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One pot reaction to synthesize allyl etherified eugenol from clove oil

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Abstract. The research to improve the value of eugenol as the main component of clove oil by modification its structure to allyl etherified eugenol through nucleophilic substitution reaction had been done. Further, the modification product was hoped to be starting material for other valuable substances. The reaction of allyl etherified eugenol synthesis was done by reacting eugenol with allylbromide using NaOH as a catalyst. The final product was analysed its structure using FT-IR spectrophotometer and Mass Spectrometer. The synthesized product was yellowish liquid with specific gravity and yield of 1.2 g/mL and 96%, respectively. IR and mass spectrum showed the presence of Csp³-H, Csp²-H, O-C and C=C for the former and the value of M⁺ = 204 for the later that revealed the functional groups and molecular weight of allyl etherified eugenol (1-allyl-4-allyloxy-3-methoxybenzene).

Keywords: eugenol, nucleophilic substitution reaction, allyl-etherified eugenol

1. Introduction

Research to improve the value of eugenol and clove oil become an interesting study. This is related to the fact that clove oil's usage is still limited and mainly exported as crude oil [1-3]. Therefore, it does not give a high contribute to the country's foreign exchange because the price is relatively cheap. One attempt to overcome this issue is to isolate and modify the component of clove oil into new compound which are expected to be used as a base material to synthesize other useful compounds.

Eugenol is the main component of clove oil (70-90%), which can be modified into other compounds as it has allyl, benzene ring, hydroxyl, and methoxy groups. Hydroxyl group (phenolic) can act as a nucleophile in nucleophilic substitution reaction with alkyl halide. Some of eugenol derivatives have been synthesized successfully, such as benzyl eugenol (4-allyl-1-(benzyloxy)-2-methoxybenzene) which was obtained through reaction with benzyl chloride [4], methyl isoeugenol (1,2-dimethoxy-4-prop-1-enylbenzene) which was obtained through reaction with methyl iodide [5-7] and allyl etherified eugenol (1-allyl-4-allyloxy-3-methoxybenzene) which was obtained through reaction with allyl bromide [8].

Reaction that occur in allyl etherified eugenol synthesis follows bimolecular nucleophilic substitution (S_N2) mechanism. To improve nucleophilicity of eugenol, NaOH as catalyst is added to attack an acidic phenolic hydrogen from eugenol to form eugenolate (phenoxy) ion. Eugenolate/phenoxy ion is a very strong nucleophile [9]. This reaction is similar with eugenol isolation from clove oil.



Therefore, this approach can be carried out into allyl etherified eugenol (1-allyl-4-allyloxy-3-methoxybenzene) synthesis directly from clove oil.

In term of chemical synthesis, an efficient method with a less step reactions and a large yield in synthesis is desired. Allyl etherified eugenol synthesis directly from clove oil offers a more efficient process because this reaction only occurs in one step reaction without going through eugenol isolation. This paper explains the synthesis of allyl etherified eugenol through nucleophilic substitution reaction with allyl bromide. This research is expected to be an alternative method for a more efficient and eco-friendly step for synthesis of allyl etherified eugenol.

2. Methods

2.1. Materials

Clove oil (obtained from traditional market in Semarang area), NaOH, HCl, Allyl bromide, petroleum ether, $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, H_2SO_4 , and anhydrous Na_2SO_4 (all are obtained from Merck).

2.2. Clove oil Purification

Clove oil was purified using distillation (redistillation) to get a purer clove oil.

2.3. Allyl Etherified Eugenol Synthesis

A pure clove oil (20 g) was added into a flask containing NaOH (5 g). The mixture was then stirred with magnetic bar for 10 minutes. The water layer was separated and an allyl bromide (13.3 g; 0.11 mol) was added dropwise over a period of 1 h at 40°C . After the addition, the mixture was stirred at 40°C for 3 h. The reaction mixture was poured into water and was extracted with petroleum ether. The organic layer was washed with water twice, and dried over sodium sulphate. A solvent from the mixture was evaporated using rotary evaporator. The product obtained was analysed using Fourier Transform Infrared Spectroscopy (FT-IR) and GC-MS.

3. Result and Discussion

The first step in this research was purification of clove oil using fractional distillation under reduced pressure. The result is presented in Table.1

Table 1. Clove leaf oil re distillation

Fraction	Temperature ($^\circ\text{C}$)	Pressure (mmHg)	Volume (mL)
I	100	10	30
II	130	10	67.5
III	200	10	412.5

The 3rd fraction from clove oil distillation was used for allyl etherified eugenol synthesis. Allyl etherified eugenol synthesis could be done from clove oil directly without going through eugenol isolation. This approach was based on eugenol isolation's principal through formation of sodium eugenolate. Sodium eugenolate is soluble in water while the oil component is still in the organic phase. The formation of sodium eugenolate is the first step of allyl etherified eugenol synthesis. Eugenolate ion is a stronger nucleophile than eugenol so that substitution reaction between eugenolate ion and allyl bromide is more preferred. Substitution reaction of allyl bromide followed bimolecular nucleophilic substitution mechanism ($\text{S}_{\text{N}}2$). The reaction is presented in Fig.1.

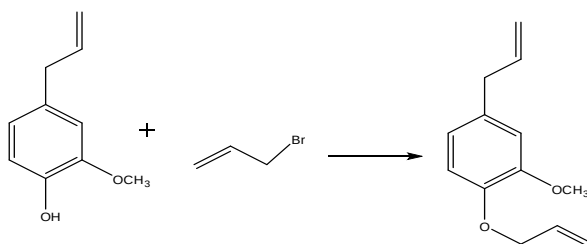


Figure 1. Reaction of Allyl etherified eugenol synthesis.

Allyl etherified eugenol product was a yellowish liquid with specific gravity of 1,2 g/mL and a yield of 96%. GC-MS analysis obtained a chromatogram which is presented in Fig 2.

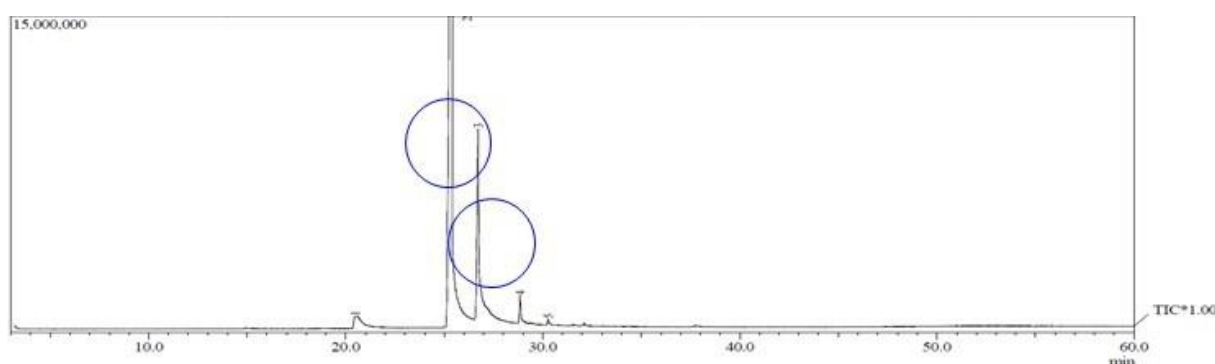


Figure 2. Chromatogram of allyl etherified eugenol.

Figure 2 showed that there were 2 dominant peaks (the 2nd and 3rd peaks) in the chromatogram. The 2nd peak has retention time and % abundance of 25.366 mins and 77.87%, respectively. While, the 3rd peak showed 26.714 mins and 17.86%, respectively.

The mass spectrum of both peaks showed similar m/z of 204 but different fragmentation. We could evaluate that both peaks were a different compound. The mass spectrum of the 2nd and 3rd peaks are showed in Fig 3 and Fig 4, respectively.

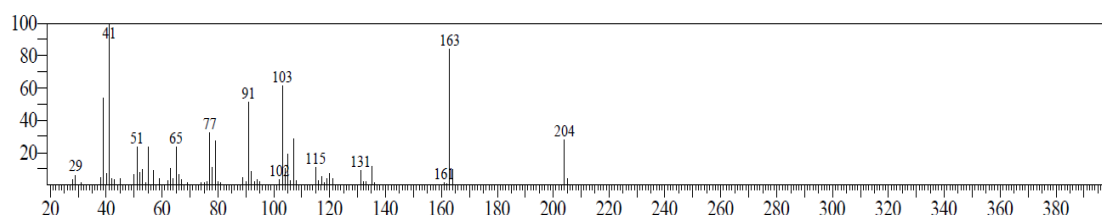


Figure 3. Mass spectrum of the 2nd peak.

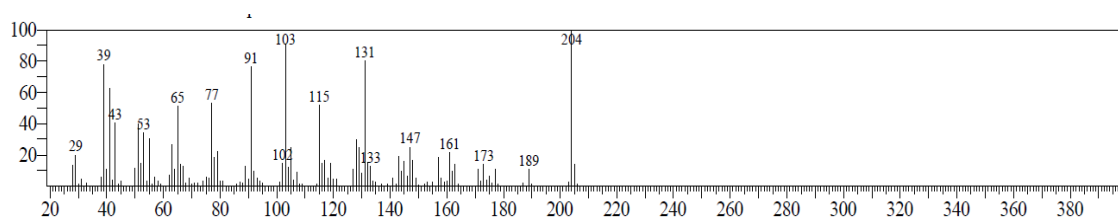


Figure 4. Mass Spectrum of the 3rd peak

From the mass spectrum data, it could be concluded that the 2nd peak (Fig. 3) was a fragmentation of allyl etherified eugenol. Its fragmentation pattern showed in Fig. 5.

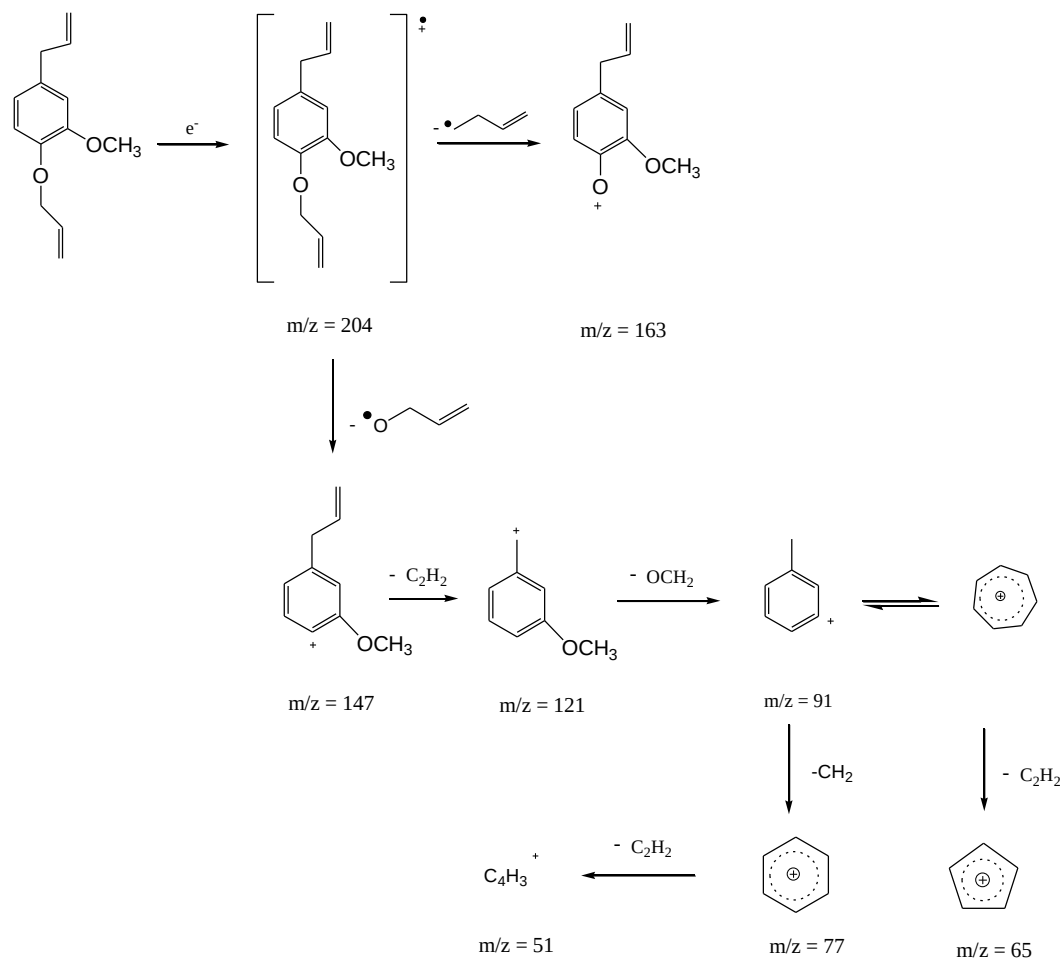


Figure 5. Fragmentation Pattern of Allyl Etherified Eugenol.

The 3rd peak mass spectrum (Fig. 4) showed that allyl etherified eugenol ran into rearrangement reaction resulting 4,6 methoxy diallyl 2 methoxy phenol. M/z value of 204 simply showed that this compound was a rearrangement reaction result [10] (Fig. 6). The fragmentation pattern can be observed from Fig 7.

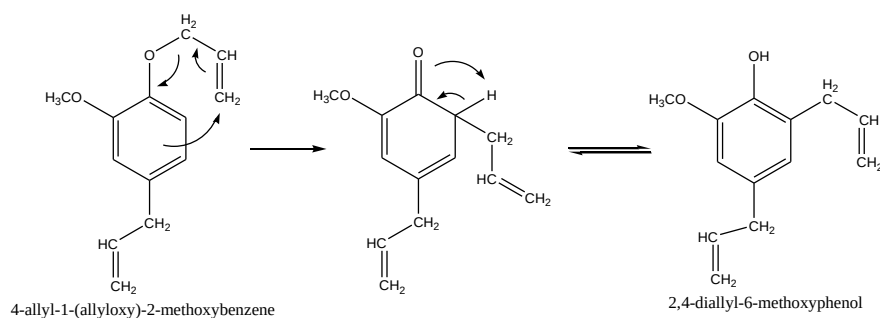


Figure 6. Rearrangement reaction of allyl etherified eugenol.

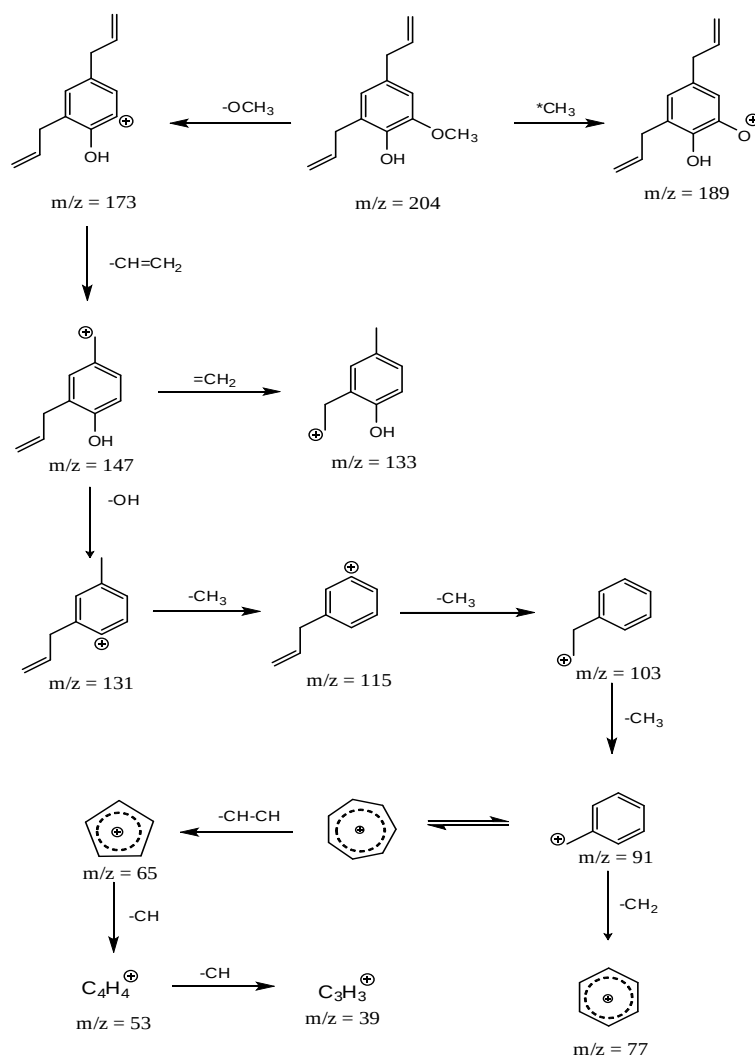


Figure 7. Fragmentation pattern of 4,6 methoxy diallyl 2 methoxy phenol rearrangement reaction.

Rearrangement reaction was strengthened by FTIR spectrum showed in Fig 8. We could qualitatively evaluate that the band at 3500 cm^{-1} was an OH vibration of 2,4-diallyl-6-methoxy phenol. Absorption band of $\text{Csp}^2\text{-H}$, aromatic $\text{C}=\text{C}$, and $\text{C}=\text{C}$ alkenes were showed respectively at 3100 cm^{-1} ; 1600 cm^{-1} ; and 1650 cm^{-1} .

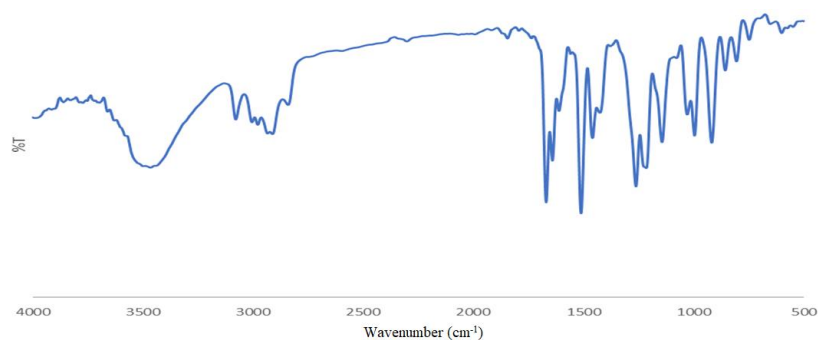


Figure 8. FTIR spectrum of rearrangement of allyl etherified eugenol.

4. Conclusion

Allyl etherified eugenol synthesis could be done by directly reacting clove oil with allyl bromide using NaOH catalyst through bimolecular nucleophilic substitution reaction. Allyl etherified eugenol is obtained as a yellowish liquid with specific gravity of 1,2 g/mL and a yield of 96%.

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