SYNLETT Spotlight 184

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

β-Cyclodextrin as Supramolecular Catalyst in Organic Synthesis

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Dedicated to my mother Kalwatibai Bhosale for her constant encouragement.



Introduction

By the end of the 1960s, the methods for the laboratoryscale preparation of cyclodextrins, their structure, physical and chemical properties had been discovered. Literature survey reveals that cyclodextrins are very interesting, promising molecules in supramolecular chemistry as well as for their industrial importance. In recent years cyclodextrins have been used as catalysts in organic reactions. In this spotlight the use of cyclodextrin in organic reactions as a supramolecular catalyst is highlighted.

Cyclodextrins (CDs) are cyclic oligomers of D-glucose and are named α -, β - and γ -CD for hexamer, heptamer and octamer, respectively. They have a toroidal cyclic structure with secondary hydroxyl glucose C-2 and C-3 on their more open face and the primary C-6 hydroxyl on the opposite secondary face. Their ability to bind organic molecules in the hydrophobic central cavity has provided a basis for the construction of receptor models. It is widely accepted that the binding forces involved in the inclusion-complex formation are van der Waals interactions, hydrophobic interactions, hydrogen bonding and electrostatic interactions between charged parts of guest molecule and CDs. 4

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Abstracts

(A) Oxiranes react smoothly with thiourea in the presence of β -cyclodextrin in water at room temperature under neutral conditions to afford the corresponding thiiranes in excellent yields and β -cyclodextrin was recycled.⁵

thiourea, r.t.

$$n = 0, 1$$
 β -CD, H_2O
thiourea, r.t.

 R

β-CD, H₂O

R = aryl, aryloxy, hexyl $R^1 = H, CH_2OH, CH_2OTBDMS$

(B) A facile, substrate-selective and transition-metal-free oxidation of benzylic and allylic alcohols catalyzed by β -cyclodextrin with NaOCl oxidant using water as only solvent was developed.

R OH
$$\frac{\beta\text{-cyclodextrin}}{\text{NaOCl, H}_2\text{O, 50 °C}}$$
 R O

(C) Recently, the bridged keto cyclodextrins were used for oxidation of alcohols to aldehydes in the presence of hydrogen peroxide in aqueous media at room temperature.⁷

(D) Mononitroarenes are reduced to azooxyarenes by NaOH in water in the presence of $\beta\text{-cyclodextrin}$. HO $^-$ acts as a one-electron reductant with enhanced reactivity. 8

(E) The one-pot synthesis of terephthalic acid from benzene has been achieved by treatment with tetrachloromethane, copper powder, and an aqueous sodium hydroxide solution using cyclodextrin as a catalyst at 30 °C under nitrogen with 100% selectivity.⁹

(F) The hydrolysis of tetrahydropyranyl ethers to alcohols catalysed by β -cyclodextrin proceeds in water under neutral conditions. ¹⁰

$$R-O$$
 $\xrightarrow{\beta\text{-CD}}$ $R-OH$

References

- Szejtli, J. Cyclodextrin Technology; Kluwer Academic Publishers: Dordrecht, 1988.
- (2) Cao, Y.; Xiao, X.; Lu, R.; Guo, Q. J. Mol. Struct. 2003, 660,
- (3) Li, S.; Purdy, W. C. Chem. Rev. 1992, 92, 1457.
- (4) Szeitli, J. Chem. Rev. 1998, 98, 1743.
- (5) Surendra, K.; Krishnaveni, N. S.; Rao, K. R. Tetrahedron Lett. 2004, 45, 6523.
- (6) Ji, H.-B.; Shi, D.-P.; Shao, M.; Li, Z.; Wang, L.-F. Tetrahedron Lett. 2005, 46, 2517.

- (7) Marinescu, L. G.; Bols, M. Angew. Chem. Int. Ed. 2006, 45, 4590
- (8) Harper, J. B.; Easton, C. J.; Stephen, S. F. *Tetrahedron Letters* 2003, 44, 5815.
- Shiraishi, Y.; Tashiro, S.; Toshima, N. Chem. Lett. 2000, 828.
- (10) Reddy, M. A.; Reddy, L. R.; Bhanumathi, N.; Rao, K. R. New J. Chem. 2001, 25, 359.