ELSEVIER

Journal of Molecular Catalysis A: Chemical 137 (1999) 31–39

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Regulatory nature of β-cyclodextrin in selective ring-opening during reduction of styrene oxide

Ramaswamy Ravichandran, Soundar Divakar *

Department of Microbiology, Central Food Technological Research Institute, Mysore-570 013, India

Received 22 December 1996; accepted 10 February 1998

Abstract

The cleavage of styrene oxide by different reagents like Raney nickel, palladium–carbon and sodium borohydride in the presence of β-cyclodextrin and its derivatives like β-CD-epichlorohydrin (β-CD-polymer) and heptakis-2,6-di-*O*-methyl-β-cyclodextrin (DMβ-CD) showed distribution in formation of ethylbenzene, 1-phenylethanol and 2-phenylethanol. Formation of deoxygenated products like styrene and ethylbenzene were suppressed by β-CD and its derivatives under hydrogenation over Raney nickel favouring increase in proportion of 2-phenylethanol. β-CD and its derivatives regulated increase in formation of 1-phenylethanol under reduction by Pd–C and $NaBH_4$. Observed selectivities have been correlated to arise directly from the disposition adopted by styrene oxide inside the β-CD cavity, the nature and manner of which has been arrived at from the spectroscopic studies (UV and NMR) of inclusion.

Keywords: β-CD; Styrene oxide; Selective ring-opening; Reduction; Deoxygenation; 1:1 Complex

1. Introduction

Most oxiranes readily undergo hydrogenolysis affording products from cleavage of both C–O as well as C–C bonds [1]. Direction of ring opening is the major problem connected with cleavage of epoxides. Based on extensive studies with various substituted styrene oxides, Mitsui et al. [2,3] reported that the ring opening of epoxides by hydrogen is not determined by the electronic effects of the substituents, but on the nature, activity and amount of the catalyst, along with reaction time and presence of alkali.

β-Cyclodextrin is a well-studied molecular catalyst and a useful enzyme mimic in the sense that it regulates reactions of bound substrates through inclusion [4,5]. The results from one such reaction, namely, ring opening of styrene oxide in the presence of β-CD and its methyl and polymer derivatives with Raney nickel, palladium–carbon and $NaBH_4$, along with UV and NMR spectroscopic investigations on the disposition of the substrate are described herein.

2. Experimental

β-Cyclodextrin was a gift from American Maize Product, USA. β-CD-polymer and DMβ-CD were prepared according to the pro-

* Corresponding author.

1381-1169/99/$ - see front matter
PII: S1381-1169(98)00073-9

cedures of Shaw and Buslig [6] and Szejtli et al. [7], respectively. Styrene oxide was prepared from styrene by Prileschajew epoxidation reaction, as described by Vogel [8]. Raney nickel (W-4) was also prepared according to the procedure described by Vogel [8].

Fluorescence spectra were recorded using an Aminco–Bowman spectrofluorophotometer at 20°C. Solutions of 6-(*p*-toludino)-2-naphthalenesulphonic acid (TNS) and β-CD were prepared in water and styrene oxide in 3% ethanol in water. Ultraviolet–visible spectra were recorded on a Shimadzu UV-240 spectrophotometer at 20°C. ^{1}H NMR spectra for structural studies were recorded on a Brüker WH 270 instrument operating at 270 MHz for ^{1}H and 67.5 MHz for ^{13}C, fitted with a Spectrospin magnet and an Aspect 2000 computer, at 20 ± 1°C. Optical activity was measured in ethanol on a Perkin-Elmer 243 polarimeter. A 1% solution in ethanol was used to measure the rotation in the sodium-D line at 20°C. Specific rotation was determined using the expression Sp. Rot. = $100\ a/c \cdot l$ where, a = rotation, c = percentage concentration and l = length in decimeters. Enantiomeric excess was determined from the difference between the specific rotation values between the pure sample and that of the reaction mixture. Styrene oxide used was found to be optically inactive.

A typical procedure employed for hydrogenation is given below. Styrene oxide (8.772×10^{-4} mole), β-CD and its derivatives (as per Tables 1 and 2) were taken in 30 ml absolute ethanol in a glass hydrogenation flask, along with about 100 mg of 5% Pd–C. The reaction mixture was hydrogenated at a pressure of 1.37 atm with mechanical agitation for 1 h. The catalyst was then filtered off, and the filtrate acidified and extracted with ether, dried and concentrated. Hydrogenation using Raney nickel was carried out under selective conditions [9].

Table 1
Deoxygenation in the catalytic hydrogenolysis of styrene oxide over Raney nickel[a]

Additive (mole ratio)	Ethylbenzene (%)	2-Phenylethanol (%)
β-CD (0)	69.0	31.0
β-CD (0.1)	60.9	39.1
β-CD (0.5)	38.2	61.8
β-CD (1.0)	20.9	79.1
β-CD-poly (1.0)	27.0	73.0
DM β-CD (1.0)	13.3	86.6

[a]Unreacted styrene oxide was zero in all the cases. GC analyses.

Table 2
Product distribution in the Pd–C catalysed hydrogenation of styrene oxide

Additive (mole ratio)	1-Phenyl ethanol (%)	2-Phenylethanol (%)
β-CD (0)	10.14[a]	89.86
β-CD (0.1)	15.80	84.20
β-CD (0.5)	22.20	77.80
β-CD (1.0)	27.70[b]	72.30
β-CD-poly (1.0)	21.70	78.30
DM β-CD (1.0)	33.80	66.20

Unreacted styrene oxide was zero in all the cases.
[a]0.74% ee of *S*(−) isomer.
[b]15% ee of *S*(−) isomer.

A typical procedure employed for $NaBH_4$ reduction is given below. A mixture of styrene oxide (8.772×10^{-4} mole), alkali and cyclodextrin (as per Table 3) were taken in 30 ml of solvent (Table 3) and stirred at room temperature with $NaBH_4$ (4 equivalents) at 50°C for 8 h. The reaction was then quenched with saturated aqueous ammonium chloride (40 ml), extracted with dichloromethane, dried over anhydrous sodium sulphate and concentrated.

The product distribution of all reaction mixtures were analysed by gas chromatography using a Shimadzu GC-15A instrument, fitted with a 20% carbowax 20 M, 3-m column with a 30-ml/min nitrogen flow rate. The analyses were performed under both a temperature programme between 70 to 150° (P) and iso at 150°C (I). The injection and FID detector port temperatures were 200 and 250°C, respectively. Retention time (RT) are (in min): ethylbenzene = 9.5 (P), styrene = 13.5 (P), styrene oxide = 5.3 (I), 20.3 (P), 1-phenylethanol = 6.9 (I) and 2-phenylethanol = 26.7 (P), 10.4 (I). The products were separated by column chromatography

Table 3
GC analyses of sodium borohydride reduction product of styrene oxide

Catalyst (mole ratio)	Unreacted styrene oxide[a] (%)	1-Phenylethanol (%)				2-Phenylethanol (%)			
Solvent[b]	S_1	S_1	S_2	E	P	S_1	S_2	E	P
β-CD (0)	28.5	31.7 (44.3)[c]	33.9[d]	71.0	80.1[e]	39.8	66.1	29.0	19.9
β-CD (0.1)	11.7	54.8 (62.1)	61.4	–	–	33.5	38.6	–	–
β-CD (0.5)	0	72.6	69.4	–	–	27.4	30.6	–	–
β-CD (1.0)	0	96.7	> 99.0[f]	96.5[i]	98.9	3.3	1.0	3.5	1.1
β-CD-polymer (1.0)	3.8	56.2 (58.4)	39.1	83.2	81.2	40.0	60.9	16.8	18.8
DM β-CD (1.0)	0	81.1	79.1	> 99.0[g]	> 99.0[h]	18.9	20.9	0	0

[a]Unreacted styrene oxide was zero in solvents S_2, E and P.
[b]S_1 = 0.12 M, 30 ml NaOH solution; S_2 = 0.17 M, 30 ml Na_2CO_3 solution; E = ethanol (30 ml); P = 2-propanol (30 ml).
[c]Values in brackets are % selectivity.
[d]0.99% ee of *R*(+) isomer.
[e]0.44% ee of *R*(+) isomer.
[f]22% ee of *S*(−) isomer.
[g]16% ee of *S*(−) isomer.
[h]19% ee of *S*(−) isomer.
[i]Unmarked values for 1-phenylethyl alcohol indicate that the product was not checked for optical activity. Styrene oxide used was optically inactive.

on silica gel with hexane as eluent and were identified by their ^{1}H NMR spectra.

3. Results and discussion

3.1. Raney nickel hydrogenation

The results of hydrogenolysis of styrene oxide(I) over Raney nickel catalyst are summarised in Table 1. The reaction proceeded to completion in all the cases studied. No unreacted styrene oxide could be detected in a reaction which gave ethylbenzene and 2-phenylethanol as products. While the control reaction gave 69% of the deoxygenated product and 31% alcohol, addition of β-CD and its derivatives showed total reversal in the proportion of both the products formed. Formation of deoxygenated products were suppressed with a corresponding increase in the alcohol formation. An increase in concentration of β-CD, showed an increase in the alcohol formation from 39.1% for 0.1 equivalent of β-CD to a maximum of 79.1% for 1 equivalent of β-CD. Both β-CD-polymer and DM β-CD showed greater inhibition than β-CD giving respectively 73.0% and 86.7% alcohol with only a minor proportion of the deoxygenated product (27.0% and 13.3%, respectively).

Hydrogen consumption profiles in the presence and absence of β-CD are shown in Fig. 1. While the control reaction showed a sigmoidal curve, that with β-CD showed an initial linear behaviour which became asymptotic after 30 min. Both the reactions consumed 1 equivalent of hydrogen at the end of 60 min.

The product profiles are shown in Fig. 2. Both control and β-CD mediated reactions

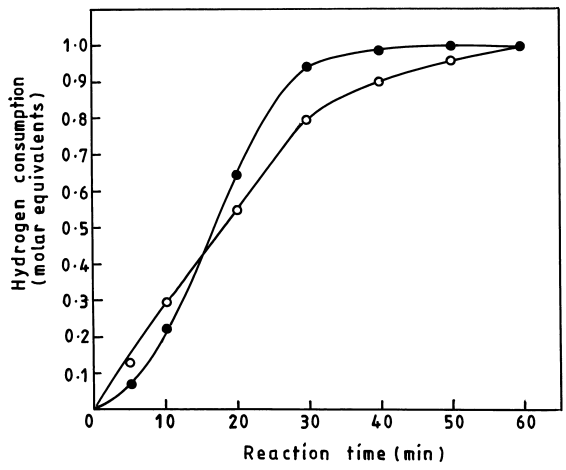


Fig. 1. Rates of hydrogen consumption by styrene oxide; ●, control; ○, β-CD.

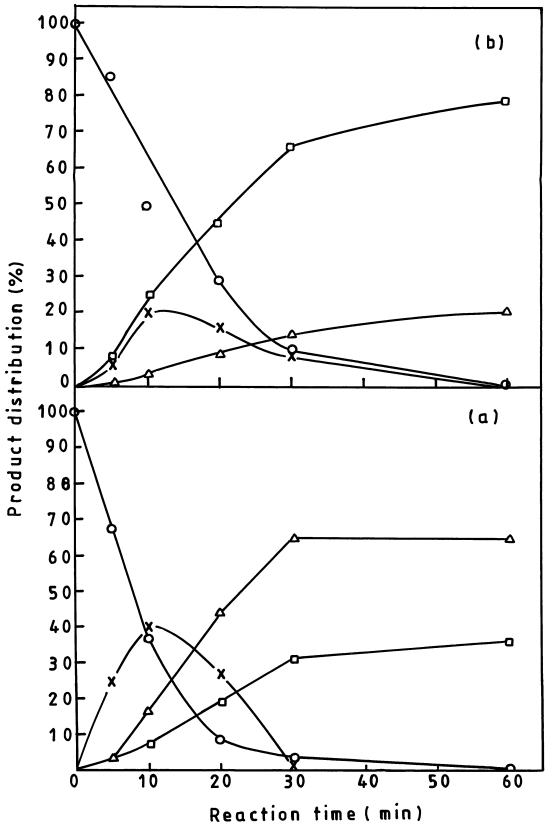


Fig. 2. Product distribution at different intervals of reaction time (a) control, (b) β-CD; ×, styrene; △, ethylbenzene; ○, styrene oxide; □, 2-phenylethyl alcohol.

showed the formation of ethylbenzene via styrene. Deoxygenation occurred in the early stages of the reaction. In the control reaction, the amount of ethylbenzene and the alcohol continuously showed an increase, whereas that of styrene reached a maximum in 10 min, and then decreased to zero in 30 min. In the β-CD mediated reaction, about 90% of styrene oxide disappeared within 20–30 min of reaction. However, β-CD suppressed the formation of deoxygenated products in the initial stage of the reaction itself and the formation of ethylbenzene could be detected only after 10 min of reaction.

3.2. Palladium–carbon hydrogenation

While the hydrogenation of styrene oxide over Pd–$BaSO_4$ [10–12] in methanol gave predominantly 2-phenylethanol, that of Pd–$BaSO_4$ in buffered alkaline methanol [13,14] gave predominantly 1-phenylethanol. In the case of either nickel in Na_2CO_3 solution [15,16] at 40 atm and above 85°C or a mixture of Raney nickel and Pd–C under mild conditions [17,18], 2-phenylethanol was obtained in 90% yield. However, in the present investigation, hydrogenation of styrene oxide over Pd–C under certain conditions yielded more 1-phenylethanol.

Use of Pd–C catalyst in the hydrogenation of styrene oxide resulted in a mixture of 1-phenylethanol and 2-phenylethanol and no deoxygenation product, implying clearly that the nature of the catalyst decides the type of products formed [19,20] (Table 2). The reaction in the absence of β-CD and its derivatives gave 2-phenylethanol in 89.9% yield, along with very little (10.1%) quantity of 1-phenylethanol. However, the addition of β-CD and its derivatives, showed an increase in proportion of 1-phenylethanol compared to the one in its absence. Thus an increase in β-CD concentration resulted in increase in proportion of 1-phenylethanol (27.7% with 1 equivalent of β-CD), the rest being 2-phenylethanol. Equivalent amounts (to styrene oxide) of β-CD-polymer and DMβ-CD resulted in 21.7% and 33.8% of the secondary alcohol, respectively.

3.3. Sodium borohydride reduction

Sodium borohydride reduction also gave a mixture of 1-phenylethanol and 2-phenylethanol on reduction in aqueous alkaline solutions, ethanol and 2-propanol (Table 3). Only the reaction in alkaline NaOH showed some unreacted styrene oxide in the control (28.5%), β-CD (11.7% with 0.1 equivalent of β-CD) and β-CD-polymer (3.8%) mediated reactions. In all the other three solvent systems, no unreacted styrene oxide could be detected. Both aqueous NaOH and Na_2CO_3 alone did not cleave the epoxide ring as also indicated by Hu et al. [21].

In aqueous NaOH the control reaction showed almost equal amounts of 1-phenylethanol (31.7%) and 2-phenylethanol (33.9%). In all the solvent systems studied, the yields of 2-phenylethanol in the β-CD-polymer mediated reaction were comparable to those from the control, those of 1-phenylethanol were better than the control. β-CD mediated reactions gave excellent yields of 1-phenylethanol (> 96.0%) in all the four solvent systems studied. In aqueous NaOH and Na_2CO_3, β-CD mediated reaction gave very good yields of 1-phenylethanol as compared to the other reactions mediated by its derivatives. In alkaline solutions, increase of β-CD also increased the yields of 1-phenylethanol. Next to β-CD, DMβ-CD mediated reactions gave very good yields of 1-phenylethanol. Among the four solvents employed, the yields of 1-phenylethanol in ethanol and isopropanol were higher in control, β-CD and its derivatives mediated reactions than that in alkaline solution. Even in ethanol and isopropanol yields greater than 96% were observed for β-CD and DMβ-CD mediated reactions. Also, the enantiomeric excesses of the $S(-)$ isomer of 1-phenylethanol obtained from these reactions were found to be in the range 16–22%.

3.4. Structure of styrene oxide–β-cyclodextrin inclusion complex

The inclusion complex formation of styrene oxide with DMβ-CD was studied by ultraviolet–visible spectroscopy. Since styrene oxide was insoluble in water, its complexation with DMβ-CD, a derivative of β-CD soluble in chloroform, was studied. Styrene oxide showed an absorption band at λ_{max} 249.8 nm ($E = 200$) in chloroform. Hyperchromicity in the absorption band at 249.8 nm of styrene oxide was noticed when DMβ-CD was added in increasing amounts. Binding constant value was determined as described elsewhere [22] and a value of $325 \pm 8\ M^{-1}$ was determined (Fig. 3, average from two experiments). Also, a plot of change in absorbance against [DMβ-CD]/[styrene oxide] showed the formation of a 1:1 inclusion complex (Fig. 3 inset).

A low molar extinction coefficient value ($E = 175$) prevented complexation studies with β-CD by UV spectroscopy in water. However, inclusion complex formation was detected indirectly by fluorescence spectroscopy. A maximum fluorescence emission (423 arbitrary fluorescence units) was observed at about 9 equiva-

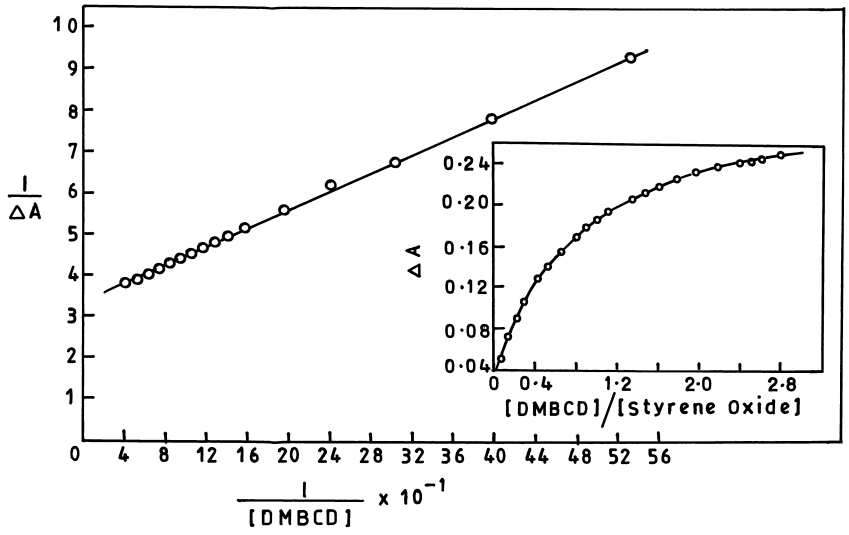


Fig. 3. Determination of binding constant value (inset: stoichiometry) for DMβ-CD–styrene oxide complex by double reciprocal plot method; [styrene oxide] = 0.0081 M; [DMβCD] = 0.079 M.

lents of β-CD, on adding β-CD to a solution of TNS (excitation = 364 nm, emission = 464 nm). On adding styrene oxide in increasing amounts to the β-CD-TNS solution, quenching of fluorescence was observed at about 8 equivalents of styrene oxide indicating probably displacement of TNS by styrene oxide.

The proposed structure in Fig. 4 was arrived at from ^{13}C and ^{1}H NMR spectroscopic studies (Table 4). ^{13}C NMR spectra of the DM β-CD–styrene oxide system showed upfield shifts for all the carbons of styrene oxide, maximum shifts being observed for C-1′, C-2′, C-6′, C-3′ and C-5′ (0.18–0.25 ppm). The epoxide carbons showed slightly lesser magnitude (0.15 and 0.22 ppm for C-1 and C-2, respectively) upfield shifts indicating phenyl ring protons being affected more by complexation than the epoxide ring. Also, C-2, C-4 and C-6 carbon of DM β-CD showed higher magnitude downfield shifts (0.04 to 0.05 ppm). Both the methoxy carbon (6-OCH_3 and 2-OCH_3) showed high upfield shifts of the order 0.13 and 0.12 ppm, respectively. ^{1}H NMR data also confirmed the orientation shown in Fig. 4. H_A, H_B and H_C protons of the epoxide moiety showed upfield shifts of magnitude (≃ 0.06–0.09 ppm). Reduced splitting in H_A and H_B arose due to broadening of signals resulting from restricted rotation of the –CH–Ph bond. Also, the phenyl ring protons showed 0.18–0.25 ppm upfield shifts. In D_2O, β-CD signals could not be detected clearly due to very little solubility of the complex. However, the observable styrene oxide signals showed high upfield shifts (≃ 0.61–0.68 ppm) with very large magnitude differences between the signals of the neat sample and those of the mixture.

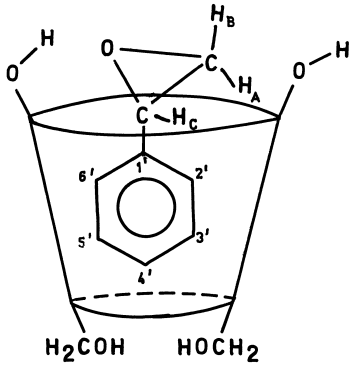
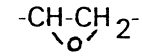


Fig. 4. Disposition of styrene oxide inside β-CD cavity.

All these observations clearly indicate, as mentioned in Section 3.3, that the phenyl ring of styrene oxide is inserted to almost middle of the cavity with the



moiety of the guest positioned close to the wider rim of the host (Fig. 4). Besides, since the alkali is employed in the reaction, β-CD in its alkoxide form, due to the dissociation of the secondary hydroxyl groups, aids in binding the styrene oxide.

Deoxygenation of styrene oxide is proposed to proceed via styrene by trans β-elimination through the strong adsorption of oxygen atom and phenyl group of styrene oxide on the nickel surface, to form the radical (II), which subsequently lose the oxygen atom to form styrene and later ethyl benzene [2] (Scheme 1). As the reaction proceeded, radical formation probably decreased due to aging of the catalyst as observed by slower deoxygenation at the later stages. Due to defined orientation of the phenyl ring of styrene oxide inside β-CD cavity (Fig. 4), and the epoxy ring outside the cavity at the wider end, deoxygenation might be suppressed as the epoxy ring was projected away from the nickel surface and not being made accessible to it.

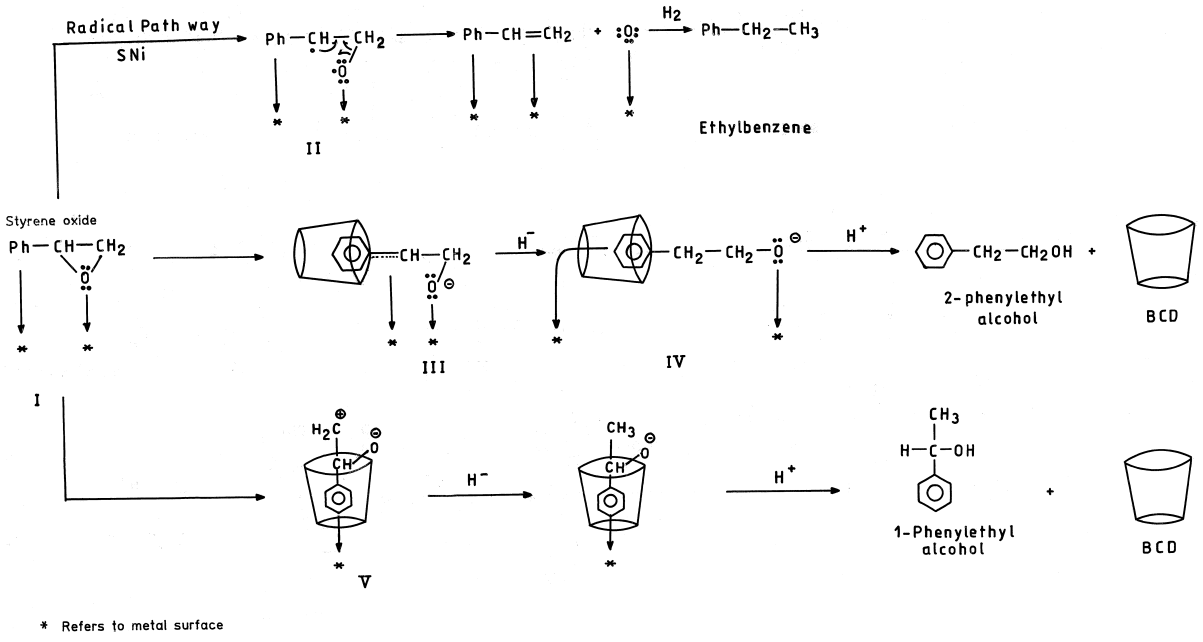
The absence of any deoxygenation product, indicates that the formation of radicals (II) is suppressed due probably to variations in extent and nature of carbon–metal bond overlap (V). Hence, the formation of π-benzyl complex (III) may yield the alkoxide anion (IV) rather than π-phenyl complex (V), resulting in 1-phenylethanol in the control reaction. Inclusion inside β-CD cavity may not permit epoxide oxygen to

Table 4
NMR chemical shift values of styrene oxide in free and complexed state

Signal	Free	Complex	Shift (ppm[a])	Signal	Free	Complex	Shift (ppm)[a]
^{13}C NMR ($CDCl_3$)							
Styrene oxide				DM β-CD			
C-1	51.81	51.59	−0.22	C-1	102.01	101.99	−0.02
C-2	53.00	52.85	−0.15	C-2	82.76	82.80	+0.04
C-1′	138.56	138.31	−0.25	C-3	71.02	71.03	+0.01
C-2′, 6′	126.32	126.10	−0.22	C-4	84.25	84.30	+0.05
C-3′, 5′	129.28	129.08	−0.20	C-5	73.90	73.92	+0.02
C-4′	128.93	128.75	−0.18	C-6	71.57	71.62	+0.05
				C-2-OCH_3	61.00	60.88	−0.12
				C-6-OCH_3	59.68	59.55	−0.13
^{1}H NMR ($CDCl_3$)							
Styrene oxide				DM β-CD			
Ph	7.48 − 7.46	7.28 − 7.25	−0.21	H-1	4.96 (3.7 Hz)	4.97	+0.01
H_A	3.10 (4.1, 5.8 Hz)	3.08 (3.65 Hz)	−0.06	H-2	3.25 (2.7, 9.4 Hz)	3.27 (9.4 Hz)	+0.02
H_B	2.83 (3.3, 5.8 Hz)	2.74 (1.95, 2.83 Hz)	−0.09	H-3	3.90 (8.9 Hz)	3.94 (8.9 Hz)	+0.04
H_C	3.92 (3.3, 4.1 Hz)	[b]		H-4	3.44 (9.0 Hz)	3.45 (9.0 Hz)	+0.01
				H-5	3.68 (8.4 Hz)	3.62	−0.06
				H-6	3.60	3.62	+0.02
				2-OCH_3	3.60	3.62	+0.02
				6-OCH_3	3.37	3.40	+0.03
				3-OH	5.05	5.10	+0.05
^{1}H NMR (D_2O)							
Styrene oxide (neat)				β-CD			
Ph	7.42 − 7.30	6.82 − 6.70	0.6	2,3-OH	–	[c]	–
H_A	3.16 (5.4, 2.7 Hz)	2.48	−0.68	H-1	5.09 (3.6 Hz)	–	−0.24
H_B	2.82 (5.4, 3.8 Hz)	2.18	−0.64	6-OH	–	–	–
H_C	3.88 (2.7, 3.8 Hz)	3.27	−0.61	H-2	3.64 (3.6, 9.4 Hz)	–	+0.03
				H-4	3.64	–	−0.28
				H-6	3.90	–	−0.23
				H-3	3.98 (9.4 Hz)	–	–
				H-5	3.90	–	–

[a] + ve and − ve indicate downfield and upfield shift, respectively, with respect to uncomplexed state. Assignments were based on Ref. [23].
[b] Could not be detected due to overlap.
[c] β-CD signals could not be detected.

get adsorbed on the metal surface. Orientation of styrene oxide inside β-CD cavity is such that, only π-phenyl complex (V) ($d\pi$–$p\pi$ interaction between metal–carbon bond) is formed and π-benzyl complex (III) formation is restricted due to inaccessibility of the buried benzyl moiety to the metal surface. This results in cleavage of the styrene oxide in such a manner that the alkoxide anion (IV) formation is suppressed at the expense of (V). While the $d\pi$–$d\pi$ metal–phenyl interaction stabilise the phenyl ring inside the cavity, the alkoxide ion (V) can



Scheme 1.

be stabilized by hydrogen bonding with the secondary hydroxy groups of β-CD resulting in more 1-phenylethanol formation.

The formation of 1-phenylethanol in excess during $NaBH_4$ reduction can also be explained by the disposition described in Fig. 4. Since the

$$-CH_2-O$$

bond projects outside the cavity near the wider end, cleavage of this bond is quite easy compared to the

$$-CH-O$$

bond, which is buried under the bracelet of secondary hydroxyl groups. Unlike $NaBH_4$ reduction of cyclic ketones such as camphor and menthone, where the attack of the hydride ion was foreseen as approaching from the bottom of the narrower end [24], due to the presence of the inserted phenyl ring, the attack of the hydride ion cannot be from the bottom of the cavity. It can come only from the upper side, resulting in the secondary alcohol. However, in the control, the selectivity seem to depend on the nature of the solvent rather than on the electronic effects of the substrates. Except in case of oxiranes with neighbouring functional groups like nitro and hydroxyl groups [25], the cleavage has been reported to be slow [26,27]. Poor chemoselectivities have also been reported with other reducing agents like lithiumaluminium hydride and lithiumtriethyl borohydride [28]. Hence, the present method offers the advantages of an easy procedure, high chemoselectivity, high yield, water as solvent, and recovery and reusage of the regulating agent namely β-CD and its derivatives.

Acknowledgements

We thank the Director, CFTRI for the facilities provided. R.R. thanks CSIR, New Delhi for a Senior Research Fellowship.

References

[1] O. Gawron, T.P. Fondy, J. Parker, J. Org. Chem. 28 (1963) 700.
[2] S. Mitsui, S. Imaizumi, M. Hisashige, Y. Sugi, Tetrahedron 29 (1973) 4093.
[3] S. Mitsui, Y. Sugi, M. Fujimoto, K. Yokoo, Tetrahedron 30 (1974) 31.
[4] M.M. Maheswaran, S. Divakar, J. Sci. Ind. Res. 53 (1994) 924.
[5] J.L. Atwood, D.D. MacNicol, J.E. Davies (Eds.), Inclusion Compounds, Vol. 3, Academic Press, 1984.
[6] P.E. Shaw, B.S. Buslig, J. Agric. Food Chem. 34 (1986) 834.
[7] J. Szejtli, A. Liptak, I. Jodal, P. Gugedi, P. Nanasi, A. Neszmelyi, Starch 32 (1980) 165.
[8] A.I. Vogel, A Text Book of Practical Organic Chemistry, 4th edn., Wiley, New York, 1978.
[9] S. Divakar, R. Ravichandran, Indian Patent Applied, NF-164/96, March 27, 1997.
[10] D. Cornet, Y. Gault, F.G. Gault, Proc. 3rd Int. Congr. Catal., Amsterdam, 1964 (1965) p. 1185.
[11] S.P. Fore, W.G. Bickford, J. Org. Chem. 26 (1961) 2104.
[12] S.P. Fore, W.G. Bickford, J. Org. Chem. 24 (1959) 620.
[13] S.A.M. Skaya, W.M. Reshetnikov, E.N. Bakhanova, K.K. Kuzembaer, M.N. Anchevskaya, Khim. Khim. Tekhnol. (Alma-Ata) P3 (1966) .
[14] S.A.M. Skaya, W.M. Reshetnikov, E.N. Bakhanova, K.K. Kuzembaer, M.N. Anchevskaya, Chem. Abstr. 69 (1968) 67027g.
[15] O. Priese, Ger (East) Patent 86, 812, Jan. 5, 1972.
[16] O. Priese, Chem. Abstr. 78 (1973) 97305Z.
[17] T.F. Wood, Ger Patent 1,918,852, Oct. 23, 1969.
[18] T.F. Wood, Chem. Abstr. 72 (1970) 43111r.
[19] G.J. Park, R. Fuchs, J. Org. Chem. 22 (1957) 93.
[20] D.R. Howton, R.W. Kaiser, J. Org. Chem. 29 (1964) 2420.
[21] Y. Hu, M. Uno, A. Harada, S. Takahashi, Chem. Lett. (1990) 797.
[22] R. Ravichandran, S. Divakar, J. Inclusion Phen. Mol. Recog. Chem. 18 (1995) 369.
[23] N.R. Easton, F.A.L. Anet, P.A. Burns, C.S. Foote, J. Am. Chem. Soc. 96 (1974) 3945.
[24] S. Divakar, M.S. Narayan, M.M. Maheswaran, Indian J. Chem. 31 (1992) 543.
[25] H.H. Baer, C.B. Madumelu, Can. J. Chem. 56 (1978) 1177.
[26] A. Hajos, Complex Hydride, Elsevier, Budapest, 1979.
[27] E.H.R. Walker, Chem. Soc. Rev. 5 (1976) 23.
[28] H.C. Brown, S. Narasimhan, V. Somayaji, J. Org. Chem. 48 (1983) 3091.