SYNLETT

Spotlight 101

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

Hydrazine Hydrate ($NH_2NH_2 \cdot H_2O$)

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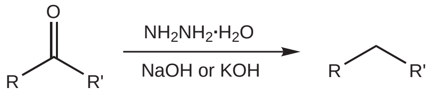
Dedicated to Dr. R. C. Malhotra on the occasion of his 58th birthday.

Introduction

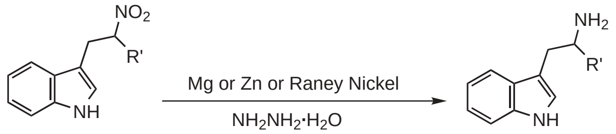
The synthetic utilities of hydrazine hydrate have been extensively investigated in organic chemistry. Among reducing agents, hydrazine hydrate stands out for its application to a broad variety of reductive transformations. It is easy to use and reduces many functional groups, such as carbonyl compounds, alkenes, alkynes and nitro groups under mild reaction conditions. Hydrazine hydrate is commercially available. It is a liquid (mp –52 °C, bp 120–121 °C, d = 1.027 g/mL), and is soluble in water, ethanol, methanol, propanol and isobutanol.

Abstracts

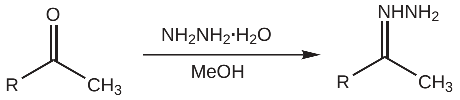
(A) Hydrazine hydrate is used in the reduction of carbonyl compounds to their corresponding methylene group via the Wolf–Kishner reduction[1] and the Huang-Minlon modification.[2]



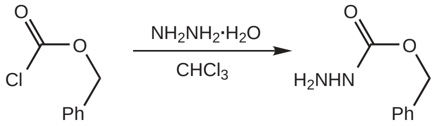
(B) Hydrazine hydrate is often used as the hydrogen donor for the transfer reduction of many organic compounds. It is used in combination with many different catalysts, including Raney Nickel,[3] platinum,[4] ruthenium,[5] palladium on carbon, iron(III) oxide, graphite, and iron(III) chloride with activated carbon. Recently, hydrazine hydrate was used with zinc[6] and magnesium[7] as a low-cost and selective reducing agent for nitro compounds to amines.



(C) A very useful reagent for simple hydrazone synthesis, hydrazine hydrate reacts with carbonyl groups.[8,9] Hydrazones are useful synthetic intermediates and have been converted to vinyl iodides[10] and vinyl selenides.[11]



(D) Carbazates are obtained simply by reacting alkyl or aryl chloroformates with hydrazine hydrate, or with alkyl or aryl hydrazine derivatives.[12]



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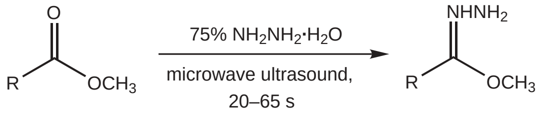
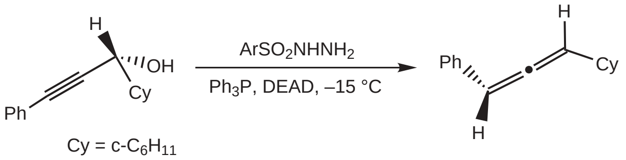
(E) The most widely used method to prepare hydrazides is hydrazinolysis of the corresponding esters with hydrazine monohydrate.[13] Recently, Toda et al. reported the use of hydroquinone and hydrazine as an alternative to hydrazine monohydrate in the solid state hydrazinolysis of esters.[14] Peng and Song reported the hydrazinolysis of esters under simultaneous microwave and ultrasound irradiation.[15]



(F) An extended application of hydrazine hydrate is in the preparation of *o*-nitrobenzenesulfonylhydrazide (NBSH). This reagent has been shown to be valuable in the synthesis of allenes from propargylic alcohols,[16] and for the reductive transposition of allylic alcohols.[17]



References

(1) (a) Todd, D. *Org. React.* **1948**, *4*, 378. (b) Szmant, H. H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 120. (c) Reusch, W. *Reduction*; Dekker: New York, **1968**, 171–185. (d) Clark, C. *Hydrazine*; Mathieson Chemical Corp.: Baltimore, **1953**.

(2) (a) Huang-Minlon, *J. Am. Chem. Soc.* **1946**, *68*, 2487. (b) Huang-Minlon, *J. Am. Chem. Soc.* **1949**, *71*, 3301. (c) Durham, L. J.; Mcleod, D. J.; Cason, J. *Org. Synth. Coll. Vol. IV* **1963**, 510. (d) Hunig, S.; Lucke, E.; Brenningesr, W. *Org. Synth.* **1963**, *43*, 34.

(3) (a) Furst, A.; Berlo, R. C.; Hooton, S. *Chem. Rev.* **1965**, *65*, 51. (b) Ayynger, N. R.; Lugade, A. C.; Nikrad, P. V.; Sharma, V. K. *Synthesis* **1981**, 640.

(4) (a) Pietra, S. *Ann. Chim. (Rome)* **1955**, *45*, 850. (b) Rondestvedt Jr., C. S.; Johnson, T. A. *Chem. Eng. News* **1977**, *55* (27), 38. (c) Bavin, P. M. G. *Org. Synth.* **1960**, *40*, 5.

(5) Weiser, H. B.; Milligan, W. O.; Cook, E. L. *Inorg. Synth.* **1946**, 215.

(6) Gowda, S.; Gowda, D. C. *Indian J. Chem., Sect. B* **2003**, *42*, 180.

(7) Srinivasa, G. R.; Abiraj, K.; Gowda, D. C. *Indian J. Chem., Sect. B* **2003**, *42*, 2885.

(8) Schonberg, A.; Fateen, A. E. K.; Sammour, A. E. M. A. *J. Am. Chem. Soc.* **1957**, *79*, 6020.

(9) Baltzly, R.; Mehta, N. B.; Russell, P. B.; Brooks, R. E.; Grivsky, E. M.; Steinberg, A. M. *J. Org. Chem.* **1961**, *26*, 3669.

(10) Barton, D. H. R.; Basiardes, G.; Fourrey, J.-L. *Tetrahedron Lett.* **1983**, *24*, 1605.

(11) Barton, D. H. R.; Basiardes, G.; Fourrey, J.-L. *Tetrahedron Lett.* **1984**, *25*, 1287.

(12) (a) Dupont, V.; Lecoq, A.; Mangeot, J. P.; Aubry, A.; Boussard, G.; Marraud, M. *J. Am. Chem. Soc.* **1993**, *115*, 8898. (b) Allcock, S. J.; Gilchrist, T. L.; Shuttleworth, S. J.; King, F. D. *Tetrahedron* **1991**, *47*, 10053.

(13) (a) Yale, H. L.; Losee, K.; Martins, J.; Holsing, M.; Perry, F. M.; Bernstein, J. *J. Am. Chem. Soc.* **1953**, *75*, 1933. (b) Bruice, T. C.; Benkovic, S. J. *J. Am. Chem. Soc.* **1964**, *86*, 418.

(14) Toda, F.; Hyoda, S.; Okada, K.; Hirotsu, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1531.

(15) Peng, Y.; Song, G. *Green Chem.* **2001**, *3*, 302.

(16) Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492.

(17) Myers, A. G.; Zheng, B. *Tetrahedron Lett.* **1996**, *37*, 4841.