



Regiospecific reduction of oxetanes with lithium under aprotic conditions

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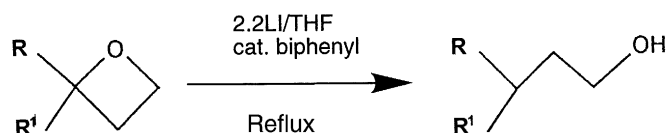
Received 27 August 1999; accepted 17 November 1999

Abstract

Substituted oxetanes have been found to give exclusively terminal alcohols by regiospecific ring-opening with lithium and biphenyl (cat.) in THF at reflux. © 2000 Elsevier Science Ltd. All rights reserved.

The synthetic applications of the cleavage of oxetane ring systems are well known. In this domain, the reductive ring-opening of oxetanes leading to alcohols has not been studied in detail. The preparation of alcohols by reducing oxetanes will be of great synthetic importance as different substituted alcohols can be prepared from the respective oxetanes. This has been accomplished by various reagents like LiAlH_4 ,^{1–3} AlH_3 ,^{2,3} Li-ethylenediamine,⁴ and $\text{H}_2/\text{Raney nickel}$.⁵ However, the cost of the reagents and the product ratio has limited the routine use of the above reagents.

While studying the action of lithium on different substituted oxetanes such as, aryl, arylalkyl, diaryl and dialkyl oxetanes, we have found that lithium in the presence of biphenyl (cat.) is capable of inducing the oxetanes to undergo regiospecific ring opening leading to the formation of terminal alcohols exclusively under aprotic conditions (Scheme 1).




Scheme 1. R, R¹-alkyl or aryl substituents

In a typical procedure, a mixture of oxetane, lithium metal and biphenyl (cat.) were heated in refluxing THF for a period of 30 min. The reaction was monitored by TLC. After workup and purification on a silica gel column, different alcohols were obtained and the results are listed in Table 1.

The reactions are general, reasonably fast, high yielding and free from side products. As oxetanes can be readily obtained from carbonyl compounds,⁶ they can be used as important intermediates in the preparation of terminal alcohols by extending the chain by two carbons.

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Table 1
Reduction of substituted oxetanes with lithium in THF

Entry	Substrate	Time (hr)	Product	Yield (%)	B.P. (°C/torr)
1	2-phenyloxetane	0.25	3-phenylpropan-1-ol	100	178/45
2	2-methyl-2 phenyloxetane	0.5	3-phenylbutan-1-ol	98	153-155/45
3	2,2-diphenyloxetane	0.5	3,3-diphenylpropan-1-ol	98	220/45
4		0.5	2-cyclohexylethan-1-ol	97	147-149/45

1. Experimental

The oxetanes were prepared from carbonyl compounds and identified from their PMR spectra.

Reduction of oxetanes. General procedure: 2-Phenyloxetane (10 mmol), lithium (2.2 g atom) and a catalytic amount of biphenyl were stirred in dry THF (15 ml) at reflux. After the completion of the reaction (15 min), water (5 ml) was added to the reaction mixture which was then extracted with ether (3×10ml) and dried over anhydrous sodium sulphate. After evaporation of the ether, the product was purified by silica gel chromatography to get 3-phenylpropan-1-ol.

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