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Tetrahedron Letters 45 (2004) 2421–2423
Tetrahedron Letters

$Pd/CaCO_3$ in liquid poly(ethylene glycol) (PEG): an easy and efficient recycle system for partial reduction of alkynes to *cis*-olefins under a hydrogen atmosphere ☆

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Received 3 November 2003; revised 7 January 2004; accepted 16 January 2004

Abstract—Lindlar's catalyst ($Pd/CaCO_3$) in PEG (400) has been found to be the most reusable reaction medium for selective reduction of alkynes to *cis*-olefins. The catalyst and PEG were recycled five times without loss of activity.

'Pollution control' demands are a source of inspiration to design and develop new catalysts and solvent media for achieving high efficiency. Towards this goal, many catalytic systems have been invented and demonstrated. More recently, attention has been drawn to the development of environmentally benign solvents viz., room temperature ionic liquids (RTILs),[1] $scCO_2$[2] poly(ethylene glycol),[3] and water[4] are a few of the new additions. It is customary to measure the efficiency of a catalyst by the number of cycles for which it can be reused (turn over number). Similarly, the value of a new solvent medium primarily depends on its environmental impact, the ease with which it can be disposed and the number of times the solvent can be recycled. Secondary issues concern a low vapor pressure, nonflammability, and high polarity for solubilization. RTILs are one of the recent additions, which meet several of the above requirements. However the high cost[5] and unproven disposal issues limit their use in industry.

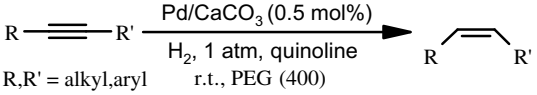
The most ideal synthetic methodology could be defined as a system wherein 100% atom economy is preserved,[6] the solvent is recycled to the fullest extent and the catalyst remains throughout in the solvent medium and without losing activity for several runs.

Many researchers worldwide have striven to achieve this ideal situation. We conceived a protocol keeping in mind all these facts. Catalytic partial hydrogenation of acetylenes to olefins with $Pd/CaCO_3$ is a perfect 'atom economy' transformation. If one could develop a solvent, which can prevent the catalyst from losing its activity while allowing one to recycle the catalyst and solvent, the whole operation would become very practical.

Poly(ethylene glycol) (PEG),[7] a biologically acceptable polymer used extensively in drug delivery and in bioconjugates as tools for diagnostics, has hitherto not been widely used as a solvent medium but has been used as a support for various transformations.[8]

We have recently demonstrated that PEG is a useful solvent medium for asymmetric dihydroxylation,[9] and $Pd(OAc)_2$ catalyzed Heck reactions.[10] Herein, we disclose a practical protocol for partial reduction of triple bonds to *cis*-olefins using Lindlar's catalyst[11] in PEG (400 Dal), (Scheme 1). The PEG and the catalyst can be recycled in all the cases studied (3–5 times) without loss in activity or yields.

In the first instance 2 g of PEG (400), 3-octyn-1-ol (630 mg, 5 mmol), 5% $Pd/CaCO_3$ (54 mg, 0.5 mol%), and



Scheme 1.

Keywords: Hydrogenation; Lindlar's catalyst; PEG; Recycling.
☆ IICT Communication No. 030701.
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0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.01.097

Figure 1. During the reaction.

Figure 2. After addition of diethyl ether.

two drops of quinoline were stirred under hydrogen for 5 h. Anhydrous ether (10 mL) was added, the mixture stirred for 5 min and the reaction allowed to settle for 10 min. Cooling in an acetone-dry ice bath caused solidification of the PEG with the catalyst entrapped in this solid. This technique allowed us to decant the ether layer without loss of PEG or catalyst. The sequence was repeated twice with 10 mL portions of ether to extract the product. The residual PEG catalyst complex was brought to room temperature for liquefacation. This

Figure 3. After decantation.

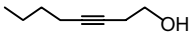
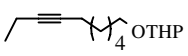
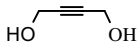
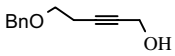
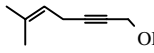
mixture was utilized in further runs by an addition of 3-octyn-1-ol (630 mg) and two drops of quinoline (catalyst poison) then exposure to hydrogen. To our pleasant surprise even after four runs consistent partial reduction with ~90% yield of products was achieved (Figs. 1–3).

To generalize the process a few other substrates were subjected to this protocol (Table 1). In all the cases studied, even after a fourth run, the quantity of catalyst and PEG was altered only to a minimal extent. Under the above mentioned conditions a hydrogenation sensitive benzyloxy group (entry 5) and an olefin (entry 6) survived.

To further substantiate our claims, a cross-over experiment was performed. After five consecutive runs of partial reduction of diphenylacetylene to *cis*-stilbene, a new substrate, 3-octyn-1-ol, was added and subjected to hydrogenation without changing the catalyst and PEG. After 5 h the corresponding reduced product (3*Z*)-octen-1-ol was obtained in over 85% yield without contamination by *cis*-stilbene. This demonstrates that the extraction of products is complete and that the reaction medium can be reused for different substrates.

The efficiency of the sequence can be attributed to the high solubility of hydrogen in PEG compared to con-

Table 1. Recycling of $Pd/CaCO_3$ catalyzed partial reduction of alkynes to *cis*-olefins in PEG

Entry	Alkyne	1st (t/y)[a,b]	2nd (t/y)[a,b]	3rd (t/y)[a,b]	4th (t/y)[a,b]	5th (t/y)[a,b]
1	Ph—≡—Ph	1/97	1/97	1/95	1/91	1/90
2		2/96	2/94	2/94	3/90	3/90
3		3/92	3/92	3/90	4/89	4/90
4		2/98	2/98	2/95	3/94	3/91
5		1/91	1/90	1/89	N.D[c]	N.D[c]
6		4/89	4/87	4/8	5/80	5/80

[a] Isolated yields of products after column chromatography.
[b] t = time in hours, y = yield in %.
[c] Not done.

ventionally used solvents,[12] and efficient retention of the catalyst by the PEG during extraction of products with ether due to solidification.

Overall, the goal of the study has been to evaluate PEG as an inexpensive, nonvolatile, nonpyrophoric, eco-friendly, and 'the appropriate' solvent for catalyzed reductions. Other catalyzed reduction reactions are presently being explored.

Acknowledgements

Ch.N., G.C.S., and T.S.S. thank CSIR, New Delhi, India for financial support.

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