Pergamon

Tetrahedron Letters 39 (1998) 8159–8162

TETRAHEDRON
LETTERS

Zirconium Sulfophenyl Phosphonate as a Heterogeneous Catalyst in Tetrahydropyranylation of Alcohols and Phenols.*

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Received 29 May 1998; accepted 28 August 1998

Abstract: Zirconium Sulfophenyl Phosphonate $Zr(O_3PCH_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}$ was found to be an efficient heterogeneous catalyst for the tetrahydropyranylation of alcohols and phenols.

Keywords: Alcohols, Phenols, Protecting group, Zirconium and compounds.

It is now well established that many acidic and basic solids act as catalysts or promoters in liquid phase organic synthesis.[1] There are many examples of better yields, shorter reaction times, and even higher selectivities achieved as the result of reactions carried out with heterogeneous catalysts under reaction conditions milder than those employed in conventional homogeneous synthetic methods. Heterogeneous catalysts are generally inorganic solids, clays and modified clays,[2] zeolites, metal oxides,[3] or organic polymers such as functionalized styrene-divinylbenzene resins.[4] We have recently found that inorgano-organic layered solids belonging to the emerging class of metal (IV) phosphonates[5,6] and bearing suitable functional groups, are excellent catalysts for organic synthesis, since they combine the properties of a stable inorganic backbone with the flexibility of the organic derivatives. Layered zirconium methane-sulfophenyl phosphonate,[7] bearing strongly acidic-$C_6H_4SO_3H$ groups anchored to the inorganic layers, has proved to be an excellent heterogeneous catalyst of acid-catalysed reactions (deprotection of nitrogen containing derivatives,[8] conversion of 1,3-dithiolanes and 1,3-dithianes to the corresponding carbonyl compound,[9] protection of alcohols as TMS-derivative[10]). It seemed of interest to test the catalyst for tetrahydropyranylation, an important

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* Dedicated to the memory of Prof. Paolo Ceccherelli.

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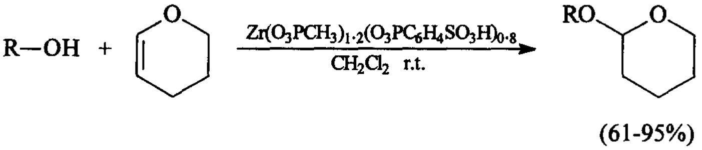
PII: S0040-4039(98)01817-6

procedure for protecting the hydroxyl function in organic synthesis due to the stability of the tetrahydropyranyl derivative in a variety of reactions such as Grignard addition, oxidation, reduction, alkylation and acylation. We have found that the inorgano-organic catalyst α-$Zr(O_3PC_6H_4SO_3H)_{0.8}(O_3PCH_3)_{1.2}$, is an excellent promoter of the tetrahydropyranylation of alcohols and phenols.



The reaction was carried out at room temperature by adding dihydro-2H-pyran to a mixture of alcohols (phenols) and the catalyst in dichloromethane. The reaction lasts from 1 h to 2.5 h and after simple work-up affords tetrahydropyranyl ethers in high yield (see Table).

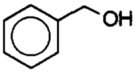
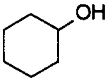
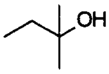
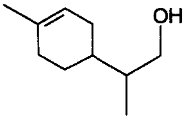
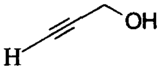
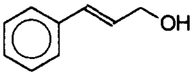
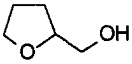
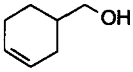
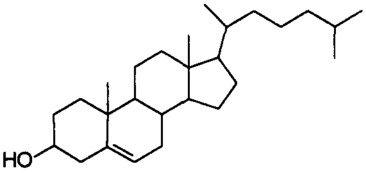
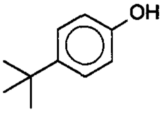
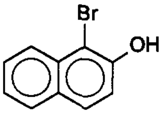
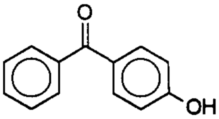
Primary, secondary, tertiary, benzylic, allylic and acetylenic alcohols as well as phenols can be protected as tetrahydropyranyl ethers under mild conditions. It is important to note that acid sensitive alcohols such as *t*-amyl alcohol undergo protection as tetrahydropyranyl ethers in 24 h (entry 3) without the formation of a dehydration product. Many homogeneous acid catalysts are available for the preparation of tetrahydropyranyl ethers using dihydro-4H-pyran as reagent and several heterogeneous catalysts such as K-10 clay,[11] H-Y Zeolite,[12] Alumina/$ZnCl_2$,[13] Envirocat EPZG®,[14] natural Kaolinic-clay[15] and Zeolite HSZ[16] have been used. However the procedure described in the present communication is effective or better than any procedure yet reported using a heterogeneous catalyst. The important features of this method are: mild reaction conditions, simple work-up and the recyclable nature of the catalyst, [17] the preparation of which does not require any particular skill.[18] Therefore the present catalytic method should be useful in synthetic organic chemistry.

Experimental.

In a typical experiment, a solution of dihydro-2H-pyran (0.5 g, 6 mmol) in dichloromethane (4 ml) was added dropwise to a stirred mixture of cyclohexanol (0.4 g, 4 mmol) and zirconium sulfophenyl phosphonate[18] (80 mg) in dichloromethane (2 ml) at room temperature. The progress of the reaction was monitored by GC-MS. Stirring was continued for 2 hours. The reaction mixture was then filtered and the residue washed with dichloromethane (10 ml). The organic layer was evaporated under reduced pressure and the residue, purified by flash chromatography (dichloromethane), gave the pure tetrahydropyranyl ether of cyclohexanol (0.64 g, 86%). The analytical and spectroscopic data of the product are identical to the data recorded in the literature.

Acknowledgement. This work was supported by M.U.R.S.T. "Progetto Chimica dei Composti Organici di Interesse Biologico" is gratefully acknowledged.

Tetrahydropyranylation of Alcohols and Phenols catalyzed by Zirconium Sulfophenyl Phosphonate.

Entry	Reagent[a]	Time (h)	Yield (%)[b, c]
1		1	94
2		2	86
3		24	70
4		1.5	87
5		0.5	95
6		0.5	88
7		1	90
8		1	90
9		1.5	95
10		1	87
11		2.5	61
12		1.5	92

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[a] All reactions were carried out at room temperature; [b] Yields of pure isolated product; [c] All tetrahydropyranyl derivatives were characterized by GC-MS and ^{1}H-NMR.

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[17] The catalyst, washed with dichloromethane and dried at 160°C, can be reused for several experiments.

[18] For the preparation and charaterisation of the catalyst see ref. 8 and 9.