SYNLETT
Spotlight 461

Glycerol

Compiled by Bin Yu

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Bin Yu was born in 1986 in Henan province, P. R. of China. He graduated from Zhengzhou University in 2012, obtaining a M.Sc. degree in pharmaceutical engineering. He is currently pursuing his Ph.D., majoring in medicinal chemistry under the supervision of Prof. Hong-Min Liu and Prof. De-Quan Yu at the same university. His research focuses on the discovery of novel small molecules with important properties using modern synthetic strategies.

Department of Medicinal Chemistry, School of Pharmaceutical Sciences, Zhengzhou University, Zhengzhou 450001, Henan, P. R. of China
E-mail: zzuyubin@hotmail.com

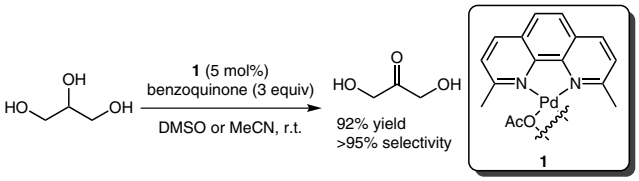
Introduction

Glycerol, a colorless and odorless liquid, is readily available as an inevitable by-product in the process of biodiesel production by transesterification of vegetable oils and can also be potentially obtained from more sustainable sources such as microalgae or cellulose.[1] It is widely used in pharmaceutical formulations because of its low price, low toxicity, and special physicochemical properties, including water solubility and hygroscopicity.[2]

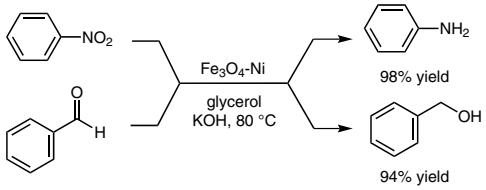
Glycerol and some of its derivatives are already used in the chemical industry as precursors to produce various more valuable products such as hydroxyacetone,[3] acrolein,[4] lactic acid,[5] and 1, 3-propanediol.[6] Besides, glycerol is also widely used in organic synthesis because it dissolves inorganic salts, acids, bases, many transition-metal complexes, and enzymes.[7] It is also used in other fields, such as protein crystallization,[8] cosmetics, pharmaceutical formulations, and foodstuffs.[9]

Abstracts

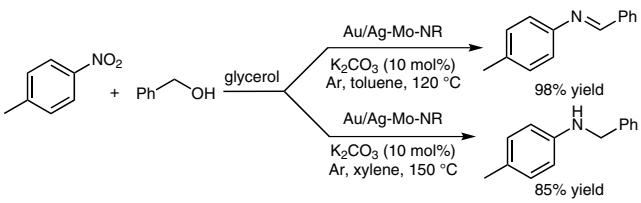
(A) Dihydroxyacetone was selectively obtained from cationic palladium catalyzed glycerol oxidation using benzoquinone or oxygen as the terminal oxidant. This protocol is especially suitable for substrates containing vicinal diol groups. The mechanism involves reversible palladium alkoxide formation with the oxidation of palladium as the turnover-limiting step.[10]



(B) A regio- and chemoselective reduction of nitroarenes and carbonyl compounds over recyclable magnetic ferrite nickel nanoparticles (Fe_3O_4-Ni) was achieved by using glycerol as the hydrogen source. The catalyst was reused eight times without any significant loss in catalytic activity and selectivity.[11]

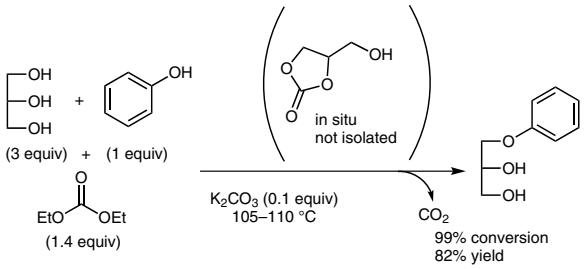


(C) Shi and co-workers used glycerol as the hydrogen source in a Au/Ag-Mo-nanorods catalyzed tandem reaction of alcohols and nitrobenzenes, which generated *N*-alkyl amines and imines. The reaction involved reduction of nitrobenzene, amine–aldehyde coupling, and imine reduction.[12]

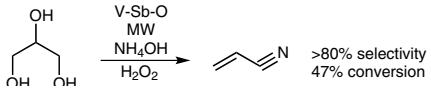


SYNLETT 2014, 25, 0601–0602
Advanced online publication: 08.01.2014
DOI: 10.1055/s-0033-1340636; Art ID: ST-2013-V0468-V

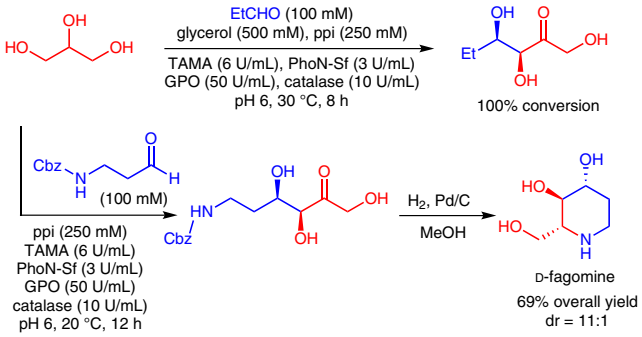
(D) Aryloxypropanediols with pharmacological properties (for example guaifenesin) are widely found in nature and are also important intermediates for the synthesis of other drugs such as methocarbamol or chlorphenesin carbamate. Glycerol was selectively converted into aryloxypropanediols under solvent-free conditions in a one-pot reaction through in situ formed glycerol carbonate.[13]



(E) Glycerol was converted into acrylonitrile in a solvent-free microwave-activated process using an alumina-supported V-Sb-O catalyst. The mild reaction conditions reported required only a short reaction time, making it a highly efficient new process for the valorization of glycerol.[14]



(F) Wever and co-workers reported a one-pot four-enzyme cascade reaction for the synthesis of enantio- and diastereomerically pure carbohydrate analogues from glycerol and a variety of aldehydes without protection–deprotection steps. This protocol was successfully applied to the total synthesis of the naturally occurring azasugar D-fagomine.[15]



References

(1) Wang, S.; Zhang, Y.; Liu, A. C. *Chem. Asian J.* **2010**, *5*, 1100.
(2) Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. *Green Chem.* **2008**, *10*, 13.
(3) Hu, W. B.; Knight, D.; Lowry, B.; Varma, A. *Ind. Eng. Chem. Res.* **2010**, *49*, 10876.
(4) Katryniok, B.; Paul, E.; Baca, V. B.; Rey, P.; Dumeignil, F. *Green Chem.* **2010**, *12*, 2079.
(5) Roy, D.; Subramaniam, B.; Chaudhari, R. V. *ACS Catal.* **2011**, *1*, 548.
(6) Dam, J. T.; Kristina, D.; Freek, K.; Hanefeld, U. *ChemCatChem* **2013**, *5*, 497.
(7) Safaei, H. R.; Shekouhy, M.; Rahmanpur, S.; Shirinfeshan, A. *Green Chem.* **2012**, *14*, 1696.
(8) Vera, L.; Czarny, B.; Georgiadis, D.; Dive, V.; Stura, E. A. *Cryst. Growth Des.* **2011**, *11*, 2755.
(9) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Pina, C. D. *Angew. Chem. Int. Ed.* **2007**, *46*, 4434.
(10) Painter, R. M.; Pearson, D. M.; Waymouth, R. M. *Angew. Chem. Int. Ed.* **2010**, *49*, 9456.
(11) Gawande, M. B.; Rathi, A. K.; Branco, P. S.; Nogueira, I. D.; Velhinho, A.; Shrikhande, J. J.; Indulkar, U. U.; Jayaram, R. V.; Ghumman, C. A. A.; Bundaleski, N.; Teodoro, O. M. N. D. *Chem. Eur. J.* **2012**, *18*, 12628.
(12) Cui, X. J.; Zhang, C. M.; Shi, F.; Deng, Y. Q. *Chem. Commun.* **2012**, *48*, 9391.
(13) Truscello, A. M.; Gambarotti, C.; Lauria, M.; Auricchio, S.; Leonardi, G.; Shisodia, S. U.; Citterio, A. *Green Chem.* **2013**, *15*, 625.
(14) Casilda, V. C.; Perez, O. G.; Bañares, M. A. *Green Chem.* **2009**, *11*, 939.
(15) Babich, L.; Hemert, L. J. C. V.; Bury, A.; Hartog, A. F.; Falcicchio, P.; Oost, J. V. D.; Herk, T. V.; Wever, R.; Rutjes, F. P. J. T. *Green Chem.* **2011**, *13*, 2895.