Intramolecular Oxidative Cyclisation of 5-Stannyl-1,3-pentanediol Derivatives with Lead Tetra-acetate

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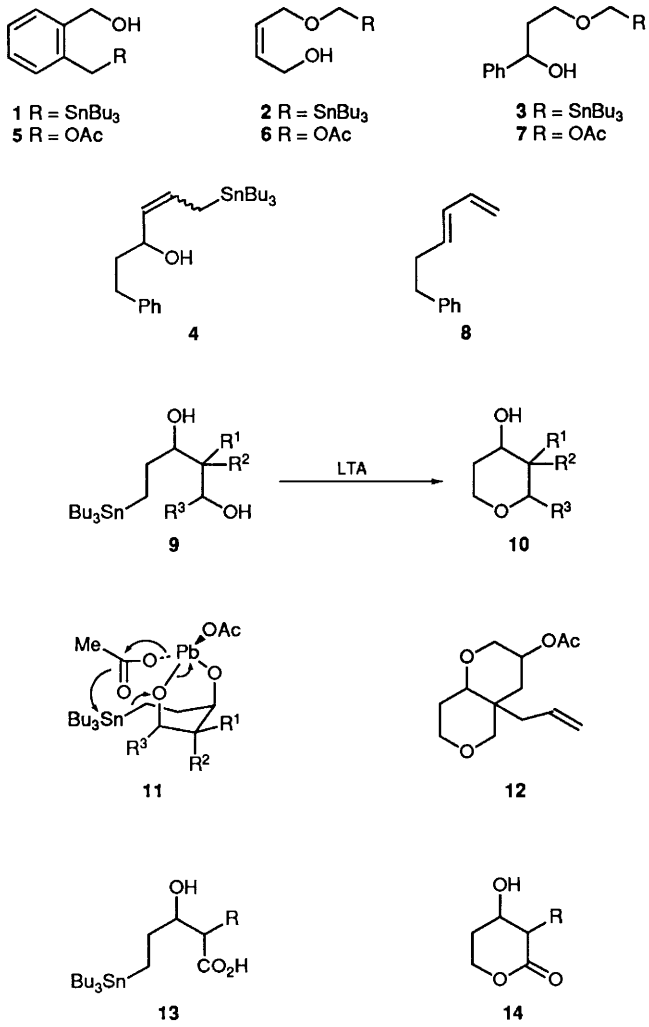
The oxidative cyclisation of 5-stannyl-1,3-pentanediol derivatives gave corresponding 4-hydroxytetrahydropyrans in excellent yields, and its applications to the synthesis of dioxabicyclodecane **12** and 4-hydroxy-δ-lactone **14** are also described.

It is well known that lead tetra-acetate (LTA) reacts with an alcohol and/or an alkene to give acetoxylated, oxidised or cyclised products.[1] Usually the reaction gives a complex mixture of products, which often renders these reactions of little synthetic value. However, from the detailed mechanistic studies of the reaction of LTA with an alcohol, it is generally accepted that an alkoxy–lead intermediate is formed in the first oxidation stage.[2,3]

However, we have previously reported that an alkoxymethyltin- or alkenyltin-group is readily oxidatively substituted to an oxygenated functionalized group by treating it with LTA.[4]

These results suggest that if a trialkyltin and a hydroxy group are located in a suitable position in the same molecule, regioselective LTA cyclisation will be possible.

We now report a novel regioselective cyclisation of 5-(tri-n-



Scheme 1

butyl)stannyl-1,3-pentanediol derivatives by LTA treatment.

Initially we selected monohydroxystannyl compounds such as **1**, **2**, **3** and **4**. These alcohols were treated with an equimolar amount of LTA in methylene chloride, benzene or acetic acid at room temperature for 40 h. But in each case only oxidative substitution products **5** (86%), **6** (68%), **7** (56%)† or an elimination product **8** (67%) were formed in good yields and none of the cyclised product was detected.

Secondly, we focused on 5-(tri-n-butyl)stannyl-1,3-pentanediol as a starting material. Treating the diol **9a** with an equimolar amount of LTA in benzene at room temperature for 2 h gave a cyclic product **10a** in 88% yield.‡ No four-membered cyclic ether nor an acetoxylated product was observed. The oxidation or the elimination of the 3-hydroxy group was not observed.

This cyclisation proceeded well when the molecule has a double or a triple bond (entry e, f and g), or bulky groups (entry a and d). Secondary alcohols (entry h and i) were also cyclised to the corresponding cyclic ethers in good yields (Table 1).

The mechanism of this cyclisation is not clear at the present stage, but from the above results we speculate that a plausible intermediate must be a dialkoxy–lead bridged one **11**.

This cyclisation was applied to the subsequent cyclisation from **9e** to **12** (45%)§, and to the lactonisation from **13** to **14** (92%).¶

A typical procedure for cyclisation is as follows. A mixture of **9a** (965 mg, 1.68 mmol) and LTA (785 mg of 95% assay, 1.68 mmol) in dry benzene (40 ml) was stirred at room temperature under nitrogen for 2 h. After quenching with saturated ammonium chloride solution (10 ml), the aqueous layer was removed and extracted further with chloroform. The combined organic layers were dried (anhydrous $MgSO_4$), concentrated and purified by silica gel column chromatography with n-hexane–ethyl acetate (4 : 1) as eluant to yield **10a** (88%, 418 mg).

Table 1 Formation of various 4-hydroxytetrahydropyrans **10**

Entry	R^1	R^2	R^3	Yield (%)[a] of **10**
a	Benzyl	Benzyl	H	88[b]
b	Benzyl	H	H	86
c	n-Hexyl	H	H	91
d	$-(CH_2)_4-$		H	88
e	Allyl	Allyl	H	83
f	Cinnamyl	H	H	86
g	Prop-2-ynyl	H	H	50
h	Benzyl	H	Me	86
i	H	H	Phenyl	82

[a] Isolated yields, based on the corresponding 5-stannyl-1,3-pentanediol **9**. [b] LTA (2.2 molar equiv.) was also used in this reaction. But the yield of **10a** was almost the same (89%) as the case of 1.0 molar equiv. of LTA.

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† In addition to **7**, 17% of a ketone ($PhCOCH_2CH_2OCH_2OAc$) was obtained.

‡ The structure of **10a** was proved from the following spectroscopic data: IR (CCl_4) 3600–3050 (broad) and 1120 cm^{-1}. ^1H NMR ($CDCl_3$) δ_H 7.32 (d, 4H), 7.25 (m, 4H), 7.07 (d, 2H), 3.96 (m, 1H), 3.71–3.66 (m, 1H), 3.64 (d, 1H), 3.26–3.20 (m, 1H), 3.22–3.19 (d, 1H), 2.89–2.86 (d, 1H), 2.72–2.69 (d, 1H), 2.21–2.18 (d, 1H), 2.06–1.98 (m, 1H), 1.68–1.64 (m, 1H) and 1.48–1.47 ppm (d, 1H). ^{13}C NMR ($CDCl_3$) δ_C 137.8 (s), 137.2 (s), 131.3 (d), 128.0 (d), 126.2 (d), 126.1 (d), 70.4 (d), 69.6 (d), 67.0 (t), 42.9 (d), 38.6 (t), 34.9 (t) and 31.2 ppm (t). High resolution mass spectrometry M^+: 282.3810, Calcd. M: 282.3816. All other new compounds showed satisfactory spectroscopic data.

§ Diol **9e** was treated with three equiv. of LTA at room temperature for 2 h, then heated to reflux in benzene for two days to give **12** (42%). In this one-pot synthesis, the product was mostly a 6-*endo*-tetrahedral-type cyclisation product **12**, together with a trace of the 5-*exo*-tetrahedral type (<5%).

¶ 5-Stannylpentanoic acid **13** was treated with an equimolar amount of LTA at room temperature for 5 min to give a lactone **14** in 92% yield.