A New Reaction for the Preparation of Acetylenic Alcohols from Lactones

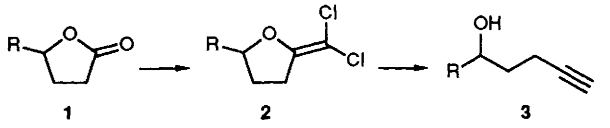
J. S. Yadav,* V. Prahlad and Madhavi C. Chander

Indian Institute of Chemical Technology, Hyderabad 500007, India

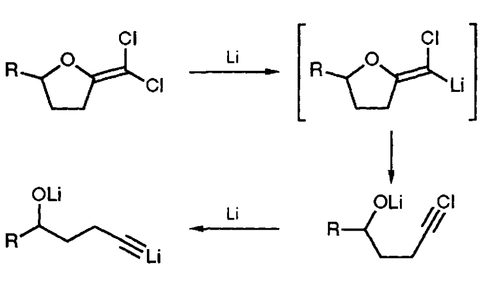
Acetylenic alcohols are synthesised for the first time from lactones; the transformation is effected *via* the corresponding dichloromethylene compound, which is converted into the acetylenic alcohol by reductive elimination.

In continuation of our studies to synthesise optically active polyfunctional acetylenic alcohols, which are very versatile intermediates in the synthesis of hydroxy fatty acids[1] of much agricultural interest, from allylic alcohols,[2] tartaric acid[3] and carbohydrates,[4] we now report a new two step conversion of lactones into acetylenic alcohols in excellent yields (Scheme 1).

The conversion of the parent lactone **1** into its corresponding dichloromethylene compound **2** was quite easily effected with the recently developed procedure of Lakhrissi and



Scheme 1



Scheme 2

Table 1 Preparation of acetylenic alcohols **3**

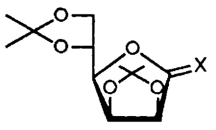
Entry	Dichloromethylene compound **2** ($[\alpha]_D$ in $CHCl_3$)	Acetylenic alcohol **3** ($[\alpha]_D$ in $CHCl_3$)	Reaction time/h	Yield[a] (%)
1	**2a** (+164.1, *c* 1.1)	**3a** (+16.7, *c* 1.4)	0.5	88
2	**2b** (+121.6, *c* 0.75)	**3b** (−23.8, *c* 0.9)	1.0	82
3	**2c** (+139.9, *c* 1.4)	**3c** (+18.3, *c* 1.25)	0.5	85
4	**2d** (−79.8, *c* 1.6)	**3d** (+16.4, *c*, 0.5)	3.0	87
5	**2e**	**3e**	0.5	82

[a] Isolated yield.

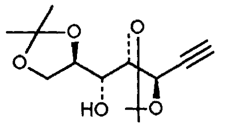
Chapleur[5] in good yields. The subject of the present communication, *i.e.* conversion of **2** into **3**, was accomplished by reductive elimination of the halo-compound **2** through metal (Li) insertion (Scheme 2).

The actual metal insertion and subsequent conversion into acetylenic alcohol was done by refluxing the dichloromethylene compound **2** in dry tetrahydrofuran (THF) with an excess (6 equiv.) of freshly prepared Li sand.† Several lactones **1a–e** were thus converted into acetylenic alcohols‡ **3a–e**. The results are summarised in Table 1.

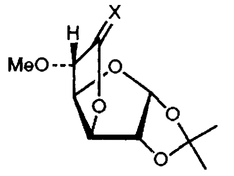
The easy availability of the parent lactones from the natural chiral pool such as carbohydrates and amino acids makes this



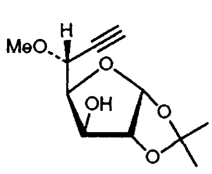
1a, 2a



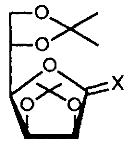
3a



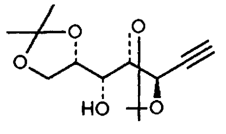
1b, 2b



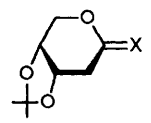
3b



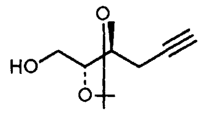
1c, 2c



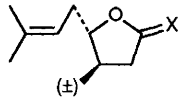
3c



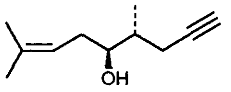
1d, 2d



3d



1e, 2e



(±)-3e

1; X = O
2; X = CCl_2

protocol a very useful synthetic tool in the preparation of versatile polyfunctional intermediates in the synthesis of natural products.

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† *Typical experimental procedure*: a freshly prepared Li sand (0.042 g, 6 mmol), suspended in THF (5 ml), was treated with **2a** (0.325 g, 1 mmol) dissolved in THF (3 ml) at room temp. under N_2 atmosphere. The reaction mixture was then refluxed for 0.5 h and brought back to room temp., quenched with a little MeOH followed by aq. NH_4Cl and extracted with diethyl ether; purification by silica gel column chromatography afforded **3a** (0.226 g, 88%).

‡ All the new compounds gave satisfactory spectral data including high resolution mass.