

Carbon-based solid acid: an efficient and reusable catalyst for the diastereoselective ring opening reaction of α -epoxyketones

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Abstract Carbon-based solid acid efficiently catalyzes diastereoselective ring opening of α -epoxyketones in the presence of methanol to produce the corresponding α -hydroxy- β -methoxyketones in excellent yield.

Keywords Epoxyketones · Carbon-based solid acid · Diastereoselective · Ring opening

Introduction

Epoxides and epoxyketones have attracted the attention of many organic chemists because of the effect of ring strain on chemical reactivity and the potential of derivatives of these compounds to act as precursors of more elaborate heterocyclic compounds. Among these transformations, ring opening reactions of α -epoxyketones have been recognized as important in thermal and photochemical transformations. These reactions are also of substantial interest synthetically and mechanistically. C–O and C–C bond cleavage in these compounds can occur via photochemical, thermal, and electrochemical processes [1–18].

Several methods have been reported for ring opening of epoxides in the presence of a catalyst, for example aluminium triflate [14], CsF [16], ZrCl₄ [17], boron trifluoride [18], vanadium(IV) tetraphenylporphyrin [19], montmorillonite K 10 [20], and (C₄H₁₂N₂)₂[BiCl₆]Cl·H₂O [21]. There are, however, no reports of ring opening of α -epoxyketones in the presence of a Lewis or Bronsted acid.

The use of heterogeneous and reusable catalysts in organic reactions has proved useful to chemists in the laboratory and in the industrial context. These reactions are

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effected by reagents immobilized on solid supports and have such advantages as operational simplicity, environmental compatibility, non-toxicity, reusability, low cost, and ease of isolation [22].

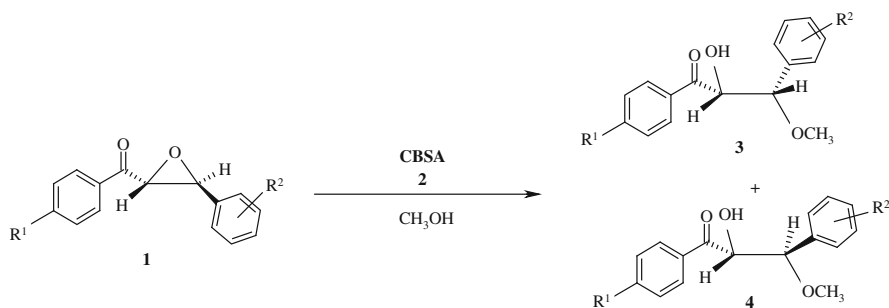
To the best of our knowledge, ring opening reactions of α -epoxyketones catalyzed by carbon-based solid acid (CBSA) with a high density of sulfonic acid (SO_3H) have not been reported in the open literature. Herein, in continuation of our interest in the use of heterogeneous catalysts in organic reactions [23, 24], we report use of CBSA as a reusable heterogeneous catalyst for diastereoselective nucleophilic opening of α -epoxyketone rings in the presence of methanol (Scheme 1).

Experimental

Chemicals were purchased from Fluka and Merck. All products obtained are known compounds and were identified by comparing their physical and spectral data with those reported in the literature. ^1H NMR spectra were recorded on an Ultra Shield spectrometer (400 MHz) using TMS as internal standard. FT-IR spectra were obtained as potassium bromide pellets in the range $400\text{--}4,000\text{ cm}^{-1}$ with a Varian 4300 spectrometer. Information about the phase of CBSA was obtained by X-ray powder diffractometry (Philips, Cu $\text{K}\alpha$, $\lambda = 1.54178\text{ \AA}$) with the Bragg angle ranging between 10° and 50° .

Catalyst preparation

Carbon-based solid acid (CBSA) was prepared as reported by Hara et al. [25]. In a typical synthesis, naphthalene (20 g) was heated in concentrated sulfuric acid (98 %, 200 ml) at 523 K under a flow of N_2 . After heating for 15 h, excess sulfuric acid was removed from the dark brown tar by vacuum distillation at 523 K for 5 h, which resulted in a black solid. The solid was then ground to a powder and washed in boiling water until impurities, for example sulfate ions, were no longer detected in the wash water. The SO_3H group density was measured by using NaOH



Scheme 1 Catalytic ring opening of α -epoxyketones by CBSA

(0.01 mol l⁻¹) as titrant in a neutralization titration. The amount of SO₃H attached to the polycyclic aromatic carbon was 4.87 mmol g⁻¹.

Typical procedure for the ring opening reaction

CBSA (0.1 g) was added to a stirred solution of α -epoxyketone (1 mmol) and MeOH (20 ml) and the mixture was stirred at room temperature for the time given in Table 1. The reaction was monitored by TLC (petroleum ether–EtOAc, 10:1). After completion of the reaction, the heterogeneous catalyst was separated by centrifugation and the solvent of resulting mixture was evaporated to give pure product (Table 1). The catalyst can be recycled by washing it with ethyl acetate and drying in an oven at 45 °C for 3 h.

Results and discussion

Synthesis of CBSA with a high density of sulfonic acid (SO₃H) was reported by Hara et al. [25]. Such CBSAs can be readily prepared by heating aromatic compounds such as naphthalene in sulfuric acid at 523 K. In this synthesis, sulfonation of the aromatic compounds is the first stage of the reaction. The resulting sulfonated aromatic compounds are completely carbonized, which results in the formation of a solid with nominal sample composition of CH_{0.35}O_{0.35}S_{0.14}. The resulting black powder is insoluble in such solvents as water, methanol, ethanol, and hexane even at boiling temperatures [26]. The X-ray diffraction (XRD) spectrum of CBSA is shown in Fig. 1. The two broad and weak peaks ($2\theta = 15^\circ$ – 30° , 35° – 50°) are attributed to amorphous carbon.

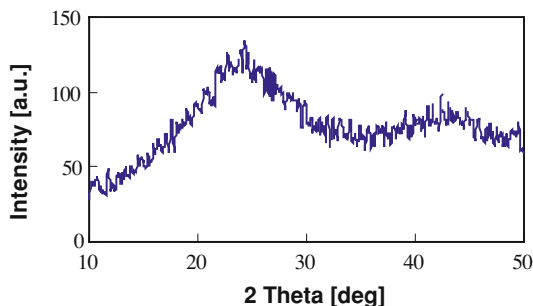
To illustrate use of the CBSA catalyst, ring opening reaction of α -epoxyketone **1e** was performed in the absence of the catalyst. In that case the product was not produced after stirring the reaction mixture in methanol for 10 h. Thus, it could be

Table 1 The ring opening reactions of **1a–j** catalyzed by CBSA in methanol solution

α -EK	R1	R2	Time (h)	Yield (%)	4/3 ^a	3 %	4 %
1a	H	H	15	95	2.88:1.00	26	74
1b	H	2-OCH ₃	0.13	97	1.00:1.99	66	34
1c	H	3-OCH ₃	20	94	2.43:1.00	29	71
1d	H	4-OCH ₃	0.13	97	1.00:1.07	52	48
1e	H	4-CH ₃	1.1	96	1.00:1.24	55	45
1f	H	4-Cl	19	93	2.77:1.00	27	73
1g	4-OCH ₃	H	16	94	5.76:1.00	15	85
1h	4-OCH ₃	4-CH ₃	0.75	97	1.26:1.00	44	56
1i	H	4-NO ₂	48	–	–	–	–
1j	4-NO ₂	H	48	–	–	–	–

^a The ratios were determined by comparison of the integral ratios of the hydrogen on C-2 (H_d and H_{d'})

Fig. 1 X-ray diffraction spectrum of CBSA



concluded that CBSA is an important component participating in this reaction. The best results were obtained by use of 0.1 g CBSA. Use of less catalyst resulted in lower yields whereas use of more catalyst did not affect reaction times and yields.

Reaction of α -epoxyketone **1e** with **2** in methanol solution produced a mixture of diastereomeric products **3e** and **4e**. The ^1H NMR spectrum of **3e** + **4e** is presented in Fig. 2.

This spectrum consists of two sharp lines for two methyl groups on phenyl rings ($\delta = 2.34$ ppm for $\text{H}^{i'}$ and 2.36 ppm for H^i), two singlets for methoxy groups ($\delta = 3.12$ ppm for H^h and 3.25 ppm for H^h), a doublet for the benzylic proton ($\delta = 4.51$ ppm for $\text{H}^{e'}$, $^3J_{\text{He}'\text{Hd}'} = 4.4$ Hz), a doublet for the benzylic proton ($\delta = 4.56$ ppm for H^e , $^3J_{\text{HeHd}} = 3.2$ Hz), a doublet for the $-\text{CO}-\text{CHOH}-$ proton ($\delta = 5.19$ ppm for H_d , $^3J_{\text{HeHd}} = 3.2$ Hz), a doublet for the $-\text{CO}-\text{CHOH}-$ proton ($\delta = 5.42$ ppm for $\text{H}^{d'}$, $^3J_{\text{He}'\text{Hd}'} = 4.4$ Hz) and four doublets, two triplet-like peaks, and four doublet of triplets for the aromatic protons ($\delta = 7.03$ ppm for H_g , d, $^3J_{\text{HgHf}} = 8$ Hz; $\delta = 7.10$ ppm for H_g , d, $^3J_{\text{Hg}'\text{Hf}'}$ = 8 Hz; $\delta = 7.18$ ppm for H_f , d, $^3J_{\text{Hg}'\text{Hf}'}$ = 8 Hz; $\delta = 7.26$ ppm for H_f , d, $^3J_{\text{HgHf}} = 8$ Hz; $\delta = 7.49$ ppm for H_b , t-like, $^3J_{\text{Hb}'\text{Ha}'}$ = 8 Hz, $^3J_{\text{Hb}'\text{Hc}'}$ = 7.6 Hz; $\delta = 7.53$ ppm for H_b , t-like, $^3J_{\text{HbHa}} = 8$ Hz, $^3J_{\text{HbHc}} = 7.2$ Hz; $\delta = 7.62$ ppm for H_a , dt, $^3J_{\text{HbHa}} = 7.2$ Hz, $^4J_{\text{HaHc}} = 1.2$ Hz; $\delta = 7.66$ ppm for H_a , dt, $^3J_{\text{Hb}'\text{Ha}'}$ = 7.2 Hz, $^4J_{\text{Ha}'\text{Hc}'}$ = 1.2 Hz; $\delta = 7.89$ ppm for H_c , dt, $^3J_{\text{Hb}'\text{Hc}'}$ = 7.2 Hz, $^4J_{\text{Ha}'\text{Hc}'}$ = 1.2 Hz; $\delta = 7.97$ ppm for H_c , dt, $^3J_{\text{HcHa}} = 7.2$ Hz, $^4J_{\text{HbHc}} = 1.2$ Hz). The **3e/4e** ratio was determined by comparison of the integral ratios of the hydrogens on C-2 (H_d and H_d'). Then, all reactions were performed under these conditions and the ratios of diastereomers were determined by the method mentioned above. The results are presented in Table 1.

As shown in Table 1, the rate and diastereoselectivity of the catalytic ring opening of α -epoxyketones **1a–h** are dependent on not only the nature of the additional substituents on the parent molecule but also their location. Whereas electron donor groups, for example methyl and methoxy, on the phenyl ring directly attached to the epoxide ring (**1b**, **1d** and **1f**) facilitate ring opening, the same substituents on the phenyl ring of the benzoyl moiety (**1g** and **1h**) have less effect. Also, for **1b**, **1d** and **1e**, the ratios of the diastereomeric products are inverted in comparison with **1a**, **1c**, **1f**, **1g**, and **1h**.

On the basis of the results obtained, we propose that activation of **1a–h** by **2** could lead to three different intermediates **5**, **6**, and **7** in the catalytic ring opening of α -epoxyketones. These intermediates are trapped by nucleophilic attack of methanol

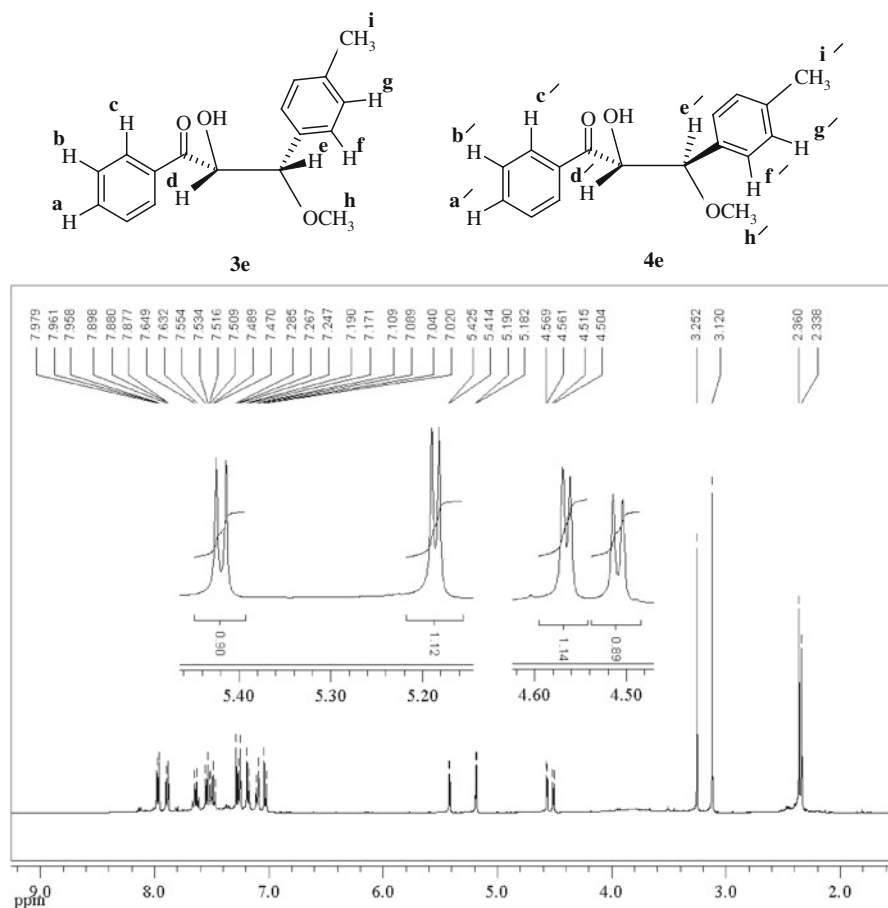
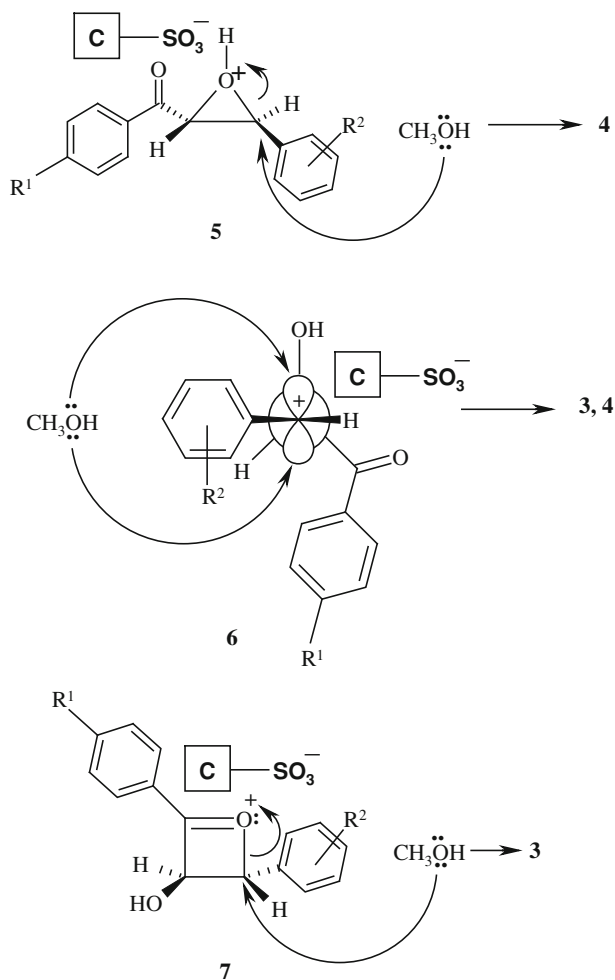


Fig. 2 The ^1H NMR spectrum of **3e** + **4e**

on the less hindered side, forming **3a–h** and **4a–h** via $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ processes [18] (Scheme 2).

The ratios of the diastereomeric products lead us to assume that the inductive effect of the *p*-methyl group (**1e**) and the resonance effect of the *o*- and *p*-methoxy groups (**1b** and **1d**) on the phenyl ring directly attached to the epoxide ring increase the contribution of the intermediates **6** and **7** because of stabilization of the carbocation. Nucleophilic attack of methanol on intermediate **7** produces predominantly **3b**, **3d**, and **3e** (Scheme 2). On the other hand, intermediates **5** and **6** can be proposed for **1a**, **1c**, **1f**, **1g**, and **1h**, in which the nucleophilic attack of methanol on intermediate **5** produces **4a**, **4c**, **4f**, **4g**, and **4h** (Scheme 2).

We also studied recycling of the used CBSA in repeated reactions. After the first run, the catalyst was recovered by filtration, washed with ethyl acetate, and reused. The catalyst can be reused ten times in sequence without loss of activity (Fig. 3).



Scheme 2 Proposed mechanism for diastereoselective ring opening of α -epoxyketones

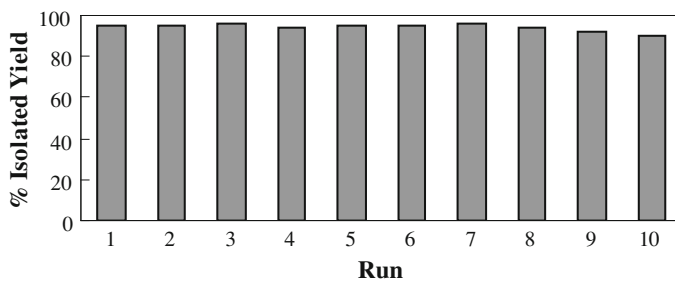


Fig. 3 Recyclability of catalyst CBSA for ring opening of **1e**

Conclusion

We have developed a simple, efficient, and green procedure for the ring opening reaction of α -epoxyketones with CBSA as catalyst in methanol solution. The rate and diastereoselectivity of catalytic ring opening of α -epoxyketones depend not only on the nature of additional substituents on the parent molecule but also on their location. Whereas electron donor groups on the phenyl ring directly attached to the epoxide ring facilitate ring opening, the same substituents on the phenyl ring of the benzoyl moiety have a smaller effect. Simple work-up in isolation of the products and high purity are features of this procedure. Further, the catalyst can be easily recovered and reused without much loss of its activity.

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References

1. H.R. Memarian, A. Saffar-Teluri, M.K. Amini, *Heterocycles* **68**, 1861 (2006)
2. E. Hasegawa, K. Ishiyama, T. Fujita, T. Kato, T. Abe, *J. Org. Chem.* **62**, 2396 (1997)
3. E. Hasegawa, A. Yoneoka, K. Suzuki, T. Kato, T. Kitazume, K. Yanagi, *Tetrahedron* **55**, 12957 (1999)
4. E. Hasegawa, T. Kato, T. Kitazume, K. Yanagi, K. Hasegawa, T. Horaguchi, *Tetrahedron Lett.* **37**, 7079 (1996)
5. E. Hasegawa, K. Ishiyama, K. Kato, T. Horaguchi, T. Shimizu, S. Tanaka, Y. Yamashita, *J. Org. Chem.* **57**, 5352 (1992)
6. E. Hasegawa, M. Kamata, in *CRC Handbook of Organic Photochemistry and Photobiology*, ed. by W.M. Horspool, F. Lenci (CRC Press, Boca Raton, 2004), pp. 1–17
7. K. Okada, E. Hasegawa, T. Mukai, *Chem. Lett.* **3**, 305 (1983)
8. E. Hasegawa, K. Ishiyama, H. Kashiwazaki, T. Horaguchi, T. Shimizu, *Tetrahedron Lett.* **31**, 4045 (1990)
9. C. Hardouin, F. Chevallier, B. Rousseau, E. Doris, *J. Org. Chem.* **66**, 1046 (2001)
10. L. Lopez, L. Troisi, *Tetrahedron Lett.* **30**, 3097 (1989)
11. J. Kagan, P.Y. Juang, B.E. Firth, J.T. Przybytek, S.P. Singh, *Tetrahedron Lett.* **18**, 4289 (1977)
12. C. Huo, X. Jia, W. Zhang, L. Yang, J. Lu, Z.L. Liu, *Synlett* **2**, 251 (2004)
13. J. Delaunay, A. Lebouc, A. Tallaec, J. Sinonet, *J. Chem. Soc. Chem. Commun.* 387 (1982)
14. D. Bradley, G. Williams, M. Lawton, *Org. Biomol. Chem.* **3**, 3269 (2005)
15. F. Fringuelli, F. Pizzo, L. Vaccaro, *J. Org. Chem.* **69**, 2315 (2004)
16. V. Polshettiwar, M.P. Kaushik, *Catal. Commun.* **5**, 515 (2004)
17. A.K. Chakraborti, A. Kondaskar, *Tetrahedron Lett.* **44**, 8315 (2003)
18. J. Izquierdo, S. Rodriguez, F.V. Gonzalez, *Org. Lett.* **13**, 3856 (2011)
19. S.A. Taghavi, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, A.R. Khosropour, V. Ahmadi, *Polyhedron* **30**, 2244 (2011)
20. A.K. Chakraborti, A. Kondaskar, S. Rudrawar, *Tetrahedron* **60**, 9085 (2004)
21. H.F. Lu, L.L. Sun, W.J. Le, F.F. Yang, J.T. Zhou, Y.H. Gao, *Tetrahedron Lett.* **53**, 4267 (2012)
22. R.S. Varma, *Green Chem.* **1**, 43 (1999)
23. A. Saffar-Teluri, S. Bolouk, *Monatsh. Chem.* **141**, 1113 (2010)
24. A. Saffar-Teluri, *Res. Chem. Intermed.* (2012). doi:10.1007/s11164-012-0846-9
25. M. Hara, T. Yoshida, A. Takagaki, T. Takata, J.N. Kondo, S. Hayashi, K. Domen, *Angew. Chem. Int. Ed.* **43**, 2955 (2004)
26. H. Toda, A. Takagaki, M. Okamura, J.N. Kondo, K. Domen, S. Hayashi, M. Hara, *Nature* **438**, 178 (2005)