TA: Seong-Min Cho

# Dimerization of Monoterpene Hydrocarbons

Turpentine oil, with a productivity of around 330,000 tons per year, is one of the most widely produced secondary metabolites of plants. Two major components of turpentine, namely α-pinene and β-pinene, can be isolated from the crude material and have extensive applications in solvent, resin, precursors, pharmaceutical intermediates and commodities. Moreover, their dimers have potential applications in lubricating oil and aerospace fuels. In particular, blended high-density fuels consisting hydrogenated dimers and distillate fuels has been developed, such kinds of high-density fuels are very promising in extending the flight distance of vehicles.

## 1. Materials and Equipment

‡ Materials: Turpentine oil (JUNSEI)

Tin (IV) chloride pentahydrate 98% ($SnCl_4 \cdot 5H_2O$, SAMCHUN)

Sodium chloride 99% (NaCl, SAMCHUN)

Sodium sulfate, anhydrous 98.5% ($Na_2SO_4$, SAMCHUN)

Ethyl acetate 99.5% (EtOAc, SAMCHUN)

‡ Equipment: Magnetic Stirrer/Hotplate, rotary evaporator, GC/MS

## 2. Methods

‡ General Procedure

(1) Mixing turpentine oil (10 g) with $SnCl_4 \cdot 5H_2O$ (2 g) at ambient temperature

(2) Heating the mixture at 90°C for 20 min at 150 rpm

(3) Cooling the reaction mixture with water

(4) Purifying the products and analyzing them with GC/MS

‡ Purification with Solvent Extraction

(1) Diluting the cooled reaction mixture with 200 mL of EtOAc

(2) Pouring the EtOAc solution into a separatory funnel and adding 100 mL of distilled water

(3) Sufficiently shaking the separatory funnel and waiting until water and EtOAc layers are separated

(4) Discarding the water layer and add 100 mL of distilled water to EtOAc solution

(5) Repeating the step (3) and (4) three times (Skip the addition of distilled water at last repetition)

(6) Adding 100 mL of aqueous saturated NaCl solution to EtOAc solution

(7) Sufficiently shaking the separatory funnel and wait until water and EtOAc layers are separated

(8) Discarding the water layer

(9) Eliminating a small quantity of water in the EtOAc solution with $Na_2SO_4$ as a drying agent

**§ Report**

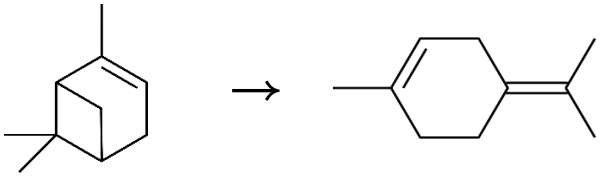
※ The report must be taken in the following order (in Korean or English); 1. Materials and Methods (Please describe your narration. Do **not** just copy and paste the above protocol!!), 2. Results (Attach an uploaded file with the simple explanation of peaks), 3. Discussion (substituted by assignments), 4. References (optional)

※ Assignment 1

Explain how terpenes are biosynthesized from D-glucose. Please include the major precursors of mono-, sesqui-, di-, and sesterterpenes.

※ Assignment 2

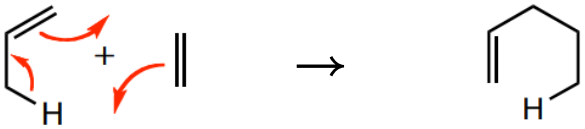
α-Pinene is a bicyclic monoterpene chemical constituting the major component of turpentine oil. Propose the possible mechanism of the below isomerization in terms of Brønsted acid-catalyzed (a) and Lewis acid-catalyzed (b) reaction.



α-pinene terpinolene

※ Assignment 3

One possible suggestion for the dimerization in our experiment is Lewis acid-catalyzed Alder-Ene reaction. The mechanism of this kind of reaction is following:




Let's assume that (1) the starting material is only α-pinene, (2) α-pinene can be easily isomerized to terpinolene by the Lewis catalyst, (3) the concentration of isomerized product increased immediately after the reaction was initiated but its level was almost constant until all α-pinene was consumed in the reaction mixture, (4) because α-pinene has the much faster rate of isomerization than rate of dimerization, it scarcely participated in dimer formation. Please propose the possible dimer products by Alder-Ene reaction in the above system.

※ Assignments should be appended to the report. (If you copy and paste them, you can not get a grade.)

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