Synlett S. Jarzyński Spotlight

Triethoxysilane

Szymon Jarzyński

Department of Organic and Applied Chemistry, Faculty of Chemistry, University of Łódź, Tamka 12, 91-403 Łódź, Poland
szymonjarzynski@wp.pl

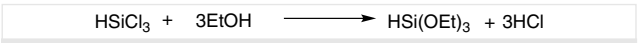
Published online: 12.03.2015
DOI: 10.1055/s-0034-1380459; Art ID: st-2014-v0512-v

Szymon Jarzyński was born in Zduńska Wola, Poland, in 1988. He obtained his B.Sc. (2010) and M.Sc. (2012) in organic chemistry and synthesis at the University of Łódź, Poland. Currently, he is working towards his Ph.D. in the Department of Organic and Applied Chemistry at the same university under the supervision of Professor Dr. Stanisław Leśniak. His work focuses on new enantiomerically pure heterocyclic ligands for asymmetric synthesis.

Introduction

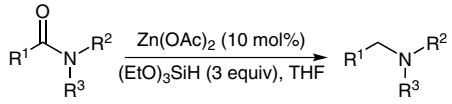
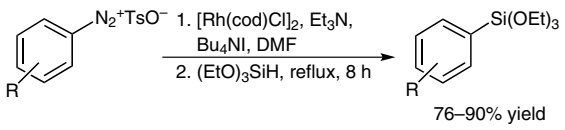
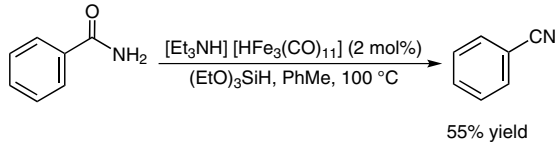
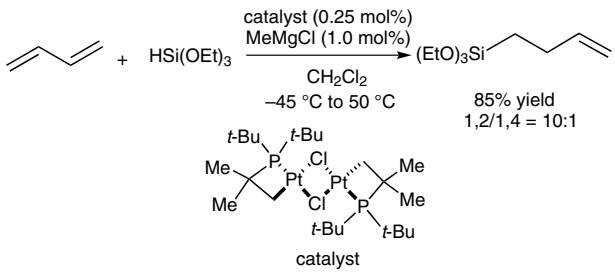
Triethoxysilane (TES) is an important chemical reagent in the synthesis of various organosilicon compounds. It is a colourless transparent liquid (bp 134–135 °C) with a characteristic ether odour. Triethoxysilane is an organosilane and has been widely used in organic synthesis as a mild reducing agent. It has been used for asymmetric hydrosilylation of ketones in order to obtain the corresponding alcohols.[1] Additionally, $(EtO)_3SiH$ is applied as silylation reagent in regio- and stereoselective hydrosilylations.[2] It is able to cleave a C–C bond of the four-membered ring of biphenylene forming the corresponding 2-silylbiphenyls.[3] TES is also used in reductive etherification of aldehydes in the presence of the catalyst system $InCl_3$/TMSCl.[4]

Triethoxysilane is commercially available but it can also easily be synthesized in the reaction of trichlorosilane with anhydrous ethyl alcohol (Scheme 1).[5]



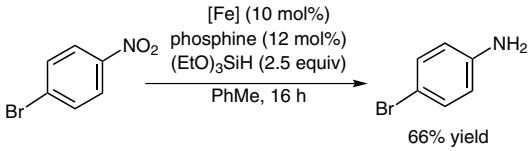
Scheme 1

Table 1 Use of Triethoxysilane

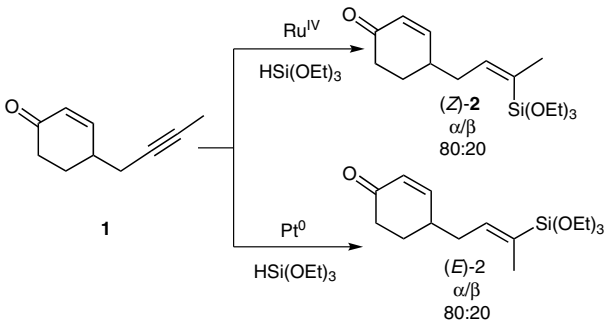
(A) Beller and co-workers described a procedure for efficient reduction of tertiary amides. The reaction was carried out in the presence of inexpensive zinc catalyst with $(EtO)_3SiH$ under mild conditions.[6] Diverse functional groups present in the molecule (ester, ether, nitro, cyano, azo) are tolerated. The desired products were isolated in good to high yields.	
(B) An efficient rhodium(I)-catalyzed reaction between arenediazonium tosylate salts and triethoxysilane led to aryltriethoxysilanes in good to high yields.[7] The synthesis was carried out in the presence of Bu_4NI and Et_3N.	
(C) The preparation of various nitriles from primary carboxylic amides can be realized by iron-catalyzed $[Et_3NH, HFe_3(CO)_{11}]$ dehydration with triethoxysilane as dehydrating agents. The experiment was carried out using toluene as a solvent in 100 °C.[8]	
(D) Ritter and co-workers reported a selective 1,2-hydrosilylation of conjugated dienes using triethoxysilane in the presence of catalytic amounts of platinum precatalyst. The catalyst was activated with methylmagnesium chloride (MeMgCl) at –45 °C, then $(EtO)_3SiH$ and diene were added. The mixture was heated to 50 °C. The product was formed with high selectivity.[9]	

Dieses Dokument wurde zum persönlichen Gebrauch heruntergeladen. Vervielfältigung nur mit Zustimmung des Verlages.

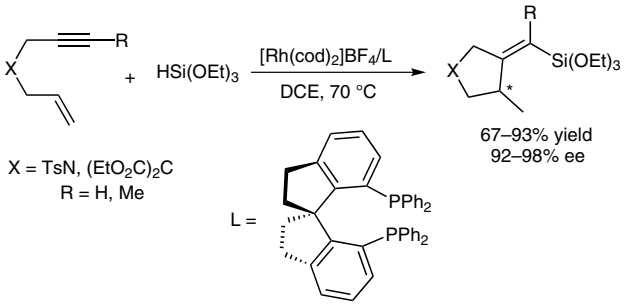
(E) Organosilanes are convenient reagents in the selective reduction of nitroarenes. The corresponding aniline was formed with $(EtO)_3SiH$ in the presence of a catalyst consisting of $FeBr_2$ and Ph_3P. The desired product was isolated in good yield (66%).[10]



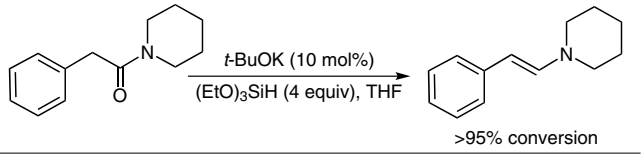
(F) Riand and co-workers described the stereodivergent synthesis of polysubstituted enynes, which are useful building blocks. Vinylsiloxanes (*Z*)-**2** and (*E*)-**2** were obtained in high yields with an α/β selectivity of 80:20. These products were then converted into trisubstituted enynes, which were isolated with full retention of the stereochemistry.[11]



(G) The asymmetric silylcyclization of 1,6-enynes with $(EtO)_3SiH$ was carried out in the presence of a rhodium catalyst generated in situ.[12] It was observed that these reactions provide optically active silylalkylidene cyclopentane and pyrrolidine derivatives. These products were formed in good yields and with high enantioselectivities.



(H) $(EtO)_3SiH$ can be applied as a mild reducing agent for catalytic reductive dehydration of tertiary amide to the corresponding enamine catalyzed by potassium *tert*-butoxide (*t*-BuOK).[13] The reaction leading to the enamine proceeded with high conversion ratio.



References

(1) Liu, S.; Peng, J.; Yang, H.; Bai, Y.; Li, J.; Lai, G. *Tetrahedron* **2012**, *68*, 1371.
(2) Ding, S.; Song, L.; Chung, L. W.; Zhang, X.; Sun, J.; Wu, Y. *J. Am. Chem. Soc.* **2013**, *135*, 13835.
(3) Matsuda, T.; Kirikae, H. *Organometallics* **2011**, *30*, 3923.
(4) Yang, M.; Xu, L.; Qiu, H.; Lai, G.; Jiang, J. *Tetrahedron Lett.* **2008**, *49*, 253.
(5) Friedel, C.; Ladenburg, A. *Justus Liebigs Ann. Chem.* **1867**, *143*, 118.
(6) Das, S.; Addis, D.; Zhou, S.; Junge, K.; Beller, M. *J. Am. Chem. Soc.* **2010**, *132*, 1770.
(7) Tang, Z. Y.; Zhang, Y.; Wang, T.; Wang, W. *Synlett* **2010**, *5*, 804.
(8) Zhou, S.; Addis, D.; Das, S.; Junge, K.; Beller, M. *Chem. Commun.* **2009**, *32*, 4883.
(9) Parker, S. E.; Börgel, J.; Ritter, T. *J. Am. Chem. Soc.* **2014**, *136*, 4857.
(10) Junge, K.; Wendt, B.; Shaikh, N.; Beller, M. *Chem. Commun.* **2010**, *46*, 1769.
(11) Cornelissen, L.; Lefrancq, M.; Riant, O. *Org. Lett.* **2014**, *16*, 3024.
(12) Fan, B.; Xie, J.; Li, S.; Wang, L.; Zhou, Q. *Angew. Chem. Int. Ed.* **2007**, *46*, 1275.
(13) Volkov, A.; Tinnis, F.; Adolfsson, H. *Org. Lett.* **2014**, *16*, 680.

Dieses Dokument wurde zum persönlichen Gebrauch heruntergeladen. Vervielfältigung nur mit Zustimmung des Verlages.