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THE CONVERSION OF PRIMARY ALCOHOLS TO THE CORRESPONDING ALDEHYDES BY A MODIFIED LEAD TETRAACETATE OXIDATION

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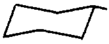
Abstract: A novel metod for obtaining aldehydes in good yield from primary alcohols has been devised, using the combination lead tetraacetate-manganous diacetate as the oxidizing agent.

When primary alcohols are treated with lead tetraacetate (LTA), they can undergo various reactions, depending upon their structure and the reaction conditions (particularly the solvent), such as functionalization of saturated (nonactivated) δ-carbons (by way of tetrahydrofuran ring closure), internal hydroxyl oxygen addition to olefinic bonds, ester formation, β-fragmentation, etc.[1] Oxidation to aldehydes is another possible pathway, but the yields are satisfactory only when pyridine is used as additive (to benzene) or as solvent, and even then structural features of the substrate can have a considerable influence on the ease of aldehyde formation.[1,2]

We have now found that the transformation of primary alcohols to the corresponding aldehydes can be performed in relatively high yield when lead tetraacetate in combination with manganous diacetate (in benzene) is used as the oxidant. The results obtained so far (see Table) indicate that this reagent could be an important addition to the present methodology and of comparable value (concerning conveniency, efficiency, economic factors) to the procedures currently in use (oxidations with LTA/pyridine,[2] with chromium containing reagents,[3-6] etc.), particularly for small to moderate scale oxid-

Table. Oxidation of alcohols R-$(CH_2)_n$-CH_2OH with LTA/$Mn(OAc)_2$

R	n	mmol ROH	ROH/LTA/$Mn(OAc)_2$	Product yield (%)[a]				
				Aldehyde				Cyclic
				A	B	C	D	ether
CH_2=CH-	4	5.9	1 : 1 : 0.2	71				24[b]
CH_2=CH-	4	7.2	1 : 1 : 0.5	74		60		9[b]
CH_3-	5	4.1	1 : 1 : 0.2	83		68		16[c]
CH_2=CH-	5	1.9	1 : 1 : 0.2	90				9[c]
CH_2=CH-	6	3.7	1 : 1 : 0.2	90		70		5[c]
CH_3-	7	7.6	1 : 1 : 0.2	79	70			10[c]
CH_3-	7	100.0	1 : 1 : 0.5	76			64	5[c]
Citronellol		5.0	1 : 1 : 0.1	71				20[c]
CH_2=CH-	8	7.2	1 : 1 : 0.2	80	73	65		13[c]
CH_2=CH-	8	30.0	1 : 1 : 0.5	77	72		65	10[c]
CH_3-	11	10.5	1 : 1 : 0.2	85	81	70		12[c]
CH_3-	14	100.0	1 : 1 : 0.5	86			70	7[c]
 CH_2OH		10.9	1 : 1 : 0.2	82	75			d

[a] The yields of aldehydes were determined: (A) by analytical gas chromatography (along with cyclic ether yields);(B)by conversion to, and titration of, oximes;[7] (C) by preparative gas-chromatographic isolation; (D) by isolation *via* the bisulfite addition compounds.[7,8] Unreacted alcohols and their acetates were usually detected as by-products.

[b] In the presence of 0.2 mol-equiv. of $Mn(OAc)_2$ 18.5% of acetoxylated 7-membered cyclic ether and 5.3% of tetrahydrofuran-type ether were produced; with 0.5 mol-equiv. of $Mn(OAc)_2$ these cyclization products were obtained in 5.1 and 4.3% yield, respectively.

[c] Tetrahydrofuran-type cyclic ethers.

[d] Not determined. A small amount of β-fragmentation acetate, i.e. cyclohexyl acetate, was detected (about 2%).

ations (the yield of aldehyde being 70-90% according to quantitative analyses and 60-75% in the preparative procedures). It should be noted that with this combination cyclic ether formation from saturated and Δ^n-olefinic ($n \geq 6$) primary alcohols was largely (but not completely) suppressed (Table), except in the case of 4-penten-1-ol and 5-hexen-1-ol, which did not afford aldehydes as major products but, instead, as with lead tetraacetate alone,[1] acetoxylated cyclic ethers. Secondary alcohols, such as 2-octanol, were converted with LTA/$Mn(OAc)_2$, in high yield (over 90%), to the corresponding ketones.

In small scale experiments, 2-10 mmol of alcohols were oxidized and the aldehyde obtained detected and quantitatively determined by analytical gas chromatography or oxime titration,[7] and isolated (in some cases) by preparative gas chromatography. The aldehyde products from the oxidation of primary alcohols on a larger scale (15-100 mmol) could be isolated *via* the corresponding bisulfite derivatives.[7,8,+]

Nonanal. - 14.4 g (0.1 mol) of nonan-1-ol, 12.2 g (0.05 mol) of $Mn(OAc)_2 \cdot 4H_2O$ and 500 ml of anh. benzene were placed in a one liter round-bottomed flask. After distilling off about 100 ml of the solvent (to remove hydrated water and traces of moisture), the reaction systems was equipped with a Dean-Stark apparatus filled with anh. K_2CO_3. With heating and vigorous stirring 57.6 g (0.13 mol) of lead tetraacetate was added in small portions, over 80-90 minutes. Stirring and refluxing were continued until all tetravalent lead had been consumed (KI starch paper control - about one hour being necessary). The reaction mixture was then cooled to room temp., diluted with 300 ml of diethyl ether and filtered. The inorganic salts, i.e. $Pb(OAc)_2$ and $Mn(OAc)_2$, were dissolved in a little water and this solution was extracted with diethyl ether. The combined organic solutions were successively washed with water, sat. aqueous $NaHCO_3$ and sat. aqueous NaCl. After drying over anh. Na_2SO_4, the solvents were removed *in vacuo*. Distillation of the residue through a Vigreux column gave 11.5 g (81%) of a fraction, b.p. 80-84°C at 13 mm Hg, containing 76% of aldehyde and 5% of 2-(pent-1-yl)tetra-

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[+] Further work is in progress in order to elucidate the mechanism of this reaction, to optimize the aldehyde yields and to explore in more detail the preparative applicability of this new method.

hydrofuran. Through the bisulfite addition product,[7,8] pure nonanal, b.p. 80-81°C at 12 mm Hg, could be isolated in 64% yield.

8-Nonenal. - The same procedure was applied to oxidize 0.52 g (3.66 mmol) of 8-nonen-1-ol, using 0.18 g (0.73 mmol) of $Mn(OAc)_2 \cdot 4H_2O$, 20 ml of anh. benzene and 1.78 g (3.66 mmol + 10% excess) of $Pb(OAc)_4$, the latter being added in one portion to the reaction mixture, upon distilling off 5 ml of solvent. The reaction was complete in about 10 minutes of refluxing. After working-up as above and careful removal of solvents, the residue was found to contain 90% of 8-nonenal and 5% of 2-(4-penten-1-yl)tetrahydrofuran (analytical GC), and, when subjected to separation by preparative GC, afforded 0.36 g (70.4%) of pure aldehyde.

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