Solid-phase reactions of lead tetraacetate with tertiary cycloalkanols and pyridine

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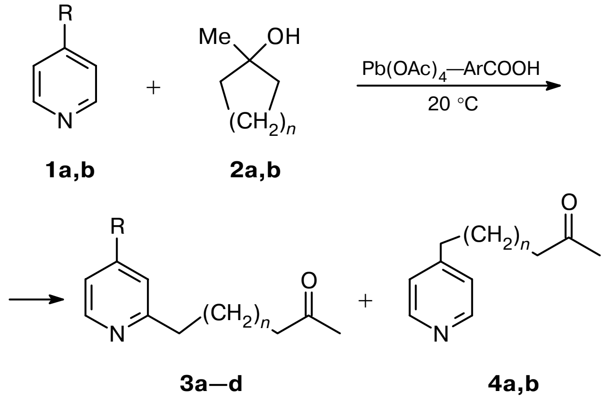
The oxidation of organic compounds with lead tetraacetate is always performed in the liquid phase using solvents.[1] For the first time, we performed solid-phase reactions of $Pb(OAc)_4$ without a solvent, which required the use of mechanical activation in a vibration mill. Under these conditions, the $Pb(OAc)_4$—metal halide system transforms naphthalene into 1-halo- and 1,4-dihalonaphthalenes[2] and C_5—C_7 *n*-alkanols into esters.[3] In the liquid phase, *n*-alkanols are oxidized by the same system by a different mechanism resulting in 4-haloalkanols.[4]

Continuing this new direction in chemistry of $Pb(OAc)_4$, we found that oxidative processes in the solid phase involving $Pb(OAc)_4$ can occur without mechanical activation. Oxidative decyclization of cycloalkanol **2** and oxoalkylation of pyridines occur in the solid-phase composition formed after mixing of pyridine or 4-picoline (**1a,b**), 1-methylcycloalkanols (**2a,b**), $Pb(OAc)_4$, and benzoic or 2-chlorobenzoic acid.

Oxoalkylation of pyridine occurs at positions 2 and 4, and 4-picoline is oxoalkylated at position 2. The results of studies are presented in Table 1 along with the data obtained under traditional conditions using AcOH as the solvent (at 80 °C).[5]



1, 3: R = H (**a**, **c**), Me (**b**, **d**)
n = 1 (**2a**, **3a**, **3b**, **4a**),
n = 2 (**2b**, **3c**, **3d**, **4b**)
Ar = Ph or 2-ClC_6H_4

It follows from Table 1 that the solid-phase reaction has higher parameters as regards the conversion of cycloalkanols **2** and the yield of oxoalkylation products **3** and **4** compared to a similar reaction in the liquid phase. However, the solid-phase state of the reacting system is not sufficient for the efficient reaction. Evidently, the chemical and structural matching of the reactants is necessary. This conclusion follows from a sharp decrease in the conversion of 1-methylcyclo-

Table 1. Solid-phase oxoalkylation of pyridines **1** by 1-methylcycloalkanols **2**

Reactants		Acid	Conversion **2**[a] (%)	Reaction products	
1	**2**			Ratio of 2- and 4-isomers (%)	Yield[b] (%)
a	**a**	PhCOOH	98	**3a** (78), **4a** (22)	86/88
a	**a**	AcOH[c]	75	**3a** (73), **4a** (27)	50/67
b	**a**	PhCOOH	95	**3b** (100)	87/92
b	**a**	AcOH[c]	67	**3b** (100)	35/52
a	**b**	2-ClC_6H_4COOH	83	**3c** (61), **4b** (39)	74/89
a	**b**	AcOH[c]	55	**3c** (71), **4b** (29)	30/55
b	**b**	2-ClC_6H_4COOH	97	**3d** (100)	76/78
b	**b**	AcOH	49	**3d** (100)	28/57

[a] Conversion of $Pb(OAc)_4$ is ~100%.
[b] With respect to initial/converted **2**.
[c] Reactions in AcOH (80 °C, 2 h).[5]

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pentanol **2b** in the oxoalkylation of compounds **1a** and **1b** when 2-chlorobenzoic acid is replaced by benzoic acid. In the case of 1-methylcyclobutanol **2a**, this replacement has no effect on the results.

A mixture of pyridine (or 4-picoline) (**1a,b**), 1-methylcycloalkanol (**2a,b**), $Pb(OAc)_4$, and PhCOOH (or $2-ClC_6H_4COOH$) (molar ratio 4 : 1 : 2 : 4, 1-methylcycloalkanol 5 mmol) was thoroughly stirred in a weighing bottle for approximately 5 min, after which the reaction mixture became liquid and then solidified after 2—6 h. After the end of the reaction (~20 h, complete conversion of $Ph(OAc)_4$), a solvent ($CHCl_3$, ether) was added to the mixture, and the conversion of the starting compound **2** and the yield of the reaction products (**3a—d**, **4a,b**) were determined by GLC using an internal standard. The reaction mixture was treated with 10% HCl and a saturated solution of Na_2CO_3, washed with water, dried with Na_2SO_4, and distilled to give products **3** and **4**. The structure of products **3** and **4** was confirmed by ^1H and ^{13}C NMR and IR spectroscopy, and by comparison with authentic samples.[5]

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