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Solid-phase reactions of alkanedicarboxylic acids with the $Pb(OAc)_4$–NH_4Cl system

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The title reactions of $HOOC(CH_2)_nCOOH$ acids afford α,ω-dichloroalkanes (n = 3, 4, 6) and lactones (n = 3, 4) as the main products.

In the last decade, the solid-phase and solvent-free reactions of organic compounds have attracted considerable attention. Interest in these reactions arises from ecological and economical factors, as well as from the fact that some solid-phase reactions are highly regioselective and stereoselective.[1–3]

We studied reactions with lead tetraacetate, which is widely used as an oxidising reagent in organic chemistry. We oxidised alkan-1-ols and 1-alkylcycloalkanols with lead tetraacetate and lead tetraacetate–metal halide systems[4,5] and found unexpected results. Thus, the mechanism of the solid-phase oxidation of alkan-1-ols is different from that in a liquid phase.[4]

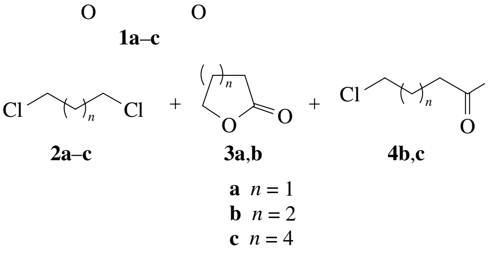
Here, we report on the solid-phase reactions of $Pb(OAc)_4$, *viz*., the oxidative decarboxylation of alkanedicarboxylic acids, such as glutaric, adipic, and suberic acids **1a**–**c**. We found that the solid-phase reactions of acids **1a**–**c** with the $Pb(OAc)_4$–NH_4Cl system gave rise to α,ω-dichloroalkanes **2a**–**c**, lactones **3a**,**b**, and ω-chloro acids **4b**,**c** (Scheme 1).†

A combination of $Pb(OAc)_4$ with NH_4Cl was used as an oxidising reagent. The solid-phase reactions were carried out in two modes (with and without mechanical activation in a vibration mill). The results are given in Table 1, together with the results of the reactions of acids **1a**–**c** and **4b** with the $Pb(OAc)_4$–NH_4Cl system in an acetic acid solution (at 80 °C) for comparison. Note that the liquid-phase decarboxylation of carboxylic acids with $Pb(OAc)_4$ and the chlorodecarboxylation with the $Pb(OAc)_4$–LiCl system have been studied in considerable detail.[6] As for alkanedicarboxylic acids, it is only known that the reactions of glutaric and adipic acids with $Pb(OAc)_4$ and I_2 in CCl_4 solutions under UV irradiation at 77 °C afforded 1,3-diiodopropane (12%) and 1,4-diiodobutane (33%), respectively.[7]

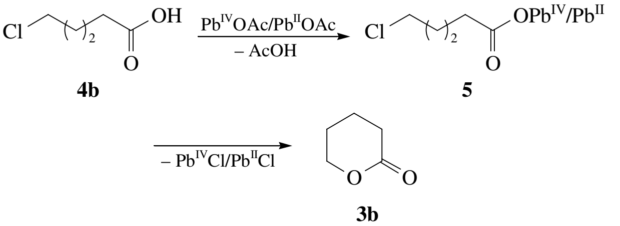
Under the reaction conditions, acids **1a**–**c** were transformed into γ-butyrolactone **3a**, δ-valerolactone **3b**, and 1,6-dichlorohexane **2c**, respectively, in high yields either in a solid phase with mechanical activation or in a liquid phase. The solid-phase reactions, which were not mechanically activated, proceeded less selectively. Thus, the reactions of acids **1b**,**c** gave predominantly dichloroalkanes **2b**,**c** along with chloro acids **4b**,**c** in a ratio of ~3–4:1. The reaction of acid **1a** produced 1,3-dichloropropane **2a** and γ-butyrolactone **3a** in a ratio of ~1:2.

In a liquid phase, lactone **3b** was derived from chloro acid **4b** through the formation of lead salt $Cl(CH_2)_4COOPb^{IV}/Pb^{II}$ **5**, as evidenced by the results of runs 7, 8 and 15 (Table 1) (Scheme 2).†

The solid-phase reaction of chloro acid **4b** without mechanical activation gave 1,4-dichlorobutane **2b** rather than lactone



Scheme 1



Scheme 2

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† *Procedures for the reactions of alkanedicarboxylic acids with the $Pb(OAc)_4$–NH_4Cl system.*

(*a*) Without mechanical activation (method A). A mixture of an acid, $Pb(OAc)_4$ and NH_4Cl was thoroughly stirred in a bottle (5–10 min) and kept at room temperature until the reaction was complete [complete conversion of $Pb(OAc)_4$]. The reaction products were extracted ($CHCl_3$, diethyl ether), and their yields were determined by GLC using an internal standard. The conversion of $Pb(OAc)_4$ was determined iodometrically.[9] The reaction products were isolated by column chromatography (silica gel, 40/100 mesh; heptane–ethyl acetate, 3:7). The structures of the reaction products were confirmed by ^1H and ^{13}C NMR (200 MHz) and IR spectroscopy (NaCl) and GC–MS (70 eV), as well as by comparison with authentic samples.

(*b*) With mechanical activation (method B). The reaction mixture (total weight of 1–2 g) was mechanically activated at room temperature using a vibration mill with a vibration frequency of 12 Hz and an amplitude of 11 mm in a sealed steel reactor with a volume of ~80 cm^3. In the reactions, steel balls 12.3 mm in diameter with a total weight of ~150 g were used for activation. The duration of mechanical treatment was 4 h. Then, the reaction mixture was treated according to the above procedure.

(*c*) In a solution in AcOH (method C). The reaction mixture of **1a**–**c** or **4b**, $Pb(OAc)_4$ and NH_4Cl in AcOH (10 ml) was heated with vigorous stirring at 80 °C until the complete conversion of lead. Then, an excess of AcOH was distilled off, and the residue was treated as described above.

For **2a**: ^1H NMR ($CDCl_3$) δ: 2.15–2.36 (m, 2H, CH_2), 3.72 (t, 4H, J 6.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 34.81 (CH_2), 41.43 (CH_2Cl).

For **2b**: ^1H NMR ($CDCl_3$) δ: 1.91–1.98 (m, 4H, CH_2), 3.59 (t, 4H, CH_2Cl, J 6.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 29.61 (CH_2), 44.11 (CH_2Cl).

For **2c**: ^1H NMR ($CDCl_3$) δ: 1.43–1.51 (m, 4H, CH_2), 1.73–1.82 (m, 4H, CH_2), 3.54 (t, 4H, CH_2Cl, J 6.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.01 (CH_2), 32.32 (CH_2), 44.85 (CH_2Cl).

For **3a**: ^1H NMR ($CDCl_3$) δ: 2.13–2.28 (m, 2H, CH_2), 2.43 (t, 2H, J 7.9 Hz), 4.30 (t, 2H, 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 (NaCl, ν/cm^{-1}): 1772 (C=O).

For **3b**: ^1H NMR ($CDCl_3$) δ: 1.79–1.83 (m, 4H, CH_2), 2.56 (t, 2H, CH_2, J 6.4 Hz), 4.36 (t, 2H, 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 (NaCl, ν/cm^{-1}): 1712 (C=O).

For **4b**: ^1H NMR ($CDCl_3$) δ: 1.79–1.82 (m, 4H, CH_2), 2.40 (t, 2H, CH_2COOH, J 6.5 Hz), 3.55 (t, 2H, 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 (NaCl, ν/cm^{-1}): 1704 (C=O). MS, m/z: 137 $[M + H]^+$.

For **4c**: ^1H NMR ($CDCl_3$) δ: 1.81–1.91 (m, 8H, CH_2), 2.42 (t, 2H, CH_2COOH, J 6.6 Hz), 3.60 (t, 2H, 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 (NaCl, ν/cm^{-1}): 1707 (C=O). MS, m/z: 165 $[M + H]^+$.

Table 1 Compositions and yields of the reaction products of alkanedicarboxylic acids **1a**–**c** and chloro acid **4b** with the $Pb(OAc)_4$–NH_4Cl system.[a]

Run	Acid	Reaction conditions[b]	Reaction time/h	Products and yields/mmol		
				2	**3**	**4**
1	**1a**	A	48	0.27	0.49	–
2		B	4	+	0.93	–
3		C	0.3	–	0.83	–
4	**1b**	A	48	0.41	–	0.14
5		A	72[c]	0.62	–	0.17
6		B	4	0.05	0.65	0.20
7		C	0.3	–	0.90	–
8		C	0.15	–	0.40	0.47
9	**1c**	A	96	0.44	–	0.11
10		A	96[c]	0.60	–	0.13
11		B	4	0.92	–	–
12		C	0.3	0.79	–	–
13	**4b**	A	48[d]	0.41	–	–
14		B	4	–	0.92	–
15		C	0.3[d]	–	0.88	–

[a] Acid, 1 mmol; $Pb(OAc)_4$, 2 mmol; NH_4Cl, 4 mmol; conversion of $Pb(OAc)_4$, ~ 100%. [b] A, solid-phase reaction without mechanical activation. B, solid-phase reaction with mechanical activation. C, reaction in a solution in AcOH (10 ml), 80 °C. [c] $Pb(OAc)_4$, 3 mmol; NH_4Cl, 6 mmol. [d] $Pb(OAc)_4$, 1 mmol; NH_4Cl, 2 mmol.

3b (run 13). In this case, lactonization is hindered because two rigidly fixed reaction centres in salt **5** are far apart. The mechanical treatment of salt **5** in a vibration mill led to the cyclization to lactone **3b** with high selectivity, apparently, due to the formation of defects in the crystal lattice (run 14).

Therefore, the solid-phase reactions of alkanedicarboxylic acids **1a**–**c** with the $Pb(OAc)_4$–NH_4Cl system with or without mechanical activation and the liquid-phase reactions provide a new approach to γ-butyro- and δ-valerolactones and 1,5- and 1,7-dichlorolalkanes, which can find use in preparative chemistry.

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