Solid-state chlorodecarboxylation of mono- and dicarboxylic acids with the $Pb(OAc)_4$—MCl system*

*G. I. Nikishin,[a] L. L. Sokova,[a] A. O. Chizhov,[a] V. D. Makhaev,[b] and N. I. Kapustina[a]**

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 137 5328. E-mail: nika@ioc.ac.ru*
[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (096) 515 3588*

Solid-state reactions of acids RCOOH (R = *n*-C_7H_{15}, BuC(Et)H, *n*-C_9H_{19}, $PhCH_2$, $PhCH_2CH_2$, $H_2C{=}CH(CH_2)_8$, or $MeOOC(CH_2)_3$) with $Pb(OAc)_4$ combined with KCl, NaCl, $CdCl_2$, or NH_4Cl in the absence of a solvent and without mechanical activation afford chlorohydrocarbons RCl. The corresponding reactions of acids $HOOC(CH_2)_nCOOH$ ($n = 3$—6) give dichloroalkanes $Cl(CH_2)_nCl$ and γ-butyrolactone ($n = 3$).

Key words: monocarboxylic acids, dicarboxylic acids, chloroalkanes, α,ω-dichloroalkanes, γ-butyrolactone, δ-valerolactone, lead tetraacetate, ammonium chloride, solid-state reactions mechanical activation.

Oxidative decarboxylation of carboxylic acids with lead tetraacetate has been studied in detail. Numerous representatives of aliphatic, alicyclic, and arylaliphatic acids were examined in this reaction.[2] The use of $Pb(OAc)_4$ and the $Pb(OAc)_4$—I, $Pb(OAc)_4$—$Cu(OAc)_2$, and $Pb(OAc)_4$—MHal oxidizing systems (M is alkali metal) opens new ways of transforming acids into unsaturated hydrocarbons and halohydrocarbons. Oxidative decarboxylation was carried out in a liquid phase generally at high temperature with the use of solvents (benzene, dichloromethane, acetic acid, *etc.*).

We were the first to use $Pb(OAc)_4$ as an oxidizer in the solid-state reactions.[3] In recent years, solid-state chemical processes involving organic compounds in the absence of a solvent have attracted considerable attention. These reactions are of interest from an economical and ecological point of view. In addition, certain solid-state reactions proceed with higher stereo- and regioselectivity compared to analogous liquid-phase processes.[4,5]

As far as we know, there is no good evidence that chemoselectivity of the process changes in going from the liquid to the solid phase. Earlier, we have demonstrated that a change in chemoselectivity can be associated with the difference in the mechanism of the reaction involving the same reagents in the solid and liquid phases.[6] This conclusion was drawn in the study of oxidation of *n*-alkanols. The alkoxy fragments generated from alkan-1-ols under the action of the $Pb(OAc)_4$—LiCl system in the liquid phase (benzene as the solvent, 80 °C) undergo isomerization (through the 1,5-H migration) to the C-centered radicals, which are oxidized to 4-chloroalkan-1-ols. In the solid phase, the intramolecular 1,5-H migration cannot occur, because the required twist conformation of the alkoxy radicals is hindered. In the presence of alkan-1-ols, these radicals are oxidized to give esters (Scheme 1).

The present study is a continuation of our research into the solid-state reactions of lead tetraacetate. We performed oxidative chlorodecarboxylation of alkanemono- and alkanedicarboxylic acids with the $Pb(OAc)_4$—MCl (M is metal) and $Pb(OAc)_4$—NH_4Cl systems. The results of chlorodecarboxylation of monocarboxylic acids are given in Table 1. The reactions were carried out in the absence of a solvent at room temperature by keeping a thoroughly stirred mixture of an acid, $Pb(OAc)_4$, and metal or ammonium chloride (1 : 1.1 : 4 molar ratio) for several days. Under these conditions, the acids undergo decarboxylation accompanied by the replacement of the carboxy group with the chlorine atom (Scheme 2).

The solid-state reaction proceeds much more slowly than the reaction in the liquid phase. In the reactions with the use of KCl and $CdCl_2$, the 90% conversion of $Pb(OAc)_4$ is attained only after 2—7 days; the yields of chlorohydrocarbons generated from acids are 55—70 and 40—50%, respectively. We succeeded in improving the characteristics of chlorodecarboxylation by replacing metal chlorides with ammonium chloride. The $Pb(OAc)_4$—NH_4Cl, system, which we have suggested for

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Scheme 1

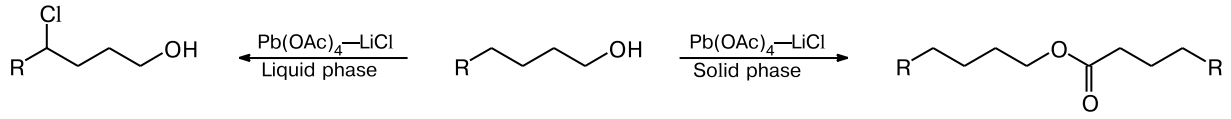


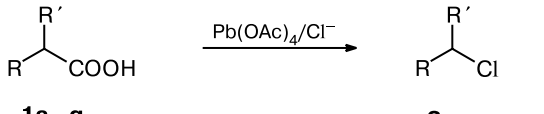
Table 1. Solid-state chlorodecarboxylation of alkanoic acids **1a—g** with the $Pb(OAc)_4$—MCl system without mechanical activation (20 °C)[a]

Entry	Acid	MCl (number of mmoles)	τ/day	C[b] (%)	Product (number of mmoles)
1	**1a**	KCl (2)	7	91	**2a** (0.37)
2	**1a**	KCl (4)	7	90	**2a** (0.67)
3	**1a**	NaCl (4)	7	67	**2a** (0.45)
4	**1a**	$CdCl_2$ (2)	7	71	**2a** (0.50)
5[c]	**1a**	$CdCl_2$ (2)	3	89	**2a** (0.64)
6	**1a**	NH_4Cl (4)	2	96	**2a** (0.62)
7	**1b**	NaCl (4)	7	75	**2b** (0.51)
8	**1b**	KCl (4)	7	86	**2b** (0.68)
9	**1b**	$CdCl_2$ (2)	7	68	**2b** (0.42)
10	**1b**	NH_4Cl (4)	2	97	**2b** (0.70)
11	**1c**	KCl (4)	3	90	**2c** (0.65)
12	**1c**	NH_4Cl (4)	1	93	**2c** (0.87)
13	**1d**	KCl (4)	2	84	**2d** (0.71)
14	**1d**	NH_4Cl (2)	1	97	**2d** (0.75)
15	**1d**	NH_4Cl (4)	1	96	**2d** (0.89)
16	**1e**	NH_4Cl (4)	1	99	**2e** (0.86)
17	**1f**	KCl (4)	2	86	**2f** (0.55)
18[d]	**1f**	NH_4Cl (4)	2	94	**2f** (0.42)
19	**1g**	KCl (4)	3	95	**2g** (0.30)
20	**1g**	NH_4Cl (4)	2	92	**2g** (0.57)

[a] Acid, 1.0 mmol; $Pb(OAc)_4$, 1.1 mmol.
[b] The conversion of $Pb(OAc)_4$.
[c] Acid, 2.0 mmol.
[d] The reaction afforded also 1.9-dichlorodecane (0.13 mmol), which was characterized by ^1H and ^{13}C NMR spectroscopy.

chlorodecarboxylation of carboxylic acids, made it possible to reduce the reaction time and increase both the conversion of the oxidizer and the yields of the products (see Table 1). The reaction can serve as a convenient procedure for the synthesis of chlorohydrocarbons, for example, of 1-chloroheptane (**2a**), 1-chlorononane (**2b**), 3-chloroheptane (**2c**), benzyl chloride (**2d**), and 2-phenylethyl chloride (**2e**) from the corresponding alkanoic and phenylalkanoic acids. The list of such examples can be extended, if required. In the case of the 94—97% conversion of $Pb(OAc)_4$, the yield of chlorohydrocarbons **2c—e** is as high as ~90% (with respect to the starting acid). This is a surprising result, because the rate of the $Pb(OAc)_4 \rightarrow Pb(OAc)_2$ conversion in the $Pb(OAc)_4$—NH_4Cl—**1a,d,e** ternary system is virtually the same as that in the $Pb(OAc)_4$—NH_4Cl system, *i.e.*, in the absence of an acid. Hence it follows that the three reagents give apparently a solid complex lead compound **C** (Scheme 3), which undergoes redox processes to form chlorohydrocarbons. It is this mechanism according to which the main amount of $Pb(OAc)_4$ is transformed into lead(II) acetate in the presence of carboxylic acid and NH_4Cl.

Scheme 2



1a—g **2a—g**

1, 2	R	R′	1, 2	R	R′
a	H	n-C_6H_{13}	**e**	H	$PhCH_2$
b	H	n-C_8H_{17}	**f**	H	$H_2C{=}CH(CH_2)_7$
c	Et	Bu^n	**g**	H	$MeOOC(CH_2)_2$
d	H	Ph			

Scheme 3

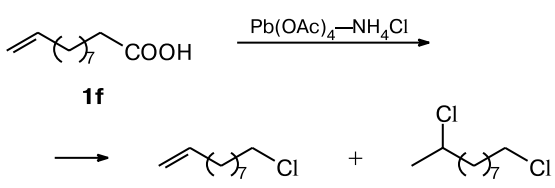
$$Pb(OAc)_4 + 2\,NH_4Cl + RCOOH \rightarrow \rightarrow [RCO_2Pb(OAc)_3Cl_2](NH_4)_2 + AcOH$$

C

At the same time, $Pb(OAc)_4$ is partially transformed into $Pb(OAc)_2$ without the involvement of carboxylic acid that undergoes oxidation (this process is most pronounced in the case of chlorodecarboxylation of acids **1a,b,g,f**), *i.e.*, directly in the reaction with ammonium chloride, *viz.*, through the formation and decomposition of the $[Pb(OAc)_4Cl_2](NH_4)_2$ complex, rather than through the step of decomposition of the ternary complex **C**.

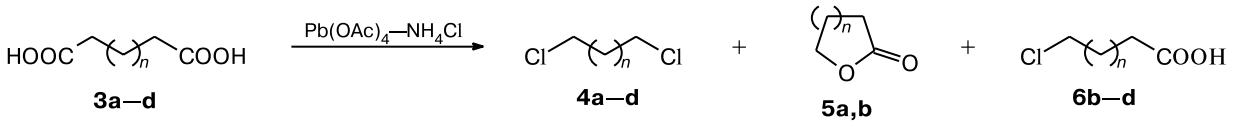
Chlorodecarboxylation of undecenoic acid **1f** with the $Pb(OAc)_4$—NH_4Cl system was accompanied by hydrochlorination of 10-chlorodec-1-ene (**2f**) that formed with

Scheme 4



1f **2f**

Scheme 5



n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**)

the resulting formation of the target product along with 1,9-dichlorodecane (Scheme 4) in a **2f** : 1,9-dichlorodecane ratio of ~ 3 : 1; their total yield was 55% (see Table 1, run *18*).

Aromatic acids, *viz.*, benzoic, *p*-methylbenzoic, and *p*-methoxybenzoic acids, do not undergo solid-state decarboxylation under the action of $Pb(OAc)_4$ and NH_4Cl. The reactivity in solid-state chlorodecarboxylation, like that in the liquid phase,[7] changes in the series ArCOOH < < RCH_2COOH < RR´CHCOOH (see Table 1).

We also studied chlorodecarboxylation of alkanedicarboxylic acids of composition C_5—C_8 with the $Pb(OAc)_4$—NH_4Cl system (Scheme 5). The reactions of alkanedicarboxylic acids involving $Pb(OAc)_4$, unlike those of monocarboxylic acids, are poorly studied. It is only known[8] that the reactions of glutaric and adipic acids with $Pb(OAc)_4$ and I_2 under UV irradiation in a CCl_4 solution afford 1,3-diiodopropane (12%) and 1,4-diiodobutane (33%), respectively. Experiments with the solid-state reactions were carried out in two modes, *viz.*, with and without mechanical activation (activation was carried out using a vibration mill). For comparative evaluation of the solid-state and liquid-phase processes, we performed chlorodecarboxylation of acids **3a—d** in an acetic acid solution at 80 °C. The results of investigation are given in Table 2.

Under the conditions used in the present study, the reactions of acid **3a—d**, $Pb(OAc)_4$, and NH_4Cl in a ratio of 1 : 2.2 : 4 both in the solid phase with mechanical activation and in the liquid phase led to the selective transformation of acid **3a** into γ-butyrolactone (**5a**) (~95% yield), acid **3b** into δ-valerolactone (**5b**) (~85% yield), and acids **3c,d** into dichloroalkanes **4c,d** (75—95% yields) (see Table 2, runs *3*, *4*, *9*, *10*, *13*, *16*, and *17*).

The solid-state reaction without mechanical activation proceeds less selectively. Thus, acids **3b—d** gave predominantly dichloroalkanes **4b—d** and ω-chloro acids **6b—d** in a ratio of (~3—4) : 1 (see Table 2, runs *7*, *12*, and *14*), whereas acid **3a** gave 1,3-dichloropropane (**4a**) and lactone **5a** in a ratio of ~1 : 2 (see Table 2, run *2*).

In the liquid phase, lactone **5b** is produced through the intermediate states of formation of chloro acid **6b** and its lead salt **7** (Scheme 6).

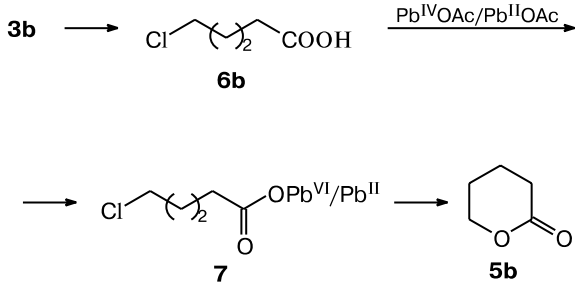
This conclusion follows from the results of experiments *10* and *11* (see Table 2). In run *11*, both lactone **5b** and chloro acid **6b** were synthesized. In run *10*, the reaction afforded exclusively lactone **5b**. In the latter case, the selectivity was attained due to an increase in the reaction

Table 2. Reactions of alkanedicarboxylic acids **3a—d** with the $Pb(OAc)_4$—NH_4Cl system without mechanical activation (***A***, 20 °C), under mechanical activation (***B***, 20 °C), and in an AcOH solution (***C***, 80 °C)[a]

Entry	Acid	Reaction type	τ/h	Product (number of mmoles)		
				4	**5**	**6**
1[b]	**3a**	***A***	72	**4a** (0.35)	**5a** (0.27)	—
2	**3a**	***A***	48	**4a** (0.27)	**5a** (0.49)	—
3	**3a**	***B***	6	—	**5a** (0.95)	—
4	**3a**	***C***	0.3	—	**5a** (0.83)	—
5[c]	**3a**	***C***	10	—	—	—
6[b]	**3b**	***A***	96	—	—	—
7	**3b**	***A***	48	**4b** (0.41)	—	**6b** (0.14)
8[d]	**3b**	***A***	72	**4b** (0.79)	—	—
9	**3b**	***B***	6	—	**5b** (0.82)	—
10	**3b**	***C***	0.3	—	**5b** (0.90)	—
11	**3b**	***C***	0.15	—	**5b** (0.40)	**6b** (0.47)
12	**3c**	***A***	96	**4c** (0.44)	—	**6c** (0.18)
13	**3c**	***B***	6	**4c** (0.72)	—	—
14	**3d**	***A***	96	**4d** (0.44)	—	**6d** (0.11)
15[d]	**3d**	***A***	96	**4d** (0.75)	—	—
16	**3d**	***B***	6	**4d** (0.94)	—	—
17	**3d**	***C***	0.3	**4d** (0.79)	—	—
18	**6b**	***A***	48	**4b** (0.41)	—	—
19	**6b**	***B***	6	—	**5b** (0.94)	—
20	**6b**	***C***	0.3	—	**5b** (0.88)	—

[a] Acid, 1.0 mmol; $Pb(OAc)_4$, 2.2 mmol; NH_4Cl, 4 mmol; the conversion of $Pb(OAc)_4$ was ~100%.
[b] Potassium chloride was used instead of NH_4Cl.
[c] The experiment was carried out without the use of NH_4Cl.
[d] $Pb(OAc)_4$, 3 mmol; NH_4Cl, 6 mmol.

Scheme 6



time (from 12 to 25 min), which provided the complete transformation of chloro acid **6b** into lactone **5b**.

An alternative free-radical mechanism of cyclization of acids **3a,b** to lactones **5a,b**, analogous to that observed[9] for the $^{\bullet}CH_2CH_2CH_2COOR$ radical, is completely ruled out. Even in the liquid phase, the reaction of glutaric acid **3a** with $Pb(OAc)_4$ in the absence of NH_4Cl did not give lactone **5a** (see Table 2, run *5*). Hence, oxidative decarboxylation of glutaric acid **3a** is not accompanied by generation of the $^{\bullet}CH_2CH_2CH_2COOR$ radicals (where R = H or Pb) as kinetically independent species.

In the solid-state reaction without mechanical activation, chloro acid **6b** was not transformed into lactone **5b**; instead, the reaction afforded 1,4-dichlorobutane **4b** (see Table 2, run *18*). In this case, lactonization is hindered due to the fact that two rigidly fixed reaction centers in salt **7** are spatially remote from each other. Under mechanical treatment using a vibration mill, salt **7** undergoes cyclization to lactone **5b** with high selectivity (see Table 2, run *19*) due, apparently, to the defect formation in the crystal lattice.

Liquid reaction products, *viz.*, chloroalkanes and acetic acid (the latter is produced as a result of the ligand exchange between $Pb(OAc)_4$ and the acid oxidized), cannot transfer a noticeable amount of lead carboxylates from the solid to the liquid phase. At room temperature, lead salts are virtually insoluble in acetic acid and chloroalkanes. In addition, it should be taken into account that the ratio between the liquid and solid compounds is nearly stoichiometric. For this reason, the liquid phase can make only an insignificant contribution to the formation of chlorodecarboxylation products.

To summarize, we demonstrated that the chemoselectivity of chlorodecarboxylation of adipic acid in the solid phase differs from that in the liquid phase. Solid-state reactions of alkanedicarboxylic acids **3a—d** with the $Pb(OAc)_4$—NH_4Cl system both with and without mechanical activation and the reaction in the liquid phase provide a new approach to the synthesis of γ-butyro- and δ-valerolactones and 1,3-, 1,4-, 1,5-, and 1,6-dichloroalkanones, which can find use in preparative chemistry.

Experimental

The GLC analysis was carried out on an LKhM-80 chromatograph equipped with a flame ionization detector and 2 m × 3-mm analytical columns with 5% FFAP and 5% SE-30 on Chromaton N-AW-HDMS (0.16—0.20 mm). The IR spectra were recorded on a UR-20 spectrometer in a thin layer between NaCl plates. The ^1H and ^{13}C NMR spectra were measured on a Bruker AC-200 spectrometer (200 and 50 MHz, respectively) in $CDCl_3$. The GLC-mass spectra were obtained on a Finnigan MAT ITD-700 spectrometer (electron impact, 70 eV, the temperature of the ion source—ion trap system was 220 °C) equipped with a Carlo Erba 4200 chromatograph with a 25 m × 0.2-mm Ultra-1 column (Hewlett—Packard); the thickness of a layer of the stationary phase (polymethylsiloxane) was 0.33 μ; helium was used as the carrier gas (1 mL min^{-1}). The reaction products were isolated by column chromatography (silica gel L 40/100 μm, a heptane—ethyl acetate mixture as the solvent). Lead tetraacetate of chemically pure grade was washed with glacial AcOH and dried over alkali *in vacuo*. The starting caprylic, capric, phenylacetic, 3-phenylpropionic, 10-undecenoic, 2-ethylhexanoic, glutaric, adipic, pimelic, suberic, and 5-chlorovaleric acids and monomethyl adipate were purchased from Lancaster and Acros and used without additional purification. Acetic acid of chemically pure grade was dried over P_2O_5 and distilled before use. The NaCl, KCl, $CdCl_2$, and NH_4Cl salts were dried *in vacuo* before use.

Oxidative chlorodecarboxylation of mono- and dicarboxylic acids (general procedures). ***A.*** Chlorodecarboxylation of carboxylic acids **1a—g**, **3a—d**, and **6b** with the $Pb(OAc)_4$—MCl and $Pb(OAc)_4$—NH_4Cl systems without mechanical activation in the absence of a solvent. A mixture of an acid, $Pb(OAc)_4$, and MCl or NH_4Cl was thoroughly stirred in air using a spatula for 5—10 min (the size of the solid particles was ~0.1—0.3 mm) and allowed to stand in a tightly closed vessel at ~20 °C until $Pb(OAc)_4$ was completely converted (the reagent ratios are given in Tables 1 and 2). The reaction mixture gradually became viscous and heterogeneous and then solidified. The duration of the transformation from one aggregate state to another depended on the structure of the acid and the nature of the chloride used (MCl or NH_4Cl), the conversion of $Pb(OAc)_4$ being no higher than 10%. After completion of the reaction (the complete conversion of $Pb(OAc)_4$ was determined iodometrically[10]), the solvents ($CHCl_3$ and diethyl ether) were successively added to the reaction mixture. The yields of the products (**2a—f**, **4a—d**, **5a—b**, and **6b**) were determined by GLC using an internal standard. For preparative isolation of the reaction products, the combined extracts were treated with 3% HCl, washed with a saturated Na_2CO_3 solution, and dried with Na_2SO_4. The solvent was distilled off. Compounds **2**, **4**, **5**, and **6** were isolated from the residue by distillation or silica gel column chromatography. The structures of the products were confirmed by ^1H and ^{13}C NMR and IR spectroscopy, GLC-mass spectrometry, elemental analysis, and comparison with authentic samples.

B. Chlorodecarboxylation of alkanedicarboxylic acids **3a—d** and acid **6b** with the $Pb(OAc)_4$—KCl and $Pb(OAc)_4$—NH_4Cl systems with mechanical activation in the absence of a solvent. Mechanical activation of the reaction mixture (the total weight was 1—2 g; the reagent ratios are given in Table 2) was performed at ~20 °C using a vibration mill with a vibration frequency of 12 Hz and the amplitude of 11 mm in a ~80-cm^3 sealed steel reactor. Steel balls with a diameter of 12.3 mm and a total weight of ~150 g were used as the milling medium. The mixture was subjected to mechanical treatment for 6 h, after whicht the reaction mixture was worked up according to the procedure ***A***.

C. Chlorodecarboxylation of alkanedicarboxylic acids **3a—d** and acid **6b** with the $Pb(OAc)_4$—NH_4Cl system in an AcOH solution. A mixture of an acid, $Pb(OAc)_4$, NH_4Cl, and AcOH (10 mL) was heated at 80 °C with vigorous stirring until Pb^{IV} was completely converted, AcOH was distilled off, and the mixture was worked up according to the procedure ***A*** (the reagent ratios are given in Table 2).

1-Chloroheptane (2a), b.p. 158—159 °C (*cf.* lit. data[11a]: b.p. 159 °C). MS, *m/z:* 134 and 136 $[M]^+$, 105 and 107 $[M - Et]^+$, 91

and 93 $[C_4H_8Cl]^+$, 69 $[C_5H_9]^+$, 55 $[C_4H_7]^+$, 43 $[C_3H_7]^+$, 41 $[C_3H_5]^+$.

1-Chlorononane (2b), b.p. 200—201 °C (*cf.* lit. data[11b]: b.p. 202—204 °C). MS, *m/z:* 162 and 164 $[M]^+$, 91 and 93 $[C_4H_8Cl]^+$, 69 $[C_5H_9]^+$, 55 $[C_4H_7]^+$, 43 $[C_3H_7]^+$, 41 $[C_3H_5]^+$.

3-Chloroheptane (2c), b.p. 153—154 °C. ^{1}H NMR ($CDCl_3$), δ: 0.85—1.10 (m, 6 H, Me); 1.31—1.53 and 1.70—1.87 (both m, 4 H each, CH_2); 3.43—3.52 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$), δ: 10.86, 13.90 (Me); 22.22, 28.65, 31.42, 37.76 (CH_2); 65.77 (CH).

Benzyl chloride (2d), b.p. 75—77 °C (20 Torr) (*cf.* lit. data[11c]: b.p. 79—80 °C (21 Torr)). ^{1}H NMR ($CDCl_3$), δ: 4.65 (c, 2 H, CH_2Cl); 7.38—7.52 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 46.20 (CH_2); 128.32, 128.51, 128.65 (C(2), C(3), C(4), C(5), C(6)); 137.40 (C(1)). MS, *m/z:* 126 and 128 $[M]^+$, 91 $[C_7H_7]^+$.

2-Phenylethyl chloride (2e), b.p. 88—90 °C (20 Torr) (*cf.* lit. data[11d]: b.p. 82—84 °C (16 Torr)). ^{1}H NMR ($CDCl_3$), δ: 3.10 (t, 2 H, CH_2, J = 3.7 Hz); 3.75 (t, 2 H, CH_2Cl, J = 3.8 Hz); 7.23—7.32 (m, 5 H, Ph). MS, *m/z:* 140 and 142 $[M]^+$, 105 $[M - Cl]^+$, 91 $[M - CH_2Cl]^+$.

10-Chlorodecen-1-ene (2f). Found (%): C, 68.69; H, 11.10; Cl, 19.65. $C_{10}H_{19}Cl$. Calculated (%): C, 68.96; H, 10.92; Cl, 20.11. ^{1}H NMR ($CDCl_3$), δ: 1.33—1.48 (m, 10 H, CH_2); 1.71—1.82 and 2.03—2.12 (both m, 2 H each, CH_2); 3.52 (t, 2 H, CH_2Cl, J = 5.6 Hz); 4.95 (t, 2 H, $C\underline{H}_2$=CH, J = 8.0 Hz); 5.72—5.89 (m, 1 H, $C\underline{H}$=CH_2).

Methyl 5-chlorovalerate (2g), b.p. 100—103 °C (30 Torr) (*cf.* lit. data[11e]: b.p. 106—107 °C (38 Torr)). Found (%): C, 48.29; H, 7.25; Cl, 23.08. $C_6H_{11}ClO_2$. Calculated (%): C, 48.00; H, 7.33; Cl, 23.33. ^{1}H NMR ($CDCl_3$), δ: 1.71—1.85 (m, 4 H, CH_2); 2.38 (t, 2 H, CH_2COO, J = 5.4 Hz); 3.52 (t, 2 H, CH_2Cl, J = 5.9 Hz); 3.68 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$), δ: 22.19 (Me); 31.79, 33.11, 44.38 (CH_2); 51.52 (Me); 173.54 (C=O).

1,3-Dichloropropane (4a), b.p. 123 °C (*cf.* lit. data[11f]: b.p. 120—122 °C). ^{1}H NMR ($CDCl_3$), δ: 2.15—2.36 (m, 2 H, CH_2); 3.72 (t, 4 H, CH_2Cl, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 34.81 (CH_2); 41.43 (CH_2Cl).

γ-Butyrolactone (5a), b.p. 202—203 °C (*cf.* lit. data[11g]: b.p. 204—205 °C). ^{1}H NMR ($CDCl_3$), δ: 2.13—2.28 (m, 2 H, CH_2); 2.43 (t, 2 H, J = 7.9 Hz); 4.30 (t, 2 H, CH_2, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.91, 27.54, 68.37 (CH_2); 177.68 (C=O). IR, ν/cm^{-1}: 1772 (C=O).

1,4-Dichlorobutane (4b), b.p. 161—162 °C (*cf.* lit. data[11h]: b.p. 46—48 °C (15 Torr)). ^{1}H NMR ($CDCl_3$), δ: 1.91—1.98 (m, 4 H, CH_2); 3.59 (t, 4 H, CH_2Cl, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 29.61 (CH_2); 44.11 (CH_2Cl).

δ-Valerolactone (5b), b.p. 220—221 °C (*cf.* lit. data[11i]: b.p. 58—60 °C (0.5 Torr)). ^{1}H NMR ($CDCl_3$), δ: 1.79—1.83 (m, 4 H, CH_2); 2.56 (t, 2 H, CH_2, J = 6.4 Hz); 4.36 (t, 2 H, CH_2, J = 5.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.00, 22.23, 29.80, 69.56 (CH_2); 171.87 (C=O). IR, ν/cm^{-1}: 1712 (C=O).

5-Chlorovaleric acid (6b), m.p. 16—17 °C (*cf.* lit. data[12]: m.p. 16—18 °C). ^{1}H NMR ($CDCl_3$), δ: 1.79—1.82 (m, 4 H, CH_2); 2.40 (t, 2 H, CH_2COOH, J = 6.5 Hz); 3.55 (t, 2 H, CH_2Cl, J = 5.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.79, 31.55, 33.08 (CH_2); 44.28 (CH_2Cl); 179.03 (C=O). IR, ν/cm^{-1}: 1704 (C=O). MS, *m/z:* 139 and 137 $[M+H]^+$.

1,5-Dichloropentane (4c), b.p. 68—70 °C (15 Torr) (*cf.* lit. data[11g]: b.p. 63—66 °C (10 Torr)). ^{1}H NMR ($CDCl_3$), δ: 1.39—1.44 (m, 2 H, CH_2); 1.79—1.85 (m, 4 H, CH_2); 3.55 (t, 4 H, CH_2Cl, J = 5.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.02, 30.11 (CH_2); 44.57 (CH_2Cl).

6-Chlorohexanoic acid (6c), b.p. 150—152 °C (10 Torr) (*cf.* lit. data[12]: b.p. 153 °C (12 Torr)). ^{1}H NMR ($CDCl_3$), δ: 1.73—1.79 (m, 6 H, CH_2); 2.38 (t, 2 H, $C\underline{H}_2COOH$, J = 6.5 Hz); 3.48 (t, 2 H, CH_2Cl, J = 5.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.22, 21.81, 32.82, 33.70 (CH_2); 44.44 (CH_2Cl); 179.45 (C=O). IR, ν/cm^{-1}: 1707 (C=O). MS, *m/z*: 151 and 153 $[M + H]^+$.

1,6-Dichlorohexane (4d), b.p. 83—85 °C (10 Torr) (*cf.* lit. data[11b]: b.p. 218—220 °C). ^{1}H NMR ($CDCl_3$), δ: 1.43—1.51 and 1.73—1.82 (both m, 4 H each, CH_2); 3.54 (t, 4 H, CH_2Cl, J = 6.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.01, 32.32 (CH_2); 44.85 (CH_2Cl).

7-Chloroheptanoic acid (6d), b.p. 168—169 °C (10 Torr) (*cf.* lit. data[12]: b.p. 171 °C (12 Torr)). ^{1}H NMR ($CDCl_3$), δ: 1.81—1.91 (m, 8 H, CH_2); 2.42 (t, 2 H, $C\underline{H}_2COOH$, J = 6.6 Hz); 3.60 (t, 2 H, CH_2Cl, J = 5.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.12, 20.65, 21.81, 31.72, 33.43 (CH_2); 44.31 (CH_2Cl); 179.21 (C=O). IR, ν/cm^{-1}: 1707 (C=O). MS, *m/z*: 165 and 167 $[M + H]^+$.

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