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Synthetic Communications

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597304>

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Online publication date: 05 August 2010

To cite this Article Saikia, Indranirekha, Kashyap, Bishwapran and Phukan, Prodeep (2010) 'Efficient Protocol for Stereoselective Epoxidation of Cinnamic Esters Using TsNBr₂', Synthetic Communications, 40: 17, 2647 – 2652

To link to this Article: DOI: 10.1080/00397910903318617

URL: <http://dx.doi.org/10.1080/00397910903318617>

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EFFICIENT PROTOCOL FOR STEREOSELECTIVE EPOXIDATION OF CINNAMIC ESTERS USING TsNBr₂

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An efficient method has been developed for the synthesis of epoxide from cinnamic esters without any catalyst. The reaction was performed in CH₃CN–water (4:1) using N,N-dibromo-p-toluenesulfonamide (TsNBr₂) in alkaline conditions. This procedure can be utilized for stereoselective synthesis of epoxides from cinnamic esters in excellent yield in a shorter reaction time with exclusive formation of the trans-isomer. The method was further extended successfully for styrenes.

Keywords: Catalyst-free; N,N-dibromo-p-toluenesulfonamide (TsNBr₂); epoxidation; epoxide; olefin; styrene; α,β -unsaturated carbonyl compounds

INTRODUCTION

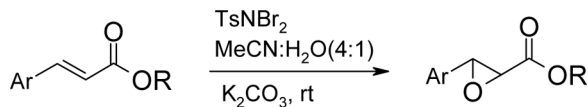
Epoxides are versatile building blocks for the manufacture of a range of pharmaceuticals, natural products, and functional materials.^[1] There are several methods for epoxidation available in the literature.^[2] Recently, new methods have been developed for epoxidation of olefins using various metallic catalysts.^[3–8] Derivatives of ketones^[9] or amines^[10] also found application in epoxidation. Although several catalytic methods have been developed in the recent past to activate the olefin for epoxide synthesis, new reagent-based noncatalytic method has rarely been reported. Geng et al. developed a procedure for epoxidation of olefins using sodium chlorite as an oxidant.^[11] However, this method suffers from the drawbacks such as long times, high temperatures, and poor yield. Synthesis of epoxide by using bromohydrin in the presence of a base has been extensively used.^[12] Recently, we have demonstrated the use of N,N-dibromo-p-toluenesulfonamide (TsNBr₂) for the synthesis of bromohydrin, alkoxybromide, and bromoazide.^[13] We report herein a procedure for the synthesis of epoxides using TsNBr₂ and a base (Scheme 1).

RESULTS AND DISCUSSION

The reagent TsNBr₂ employed for this purpose was prepared from chloroamine-T by following a literature procedure.^[14] We found that bromohydrins

Received May 2, 2009.

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Scheme 1. Epoxidation using TsNBr₂.

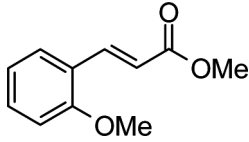
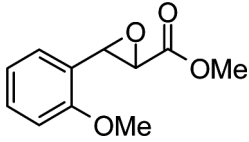
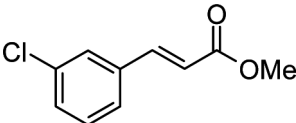
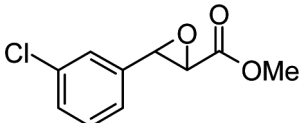
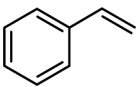
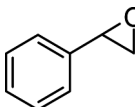
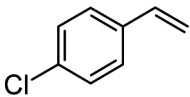
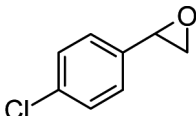
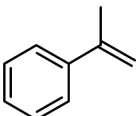
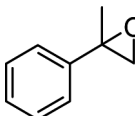
form instantaneously upon addition of TsNBr₂ to olefins in aqueous acetonitrile.^[13a] We desired to extend the method for epoxidation of olefins by treating the bromohydrin in situ with a base. Thus, TsNBr₂ (1.2 mmol) and the substrate (1.1 mmol) in acetonitrile–water (4:1) were stirred for 10 min at room temperature, and then K₂CO₃ was added. After 40 min, the epoxide was isolated in good yield (Table 1). When the reaction was evaluated with varying amounts of K₂CO₃, we found that addition of 1.4 equivalents of the base (based on the substrate) is enough to get the best result. Epoxidation of cinnamic esters is stereoselective, and only the *trans* isomer was observed as evidenced by the analysis of ¹H NMR data. After initial success with various cinnamic esters, the procedure could be extended to other olefins such as styrenes (Table 1, entries 8–10).

Table 1. Epoxidation of various olefins using TsNBr₂^a

Entry	Olefins (a)	Products (b)	Time (min)	Yield ^b (%)
1			50	85
2			45	70
3			40	73
4			40	75
5			45	74

(Continued)

Table 1. Continued

Entry	Olefins (a)	Products (b)	Time (min)	Yield ^b (%)
6			45	70
7			40	75
8			30	50
9			30	80
10			60	50

^aReaction conditions: ethyl cinnamate (1.1 mmol), MeCN (4 mL), H₂O (1 mL), TsNBr₂ (1.2 mmol), K₂CO₃ (1.5 mmol), room temperature.

^bIsolated yield after chromatographic purifications.

CONCLUSION

In conclusion, an efficient protocol for epoxidation of olefins has been established by using *N,N*-dibromo-*p*-toluenesulfonamide in the presence of K₂CO₃ as base.

EXPERIMENTAL

General Procedure for Synthesis of Epoxides

TsNBr₂ (1.2 mmol) was added at room temperature to a solution of olefin (1.1 mmol) in a mixture of acetonitrile (4 mL) and water (1 mL). After stirring the reaction mixture for 10 min, K₂CO₃ (1.5 mmol) was added, and stirring was continued for another 45 min at room temperature. The reaction was quenched by adding sodium thiosulfate (200 mg approximately), and stirring continued for another 20 min. The reaction mixture was extracted with ethyl acetate (3 × 20 mL), dried (Na₂SO₄), and concentrated. The crude product was purified by flash chromatography on silica gel (230–400 mesh) with petroleum ether–ethyl acetate (5%) as

eluent. The product was confirmed by analyzing NMR, infrared, and mass spectroscopic data.

ACKNOWLEDGMENT

Financial support from the Department of Science and Technology (Grant No. SR/S1/RFPC-07/2006) is gratefully acknowledged.

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