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Studies on Natural Products: A Facile Epoxidation of Eugenol

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Abstract

Oxidation of the alkene group of eugenol by various reagents and solvents is investigated. This method is used for a simple synthesis of eugenol epoxide in excellent yield.

Keywords: Eugenol; Epoxidation; Alkene; Natural product

Introduction

Eugenol is a natural product obtained from the dried flower buds of clove, *Eugenia caryophyllata* [1]. It is a light yellow oil-type of molecule that is extracted from nutmeg, cinnamon, cloves and bay leaf. Cloves are cultivated in India, Indonesia, Sri-Lanka, Madagascar, Tanzania and Brazil. The medicinal uses of cloves are well-known for many centuries. It can mask bad smell of human's mouth, dental treatment, reduction of fever, and sexual disorders [2-4]. It has been demonstrated that the medicinal use of cloves is due to the presence of Eugenol, a monocyclic benzene derivative that has a methoxy, a phenolic and an allyl group. In one of earlier publication, we have demonstrated nitration of eugenol and biological studies of some eugenol derivatives [5]. Chemical modifications of eugenol are not performed like many other spices. But, this molecule is well suited for structural modifications in a number of ways. In this paper, oxidation of the alkene group of eugenol and its derivatives is discussed.

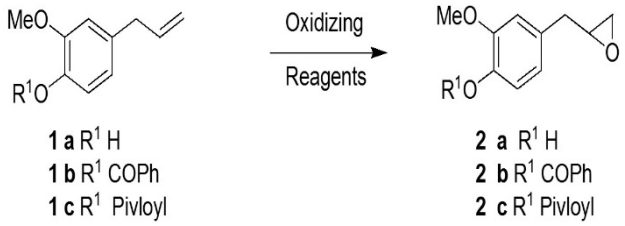
Experimental Section

Compound 1 (1 mmol) and DMDO (1.5 mmol) were taken in dichloromethane or chloroform (5 mL). The reaction mixture was stirred at room temperature (Table 1). After the reaction is completed, the organic part was washed with aqueous saturated sodium bicarbonate solution (2 mL), brine (2 mL) and dried over sodium sulfate (1 g). It was then filtered and solvent was evaporated to afford the crude epoxide 2. The crude 2 was purified through a small column of silica gel (4-5 gm) using ethylacetate-hexanes (20:80) as the solvent. Pure product 2 was identical with the compound reported earlier [5].

Results and Discussion

Oxidation is a very common organic reaction. The alkene group oxidation of eugenol to a 3-membered epoxide ring is an important objective. This reaction is sensitive because of the precise structural features present in eugenol. For example, the presence of phenolic hydroxyl group makes this molecule highly sensitive in the presence of oxidizing agents. The methoxy group next to the phenolic hydroxyl group makes the molecule even more vulnerable. This type of system in the aromatic ring is susceptible to facile oxidation to a number of known and unknown species. The alkene group is also reactive and sometimes it migrates during reaction of eugenol to maintain a conjugated system with the benzene ring.

Selective oxidation of the alkene group was attemted with eugenol and its derivatives (1a, 1b and 1c) by aqueous alkaline hydrogen peroxide at room temperature. However, the yield of the eugenol epoxide (2a, 2b and 2c) was too low. An increase of reaction time was necessary to obtain moderate yield of the product with protected eugenol (1b and 1c). An increase of time with 1a was not helpful to obtain better yield (Scheme 1 and Table 1). 3-Chloroperoxybenzoic acid and dimethyldioxiran in chloroform or dichloromethane was proved to be the reagents of choice for this oxidation reaction leading to epoxide 2 in excellent yield. No oxidation of the aromatic system, removal of the protective groups, isomerization-oxidation of the alkene functionality and cleavage of the epoxide ring was observed under these reaction conditions.



1 a R^1 H
1 b R^1 COPh
1 c R^1 Pivloyl

2 a R^1 H
2 b R^1 COPh
2 c R^1 Pivloyl

Scheme 1: Epoxidation of Eugenol and its derivatives.

Entry	Oxidizing Reagents	Solvents	Reaction time (hrs.)	Yields (%)	Products
1	H_2O_2, NaOH, H_2O	THF: H_2O (2:1)	43192	20-30	2a
	H_2O_2, NaOH, H_2O	THF: H_2O (2:1)	43256	40-50	2b
	H_2O_2, NaOH, H_2O	THF: H_2O (2:1)	43381	40-50	2c
2	Meta-Chloroperoxybenzoic acid (mCPBA)	DCM/$CHCl_3$	43255	60-70	2a
	Meta-Chloroperoxybenzoic acid (mCPBA)	DCM/$CHCl_3$	43255	60-70	2b
	Meta-Chloroperoxybenzoic acid (mCPBA)	DCM/$CHCl_3$	43285	60-70	2c
3	Dimethyldioxirane (DMDO)	DCM/$CHCl_3$	43193	70-80	2a
	Dimethyldioxiran (DMDO)	DCM/$CHCl_3$	43193	70-80	2b
	Dimethyldioxirane (DMDO)	DCM/$CHCl_3$	43193	70-80	2c

Table 1: Optimization of reaction condition of the epoxidation of Eugenol and its derivatives.

Conclusion

In conclusion, we have identified a facile route for the preparation of epoxide of eugenol and its derivatives in excellent yield. The epoxide group can be used for additional functionalization towards bioactive molecules.

Acknowledgements

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