## **Glass Wool Catalysed Regioselective Isomerization of Styrene Oxides**

Govindarajan K. Ramaswamy,<sup>a,b,\*</sup> Angalan Somasundaram,<sup>a</sup> Balasubramanian K. Kuppuswamy<sup>a</sup> and Murugesan Velayudham<sup>b</sup>

<sup>a</sup>Shasun Research Centre, Vandaloor-Kelambakkam Rd, 27 Keelakottaiyur, Chennai, India <sup>b</sup>Centre for Research, Anna University, Guindy, Chennai, India

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Glass wool is widely used as an insulating material. Here we report for the first time, the function of glass wool as a mild heterogeneous catalyst under vapor phase conditions – particularly for the rearrangement of styrene oxides including halogen-substituted styrene oxides to the corresponding phenyl acetaldehydes. Using this methodology, 4-isobutyl- $\alpha$ -methyl styrene oxide is smoothly converted to 4-isobutyl  $\alpha$ -methyl phenyl acetaldehyde which is the precursor of the API "Ibuprofen" – an important pharmaceutical agent.

Keywords: Glass wool; Heterogeneous catalysis; Styrene oxide; 4-Isobutyl- $\alpha$ -methyl phenyl acetaldehyde.

### INTRODUCTION

Epoxides are one of the most useful and versatile substances in organic chemistry due to their high reactivity and easy availability through a wide variety of methods that permit relative and absolute stereo control.<sup>1,2,3</sup> One of the most frequently used atom-economical reactions of epoxides is their rearrangement to carbonyl compounds. A number of reagents - including a variety of Lewis acids, palladium catalysts and Indium(III) chloride - have been demonstrated as being effective for this rearrangement reaction.<sup>4,5,6</sup> One of the well-known procedures for preparation of phenyl acetaldehydes in an industrial scale is by dehydrogenation of phenyl ethanols.<sup>7</sup> However, in this approach, only partial conversion is possible, and separation of starting material from the end product involves huge losses (mainly owing to phenyl acetaldehydes being thermally unstable). Additionally, formation of auto-condensation products during fractionation is another drawback of this approach. Finally, halogen-substituted phenyl acetaldehydes cannot be prepared by this approach since elimination of halogen can occur.<sup>7</sup> An alternate approach involves rearrangement of epoxides using homogeneous or heterogeneous catalysts.<sup>8</sup> For instance, the isomerization of styrene oxide to phenyl acetaldehyde is an acid catalyzed reaction, which is used for the production of fragrant chemicals in an industrial scale as well as production of pharmaceuticals, insecticides, fungicides and herbicides.<sup>8</sup> Furthermore, phenyl acetaldehyde is a valuable intermediate for producing more stable acetals with a honey aroma (glycol

acetals), a sweet leaf odour (diethyl acetals), or a tangy aroma (diphenyl acetals).<sup>9</sup>

Homogeneous catalysts such as phosphoric acid, BF<sub>3</sub>, FeCl<sub>3</sub>, ZnBr<sub>2</sub>, as well as heterogeneous catalysts such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, WO<sub>3</sub>, supported metals and various precipitated phosphates have been employed for isomerization reactions.8 These acid catalysts are generally used in stoichiometric quantities. However, these catalysts are corrosive on the equipments used, in addition to necessitating procedures involving aqueous work up and challenging isolation techniques. In addition, large amounts of salts are produced during neutralization which can lead to heavy metal pollution. Chemo- and regio-selective conversion of epoxides to carbonyl compounds in 5 M lithium perchlorate (in diethyl ether medium) has been reported.<sup>10</sup> Lithium perchlorate in refluxing benzene may be a useful reagent for the rearrangement of several epoxides since this reagent shows higher selectivity compared to strong Lewis acids.<sup>11</sup> However, the perchlorate salts are not eco-friendly and are explosive in nature, and this method is not suitable for large scale preparation. Several solid catalysts have been used to study the rearrangement of various styrene oxides under gas and liquid conditions.<sup>12</sup> Homogeneous catalysts are used in industry although they are not regenerable and produce voluminous corrosive waste streams. On the other hand, heterogeneous catalysts like TiO2, P2O5/SiO2, Y-alumina, B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> and bentonite have been used for this reaction.<sup>8</sup> One of their advantages is that they can be used in gas-phase reactions and therefore continuous processes

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<sup>\*</sup> Corresponding author. Tel: +91-44-23642210; Fax: +91-44-47406190; E-mail: krg.geetha@gmail.com

can be created with relatively little technical effort. However, they do have some drawbacks including incomplete conversion, formation of mixtures of ketones and aldehydes and the formation of aldol condensation products. The formation of these condensation products is the first step in the formation of coke and therefore limits the lifetime of these catalysts.<sup>13</sup> Different styrene oxides can be rearranged in a fixed bed reactor under gas phase conditions.14 When conventional oxides are used, one of the major side products is 1,3,5-triphenyl benzene formed via aldol condensation mechanism. The side reactions can be suppressed by the use of zeolites such as ZSM-5 (Si/Al = 18.8) that hinder aldol condensation and subsequent products because of steric constraints on the framework of the catalyst.<sup>8</sup> Some of the problems associated with these catalysts are challenging preparation methods, poor selectivity, difficulty in separating the by-products formed (due to auto-cyclization) and poor lifetime of the catalyst (caused by coating of the surface). Moreover, these catalyst systems are not useful for halogenated starting materials. While studying the isomerization of halogen substituted styrene oxides, we found that glass wool<sup>15</sup> can effectively and selectively isomerize styrene oxides to phenyl acetaldehydes under vapor phase conditions.

#### **RESULTS AND DISCUSSIONS**

Styrene oxides isomerization is schematically represented in Scheme I. Styrene oxide 1 served as the model compound for our studies and the reaction conditions for this vapor phase isomerization reactions were evaluated (Table 1). Styrene oxide (1) vapors (6 mL/h) were fed in to the pre-activated glass wool (450 mg) placed inside the tubular reactor kept at 300 °C under N<sub>2</sub> flow, the product collected at the receiver was found to be phenylacetalydyde (Table 1 entry 3), identified on the basis of its spectral data

Table 1. Styrene oxide 1 (density 1.052 g/mL) isomerization

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and by comparison with an authentic sample. It is important to note that this isomerization did not take place to an appreciable extent in the absence glass wool, (Table 1 entry 5). We have also observed that silica gel (desiccant form as well as silica gel for column chromatography) and aluminum oxide (used as pellets) did not catalyze the reaction to the same extent as that of glass wool under identical conditions. It is interesting to note that synthesis of aldehydes from oxiranes using silica gel as reagent is known under liquid phase conditions.<sup>16</sup>

We have attempted styrene oxide isomerization under reflux conditions as such without any catalyst (194-196 °C) and also in presence of ceramic beads and glass wool separately. We did not observe any rearrangement and obtained the starting material as such in all the cases, indicating that styrene oxide was stable under reflux conditions and in presence of these materials. We have successfully isomerized various styrene epoxides using glass wool as the heterogeneous catalyst under vapor phase condition as shown in Table 2. Halogen substituted styrene oxides like 4-chlorostyrene oxide **3** (Table 2 entry 1); 3-chlorostyrene oxide **5** (Table 2 entry 2) underwent rearrangement smoothly to the corresponding phenyl acetaldehydes under vapor phase

Entry	T ℃	Flow rate of 1 mL/h	Glass wool- mg	WHSV*	GC purity of 2-% area	Yield w/w	Remarks % of styrene oxide in the product by GC
1	300	1.5	450	3.50	80	34.6	Nil
2	300	3	450	7.01	89.4	54.5	Nil
3	300	6	450	14.02	91.5	91 <sup>17</sup>	0.28
4	300	90	450	210.3	21	87	76.6
5	300	3	Nil	-	22	60	77

\*WHSV-Weight Hourly Space Velocity. (Weight of feed flowing per unit weight of catalyst per hour).

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Entry	Epoxide	Temp	Glass wool Loading (mg)	Rate of flow (mL/h)	Product	Yield w/w
1	CI (3)	300 °C	450	3	CI (4) CHO 21	62%
2		300 °C	450	3	CI CHO <sup>23</sup>	70%
3	(5) CI (7) CI	300 °C	450	3		80%
4	(9)	300 °C	450	3	(10) 27	60%
5	H <sub>3</sub> CO (11)	300 °C	450	3	H <sub>3</sub> CO (12)	52%
6	(11) CI ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	300 °C	450	3	No isomerization has occurred. Starting epoxide was obtained with GC purity of 93.4%	-
7	0 29 29	300 °C	450	3	No isomerization has occurred. Starting epoxide was obtained with GC purity of 96.02%	-
8	(14) 0 30 CHO (15)	300 °C	450	3	No isomerization has occurred. Starting epoxide was obtained with GC purity of 89.2%	-

Table 2.	Various	epoxides	isomerizati	on using	glass wool	l as catalyst	under gas phase
		1		<u> </u>	0	-	0 1

conditions using glass wool as the heterogeneous catalyst while our attempts to rearrange them using conventional systems did not yield desired results.<sup>10,11</sup> Likewise, 3-chloro- $\alpha$ -methyl styrene oxide 7 underwent smooth rearrangement to the corresponding phenyl acetaldehyde under vapor phase conditions using glass wool as catalyst (Table 2 entry 3). 4-Isobutyl- $\alpha$ -methyl phenyl acetaldehyde **10** which is precursor of the API "Ibuprofen", a popular antiinflammatory and analgesic drug, has been prepared by the isomerisation of 4-isobutyl- $\alpha$ -methylstyrene oxide **9** (Table 2 entry 4) in moderate yield of 60% (Table 2 entry 4). 4-Methoxystyrene oxide **11** also underwent this transformation without any problem. (Table 2 entry 5). *The catalytic activity of glass wool is specific to rearrangement of styrene oxides*. Epoxides that are not attached to aromatic systems did not undergo isomerization under these conditions. For example, epichlorohydrin **13** (Table 2 entry 6), phenyl glycidyl ether **14**. (Table 2 entry 7) and 4-oxiranylmethoxy benzaldehyde **15** (Table 2 entry 8) did not undergo the rearrangement to the corresponding aldehydes under these conditions.<sup>18,19</sup> Time Controlled Desorption measurement and Temperature Programmed Desorption profile which are simple and inexpensive methods normally used to measure the number and strength of acid sites

Scheme II Possible mechanism of styrene epoxides isomerization over glass wool



on solid catalysts were extended to glass wool.<sup>31</sup> Time Controlled Desorption (TCD) measurement and Temperature Programmed Desorption –  $NH_3$  (TPD) measurement on glass wool revealed strong and weak acidic sites in the glass wool molecule. These acidic sites are believed to aid in the isomerization reaction of aryl ethylene oxides to corresponding aryl aldehydes. This transformation can be rationalized as shown in Scheme II. Non-benzylic epoxides did not undergo rearrangement in presence of glass wool due to the difficulty in the formation of the carbocations that are not resonance stabilized.

#### CONCLUSION

In conclusion we have shown that glass wool behaves as a heterogeneous catalyst system under vapor phase conditions, particularly for the regioselective rearrangement of styrene oxides to the corresponding phenyl acetaldehydes. This method also provides very good yields with halogen-containing starting materials which are very difficult to prepare by other methods. Further, the use of glass wool as a catalyst appears to be associated with several advantages over current approaches, including green transformation, enhanced selectivity, increased catalyst lifetime, heightened availability and lower cost. Taken together, these results establish that glass wool could be used as a novel heterogeneous mild acid catalyst in organic chemistry reactions under vapor phase.

# General Procedure for the isomerization of styrene epoxides to phenyl acetaldehydes

A tubular catalyst chamber of desired width and length is loaded with the catalyst glass wool of desired volume. The catalyst is activated by heating to 500 °C for 5 h and cooled to the desired temperature under nitrogen. The aryl ethylene oxide is vaporized and the vapors are passed through the externally heated tubular reactor loaded with the catalyst, at a desired flow rate using a syringe infusion pump. The vapors flow through the hot catalyst and the resultant product vapors are cooled and collected.

Example 1: Phenyl acetaldehyde (2) (Table 1, entry 3)

Styrene oxide (1) vapors are fed in to the pre-acti-

vated glass wool placed inside the tubular reactor at a flow rate of 6 mL/h. The temperature for the rearrangement reaction was maintained at 300 °C. The product vapors are cooled and collected downwards at the receiver, with 91% recovery of phenyl acetaldehyde (**2**) with a GC purity of 91.3% a/a.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.7 (d, 2H, *J* = 3 Hz), 7.31-7.23 (m, 2H), 7.41-7.33 (m, 3H), 9.75 (t, 1H, *J* = 3 Hz).

**Example 2:** 4-Chloro phenyl acetaldehyde (4) (Table 2, entry 1)

4-Chloro styrene oxide (3) vapors are fed in to the pre-activated glass wool, placed inside the tubular reactor at a flow rate of 3 mL/h. The rearrangement reaction was conducted under  $N_2$  flow at 300 °C. The product vapors are cooled and collected at the receiver, with 62% recovery of 4-chloro phenyl acetaldehyde (4).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.69 (d, 2H, 2 Hz), 7.16 (d, 2H, *J* = 8 Hz), 7.36 (d, 2H, *J* = 8 Hz), 9.75 (t, 1H, *J* = 2 Hz).

**Example 3:** 3-Chloro phenyl acetaldehyde (6) (Table 2, entry 2)

3-Chloro styrene oxide (5) vapors are fed in to the pre-activated glass wool, placed inside the tubular reactor at a flow rate of 3 mL/h. The temperature for the rearrangement reaction was maintained at 300 °C. The product vapors are cooled and collected at the receiver, with 70% recovery of 3-chloro phenyl acetaldehyde (6) with a GC purity of 94.3% a/a.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.68 (d, 2H, *J* = 2 Hz), 7.09 (d, 1H), 7.15 (s, 1H), 7.21-7.34 (m, 2H), 9.74 (t, 3H, *J* = 2 Hz); *m/z* value is 154.

**Example 4:** 3-Chloro-α-methyl phenyl acetaldehyde (8) (Table 2, entry 3)

3-Chloro- $\alpha$ -methyl styrene oxide (7) was prepared according to the literature procedure. This epoxide was fed into the reactor over the pre-activated glass wool at 300 °C, at a flow rate of 3 mL/h, with 80% yield of 3-chloro- $\alpha$ methyl phenyl acetaldehyde and a GC purity of 94.3% a/a.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.45 (d, 3H, *J* = 7 Hz), 3.63 (q, 1H, *J* = 7 Hz), 7.08 (d, 1H), 7.15 (s, 1H), 7.21-7.34 Glass Wool Catalysed Isomerization of Styrene Oxides

#### (m, 2H), 9.67 (d, 1H, 1Hz).

**Example 5:** 4-Isobutyl-α-methyl phenyl acetaldehyde (**10**) (Table 2, entry 4)

4-Isobutyl- $\alpha$ -methylstyrene oxide (**9**) was prepared according to the literature procedure. This epoxide was fed into the reactor over the pre-activated glass wool at 300 °C, at a flow rate of 3 mL/h. 61% yield of 4-isobutyl- $\alpha$ -methyl phenyl acetaldehyde<sup>25</sup> (**10**) was obtained; with a HPLC purity of 90% a/a. The IR spectrum is superimposible with that of a reference material.

IR (cm<sup>-1</sup>) – 1720-1740 - Aliphatic aldehyde stretching C=O.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.91 (d, 6H, *J* = 6 Hz), 1.43 (d, 2H, *J* = 6 Hz), 1.90-1.81 (m, 1H), 2.48 (d, 3H, *J* = 9 Hz), 3.63-3.57 (q, 1H, *J* = 6 Hz), 7.17-7.03 (m, 4H), 9.66 (d, 1H).

**Example 6:** 4-Methoxy phenyl acetaldehyde (12) (Table 2, entry 5)

4-Methoxy styrene oxide (11) was prepared according to the literature procedure. This epoxide was fed into the reactor over the pre-activated glass wool at 300 °C, at a flow rate of 3 mL/h. 52% yield of 4-methoxy phenyl acetaldehyde (12).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.63 (d, 2H, *J* = 2 Hz), 3.80 (s, 3H), 6.92 (d, 2H, *J* = 8 Hz), 7.148 (d, 2H, *J* = 8 Hz), 9.72 (t, 1H, *J* = 2 Hz).

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#### REFERENCES

- a) Rao, A. S.; Paknikar, S. K.; Kirtane, J. C. *Tetrahedron* 1983, *39*, 2323. b) Smith, J. G. *Synthesis* 1984, 629. c) Ruiz-Hitzky, E.; Casal, B. J. *Catal.* 1985, *92*, 291.
- a) Parker, R. E.; Issacs, N. S. Chem. Rev. 1959, 59, 737. b) Schwartz, N. N.; Blumbergs, J. H. J. Org. Chem. 1964, 20, 1976. c) Fringuell, F.; Germani, R.; Pizzo, F.; Savelli, G. Tetrahedron Lett. 1989, 30, 1427. d) Ishizuka, N. J. Chem. Soc., Perkin. Trans. 1990, 1, 813.
- a) Imuta, M.; Ziffer, H. J. Org. Chem. 1999, 44, 1351. b) Besse, P.; Veschambre, H. Tetrahedron 1994, 40, 8885.
- 4. a) Rickborn, B. In Comprehensive Organic Synthesis; Trost,

B. M., Ed.: Pergamon: Oxford, 1991; Vol 3, Chapter 3.3, pp 733-735 and references cited there in. b) Manioka, K.; Miirase, N.; Bureau, R.; Ool, T.; Yamammota, H. *Tetrahedron* **1994**, *50*, 3663. c) House, H. O. *J. Am. Chem. Soc.* **1955**, *77*, 3070.

- a) Kulasegaram, S.; Kulawlec, R. J. J. Org. Chem. 1994, 59, 7195; *ibid*, 1997, 62, 6547; *Tetrahedron* 1998, 54, 1361. b) Takanami, T.; Hirabe, R.; Ueno, M.; Hino, F.; Suda, K. Chem. Lett. 1996, 1031.
- a) Loh, T. P.; Pei, J.; Lin, M. J. Chem. Soc., Chem. Commun. 1996, 2135. b) Loh, T. P.; Pei, J.; Cao, G.-Q. J. Chem. Soc., Chem. Commun. 1996, 1810. c) Babu, G.; Perumal, P. T. Tetrahedron Lett. 1997, 38, 5025. d) Loh, T. P.; Wei, L. L. Tetrahedron Lett. 1998, 39, 323. e) Brindaban, C. R.; Umasish, J. J. Org. Chem. 1998, 63(23), 8212.
- Holderich, W.; Mross, W. D.; Merger, F.; Fouquet, F. US Patent 4,929,765. 1998. (*Chem. Abstr. Vol 111*: 232300 m).
- Hölderich, W.; Barsnick, U. In *Fine Chemicals through Heterogeneous Catalysis*; Sheldon, R. A.; van Bekkum, H., Eds.; Wiley-VCH: Germany, 2001; pp 217-222, and references cited there in.
- Hoelderich, W.; Laufer, M. C. In *Zeolites for Cleaner Technologies*; Guisnet, M.; Gilson, J. P., Eds.; Imperial College Press: London, 2002; p 301.
- Sudha, R.; Narasimhan, K. M.; Saraswathy, V. G.; Sankararaman, S. J. Org. Chem. 1996, 61, 1877.
- 11. Trost, B. M.; Bogdanowicz, M. J. J. Am. Chem. Soc. 1973, 95, 5321.
- 12. a) Hölderich, W.; Goetz, H.; Hupfer, L. US Patent 4,990,684, 1989, (*Chem. Abstr. Vol 111*: 232300 m). b) Taramasso, M.; Perego, G.; Notari, B. US Patent 4,410,501.1983. (*Chem. Abstr. Vol 95*, 206272 k).
- Kochkar, H.; Clacens, J. M.; Figueras, F. Catal. Lett. 2002, 78, 91.
- 14. a) Holderich, W.; Mross, W. D.; Merger, F.; Fouquet, F. US Patent 4,929,765, 1998. (*Chem. Abstr. Vol 111*: 232300 m). b) Holderich, W.; Norbert, G.; Leopold, H.; Helmut, H. US Patent 4,980,511.1987 (*Chem. Abstr. Vol 109*, 151902 r).
- 15. Draft Report on Carcinogens: Substance Profile for Glass Wool Fibers (Respirable) as a Class (National Toxicology Program, 2010) and references and reports cited there in website: ntp.niehs.nih.gov/NTP/roc/twelfth/2010/.../ GWF20100421.pdf (Accessed May 2, 2012)
- Lemini, C.; Ordonez, M.; Perez-Flores, J.; Cruz-Almanza, R. Synth. Commun. 1995, 25(18), 2695.
- For Styrene oxide- Aldrich Library of 13C and 1H FT NMR Spectra, 2, 219C, 220A For Phenyl acetaldehyde- Aldrich Library of 13C and 1H FT NMR Spectra, 2, 230A, 239A.
- Khadilkar, B. M.; Bendale, P. M. Synth. Commun. 1997, 27(12), 2051.
- Baldwin, J. J.; Engelhardt, E. L.; Hirschmann, R.; Lundell, G. F.; Ponticello, G. S.; Ludden, C. T.; Sweet, C. S.; Scriabine, A.; Share, N. N.; Hall, R. J. Med. Chem. 1979, 22, 689.

- 20. Cleij, M.; Archelas, A.; Furstoss, R. J. Org. Chem. **1999**, 64, 5029.
- 21. Shou-Ri, S.; Qiu-Ying, W.; Yi-Xiang, H.; Qin, X.; Xiao-Ling, L. Synth. Commun. 2006, 36(4), 429.
- 22. Sarma, K.; Bhati, N.; Borthakur, N.; Goswamy, A. *Tetrahedron* **2007**, *63*(36), 8735.
- 23. Hiroyoshi, O.; Takashi, N.; Yoshihisa, K.; Harukichi, H. Bull. Chem. Soc. Jpn. 1968, 41, 1395.
- Ciaccio, J. A.; Drahus, A. L.; Meis, R.; Tingle, C. T.; Smrtka, M.; Geneste, R. Synth. Commun. 2003, 33, 2135.
- 25. Fu, J.-Y.; Xu, X.-Y.; Li, Y.-C.; Huang, Q.-C.; Wang, L.-X. Org. Biomol. Chem. 2010, 8(20), 4524.
- 26. Cleij, M.; Archelas, A.; Furstoss, R. J. Org. Chem. 1999, 64, 5029.

- 27. a) Friest, J. A.; Maezato, Y.; Broussy, S.; Blum, P.; Berkowitz, D. B. *J. Am. Chem. Soc*, **2010**, *132*(17), 5930. b) Galletti, P.; Emer, E.; Gucciardo, G.; Quintavalla, A.; Pori, M.; Giacomini, D. Org. Biomol. Chem. **2010**, *8*(18), 4117.
- 28. Ranu, B. C.; Jana, U. J. Org. Chem. 1998, 63(23), 8212.
- 29. Khadilkar, B. M.; Bendale, P. M. Synth. Commun. 1997, 27(12), 2051.
- Baldwin, J. J.; Engelhardt, E. J.; Hirschmann, R.; Lundell, G.
  F.; Ponticello, G. S.; Ludden, C. T.; Sweet, C. S.; Scriabine,
  A.; Share, N. N.; Hall, R. J. Med. Chem. 1979, 22, 689.
- Viswanathan, B.; Sivashankar, S.; Ramaswamy, A. V. *Catal*ysis-Principles and Application, 2<sup>nd</sup> ed.; Narasa Publishing House: New Delhi, India, 2006.