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Generation of alkyl hypochlorites in oxidation of alcohols with carbon tetrachloride catalyzed by vanadium and manganese compounds

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Primary alcohols and diols with various structures were subjected to transformations into esters, aldehydes, ketones, and lactones under the action of carbon tetrachloride in the presence of manganese compounds ($MnCl_2$, MnO_2, $Mn(OAc)_2$, $Mn(acac)_3$) and vanadium compounds (VCl_5, V_2O_5, $VO(acac)_2$) as catalysts. These transformation proceeded with the involvement of alkyl hypochlorites, which were generated in the course of oxidation of alcohols with carbon tetrachloride catalyzed by manganese or vanadium compounds. The optimum molar ratios between the catalyst and reagents were determined, and the reaction conditions for the highly selective synthesis of esters, aldehydes, ketones, and lactones from alcohols were found.

Key words: alkyl hypochlorites, oxidation, primary alcohols, diols, manganese and vanadium compounds, carbon tetrachloride, esters, aldehydes, ketones, lactones.

In the previous study,[1] we have reported that the reactions of secondary alcohols with CCl_4 in the presence of catalysts, *viz.*, manganese compounds, proceeded through the intermediate formation of alkyl hypochlorites and have considered the role of the latter compounds in subsequent oxidation of secondary alcohols to the corresponding ketones.

Further studies demonstrated that alkyl hypochlorites can also be generated in reactions with primary alcohols and diols. In addition, it was found that these transformations are catalyzed not only by manganese compounds but also by vanadium(IV,V) compounds. Moreover, the formation of ROCl in the presence of vanadium compounds occurs at lower temperature (125—150 °C) compared to that in the presence of manganese compounds (200 °C). Taking into account the chemical nature of alkyl hypochlorites and the presence of the catalyst in the reaction medium, ROCl would be expected to be actively involved in oxidative transformations of the starting alcohols.

We studied the characteristic features of the formation of alkyl hypochlorites and subsequent oxidative transformations of ROCl and primary alcohols **1a—i** using the model reaction with Bu^nOH (**1d**) as an example. This reaction was chosen because the resulting compounds are simple to analyze.

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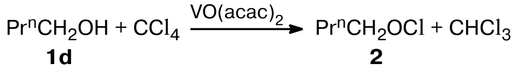
The reaction of alcohol **1d** (like those of other alcohols) with CCl_4 was carried out in sealed Pyrex tubes or in stainless steel microautoclaves.* The reaction in the presence of catalytic amounts of $VO(acac)_2$ afforded a complex mixture of products containing $CHCl_3$, butyl hypochlorite (**2**), and trace amounts of CH_2Cl_2 along with other compounds. The presence of $CHCl_3$ and compound **2** indicates that the reaction proceeded according to Scheme 1.

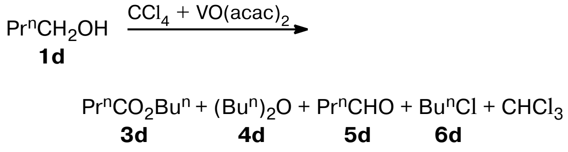
Scheme 1



$$\underset{\textbf{1d}}{Pr^nCH_2OH} + CCl_4 \xrightarrow{VO(acac)_2} \underset{\textbf{2}}{Pr^nCH_2OCl} + CHCl_3$$

The concentration of active chlorine, which was proportional to the amount of hypochlorite **2**, was 1.5—2 and 3.5 mg mL^{-1} at a time of 5 and 20 min, respectively, after the start of the reaction (at 150 °C). In addition to the above-mentioned products, butyl butanoate (**3d**), dibutyl ether (**4d**), *n*-butanal (**5d**), and *n*-butyl chloride (**6d**) were detected in the reaction mixture (Scheme 2). Their contents depend primarily on the nature of the vanadium catalyst. Thus, the reaction catalyzed by $VO(acac)_2$ afforded ester **3d** (87%) as the major product and compounds **4d** (7%), **5d** (4%), and **6d** (2%) as the minor products (Table 1, entry *1*).

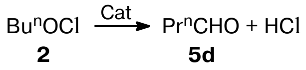
Scheme 2



$$\underset{\textbf{1d}}{Pr^nCH_2OH} \xrightarrow{CCl_4 + VO(acac)_2} \underset{\textbf{3d}}{Pr^nCO_2Bu^n} + \underset{\textbf{4d}}{(Bu^n)_2O} + \underset{\textbf{5d}}{Pr^nCHO} + \underset{\textbf{6d}}{Bu^nCl} + CHCl_3$$

Apparently, the formation of ester **3d** and ether **4d** is favored by HCl that liberated in a stoichiometric amount upon decomposition of Bu^nOCl (Scheme 3).

Scheme 3



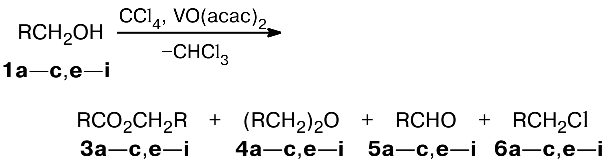
$$\underset{\textbf{2}}{Bu^nOCl} \xrightarrow{Cat} \underset{\textbf{5d}}{Pr^nCHO} + HCl$$

In the reactions catalyzed by V_2O_5 or VCl_5, the conversion of alcohol **1d** was at most 35—42% (see Table 1, entries *2—4*).

The conversion of compound **1d** depends substantially on the molar ratio between this compound and CCl_4. The complete conversion was achieved with the use of at least a threefold excess of CCl_4. The preferred molar ratio of the catalyst to alcohol **1d** is 1 : 500. If the catalyst is taken at low concentrations (1 : 750—1000), a 2—3-fold increase in the reaction time is required for the complete conversion of alcohol even under the optimum temperature conditions (see Table 1, entry *5*).

The reactivities of primary alcohols in the reaction under consideration depend on the size of the alkyl group. Thus, the reactions of MeOH (**1a**) and EtOH (**1b**) with CCl_4 at 150 °C in the presence of $VO(acac)_2$ afforded methyl formate (**3a**) in 78% yield and ethyl acetate (**3b**) in 92% yield, respectively, and the reactions were completed in 1 h (see Table 1, entries *6* and *7*). The $Mn(acac)_3$-catalyzed reaction of EtOH with CCl_4 at 200 °C proceeded even more rapidly (20 min) but less selectively (see Table 1, entry *27*). Propanol (**1c**), isobutyl alcohol (**1e**), and amyl alcohol (**1f**) exhibited virtually identical reactivities in the $VO(acac)_2$-catalyzed reactions. Their oxidation was completed in 3 h. The conversions of hexan-1-ol (**1g**), octan-1-ol (**1h**), and decan-1-ol (**1i**) into products **3**—**6** (Scheme 4) during the same period of time were 92, 71, and 45%, respectively (see Table 1, entries *11*, *13*, and *15*).

Scheme 4

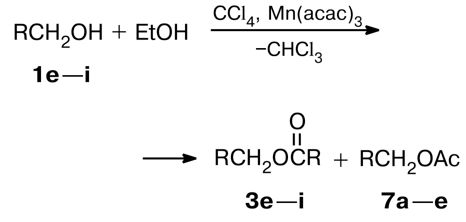


$$\underset{\textbf{1a—c,e—i}}{RCH_2OH} \xrightarrow[-CHCl_3]{CCl_4,\ VO(acac)_2} \underset{\textbf{3a—c,e—i}}{RCO_2CH_2R} + \underset{\textbf{4a—c,e—i}}{(RCH_2)_2O} + \underset{\textbf{5a—c,e—i}}{RCHO} + \underset{\textbf{6a—c,e—i}}{RCH_2Cl}$$

R = H (**a**), Me (**b**), Et (**c**), Pr^i (**e**), Bu^n (**f**), $n\text{-}C_5H_{11}$ (**g**), $n\text{-}C_7H_{15}$ (**h**), $n\text{-}C_9H_{19}$ (**i**)

Oxidation of alcohols **1e—i** can be accelerated by adding an equimolar amount of ethanol, which made it possible to obtain esters **3** and **7** in a ratio of 2 : 3 in a total yield of 92—98% at 200 °C during 1 h (Scheme 5). The fact that esters RCO_2Et were virtually absent among the reaction products is attributable to the high rate of oxidation of EtOH to AcOH under the reaction conditions used.

Scheme 5



$$\underset{\textbf{1e—i}}{RCH_2OH} + EtOH \xrightarrow[-CHCl_3]{CCl_4,\ Mn(acac)_3} \underset{\textbf{3e—i}}{RCH_2O\overset{O}{\overset{\|}{C}}R} + \underset{\textbf{7a—e}}{RCH_2OAc}$$

7: R = Pr^i (**a**), Bu^n (**b**), $n\text{-}C_5H_{11}$ (**c**), $n\text{-}C_7H_{15}$ (**d**), $n\text{-}C_9H_{19}$ (**e**)

Noteworthy is the high selectivity of oxidation of 2,2,3,3-tetrafluoropropanol (**1j**) (Scheme 6), which was

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* Special experiments demonstrated that iron and its compounds ($FeCl_3$ and $Fe(acac)_3$) do not exhibit catalytic activity in the reaction under study.

Table 1. Influence of the conditions of oxidation of alcohols by carbon tetrachloride on their conversion and yields of the reaction products

Entry	R (RCH_2OH)	Catalyst (Cat)	Molar ratio [Cat] : [RCH_2OH] : [CCl_4]	T/°C	Time /h	Conversion (%)	Internal standard[a]	Yield of the product[b] with respect to the consumed alcohol (%)			
								3	**4**	**5**	**6**
1	Pr^n (**1d**)	VO(acac)$_2$	1 : 500 : 1500	150	1	100	*A*	87	7	4	2
2	Pr^n (**1d**)	V_2O_2	1 : 500 : 1500	150	1	35	*A*	50	21	20	9
3	Pr^n (**1d**)	VCl_5	1 : 500 : 1500	150	1	38	*A*	58	20	17	15
4	Pr^n (**1d**)	VCl_5	1 : 500 : 1500	150	3	42	*A*	55	10	15	20
5	Pr^n (**1d**)	VO(acac)$_2$	1 : 750 : 1000	150	3	100	*A*	85	5	8	2
6	H (**1a**)	*Ditto*	1 : 500 : 1500	150	1	100	*B*	78	12	10	—
7	Me (**1b**)	»	1 : 500 : 1500	150	1	100	*A*	92	2	5	—
8	Et (**1c**)	»	1 : 500 : 1500	150	1	100	*C*	84	5	9	2
9	Pr^i (**1e**)	»	1 : 500 : 1500	150	3	100	*A*	79	—	13	8
10	Bu^n (**1f**)	»	1 : 500 : 1500	150	3	100	*A*	82	4	11	3
11	n-C_5H_{11} (**1g**)	»	1 : 500 : 1500	150	3	92	*A*	78	7	12	3
12	n-C_5H_{11} (**1g**)	»	1 : 500 : 1500	150	8	100	*A*	72	9	14	5
13	n-C_7H_{15} (**1h**)	»	1 : 500 : 1500	150	3	71	*D*	77	5	14	2
14	n-C_7H_{15} (**1h**)	»	1 : 500 : 1500	150	8	95	*D*	73	7	16	4
15	n-C_9H_{19} (**1i**)	»	1 : 500 : 1500	150	3	45	*D*	70	8	20	2
16	n-C_9H_{19} (**1i**)	»	1 : 500 : 1500	150	8	73	*A*	100	—	—	—
17	CHF_2CF_2 (**1j**)	»	1 : 500 : 1500	150	3	97	*A*	100	—	—	—
18	1-Ad (**1k**)	»	1 : 500 : 1500	150	3	100	*E*	—	—	92	8
19	Ph (**1l**)	»	1 : 500 : 1500	150	3	91	*E*	12	—	73	15
20	Furfuryl (**1m**)	»	1 : 500 : 1500	150	3	100	*E*	—	—	98	—
21	Pr^n (**1d**)	$MnCl_2$	1 : 100 : 200	200	3	31	*A*	62	15	12	9
22	Pr^n (**1d**)	MnO_2	1 : 100 : 200	200	3	48	*A*	77	3	19	1
23	Pr^n (**1d**)	Mn(OAc)$_2$	1 : 100 : 200	200	3	87	*A*	80	6	11	3
24	Pr^n (**1d**)	Mn(acac)$_3$	1 : 100 : 300	200	3	91	*A*	65	14	15	4
25	Pr^n (**1d**)	*Ditto*	1 : 500 : 1500	200	2	100	*A*	68	12	9	11
26	Pr^n (**1d**)	»	1 : 500 : 1500	200	1	100	*A*	70	15	7	8
27	Me (**1b**)	»	1 : 500 : 1500	200	0.2	100	*A*	70	15	7	8
28[c]	Pr^n (**1d**)	VO(acac)$_2$	1 : 500 : 1500	200	0.2	100	*A*	31	34	30	5
29[c]	1-Ad (**1k**)	VO(acac)$_2$	1 : 500 : 1500	200	1	100	*E*	—	2	98	—
30[c]	Pr^n (**1d**)	Mn(acac)$_3$	1 : 500 : 1500	200	1	100	*A*	73	16	9	2

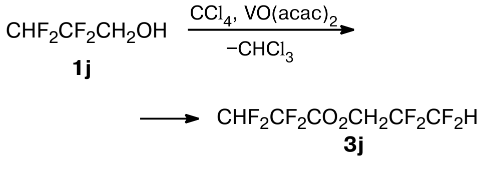
[a] The internal standards used for the determination of the yields of the products by GLC: *A*, propyl acetate; *B*, ethyl acetate; *C*, butyl acetate, *D*, hexyl acetate; *E*, cyclohexanone.

[b] RCO_2CH_2R (**3**), $R(CH_2)_2O$ (**4**), RCHO (**5**), RCH_2Cl (**6**).

[c] The experiment was carried out in a glass tube.

converted into 2,2,3,3-tetrafluoropropyl 2,2,3,3-tetrafluoropropionate (**3j**) in virtually quantitative yield (see Table 1, entry *17*).

Scheme 6



An increase in the volume of the alkyl group in the series of alcohols **1b**,**c**,**e** is accompanied by a decrease in selectivity of their conversion into esters **3b**,**c**,**e** from 92 to 79% with a simultaneous increase in the yield of aldehydes **5b**,**c**,**e** from 5 to 13% (see Table 1, entries *7—9*). Alcohol **1e** involved in the reaction together with ethanol was readily oxidized to ester **3e** and isobutyl acetate (**7a**) in a ratio of 1 : 1. In this connection, noteworthy is the behavior of 1-adamantylmethanol (**1k**). Under the standard conditions, this compound was converted into 1-adamantane carbaldehyde in high yield, whereas the reaction of compound **1k** in the presence of 4 equiv. of EtOH afforded ethyl adamantanecarboxylate (**8**) and 1-adamantylmethanol acetate (**7f**) in a ratio of 2 : 3.

Benzyl alcohol (**1l**) was oxidized predominantly to benzaldehyde. The reaction also gave small amounts of benzyl benzoate and benzyl chloride (see Table 1, entry *19*). The reaction involving $PhCH_2OH$ together with EtOH afforded benzyl acetate in 73% yield.

Furfuryl alcohol (**1m**) was oxidized to furfurol in almost quantitative yield (see Table 1, entry *20*).

Of manganese catalysts, freshly prepared and vacuum dried $Mn(acac)_3$ exhibited the highest activity in the reactions of CCl_4 with alcohols (see Table 1, entries *21—27*). In the presence of this catalyst, the reactions of alcohols with CCl_4 proceeded less selectively than those in the presence of $VO(acac)_2$ due, apparently, to the somewhat more drastic reaction conditions (200 °C, 1 h). The yield of ester **3d** obtained in the reaction in the presence of this catalyst decreased to 70%, while the yields of compounds **4d** (16%), **5d** (7%), and **6d** (8%) simultaneously increased (see Table 1, entry *26*).

Phenol did not underwent transformations in the presence of CCl_4 and catalytic amounts of $VO(acac)_2$ even upon prolonged heating (150 °C, 8 h), whereas its reactions with ethyl hypochlorite generated *in situ* from EtOH and CCl_4 afforded phenyl acetate in 84% yield.

Oxidation of diols with CCl_4 catalyzed by $VO(acac)_2$ proceeded under milder conditions (100 °C, 1 h) than oxidation of monobasic alcohols. The structures and compositions of the resulting products depend substantially on the nature of the starting diol (Scheme 7). Thus, oxidation of ethylene glycol (**9a**) afforded chloroacetaldehyde (**10**) in 72% yield along with 1,4-dioxane (**11**) in ~20% yield.

Under analogous conditions, the reaction of propane-1,3-diol (**9b**) gave β-propiolactone (**12**) in 98% yield. Butane-1,4-diol (**9c**) was converted into a mixture of γ-butyrolactone (**13**) (82%) and 4-chlorobutanal (**14**) (10%).

α,ω-Diols are readily oxidized to the corresponding lactones. However, as one would expect, the yields of these lactones gradually decreased as the length of the methylene chain was increased. Thus, oxidation of hexane-1,6-diol (**9d**) and dodecane-1,12-diol (**9e**) gave hexan-6-olide (**15a**) and dodecan-12-olide (**15b**) in 82 and 30% yields, respectively.

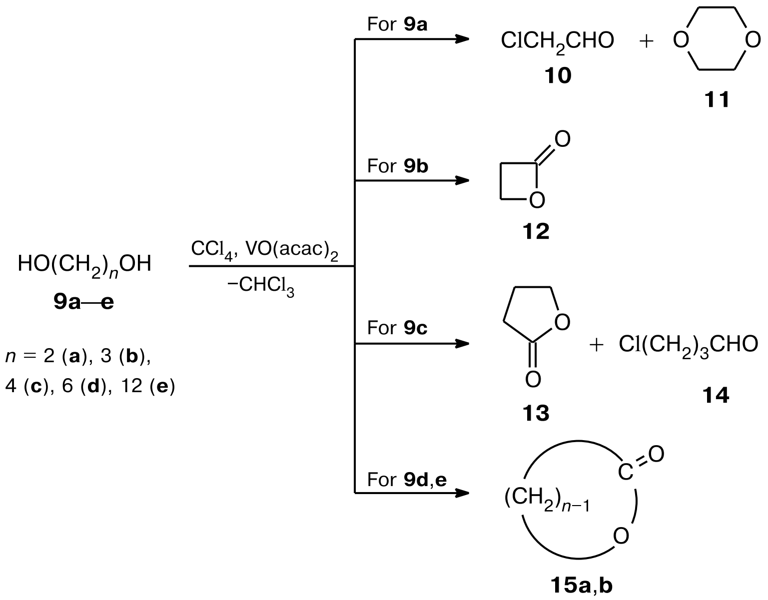
Butane-1,3-diol (**16a**) was subjected to selective oxidation at the primary alcoholic group. However, the reaction did not stop at the formation of 3-hydroxybutyraldehyde because the second molecule of diol **16a** rapidly added to the latter compound to give 2-(2-hydroxypropyl)-4-methyl-1,3-dioxane (**17**) (Scheme 8). An analogous reaction pathway has been observed previously in the oxidation of 1,3-butanediol with 4-methoxy-2,2,6,6-tetramethyl-1-oxopiperidinium chloride.

Butane-2,3-diol (**16b**) containing two equivalent secondary OH groups was oxidized only to 3-hydroxybutan-2-one (**18**) even upon prolonged heating.

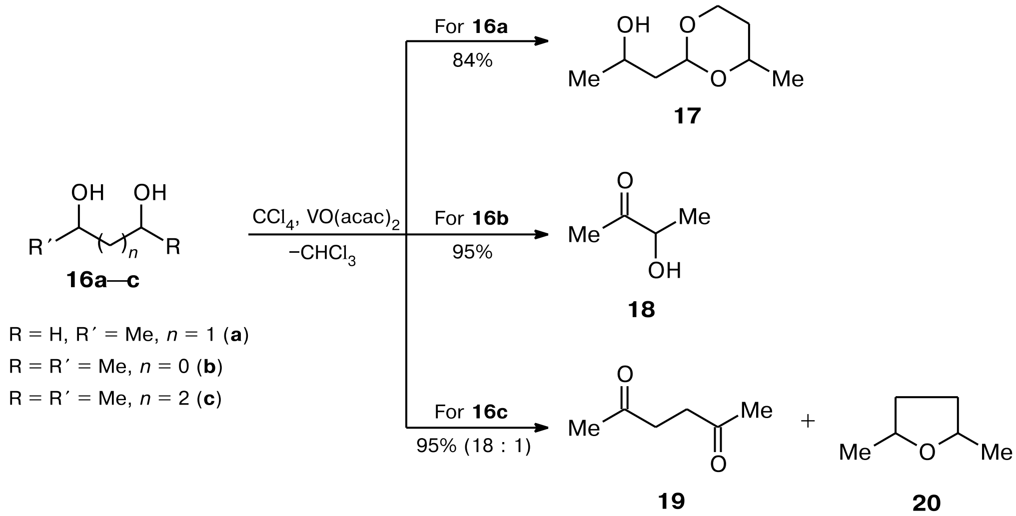
In this connection, noteworthy is the behavior of hexane-2,5-diol (**16c**), which was readily oxidized to the corresponding diketone **19** under the standard conditions. Simultaneously, the reaction afforded 2,5-dimethyltetrahydrofuran (**20**) as a by-product formed through intramolecular dehydration of hexane-2-diol (see Scheme 8).

To summarize, we developed a new convenient catalytic procedure for oxidation of primary alcohols and diols to aldehydes, ketones, esters, and lactones with the use of carbon tetrachloride as an oxidizing agent. Oxidation proceeded through the intermediate formation of alkyl hypochlorites generated *in situ* in the reactions of alcohols or diols with CCl_4 under the action of manganese or vanadium compounds.

Scheme 7



Scheme 8



Experimental

The IR spectra were measured on a UR-20 instrument in KBr pellets or Nujol mulls. The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol FXQ instrument (90 and 22.5 MHz, respectively) in $CDCl_3$ with respect to Me_4Si. The mass spectra (EI, 70 eV) were obtained on a Finnigan MAT-112S GLC-mass spectrometer. Chromatographic analysis was carried out on a Chrom-5 instrument (length of the column was 1.2 or 2 m, silicone SE-30 (5%) on Chromaton N-AW-HMDS as the stationary phase, helium as the carrier gas).

The reactions were carried out with the use of purified and degassed CCl_4. The commercially available manganese and vanadium compounds used as catalysts were purified according to standard procedures. The starting 1-adamantylmethanol (**1k**) was prepared according to a procedure described previously.[3] Furfuryl alcohol (**1m**) was prepared according to a known procedure.[4] Other starting alcohols, *viz*., methanol (**1a**), ethanol (**1b**), *n*-propanol (**1c**), *n*-butanol (**1d**), isobutyl alcohol (**1e**), pentan-1-ol (**1f**), tetrafluoropropan-1-ol (**1j**), hexan-1-ol (**1g**), octan-1-ol (**1h**), decan-1-ol (**1i**), benzyl alcohol (**1l**), ethylene glycol (**9a**), propane-1,3-diol (**9b**), butane-1,4-diol (**9c**), butane-1,3-diol (**16a**), butane-2,3-diol (**16b**), hexane-2,5-diol (**16c**), hexane-1,6-diol (**9d**), and dodecane-1,12-diol (**9e**), were commercially available reagents, which were purified and dried according to standard procedures.[4]

In the experiments, the starting alcohol (50 mmol) or diol (25 mmol), CCl_4 (100 mmol), and the catalyst (0.1 mmol) were placed in a hermetically sealed autoclave under argon and heated with constant stirring at 150—200 °C for 1—8 h. Then the autoclave was cooled to ~20 °C and the reaction mixture was filtered through a layer of silica gel (hexane—ether, 1 : 1, as the eluent). The solvent was distilled off and the residue was distilled under atmospheric pressure or *in vacuo*. The experiments *27—30* (see Table 1) were carried out in sealed glass tubes.

The structures of most of the resulting compounds were confirmed by comparing their physical properties with those of authentic samples and the data published in the literature.[1—8]

***n*-Propyl propionate (3c)** (see Ref. 5). B.p. 123—123.5 °C. Found (%): C, 62.00; H, 10.52. $C_6H_{12}O_2$. Calculated (%): C, 62.04; H, 10.41. IR, ν/cm^{-1}: 1730 (O—C=O). ^{13}C NMR, δ: 9.25 (C(1)); 13.65 (C(6)); 27.20 (C(2)); 36.26 (C(5)); 64.09 (C(4)); 173.32 (C(3)).

***n*-Butyl butyrate (3d)** (see Ref. 5). B.p. 87 °C (60 Torr). Found (%): C, 66.62; H, 11.08. $C_8H_{16}O_2$. Calculated (%): C, 66.63; H, 11.18. IR, ν/cm^{-1}: 1740 (O—C=O). ^{13}C NMR, δ: 13.65 (C(1)); 13.70 (C(8)); 18.51 (C(2)); 19.16 (C(7)); 30.73 (C(6)); 36.26 (C(3)); 64.09 (C(5)); 173.80 (C(4)).

Isobutyl isobutyrate (3e) (see Ref. 5). B.p. 146—146.5 °C (10 Torr). Found (%): C, 66.61; H, 11.02. $C_8H_{16}O_2$. Calculated (%): C, 66.63; H, 11.18. IR, ν/cm^{-1}: 1730 (O—C=O). ^{13}C NMR, δ: 13.76 (C(7)); 14.35 (C(8)); 18.57 (C(1)); 19.22 (C(2)); 30.80 (C(6)); 36.33 (C(3)); 64.09 (C(5)); 173.80 (C(4)).

***n*-Pentyl pentanoate (3f).** B.p. 98 °C (20 Torr). Found (%): C, 69.75; H, 11.61. $C_{10}H_{20}O_2$. Calculated (%): C, 69.72; H, 11.70. IR, ν/cm^{-1}: 1735 (O—C=O). ^{13}C NMR, δ: 13.70 (C(1)); 14.01 (C(10)); 20.59 (C(9)); 22.08 (C(8)); 26.83 (C(7)); 27.87 (C(2)); 28.13 (C(3)); 33.73 (C(4)); 64.22 (C(6)); 173.28 (C(5)).

***n*-Hexyl hexanoate (3g)** (see Ref. 6). B.p. 91—92 °C (20 Torr). Found (%): C, 70.95; H, 11.98. $C_{12}H_{24}O_2$. Calculated (%): C, 71.95; H, 12.08. IR, ν/cm^{-1}: 1745 (O—C=O). ^{13}C NMR, δ: 13.78 (C(12)); 13.92 (C(1)); 22.64 (C(11)); 23.35 (C(2)); 24.58 (C(4)); 25.69 (C(10)); 28.90 (C(8)); 29.92 (C(9)); 31.22 (C(3)); 34.63 (C(5)); 173.19 (C(6)).

***n*-Octyl octanoate (3h)** (see Ref. 6). B.p. 125—126 °C (2 Torr). Found (%): C, 74.93; H, 12.48. $C_{16}H_{32}O_2$. Calculated (%): C, 74.94; H, 12.58. IR, ν/cm^{-1}: 1745 (O—C=O). ^{1}H NMR, δ: 0.89 (t, 6 H, Me, J = 6.6 Hz); 1.23 (m, 18 H, Me); 1.65 (m, 4 H, CH_2); 2.25 (t, 2 H, CH_2COO, J = 7.6 Hz); 4.00 (t, 2 H, CH_2OCO, J = 6.6 Hz). ^{13}C NMR, δ: 13.87 (C(1)); 13.88 (C(16)); 22.70 (C(2)); 22.82 (C(15)); 25.12 (C(6)); 26.33 (C(11)); 28.66 (C(10)); 29.20 (C(4)); 29.25 (C(5)); 29.50 (C(12)); 29.60 (C(13)); 31.80 (C(3)); 32.81 (C(14)); 34.15 (C(7)); 64.23 (C(9)); 173.31 (C(8)).

***n*-Decyl decanoate (3i).** B.p. 158—159 °C (2 Torr). Found (%): C, 76.89; H, 12.78. $C_{20}H_{40}O_2$. Calculated (%): C, 76.86; H, 12.90. IR, ν/cm^{-1}: 1740 (O—C=O). ^{1}H NMR, δ:

0.89 (t, 3 H, Me, J = 6.6 Hz); 0.91 (t, 3 H, Me, J = 6.6 Hz); 1.24 (m, 26 H, Me); 1.62 (m, 4 H, CH_2); 2.34 (t, 2 H, CH_2OCO, J = 7.2 Hz); 4.40 (t, 2 H, CH_2OCO, J = 6.6 Hz). ^{13}C NMR, δ: 14.00 (C(20)); 14.02 (C(1)); 22.60 (C(2)); 22.67 (C(19)); 26.25 (C(8)); 26.33 (C(13)); 28.65 (C(12)); 29.15 (C(6)); 29.20 (C(4)); 29.25 (C(5)); 29.30 (C(7)); 29.56 (C(14)); 29.60 (C(17)); 29.80 (C(15)); 30.10 (C(16)); 31.80 (C(3)); 31.90 (C(18)); 34.31 (C(9)); 64.22 (C(11)); 173.80 (C(10)). MS, m/z (I_{rel} (%)): 85 (20), 84 (21), 83 (24), 82 (12), 81 (6), 73 (19), 71 (32), 70 (32), 69 (35), 68 (12), 67 (9), 61 (18), 60 (10), 53 (53), 51 (32), 50 (53), 43 (100), 42 (23), 41 (58).

2,2,3,3-Tetrafluoropropyl 2´,2´,3´,3´-tetrafluoropropionate (3j). B.p. 75 °C (100 Torr). Found (%): C, 27.67; H, 1.52; F, 58.42. $C_6H_4F_8O_2$. Calculated (%): C, 27.71; H, 1.55; F, 58.44. IR, ν/cm^{-1}: 910, 925, 1110, 1190, 1210, 1725, 2940. ^1H NMR, δ: 5.30—6.54 (m, 2 H, CF_2H); 3.41—3.95 (m, 2 H, CH_2). ^{13}C NMR, δ: 59.80 (C(4)); 98.37 (C(1)); 109.42 (C(6)); 115.40 (C(2)); 120.47 (C(5)); 168.60 (C(3)).

***n*-Octyl acetate (7d).** B.p. 105 °C (10 Torr). Found (%): C, 69.74; H, 11.60. $C_{10}H_{20}O_2$. Calculated (%): C, 69.72; H, 11.70. IR, ν/cm^{-1}: 1745 (O—C=O). ^{13}C NMR, δ: 13.85 (C(10)); 20.84 (C(1)); 22.63 (C(9)); 26.33 (C(5)); 28.66 (C(4)); 29.33 (C(8)); 29.50 (C(6)); 29.90 (C(7)); 64.48 (C(3)); 174.01 (C(2)).

***n*-Decyl acetate (7e).** B.p. 121—122 °C (10 Torr). Found (%): C, 71.96; H, 11.97. $C_{12}H_{24}O_2$. Calculated (%): C, 71.95; H, 12.08. IR, ν/cm^{-1}: 1740 (O—C=O). ^{13}C NMR, δ: 13.87 (C(12)); 20.82 (C(1)); 22.80 (C(11)); 26.33 (C(5)); 28.66 (C(4)); 29.52 (C(6)); 29.65 (C(9)); 29.78 (C(7)); 29.92 (C(8)); 32.00 (C(10)); 64.48 (C(3)); 173.29 (C(2)).

1-Adamantylmethanol acetate (7f). B.p. 78—79 °C (0.5 Torr). Found (%): C, 74.93; H, 9.63. $C_{13}H_{20}O_2$. Calculated (%): C, 74.96; H, 9.68. IR, ν/cm^{-1}: 1720 (O—C=O). ^{13}C NMR, δ: 20.94 (C(13)); 28.30 (C(3), C(5), C(7)); 33.43 (C(1)); 37.35 (C(4), C(6), C(10)); 39.38 (C(2), C(8), C(9)); 67.62 (C(11)); 170.90 (C(12)).

1-Adamantane carbaldehyde (see Ref. 7). M.p. 125—126 °C (MeOH). Found (%): C, 80.42; H, 9.74. $C_{11}H_{16}O$. Calculated (%): C, 80.44; H, 9.83. IR, ν/cm^{-1}: 1725 (CHO). ^1H NMR, δ: 1.59 (m, 12 H, CH_2); 1.75 (m, 3 H, CH); 9.46 (s, 1 H, CHO). ^{13}C NMR, δ: 28.14 (C(3), C(5), C(7)); 36.17 (C(4), C(6), C(10)); 36.80 (C(2), C(8), C(9)); 48.80 (C(1)); 204.89 (C(11)). MS, m/z (I_{rel} (%)): 164 $[M]^+$ (25), 137 (100), 107 (24), 91 (33), 79 (45), 67 (39), 65 (21).

Ethyl 1-adamantanecarboxylate (8). B.p. 121—122 °C (4 Torr). Found (%): C, 74.95; H, 9.58. $C_{13}H_{20}O_2$. Calculated (%): C, 74.96; H, 9.68. ^{13}C NMR, δ: 14.57 (C(13)); 28.24 (C(3), C(5); C(7)); 36.80 (C(4), C(6), C(10)); 39.01 (C(2), C(8), C(9)); 40.72 (C(1)); 59.21 (C(12)); 177.33 (C(11)). MS, m/z (I_{rel} (%)): 208 $[M]^+$ (26), 180 (13), 163 (3), 136 (44), 135 (100), 107 (18), 93 (45), 91 (17), 79 (54), 67 (24).

Benzyl benzoate. B.p. 142 °C (3 Torr). Found (%): C, 79.23; H, 5.63. $C_{14}H_{12}O_2$. Calculated (%): C, 79.22; H, 5.70. IR, ν/cm^{-1}: 1720 (O—C=O). ^{13}C NMR, δ: 64.30 (C(8)); 128.75 (C(12)); 128.82 (C(9), C(14)); 128.96 (C(2), C(6)); 129.15 (C(11), C(13)); 129.64 (C(1)); 133.95 (C(4)); 140.90 (C(9)); 166.98 (C(7)); 309.15 (C(3), C(5)).

Chloroacetaldehyde (10) (see Ref. 5). B.p. 51—52 °C. IR, ν/cm^{-1}: 1720, 800. ^{13}C NMR, δ: 40.74 (C(1)); 176.85 (C(2)).

1,4-Dioxane (11) (see Ref. 5). B.p. 102—103 °C. ^{13}C NMR, δ: 66.82.

4-Chlorobutanal (14). B.p. 85 °C (95 Torr). Found (%): C, 45.31; H, 6.54; Cl, 32.98. C_4H_7ClO. Calculated (%): C, 45.09; H, 6.62; Cl, 33.28. IR, ν/cm^{-1}: 790, 1730. ^1H NMR, δ: 3.47 (t, 2 H, CH_2Cl, J = 6.5 Hz); 1.81 (m, 2 H, CH_2, H(3)); 2.42 (m, 2 H, CH_2, H(2)); 9.75 (s, 1 H, CHO). ^{13}C NMR, δ: 26.32 (C(3)); 45.75 (C(2)); 46.82 (C(4)); 207.64 (C(4)).

Hexan-6-olide (15a). B.p. 109 °C (20 Torr). Found (%): C, 63.21; H, 8.90. $C_6H_{10}O_2$. Calculated (%): C, 63.13; H, 8.83. ^{13}C NMR, δ: 23.15 (C(3)); 28.92 (C(5)); 29.44 (C(4)); 34.55 (C(2)); 68.86 (C(6)); 176.08 (C(1)).

Dodecan-12-olide (15b). B.p. 118 °C (10 Torr). Found (%): C, 72.68; H, 11.09. $C_{12}H_{22}O_2$. Calculated (%): C, 72.68; H, 11.18. IR, ν/cm^{-1}: 1050, 1160, 1245, 1365, 1470, 1730, 2920. ^1H NMR, δ: 1.28 (s, 14 H, CH_2); 1.62 (m, 2 H, CH_2); 2.05 (s, 2 H, CH_2); 3.68 (m, 2 H, CH_2); 4.05 (m, 2 H, CH_2). ^{13}C NMR, δ: 25.66 (C(2)); 28.39 (C(3)); 29.24 (C(4)—C(9)); 29.69 (C(10)); 34.12 (C(11)); 65.13 (C(1)); 173.87 (C(12)).

2-(2-Hydroxypropyl)-4-methyl-1,3-dioxane (17) (see Ref. 2). B.p. 75—76 °C (2 Torr). Found (%): C, 60.08; H, 10.05. $C_8H_{16}O_3$. Calculated (%): C, 59.98; H, 10.07. IR, ν/cm^{-1}: 780, 850, 900, 1050, 1090, 1126, 1380, 2860, 2930, 2965, 3460. ^1H NMR, δ: 1.15 (d, 3 H, Me, J = 6.2 Hz); 1.20 and 1.27 (both d, 3 H each, Me, J = 6.0 Hz); 1.44—1.51 (m, 1 H, $H(5)_{ax}$); 1.66—1.72 (m, 1 H, $H(5)_{eq}$); 1.78 (t, 2 H, CH_2, H(8), J = 3.7 Hz); 2.98 (s, 1 H, OH); 3.74—3.85 (m, 2 H, H(4) and $H(6)_{ax}$); 4.02—4.13 (m, 2 H, H(9) and $H(6)_{eq}$); 4.78 (t, 1 H, H(2)). ^{13}C NMR, δ: 21.69 (C(7)); 23.26 (C(10)); 32.88 (C(5)); 43.55 (C(8)); 64.42 (C(9)); 66.37 (C(6)); 72.87 (C(4)); 100.84 (C(2)).

3-Hydroxybutan-2-one (18) (see Ref. 8). M.p. 89—90 °C (MeOH). Found (%): C, 54.51; H, 9.02. $C_4H_8O_2$. Calculated (%): C, 54.53; H, 9.15. IR, ν/cm^{-1}: 1100, 1710, 3450. ^{13}C NMR, δ: 18.90 (C(4)); 28.26 (C(1)); 64.08 (C(3)); 200.62 (C(2)).

Hexane-2,5-dione (19) (see Ref. 8). B.p. 85 °C (20 Torr). IR, ν/cm^{-1}: 1715 (C=O).

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