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ORIGINAL ARTICLE

Synthesis, spectral studies, antimicrobial and insect antifeedant potent keto oxiranes

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Abstract A series of ee (α*S*, β*R*) biphenyl keto oxiranes (biphenyl-4-yl[3-(substituted phenyl)oxiran-2-yl]methanones) have been synthesized by phase transfer catalysed epoxidation of biphenyl 2*E*-chalcones. The yields of oxiranes are more than 95%. The synthesized oxiranes have been characterized by IR, ^{1}H, ^{13}C and GC–MS spectra. The spectral data are correlated with Hammett substituent constants and Swain–Lupton parameters. From the regression analyses, the effect of substituent on the group frequencies has been predicted. The antimicrobial and insect antifeedant activities of all synthesized oxiranes have been evaluated.

1. Introduction

Synthetic and natural oxiranes possess various multipronged activities such as, anti-microbial (Contelles et al., 2004), anti-cancer and anti-tumour activities (Misra et al., 2008), etc. Chemists have studied a small number of natural oxiranes (Contelles et al., 2004). Many synthetic aryl oxiranes have been reported with their synthetic methods (Poter and Skidmore, 2000; Nemoto et al., 2002; Yao and Zhang, 2003) in literature. Many reagents and catalysts have been used for synthesizing oxiranes from chalcones and alkenes (Benjamin and Burgees, 2003). Alkaline hydroxides–hydrogen peroxide (Yang and Finnegan, 1958), alkaline carbonates–hydrogen peroxides (Payne, 1959), potassium hypochlorite at −40 °C (Corey and Zhang, 1999), Mn(III) complexes (Song et al., 2005; Tayebee, 2006), chromium salts (Sung and Ananthakrishna Nadar, 1999), metal hydroxides, oxides–hydrogen peroxide have been applied for epoxidation reactions (Andic et al., 2003; Ye et al., 2003; Arari et al., 2004; Bako et al., 2004; Reddy et al., 2005) in the past decade. Numerous investigations have been carried out on the catalytic asymmetric epoxidation of α,β-unsaturated ketones (Thirunarayanan and Vanangamudi, 2010; Adam et al., 2002; Allingham et al., 2003; Hashimoto and Maruoka, 2003). Catalytic asymmetric epoxidation has been given a unique place (Poter and Skidmore, 2000; Nemoto et al., 2002; Yao and Zhang, 2003) in the synthesis of organic substrates, featuring many advantages including operational

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simplicity, non-metal catalysts and highly environmental consciousness. During the last decade, greener smethods have been employed for epoxidation (Santos et al., 2004). Phase transfer catalysts (Thirunarayanan and Vanangamudi, 2010; Ooi et al., 2004) have also been applied for epoxidation reactions for obtaining the effective yields upto 96%. The effects of substituent on the group frequencies through ultraviolet–visible, infrared, nuclear magnetic both proton and carbon-13 spectra of ketones (Brown and Okamoto, 1957), unsaturated ketones (Thirunarayanan et al., 2007; Thirunarayanan, 2007a,b, 2008a), acid chlorides (Flett, 1948), acyl bromides, and their esters (Thirunarayanan and Vanangamudi, 2011) have been studied. However, literature survey shows that the study of effects of substituent on the group frequencies of oxiranes is almost absent. Therefore the authors have attempted to study the spectral linearity of the group frequencies by Hammett equation with the help of linear regression analysis for oxiranes. The epoxy ring, polar nature of carbonyl group and the substituents in phenyl rings have been found to be responsible for the medicinal activities of the oxirane compounds. Some natural epoxides have shown the biological activities (Contelles et al., 2004) and they have been used for synthesizing aziridines. Ab intio-computational studies of biological activities of some epoxides provide the information about electronic effects and steric effects (Peter and Laurence, 1984) on CO and CH bonds. Generally epoxides possess many biological activities such as vasoactivity (Carroll et al., 1987), cardiovascular activity (Imig and Hammock, 2009), EETs (Inceoglua et al., 2007), mutagenicity (Wu et al., 1993), K-region cure property (Swaisland et al., 1973), regulators of blood pressure, hypertension, pain, inflammation (Morisseau et al., 2008; Fang, 2006), anti-analgesic activity (Inceoglua et al., 2008), cytotoxicity (Yu et al., 1998) mutagenic and cell-transforming activities (Glatt et al., 1986), mutagenicity and tumorigenicity (Kumar et al., 1989, 2001). Hence the authors have attempted to study the antimicrobial and insect antifeedant activities of biphenyl keto-oxiranes.

2. Experimental

2.1. Materials and methods

All chemicals used were purchased from Sigma–Aldrich and E-Merck chemical company. Melting points of all oxiranes have been determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000–400 cm^{-1}) have been recorded on AVATAR-300 Fourier transform spectrophotometer. INSTRUM AV300 NMR spectrometer operating at 300 MHz has been utilized for recording ^{1}H NMR spectra and 75.46 MHz for ^{13}C spectra in $CDCl_3$ solvent using TMS as internal standard. Electron impact (EI) (70 eV) and chemical ionization mode FAB^+ mass spectra have been recorded with a JEOL JMS600H spectrometer.

2.2. Synthesis of substituted biphenyl chalcones

All substituted styryl biphenyl ketones were synthesized by the literature procedure (Thirunarayanan and Vanangamudi, 2006).

2.3. Synthesis of biphenyl keto oxiranes (Thirunarayanan and Vanangamudi, 2010)

Appropriate mixture of substituted styryl biphenyl ketones (0.10 mmol) and a chiral quaternary ammonium bromide–PF_6 catalyst (6 mg, 0.003 mmol, 3 mol%) in toluene (3 mL) was added to 15% aqueous sodium hypochlorite (NaOCl, 0.15 mL) and the mixture was stirred for 14 h (minimum 10 h) at 0 °C under inert atmosphere (Scheme 1). The resulting mixture was diluted with water and the organic phase was separated. Using dichloromethane, the aqueous medium was extracted and the same was repeated thrice. Then the resulting organic extract was dried using anhydrous sodium sulfate. After evaporating the solvent, the resulting product was purified using flash column chromatography on silica gel (ethyl acetate/hexane) as eluent afforded the epoxide. An optical purity of the epoxy ketone was determined by chiral stationary phase HPLC analysis. The spectral data are presented in Table 1.

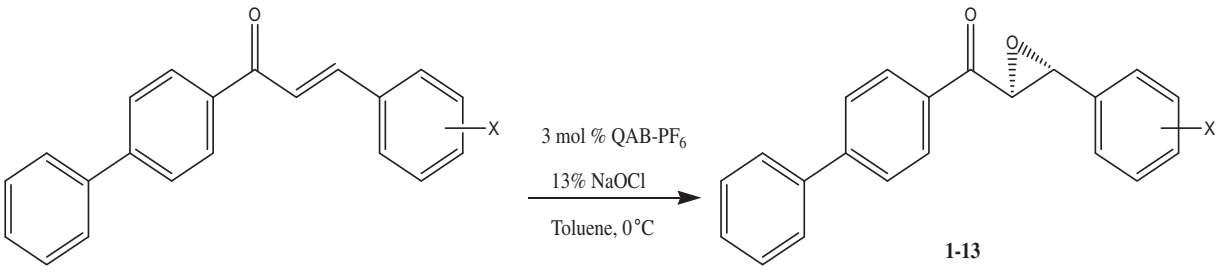
3. Results and discussion

3.1. IR spectral study

The synthesized oxiranes in the present study are shown in Scheme 1. The infrared ν_{CO} and ν_{C-O-C} stretching frequencies (cm^{-1}) of these oxiranes were recorded and are presented in Table 1. These data have been correlated with Hammett substituent constants and Swain–Lupton constants (Swain and Lupton, 1968). In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

$$v = \rho\sigma + v_o \quad (1)$$

where v_o is the frequency for the parent member of the series.



Where X = H, 3-NH_2, 4-NH_2 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO2 and 4-NO2

Scheme 1 Synthesis of epoxy ketones.

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