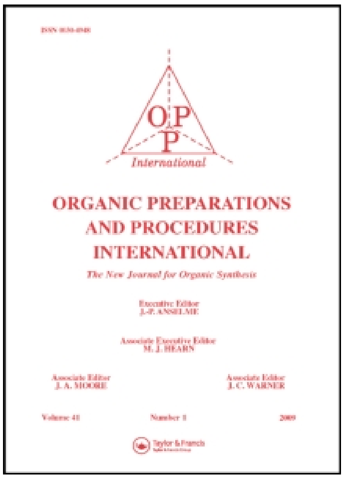


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A NOVEL AND EFFICIENT BIOMIMETIC HYDROLYSIS OF OXIRANES TO 1,2-DIOLS CATALYSED BY β-CYCLODEXTRIN IN WATER UNDER NEUTRAL CONDITIONS

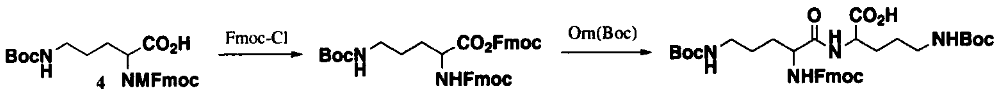
M. Anjun Reddy[a]; L. Rajender Reddy[a]; N. Bhanumathi[a]; K. Rama Rao[a]
[a] Organic Chemistry Division-1, Indian Institute of Chemical Technology, Hyderabad, India

To cite this Article Reddy, M. Anjun , Reddy, L. Rajender , Bhanumathi, N. and Rao, K. Rama(2002) 'A NOVEL AND EFFICIENT BIOMIMETIC HYDROLYSIS OF OXIRANES TO 1,2-DIOLS CATALYSED BY β-CYCLODEXTRIN IN WATER UNDER NEUTRAL CONDITIONS', Organic Preparations and Procedures International, 34: 5, 537 — 540

To link to this Article: DOI: 10.1080/00304940209355776

URL: http://dx.doi.org/10.1080/00304940209355776

remains unreacted Fmoc–Cl, it reacts with the main product Fmoc-Orn(Boc) (**4**) to give a reactive mixed anhydride, which in turn reacts with still unreacted Orn(Boc) to furnish dipeptide Fmoc-Orn(Boc)-Orn(Boc). This, after the Boc removal process, yields dipeptide Fmoc-Orn-Orn that cannot be removed from the final derivative, Fmoc-Orn (**7**) which remains as 2% contaminant.



29. L. Zervas, T. T. Otani, M. Winitz and J. P. Greenstein, *J. Am. Chem. Soc.*, **81**, 2878 (1959).

****

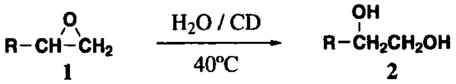
A NOVEL AND EFFICIENT BIOMIMETIC HYDROLYSIS OF OXIRANES TO 1,2-DIOLS CATALYSED BY β-CYCLODEXTRIN IN WATER UNDER NEUTRAL CONDITIONS[†]

Submitted by
(12/04/00)

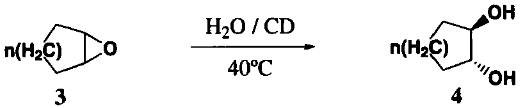
M. Anjun Reddy, L. Rajender Reddy, N. Bhanumathi and K. Rama Rao*

Organic Chemistry Division-1
Indian Institute of Chemical Technology
Hyderabad-500 007, INDIA

The 1,2-diol functionality has great significance in pharmaceutical and industrial chemistry[1] due to its utility in the synthesis of bacteriostatic[2] and antifogging agents,[3] β-blockers,[4] perfumes[5] and in the polymer industry.[6] However, the facile synthesis of these commercially important 1,2-diols consists of the ring opening of the easily accessible epoxides under acidic conditions at room temperature or at high temperatures under basic conditions.[7] Since these harsh experimental conditions involving either acid or base are not suitable for the epoxides bearing labile substituents, there is need to develop milder methods. Cyclodextrins (CDs) which are cyclic oligosaccharides, exert microenvironmental effect leading to selective reactions. They catalyze reactions by supramolecular catalysis through non-covalent bonding as in enzymes. These biomimetic reactions can be carried out efficiently in water.[8] This biomimetic approach of chemical reactions involving supramolecular catalysis has several advantages over chemical methodologies since these reactions can be carried out under mild and neutral conditions in water. Hence, in our effort to develop biomimetic approaches of chemical reactions involving cyclodextrins,[9] the synthesis of 1,2-diols from epoxides (derived from cyclic and terminal alkenes) catalyzed by cyclodextrins (α and β) in water under neutral conditions was developed.



a) R = $C_6H_5OCH_2$ b) R = 4-$ClC_6H_4OCH_2$ c) R = 4-$CH_3COC_6H_4OCH_2$
d) R = 4-$CH_3OCH_2CH_2C_6H_4OCH_2$ e) R = C_6H_5 f) R = $ClCH_2$
g) R = CH_3CH_2 h) R = $CH_3(CH_2)_4CH_2$



a) n = 1 b) n = 2

Table. Conversion of Epoxides to 1,2-Diols with β-CD/H2O

Cmpd[a]	Yield (%)	mp. (°C)	*lit.* (°C)	Time (hrs)	Ms (M^+)	^{1}H NMR (δ)
2a	86	55-56	54-56[10]	13	168	3.64 -3.85 (m, 2H), 3.98-4.15 (m, 3H), 6.82-7.01 (m, 3H), 7.15-7.35 (m, 2H).
2b	85	79-80	77-79[11]	10	202	3.70- 3.95 (m, 2H), 4.05- 4.22 (m, 3H), 6.85 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H).
2c	82	89-90	88-89[11]	10	210	2.55 (s, 3H), 3.71-3.95 (m, 2H), 4.05-4.20 (m, 3H), 6.98 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 2H).
2d	85	Oil	Oil[14]	6	226	2.75 (t, J = 7.0 Hz, 2H), 3.30 (s, 3H), 3.52 (t, J = 7.0 Hz, 2H), 3.60–4.45 (m, 5H), 6.75 (d, J = 9.0 Hz, 2H), 7.05 (d, J = 9.0 Hz, 2H).
2e	89	66-67	66-68[10]	10	138	3.55-3.75 (m, 2H) 4.73-4.85 (m, 1H), 7.30 (s, 5H).
2f	90	Oil	Oil[15]	12	----	3.55-3.85 (m, 4H), 3.87-4.05 (m, 1H).
2g	90	Oil	Oil[13]	12	----	0.95 (t, J= 7Hz, 3H), 1.32-1.65 (m, 2H), 3.35-3.50,(m, 1H), 3.62-3.75 (m, 2H).
2h	92	Oil	36-38[12]	12	----	0.90 (t, J = 7Hz, 3H), 1.25-1.52(m, 10H), 3.38-3.50 (m, 1H), 3.65-3.80 (m, 2H).
4a	80	50-51	50-51[7]	14	102	0.75 –0.97 (m, 2H), 1.15 –1.40 (m, 2H), 1.70 - 1.95 (m, 2H), 3.90- 4.12 (m, 2H).
4b	96	102-103	102-103[7]	14	116	1.15-1.40 (m, 4H), 1.65-1.80 (m, 2H), 1.95-2.05 (m, 2H), 3.25- 3.40 (m, 2H).

a) All the products are colorless solids or oils

The yields are nearly quantitative and only catalytic amount (0.1 mole per mole of the substrate) of cyclodextrin is required. No optical induction was observed in the products. These reactions do not take place in the absence of CD. Here, the role of CD appears to be to activate the epoxide by supramolecular catalysis through the formation of hydrogen bonds. Though these reactions are also catalysed by α-CD, β-CD is the preferred catalyst due to its easy accessibility and low cost.

In conclusion, our studies have shown that a wide range of epoxides can be transformed to 1,2-diols under neutral conditions using water as the solvent in a biomimetic fashion. This method also avoids the use of acid or base and thus can be used with substrates bearing labile groups.

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded on Gemini-200 MHz spectrometer in $CDCl_3$ as the solvent with TMS as an internal standard. The mass spectra were determined on VG Autospect M. The IR spectra were obtained on Nicolet FT-IR Spectrometer.

General Procedure: To β-Cyclodextrin (0.123g, 0.108 mmol) in water (40 mL) at 60° was added the epoxide (1.08 mmol) in methanol (1 mL) dropwise with stirring. Stirring was continued at 40° for the specified time (Table), then the mixture was cooled to r.t. and extracted with ethyl acetate (2 x 25 mL). The crude product was purified by column chromatography on silica gel (100-200 mesh) using dichloromethane and methanol (8:2) as eluent. The pure 1,2-diols were obtained in 80-96% yield (Table). The analytical data of compounds 2a to 2h and 4a, 4b were identical to those reported in the literature.[10-15]

Acknowledgement.- MAR and LRR thank CSIR, New Delhi for the award of research fellowships

REFERENCES

† IICT communication No.4507

1. H. C. Kolb, M. S. Vaunieuwenhze and K. B. Sharpless, *Chem. Rev.*, **94,** 2483 (1994).

2. A. Kil patrick and J. P. Lambooy, *Proc. Soc. Exp. Biol. Med,* **126,** 237 (1967).

3. M. Sonoda, N. Yamamoto and A. Mikawa, *Ger. Offen.* 1,934, 626 (1970); *Chem. Abstr.*, **73,** 82505^n (1970).

4. W. L. Nelson, J. E. Wennerstrom and S. R. Sanker, *J. Org. Chem.*, **42,** 1006 (1997).

5. Y. Tsumoda and A. Kado, Kokai Tokkyo Koho JP 08,113,522 (1996); *Chem. Abstr.*, **125,** 95609[s] (1996).

6. J. Wintzer and V. Strobel Ger. Offen. DE, 4,106,665 (1992); *Chem. Abstr.*, **118** 103723[x] (1993).

7. F. Fringuelli, R. Germani, F. Pizzo and G. Savelli, *Synth. Commun.*, **19**, 1939 (1989).

8. V. T. D. Souza and K. B. Lipkowitz *Chem. Rev.,* **98**, 1743(1998).

9. a) K. Rama Rao and P. B. Sattur, *Chem. Commun.*, 342 (**1989**). b) K. Rama Rao and H. M. Sampath Kumar, *Synth. Commun.*, **23**, 1877 (1993). c) K. Rama Rao, N. Bhanumathi and L. Rajender Reddy, *Synth. Commun.*, **29**, 1703 (1999). d) L. Rajender Reddy, M. Arjun Reddy, N. Bhanumathi and K. Rama Rao, *Synlett.*, 339 (**2000**).

10. V. Ulbrich, J. Makes and M. Jurecek, *Coll. Czech. Chem. Commun.*, **29**, 1466 (1964).

11. Karl Thomae (GmbH) Fr 1445 013 (1966); *Chem. Abstr.*, **68**, 21920[u] (1968).

12. D. Swern, G. N. Billen and J. T. Scanlan, *J. Am. Chem. Soc.*, **68**, 1504 (1946).

13. H. J. Bernstein, *J. Am. Chem. Soc.*, **74**, 2674 (1952).

14. M. K. Gurjar, S. V Joshi, B. S. Sastry and A.V. Rama Rao, *Synth. Commun.*, **20**, 3489(1990).

15. H. Kelker and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, Decrfield Beach, Florida, Basel (1980).

****

IMPROVED LARGE SCALE SYNTHESIS OF 2-TRIMETHYLSILOXY-1,3-BUTADIENE

Submitted by (09/10/01)

Roy T. Uyeda, Phong Vu and Daniel D. Holsworth*

Ontogen Corporation, 2325 Camino Vida Roble
Department of Chemistry, Carlsbad, CA, 92009

We recently required multigram quantities of 2-trimethylsiloxy-1,3-butadiene (**1**), a versatile Diels-Alder reaction component used to synthesize a number of ring systems, including substituted pyranones,[1] pyridones,[2] and cyclohexanones.[1] A number of methods exist for the synthesis of this compound,[3] the procedure outlined by Jung[4] being the most convenient. Although, Jung's procedure