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Efficient Transformation of α,β-Enone to Substituted Furans via Phosphoniosilylation

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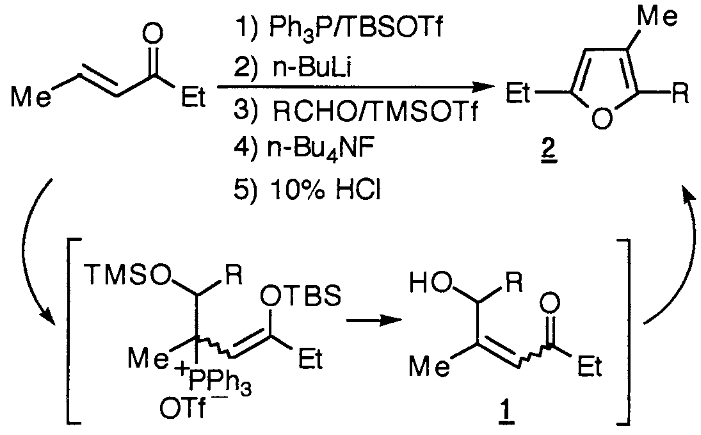
It was found that 2,3,5-trisubstituted furans were prepared from 4-hexen-3-one and various aldehydes via phosphoniosilylation.

Furans represent one of the most common of the five-membered oxygen-containing heterocyclic compounds and are found in a number of natural products.[1)] Therefore, a new method for preparing furan heterocycles is of particular interest of organic chemist.[2)] Especially, polysubstituted furans are the important key intermediate in organic synthesis. In this regard, we have recently described that furans were prepared from 1-alkenyl-1-methoxycyclopropane derivatives derived from the conjugate addition of 1-methoxy-2-alkenylidenephosphoranes to activated olefins.[3)] As an extension of this work, we have investigated a new route for synthesis of 2,3,5-trisubstituted furans to report herein an efficient conversion of α,β-enone to substituted furans via phosphoniosilylation.[4)] The present method is based on the Wittig reaction of ylides with aldehydes, quenching betaine intermediate with TMSOTf, and facile elimination of phosphonium salts via desilylation followed by cyclization of β-hydroxy-α,β-enones.



R	isolated yield/%	
	1	2
$CH_3CH=CH$	72	71
n-$C_6H_{13}CH=CH$	64	80
PhCH=CH	64	69
Ph	68	88
n-C_8H_{17}	34	80
c-C_6H_{11}	60	64

A typical procedure is as follows: 4-hexen-3-one(80.6 mg, 0.82 mmol) and TBSOTf(227.6 mg, 0.86 mmol) were added to a solution of triphenylphosphine(215.4 mg, 0.82 mmol) in THF(3 ml) at 0 °C. The reaction mixture was stirred for 30 min and cooled to -78 °C. After n-butyllithium(0.7 ml, 0.98 mmol) was added at -78 °C followed by stirred for 30 min, benzaldehyde(104.4 mg, 0.98 mmol) and TMSOTf(219 mg, 0.98 mmol) were added to the ylide separately. The reaction mixture was stirred at -78 °C for 1 h, treated with TBAF(2.24 ml, 2.46 mmol) and allowed to warm to room temperature over 1 h and the extractive work-up and chromatographic separation gave 5-(1-hydroxyphenyl)-4-hexen-3-one(113.4 mg, 68%). 10% HCl was added to a solution of 5-(1-hydroxyphenyl)-4-hexen-3-one(113.4 mg, 0.56 mmol) in THF(4 ml). The reaction mixture was stirred at r.t. for 5 h and the extractive work-up and chromatographic separation gave 5-ethyl-3-methyl-2-phenylfuran(91.1 mg, 88%).

In a similar manner, furans were prepared in good yield from 4-hexen-3-one and various aldehydes. In case of methyl vinyl ketone, when the ylide was treated to an equimolar amount of benzaldehyde, 4-benzoyl-2-butanone was produced in 30% yield. Although there have been reported a lot of methods for the preparation of furan derivatives, their preparations consist of multi-steps and starting materials are not easily available.$^{2)}$ The present method affords a procedure for the preparation of substituted furans because of brevity in procedure and of introduction of substituents at 2,3,5-position of furans. We consider the present method as very useful addition to previously known methods. Further investigations in the related area are now in progress. We gratefully acknowledge financial support from KOSEF and the Basic Science Research Institute Program, Ministry of Education.

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