

REGIOSELECTIVE EPOXIDATION OF GERANIOL WITH  
m-CHLOROPERBENZOIC ACID IN EMULSION SYSTEMS

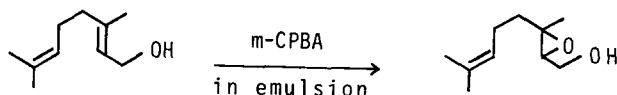
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Summary: Oxidation of geraniol with m-chloroperbenzoic acid (m-CPBA) in emulsion systems gave 2,3-epoxygeraniol selectively in high yield.

The regioselective epoxidation of allylic double bond of polyolefinic alcohols with t-butyl hydroperoxide in the presence of  $\text{Mo}^{6+}$  or  $\text{V}^{5+}$  complexes is well known.<sup>1)</sup>

We have now found that geraniol is oxidized with m-CPBA in the emulsion systems formed by surfactant to yield 2,3-epoxygeraniol with high selectivity.



The epoxidation of geraniol was carried out as follows: To a stirred emulsion consisting of geraniol (100 mg, 0.648 mmol), n-hexane (2 ml), n-octanol (100 mg), water (20 ml), NaOH (120 mg), and dioctadecyl dimethylammonium chloride (50 mg)<sup>2)</sup> was added m-CPBA (2 eq.)<sup>3)</sup> in several portions at 25 °C during 5 hr and the stirring was continued for additional 15 hr. The reaction mixture was extracted with two 30 ml portions of chloroform<sup>4)</sup> and the organic layer was washed with aqueous solution of  $\text{NaHCO}_3$ , NaCl and dried over  $\text{Na}_2\text{SO}_4$ . Removal of solvent gave 2,3-epoxygeraniol in 93 % yield. Neither the regioisomeric 6,7-epoxygeraniol nor diepoxygeraniol were detected.

Other surfactants were also effective for this highly selective epoxidation reaction as shown in Table I. The use of cationic surfactants resulted in higher conversion ratio than that of anionics. This would be explained by easy approach of m-CPBA anion<sup>5)</sup> to substrate in the cationic emulsion systems. In the anionic systems the contact of the reagent to substrate would be prevented. These behaviors are believed to be caused by a well-known Coulombic attraction or repulsion at the micelle surface.<sup>6)</sup>

The observed high selectivities would be resulted from the orientation of geraniol molecule of which polar hydroxy group was faced to water phase. Therefore, the double bond at 6,7-position apart from polar head group was protected with long alkyl chains of surfactants or with hexane phase and was not attacked by m-CPBA anion in water phase or at the interface. This led to the highly selective formation of 2,3-epoxygeraniol. Similarly, nerol was selectively oxidized with 2.0 eq. of m-CPBA in this emulsion system containing 18,18-AC to yield 2,3-epoxynerol in 93 % yield. The regioisomeric 6,7-epoxynerol or diepoxynerol were not detected.

Table I ; Epoxidation of geraniol in the emulsion systems<sup>a)</sup>

| Surfactant <sup>b)</sup> | Conv.% <sup>c)</sup> | Select.% <sup>d)</sup> |
|--------------------------|----------------------|------------------------|
| S L                      | 10                   | 98 <sup>e)</sup>       |
| 8,8-AC                   | 48                   | 98 <sup>e)</sup>       |
| S D S                    | 14                   | 100                    |
| CTABr                    | 33                   | 100                    |
| 18,18-AC                 | 65                   | 100                    |
| 18,18-AC <sup>f)</sup>   | 93                   | 100                    |

- a) The conversion and products ratio were determined by GLC(3 %,OV-17) after acetylation (Py.-Ac<sub>2</sub>O) using n-decyl acetate as a internal standard.
- b) 50 mg of surfactant was used. 8,8-AC(dioctyl dimethylammonium chloride), SDS(sodium dodecylsulfate), CTABr(hexadecyl trimethylammonium bromide), SL(sodium laurate), 18,18-AC(dioctadecyl dimethylammonium chloride).
- c) Conversion of geraniol.
- d) Percentage of 2,3-epoxygeraniol in the products.
- e) Only byproduct detected was 6,7-epoxygeraniol and the diepoxygeraniol was not detected. All spectral and analytical deta of the products isolated by the chromatography on a silica gel column were consonant with the assigned structures.
- f) 2 eq. of m-CPBA was added only for this run, others under 1.1 eq. of reagent.

#### References and Notes

- 1) K.B.Sharpless,R.C.Michaelson, J.Amer.Chem.Soc.,95,6136(1973).
- 2) Dioctadecyl and dioctyl dimethylammonium chloride were used after drying of commercial products (Nikkoh Chemicals Co.) without further purifications.
- 3) Commercial m-CPBA (80 % active oxygen) was used without further purifications.
- 4) 18,18-AC is more soluble in CHCl<sub>3</sub> than in water and most of the surfactant is extracted together with reaction products.
- 5) m-CPBA is considered to exist as anion form because of the presence of excess NaOH in the reaction mixture.
- 6) J.W.Larsen,L.J.Magid, J.Amer.Chem.Soc.,96,5774(1974). J.H.Fendler,E.J.Fendler,"Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York,1975.

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