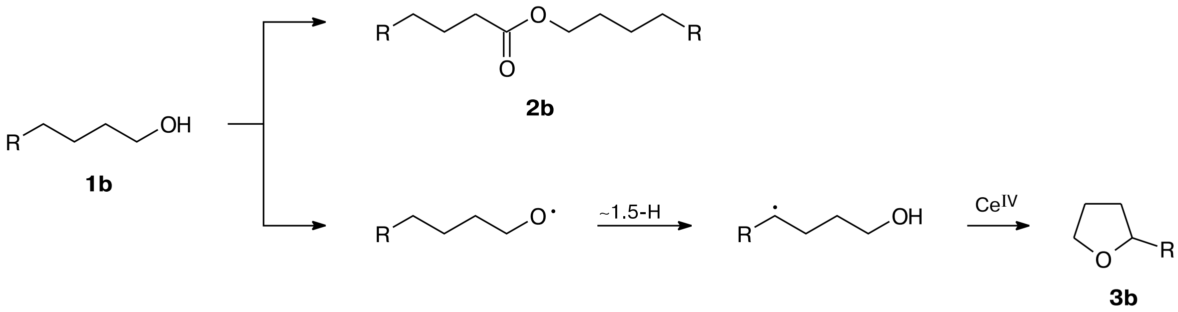
The choice of CS instead of CAN is caused by the high chemical activity of CAN, upon reaction of which with the spin trapping agents, such as PBN, 2-methyl-2-nitrosopropane (MNP), and nitrosodurene (ND), in the absence of alcohols, the signals of nitroxyl radicals were observed in the ESR spectra. The similar picture appeared for the combination of CS with MNP and ND, and only

Scheme 4



i. CAN; *ii.* CAN—LiBr.

Scheme 5



Reagents and conditions: CAN—LiBr, 20 °C, in $CH_3CN—H_2O$.

for PBN—CS system, no signals of paramagnetic species were registered. Therefore, this system was used for determining of the mechanism of alcohols oxidation with Ce^{IV} salts.

Such an approach to the choice of CS is fully justified, since, as it was established, CS does not in principal differ from CAN in the reaction with alcohols. Indeed, the solvent-free oxidation of alcohol **1b** with CS—LiBr system gave a small amount of ester **2b** (3%), while the oxidation in $CH_3CN—H_2O$ (or H_2O) afforded two products, *viz.,* ester **2b** and 2-propyltetrahydrofuran (**3b**), in the ratio 6 : 1 and total yield 85%, *i.e.*, the oxidation process with participation of CAN—LiBr or CS—LiBr systems can be alike presented by Schemes 1 and 5.

In the conclusion, the solvent-free oxidation of alkan-1-ols with CAN—LiBr system proceeds with participation of the generated from LiBr bromine and leads to esters, the acid and alcohol parts of which are formed from the starting compounds. The reaction can be used for the preparative synthesis of esters.

Experimental

GLC analysis was performed on a Chrom-5 chromatograph with the flame-ionization detector and 3 m × 3 mm analytical glass column with 5% SE-30 and 5% FFAP on Chromaton N-AW-HMDS (0.16—0.20 mm) (with heptan-2-one as the internal standard). The product yields were determined by the internal standard method with the experimentally found correction factors. IR spectra were recorded on a Perkin—Elmer 577 spectrophotometer for neat samples. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$ under standard conditions, chromato mass spectra were recorded on a Finigan MAT ITD-700 spectrometer (electron ionization, 70 eV, the source of ions — ions trap system temperature, 220 °C) and Carlo Erba 4200 chromatograph, provided with 25 m × 0.2 mm Ultra-1 column (Hewlett—Packard), the stationary phase (polymethylsiloxane) film thickness, 0.33 m, carrier gas, helium. ESR spectra were recorded on a Varian-E12 radiospectrometer. The starting primary alcohols (pentan-1-ol (**1a**), heptan-1-ol (**1b**), and nonan-1-ol (**1c**)) and secondary octan-2-ol (**1d**) were purchased from Acros and redistilled before use. Ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$) and ceric sulfate ($Ce(SO_4)_2{\times}4H_2O$), the pure for analysis reagents (Acros), were used without additional purification. Acetonitrile, pure reagent grade (Acros) was redistilled before use. Commercial lithium bromide was dried in a drying oven before use.

ESR spectra were recorded during oxidation of heptan-1-ol (**1b**) with ceric sulfate in the presence of *C*-phenyl-*N*-*tert*-butylnitrone as the spin trapping agent. Ceric sulfate and solution of alcohol with PBN (0.05 mol L^{-1}) were placed in a glass cylindrical tube (with internal diameter ~3 mm). The tube was degassed by a few cycles of freezing-evacuation-thawing, sealed *in vacuo* and placed in the spectrometer resonator. The spectra were registered at ~20 °C.

Solvent-free oxidation of alcohols (1a—d) with CAN—LiBr system (general procedure). A mixture of alcohols **1a—d**, CAN and LiBr (ratios of reagents are given in Tables 1 and 2) was thoroughly mulled in air in a porcelain mortar for 5—10 min, then it was placed in a glass flask, which was then tightly capped, and kept for 20 h at 20 °C until complete conversion of CAN. After the reaction was over (the orange color of reaction mixture turned pale yellow), water (10—15 mL) was added and this was extracted with ether (3×20 mL). The combined extract was washed with saturated aq. $NaHCO_3$ (10—15 mL), water (10—15 mL) and dried with $MgSO_4$. After removal of the volatiles, the conversion of the starting alcohols and the yields of the reaction products were determined by GLC with the use of the internal standard. Structures of the synthesized compounds were established by ^1H and ^{13}C NMR and chromato-mass spectrometry, IR spectroscopy, elemental analysis data, and by comparison with authentic samples.

Oxidation of heptan-1-ol (1b) with CAN—LiBr system in $CH_3CN—H_2O$ (or H_2O). A mixture of **1b** (1 mmol), CAN (3 mmol), and LiBr (1 mmol) in 70% aq. CH_3CN (20 mL) was vigorously stirred at ~20 °C until complete conversion of the oxidant for 3.5—4 h. Then this was extracted with ether (3 × 25 mL), the extracts were washed with saturated aq. $NaHCO_3$ and water, dried with $MgSO_4$ and the solvent was evaporated. The yield of the reaction products and conversion of the alcohol were determined by GLC (see Table 1).

Oxidation of heptan-1-ol (1b) with CS—LiBr system. The solvent-free reaction and reaction in $CH_3CN—H_2O$ (or H_2O) were carried out similarly to the procedures with the use of CAN—LiBr (see Table 1).

Solvent-free combined oxidation of alcohols 1a,b and heptanal with CAN—LiBr system (general procedure). A mixture of alcohol (1 mmol), heptanal (1 mmol), CAN (3 mmol), and LiBr (1 mmol) was mulled in a porcelain mortar, kept for 20 h in a capped glass flask until complete conversion of CAN, and this was treated according to the aforementioned procedure (see Table 3).

***n*-Pentyl pentanoate (2a).** IR, ν/cm^{-1}: 1728 (O—C=O). MS, *m/z*: 173 $[M + H]^+$. ^1H and ^{13}C spectra agree with the described earlier ones.[18]

***n*-Heptyl heptanoate (2b)** (see Ref. 20). IR, ν/cm^{-1}: 1740 (O—C=O). ^1H NMR ($CDCl_3$), δ: 0.85 (t, 6 H, CH_3, *J* = 6.4 Hz); 1.32 (m, 14 H, CH_2); 1.57 (m, 4 H, CH_2); 2.25 (t, 2 H, CH_2COO, *J* = 7.3 Hz); 4.01 (t, 2 H, CH_2OCO, *J* = 6.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.85 (CH_3); 21.89, 22.45, 24.83, 25.79, 25.87, 28.65, 29.97, 30.98, 31.70 (CH_2); 35.01 ($\underline{C}H_2COO$); 65.21 ($\underline{C}H_2OCO$); 173.34 (C=O). MS, *m/z*: 229 $[M + H]^+$.

***n*-Nonyl nonanoate (2c)** (see Ref. 21). IR, ν/cm^{-1}: 1740 (O—C=O). ^1H NMR ($CDCl_3$), δ: 0.88 (t, 6 H, CH_3, *J* = 6.4 Hz); 1.27 (m, 24 H, CH_2); 1.61 (m, 2 H, CH_2); 2.29 (t, 2 H, CH_2COO, *J* = 7.2 Hz); 4.05 (t, 2 H, CH_2OCO, *J* = 6.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.08 (CH_3); 21.94, 22.50, 22.64, 24.77, 24.83, 25.01, 25.97, 28.63, 29.02, 29.14, 29.23, 29.47, 31.81 (CH_2); 34.39 ($\underline{C}H_2COO$); 64.38 ($\underline{C}H_2OCO$), 174.02 (C=O). MS, *m/z*: 285 $[M + H]^+$.

2-Propyltetrahydrofuran (3d) (see Ref. 16). ^1H NMR ($CDCl_3$), δ: 0.87 (t, 3 H, CH_3, *J* = 7.0 Hz); 1.45 (m, 4 H, CH_2); 1.55 (m, 2 H, $CH_2(3)$); 1.80 (m, 2 H, $CH_2(4)$); 3.65 (m, 3 H, $C(5)H_2$, C(2)H).

Octan-2-one (4). IR, ν/cm^{-1}: 1716 (C=O). ^1H and ^{13}C NMR spectra agreed with the described earlier ones.[18]

3-Bromooctan-2-one (5) (see Ref. 22). ^1H NMR ($CDCl_3$), δ: 0.87 (t, 3 H, CH_3, *J* = 6.4 Hz); 1.28 (m, 4 H, CH_2); 1.62, 1.97 (both m, 2 H each, CH_2); 2.34 (s, 3 H, CH_3CO); 4.22 (m, 1 H, CHBrCO). ^{13}C NMR (CDCl$_3$), δ: 14.05 (CH$_3$); 25.87 ($\underline{C}$H$_3$CO); 22.37, 28.99, 31.14, 33.36 (CH$_2$); 54.87 (CHBr); 201.78 (C=O). MS, *m/z*: 209 [M + H]$^+$ (^{81}Br); 207 [M + H]$^+$ (^{79}Br).

1-Bromooctan-2-one (6) (see Ref. 22). ^{1}H NMR (CDCl$_3$), δ: 0.87 (t, 3 H, CH$_3$, *J* = 6.4 Hz); 1.40 (m, 8 H, CH$_2$); 2.58 (t, 2 H, CH$_2$CO, *J* = 7.1 Hz); 3.88 (s, 2 H, CH$_2$Br). ^{13}C NMR (CDCl$_3$), δ: 13.98 (CH$_3$); 22.36, 23.30, 27.99, 31.40 (CH$_2$); 33.70 (CH$_2$Br); 42.56 ($\underline{C}$H$_2$CO); 200.08 (C=O). MS, *m/z*: 209 [M + H]$^+$ (^{81}Br); 207 [M + H]$^+$ (^{79}Br).

Pentyl 2-bromoheptanoate (7a). Found (%): C, 51.61; H, 8.24; Br, 28.67. $C_{12}H_{23}O_2Br$. Calculated (%): C, 51.10; H, 8.66; Br, 28.30. ^{1}H NMR (CDCl$_3$), δ: 0.91 (t, 6 H, CH$_3$, *J* = 6.4 Hz); 1.31 (m, 8 H, CH$_2$); 1.62 (m, 4 H, CH$_2$); 1.97 (m, 2 H, C$\underline{H}_2$CHBr); 4.04 (t, 2 H, CH$_2$OCO, *J* = 6.3 Hz); 4.19 (m, 1 H, CHBr). ^{13}C NMR (CDCl$_3$), δ: 13.98 (CH$_3$); 22.55, 23.11, 27.67, 27.89, 28.64, 35.01, 39.23 (CH$_2$); 45.27 (CHBr); 64.33 ($\underline{C}$H$_2$OCO); 172.02 (C=O). MS, *m/z*: 281 [M + H]$^+$ (^{81}Br); 279 [M + H]$^+$ (^{79}Br).

Heptyl 2-bromoheptanoate (7b). Found (%): C, 54.72; H, 8.79; Br, 26.06. $C_{14}H_{27}O_2Br$. Calculated (%): C, 54.98; H, 9.10; Br, 26.35. ^{1}H NMR (CDCl$_3$), δ: 0.89 (t, 6 H, CH$_3$, *J* = 6.4 Hz); 1.27 (m, 12 H, CH$_2$); 1.61 (m, 4 H, CH$_2$); 2.10 (m, 2 H, CH$_2$CHBr); 3.97 (t, 2 H, CH$_2$OCO, *J* = 6.5 Hz); 4.13 (m, 1 H, CHBr). ^{13}C NMR (CDCl$_3$), δ: 14.08 (CH$_3$), 22.78, 23.15, 25.64, 27.90, 28.59, 32.23, 33.01, 34.99, 39.85 (CH$_2$), 45.00 (CHBr), 64.01 ($\underline{C}$H$_2$OCO), 171.77 (C=O). MS, *m/z*: 309 [M + H]$^+$ (^{81}Br); 307 [M + H]$^+$ (^{79}Br).

***n*-Pentyl heptanoate (8)** (see Ref. 20). IR, ν/cm^{-1}: 1735 (O—C=O). ^{1}H NMR (CDCl$_3$), δ: 0.89 (t, 6 H, CH$_3$, *J* = 6.4 Hz); 1.30 (m, 10 H, CH$_2$); 1.66 (m, 4 H, CH$_2$); 2.28 (t, 2 H, CH$_2$COO, *J* = 7.1 Hz); 3.99 (t, 2 H, CH$_2$OCO, *J* = 6.4 Hz). MS, *m/z*: 201 [M + H]$^+$.

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