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Oxidation of 1-alkylcycloalkanols with Pb^{IV} and Mn^{III} compounds under mechanical activation

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A mechanoactivated solid-state oxidative decyclization of 1-alkylcycloalkanols under the action of the $Pb(OAc)_4$—MX or $Mn(OAc)_3$—MX systems (MX is a metal halide) was carried out for the first time. The reaction affords exclusively ω-haloalkanones.

Key words: mechanical activation, oxidative decyclization, tertiary cyclic alcohols, lead tetraacetate, manganese triacetate, ω-haloalkanones.
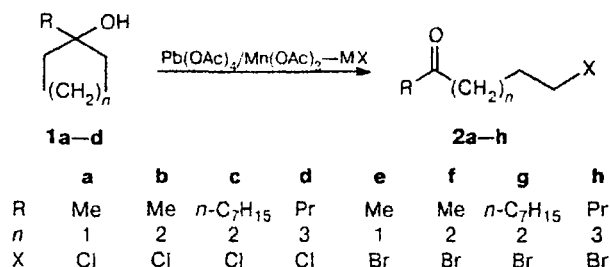
Oxidative decyclization of 1-alkylcycloalkanols (1) with lead tetraacetate is one of the most convenient methods for the synthesis of substituted ketones. Oxoalkyl radicals $RCOCH_2(CH_2)_nC^\cdot H_2$ (R = C_1—C_9 alkyl; n = 2—5) generated in the reaction of cycloalkanols 1 with lead tetraacetate[1] are oxidized with a $Pb(OAc)_4$—$Cu(OAc)_2$ system into unsaturated ketones in quantitative yields,[2] selectively transformed into ω-halo- or ω-pseudohaloalkanones under the action of a $Pb(OAc)_4$—metal halide(pseudohalide) system,[3,4] and recombined with each other in the presence of a $Pb(OAc)_4$—AgOAc system to give dicarbonyl compounds.[5] All the above processes needed a solvent (benzene) and pyridine, which accelerates the oxidation, and were carried out at 80 °C.

Unlike lead tetraacetate, manganese triacetate efficiently oxidizes only 1-methylcyclobutanol (1a), while cycloalkanols 1 with a larger ring size are inert with respect to this oxidant.[6]

In the present work, in continuation of the study of mechanoactivated oxidation of organic compounds with Pb^{IV} and Mn^{III} compounds in the absence of a solvent[7] we carried out for the first time the oxidation of cycloalkanols 1 (ring size C_4—C_6) with the $Pb(OAc)_4$—MX or $Mn(OAc)_3$—MX systems (M = Li, Na, or K; X = Cl or Br). Reaction mixtures were mechanically activated using vibration ball mills in sealed steel reactors. The reaction began at 20 °C, but the mechanical energy supplied to the reactants increased the temperature by 10 to 15 °C over 4 h.

Cycloalkanols 1 react with the oxidizing systems to give ω-chloro(bromo)alkanones (2).

At the first stage, when the reaction mixture (a solid mass of lead tetraacetate and halide MX, saturated with cycloalkanol 1) is mechanically activated, complex compounds $M_2[Pb(OAc)_4X_2]$ seem to be formed. The formation of such complexes from $Pb(OAc)_4$, $K_2[Pb(OAc)_6]$, and $K_2[Pb(OAc)_4Cl_2]$ was reported previously.[8,9]

	a	b	c	d	e	f	g	h
R	Me	Me	n-C$_7$H$_{15}$	Pr	Me	Me	n-C$_7$H$_{15}$	Pr
n	1	2	2	3	1	2	2	3
X	Cl	Cl	Cl	Cl	Br	Br	Br	Br

Apparently, these complexes cause decyclization of cycloalkanols 1 to give alkanones 2. In the case of manganese triacetate, the oxidation probably involves manganese halides formed in an exchange reaction.
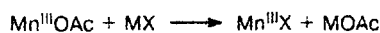
$$Mn^{III}OAc + MX \longrightarrow Mn^{III}X + MOAc$$

Table 1 presents data on the mechanoactivated oxidation of cycloalkanols 1 under the action of the Pb(OAc)$_4$—MX and Mn(OAc)$_3$—MX systems. It was exemplified with the oxidation of 1-methylcyclobutanol (1a) with the Pb(OAc)$_4$—LiCl system that an increase

Table 1. Oxidation of 1-alkylcycloalkanols (1a—d) with Pb^{IV} and Mn^{III} compounds under mechanical activation[a]

Entry	1-Alkyl-cyclo-alkanol (1)	Oxidizing system[b]	Degree of conversion of 1 (%)	Yield of ω-halo-alkanone[c] 2 (%)
1	1a	Pb(OAc)$_4$—LiCl[d]	52	2a, 36/69
2		Pb(OAc)$_4$—LiCl	95	2a, 85/91
3		Pb(OAc)$_4$—KCl	68	2a, 53/78
4		Pb(OAc)$_4$—LiBr	34	2e, 22/65
5		Pb(OAc)$_4$—NaBr	57	2e, 53/93
6		Pb(OAc)$_4$—KBr	75	2e, 59/78
7	1a	Mn(OAc)$_3$—LiCl	61	2a, 59/98
8		Mn(OAc)$_3$—LiCl[e]	87	2a, 70/80
9		Mn(OAc)$_3$—LiCl[f]	84	2a, 72/86
10		Mn(OAc)$_3$—LiBr	27	2e, 19/70
11	1b	Pb(OAc)$_4$—LiCl	62	2b, 51/82
12		Pb(OAc)$_4$—LiBr	28	2f, 18/65
13		Pb(OAc)$_4$—KBr	51	2f, 45/88
14	1c	Pb(OAc)$_4$—LiCl	57	2c, 44/77
15		Pb(OAc)$_4$—KBr	45	2g, 34/76
16	1d	Pb(OAc)$_4$—LiCl	53	2d, 48/90
17		Pb(OAc)$_4$—NaBr	28	2h, 24/86
18		Pb(OAc)$_4$—KBr	47	2h, 39/83

[a] Reaction conditions: reaction duration 4 h; frequency 12 Hz; molar ratio of alcohol : Pb(OAc)$_4$ or Mn(OAc)$_3$: MX = 1 : 2 : 5; amount of alcohol 0.025 mol.
[b] The degree of conversion of Pb(OAc)$_4$ is 100%.
[c] The yield is cited with respect to the initial/consumed alcohol.
[d] Molar ratio of alcohol : Pb(OAc)$_4$: LiCl = 1 : 1.2 : 5.
[e] Molar ratio of alcohol : Mn(OAc)$_3$: LiCl = 1 : 3 : 5.
[f] Molar ratio of alcohol : Mn(OAc)$_3$: LiCl = 1 : 4 : 5.

in the amount of lead tetraacetate in the reaction mixture from 1.2 to 2 mol per mol of 1a results in a virtually doubled degree of conversion of 1a and increases the yield of 5-chloropentan-2-one (2a) from 36 to 85% (with respect to the starting cyclobutanol 1a). The selectivity with respect to 1a is higher than 90%. Lead tetraacetate is consumed almost completely (entry 2). In this reaction, LiCl and KBr are the most effective compounds among chlorides and bromides, respectively. The yield of ω-chloro(bromo)alkanones 2 amounts to ~75—95% per the converted 1. The degree of conversion of cycloalkanol 1 ranges from 30 to 90% depending on the ring size and the nature and amount of the oxidizing system. A similar dependence was also observed in the case of liquid-phase oxidation of these alcohols with the above systems.[3]

Among the cycloalkanols 1 studied, only the alcohol with a ring size of C$_4$ (1a) undergoes decyclization in mechanoactivated oxidation with a system based on manganese triacetate (entries 7—10). As in the case of lead tetraacetate, a Mn(OAc)$_3$—metal halide system affords 5-chloro- (2a) and 5-bromopentan-2-ones (2e). Note that the yields of the reaction products and the degree of conversion of alkanol 1a were nearly the same as the corresponding characteristics of a common reaction in the presence of a solvent.[6]

The reactivity of cycloalkanols 1 under mechanical activation in the absence of a solvent decreases in the same order (C$_4$ > C$_5$ > C$_6$) as that observed for liquid-phase oxidation with a Pb(OAc)$_4$—MX system in the presence of a solvent,[3] ring opening being the sole pathway of the solid-state process (entries 2, 11, 14, and 16).

Experimental

GLC analysis was performed on an LKhM-80 chromatograph with a flame ionization detector and an analytical glass column (3000 × 3 mm) with 5% SE-30 on Chromaton N-AW-HDMS (0.16—0.20 mm). ^{1}H and ^{13}C NMR spectra were recorded using standard conditions on a Bruker AC-250P spectrometer (CDCl$_3$). IR spectra were recorded on a UR-20 instrument (thin film). The starting 1-alkylcycloalkanols were synthesized by the Grignard reaction from the corresponding cycloalkanols and alkylmagnesium halides. Commercial 1-methylcyclobutanol was distilled before use. Lead tetraacetate (of "pure" grade) was washed with glacial AcOH and dried over alkali *in vacuo*. Manganese triacetate was prepared according to the known procedure.[10] Commercial LiCl, KCl, LiBr, NaBr, and KBr were dried before use.

Solid-state oxidative decyclization of 1-alkylcycloalkanols under the action of a Pb(OAc)$_4$—MX or Mn(OAc)$_3$—MX system (general procedure). The reaction mixture composed of 1-alkylcycloalkanol, Pb(OAc)$_4$ or Mn(OAc)$_3$, and a metal halide (overall weight ~2 g) was mechanically activated using a vibration mill with a frequency of 12 Hz and an amplitude of 11 mm in a hermetically sealed steel reactor (~80 cm^3 volume) packed with steel balls 12.3 mm in diameter with an overall weight of ~150 g. The mechanical activation was carried out for 4 h, the reaction temperature increasing from 20 to 30—35 °C. After the process was terminated, the reaction mixture (a gray

sintered solid) was withdrawn from the reactor and washed with ether (2×30 mL) and chloroform (2×30 mL) to extract reaction products. The degree of conversion of cycloalkanols 1 and the yield of haloalkanones 2 were determined by GLC with the use of an internal standard. The degree of conversion of the oxidant was measured by iodometry.[11] The organic layer was washed with a 3% aqueous solution of HCl and an aqueous solution of $NaHCO_3$, dried with Na_2SO_4, and distilled to isolate the reaction products. The structures of compounds 2 were determined by ^1H and ^{13}C NMR spectroscopy.

5-Chloropentan-2-one (2a), b.p. 71 °C (20 Torr).[6] ^1H NMR (CDCl₃), δ: 1.95—2.10 (m, 2 H, $CH_2CH_2CH_2Cl$); 2.18 (s, 3 H, CH₃CO); 2.65 (t, 2 H, CH₂CO, J = 7.48 Hz); 3.60 (t, 2 H, CH₂Cl, J = 6.64 Hz). ^{13}C NMR (CDCl₃), δ: 26.2, 40.2, and 44.4 (CH₂); 30.0 (CH₃); 207.9 (C=O).

5-Bromopentan-2-one (2e), b.p. 68 °C (10 Torr).[6] ^1H NMR (CDCl₃), δ: 1.82—2.05 (m, 2 H, CH₂); 2.10 (s, 3 H, CH₃CO); 2.45 (t, 2 H, CH₂CO, J = 7.62 Hz); 3.42 (t, 2 H, CH₂Br, J = 6.46 Hz). ^{13}C NMR (CDCl₃), δ: 24.9, 27.7, and 42.0 (CH₂); 29.9 (CH₃); 209.2 (C=O).

6-Chlorohexan-2-one (2b), b.p. 77—78 °C (10 Torr).[3] ^1H NMR (CDCl₃), δ: 1.50—1.75 (m, 4 H, $CH_2CH_2CH_2CH_2Cl$); 2.03 (s, 3 H, CH₃CO); 2.37 (t, 2 H, CH₂CO, J = 7.50 Hz); 3.44 (t, 2 H, CH₂Cl, J = 6.61 Hz). ^{13}C NMR (CDCl₃), δ: 20.7, 20.9, 41.0, and 44.5 (CH₂); 29.8 (CH₃); 208.8 (C=O).

6-Bromohexan-2-one (2f), b.p. 85 °C (7 Torr).[3] ^1H NMR (CDCl₃), δ: 1.48—1.58 (m, 4 H, $CH_2CH_2CH_2CH_2Br$); 2.11 (s, 3 H, CH₃CO); 2.38 (t, 2 H, CH₂CO, J = 7.58 Hz); 3.46 (t, 2 H, CH₂Br, J = 6.47 Hz). ^{13}C NMR (CDCl₃), δ: 22.2, 24.3, 28.5, and 42.0 (CH₂); 29.9 (CH₃); 212.1 (C=O).

12-Chlorododecan-5-one (2c), b.p. 89 °C (0.5 Torr).[3] ^1H NMR (CDCl₃), δ: 0.88 (t, 3 H, CH₃, J = 7.40 Hz); 1.10—1.30 (m, 8 H, CH₂); 1.65—1.80 (m, 6 H, CH₂); 2.38 (t, 2 H, CH₂CO, J = 7.15 Hz); 2.40 (t, 2 H, COCH₂, J = 7.52 Hz); 3.50 (t, 2 H, CH₂Cl, J = 6.60 Hz). ^{13}C NMR (CDCl₃), δ: 14.0 (CH₃); 21.0, 22.6, 23.8, 23.8, 29.0, 29.2, 30.2, 31.9, 41.6, and 44.6 (CH₂); 210.9 (C=O).

12-Bromododecan-5-one (2g), b.p. 114—115 °C (0.7 Torr). IR, ν/cm⁻¹: 650 (CH₂Br), 1720 (C=O). ^1H NMR (CDCl₃), δ: 0.90 (t, 3 H, CH₃, J = 6.42 Hz); 1.25—1.38 (m, 8 H, CH₂); 1.60—1.80 (m, 6 H, CH₂); 2.40 (t, 2 H, CH₂CO, J = 7.44 Hz); 2.44 (t, 2 H, COCH₂, J = 7.60 Hz); 3.41 (t, 2 H, CH₂Br, J = 6.44 Hz). ^{13}C NMR (CDCl₃), δ: 13.9 (CH₃); 20.9, 22.0, 23.5, 24.5, 28.1, 29.1, 30.2, 31.9, 42.0, and 44.0 (CH₂); 213.0 (C=O). Found (%): C, 55.04; H, 8.69; Br, 30.09. $C_{12}H_{23}BrO$. Calculated (%): C, 54.75; H, 8.74; Br, 30.41.

9-Chlorononan-4-one (2d), b.p. 126 °C (20 Torr). IR, ν/cm⁻¹: 725 (CH₂Cl), 1715 (C=O). ^1H NMR (CDCl₃), δ: 0.90 (t, 3 H, CH₃, J = 7.38 Hz); 1.30—1.65 (m, 6 H, CH₂); 1.65—1.85 (m, 2 H, CH₂); 2.37 (t, 2 H, CH₂CO, J = 7.13 Hz); 2.41 (t, 2 H, COCH₂, J = 7.54 Hz); 3.52 (t, 2 H, CH₂Cl,

J = 6.58 Hz). ^{13}C NMR (CDCl₃), δ: 13.7 (CH₃); 17.2, 20.7, 22.9, 26.4, 32.3, 42.4, and 44.7 (CH₂); 211.1 (C=O). Found (%): C, 61.06; H, 9.80; Cl, 19.80. $C_9H_{17}ClO$. Calculated (%): C, 61.36; H, 9.64; Cl, 19.89.

9-Bromononan-4-one (2h), b.p. 125 °C (0.5 Torr). IR, ν/cm⁻¹: 655 (CH₂Br), 1720 (C=O). ^1H NMR (CDCl₃), δ: 0.86 (t, 3 H, CH₃, J = 6.45 Hz); 1.40—1.70 (m, 6 H, CH₂); 1.75—1.90 (m, 2 H, CH₂); 2.38 (t, 2 H, CH₂CO, J = 7.43 Hz); 2.50 (t, 2 H, COCH₂, J = 7.61 Hz); 3.42 (t, 2 H, CH₂Br, J = 6.44 Hz). ^{13}C NMR (CDCl₃), δ: 13.8 (CH₃); 17.3, 22.8, 27.7, 32.5, 33.6, 42.4, and 44.8 (CH₂); 210.2 (C=O).

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