Synthesis of Camphor by the Oxidation of Borneol

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Introduction

Oxidation and reduction reactions, or redox reactions, are extremely important in organic chemistry. The majority of carbonyl chemistry involves redox reactions to either oxidize alcohols to form carbonyl groups or reduce carbonyl groups to produce an alcohol$^1$. The preparation of camphor is one example of the use of redox reactions. One method of synthesis of camphor involves the oxidation of the secondary alcohol in borneol to produce the ketone present in camphor.

Camphor is a naturally occurring compound that can be isolated from a certain evergreen tree ($Laurus camphora$)$^2$. In the past, due to the natural occurrence of the compound and its ease of isolation, camphor has mainly been used for medicinal purposes. However, recently, more uses of camphor have been explored. Today, the best estimates of the uses of camphor are as follows: 80% in manufacturing celluloid and film, 10% in medicine, 6% in Indian incense and religious ceremonies, 2% in gunpowder and fireworks, and 2% in perfumes$^2$. There has also been increased research into the use of camphor as an antiseptic, analgesic, anti-pruritic, and counterirritant$^3$. Another more recent field of research involving camphor is the use of nanotechnology. Camphor is a very eco-friendly and easily obtained compound that shows about 50% efficiency in the production of carbon nanotubes$^4$.

Although camphor can be easily steam-distilled from a specific tree, that tree is not always readily available. Therefore, there are various methods available to synthesize camphor. One method involves the oxidation of borneol using Oxone as an environmentally friendly oxidizer and sodium chloride as a catalyst. The reaction mechanism is shown below.
The mechanism for the synthesis of camphor involves the oxidizer formation using chloride and Oxone to produce chlorine hydroxide and release sulfate. The chlorine hydroxide is then protonated to produce a $\text{ClH}_2\text{O}^+$ ion. The oxygen on borneol then attacks the chlorine in the ion and chlorine oxygen bond electrons are pushed to the oxygen to add chlorine to borneol and a water molecule. The oxygen from the water molecule then deprotonates borneol and the hydrogen carbon bond electrons are pushed to the oxygen carbon bond to produce a double bond while the chlorine acts as a leaving group.

Oxone is used for the oxidation because it is considered to be environmentally friendly, relatively inexpensive, and an appropriate reagent for a “green” reaction. Green chemistry is the term given to the effort to reduce waste, especially hazardous waste, generated by chemical reactions. Green chemistry also refers to the effort to create products and processes that accomplish specific goals in terms of reducing waste. The byproducts produced by the reaction using Oxone do not pose the environmental threats to aquatic life upon disposal that the same reaction using a different oxidizer, such as chromium trioxide, would produce.
The experiment was an excellent example of the benefits of green chemistry and how one method of synthesis may be better than another. The purpose of the experiment was to efficiently synthesize camphor in an environmentally friendly way. The experiment also provided an opportunity to purify a compound by sublimation and analyze a compound using methods such as melting point, $^1$H NMR, IR spectroscopy, GC-MS. These are all very useful and commonly used techniques in fields that involve any amount of organic chemistry.

**Experimental**

**Camphor.** Borneol (0.50 g) was added to ethyl acetate (2 mL). The solution was stirred and Oxone (1.21 g), sodium chloride (0.04 g), and distilled water (0.75 mL) were added. After one hour, sodium chloride (0.02 g) was added. After 15 minutes, distilled water (7.5 mL) and a scoop of sodium bisulfate were added. The product was extracted using ethyl acetate (3 x 5 mL) and washed with saturated sodium chloride solution (5 mL). The organic layer was decanted off and isolated to yield (0.4600 g, 94%). The product was then purified by sublimation (0.20 g, 42%) mp178-184°C; $^1$H NMR (60 MHz, CDCl$_3$: $\delta$ (ppm) 2.0 (m, 4H), 1.4 (m, 4H), 0.9 (t, 9H); IR (ATR) $\nu_{\text{max}}$ (cm$^{-1}$) 2956, 1739, 1449, 1388; GC-MS (5% phenyl methyl silicone, 40°C to 250°C at 10°C per min) RT 13.00 min, m/z 151.99.

**Results and Discussion**

In this experiment, camphor was synthesized from borneol using Oxone in a reaction that exemplifies the advantages of “green” chemistry. Camphor was then purified by sublimation. The synthesis involved the use of sodium chloride as a catalyst. Therefore, with Oxone as the oxidizer and sodium chloride as the catalyst, the reaction environment occurs under acidic conditions and sodium bisulfate was added at the end of the reaction to quench it. The synthesis was followed by the extraction.
of the aqueous layer by ethyl acetate. Finally, any water molecules left in the organic layer were extracted using a wash of saturated sodium chloride solution and anhydrous sodium sulfate. The purification was made possible by the compact and symmetrical structure of camphor, resulting in its tendency to sublime when heated. The purification was carried out using a test tube and hot sand bath, leaving a white, crystalline solid in a ring around the inside of the test tube, about halfway up the glass.

The percent yield before the purification was 94% and the final percent yield was 40%. The percent recovery from the purification was 42%. The 94% conversion of borneol to camphor is consistent with what could be expected. Other experiments averaged a conversion rate of anywhere from 75% to 97%. The same experiments yielded an average yield of about 70% for the pure product. This puts the 40% yield that was achieved on the very low end of the spectrum. This low yield is due to a very low percent recovery that could stem from a few problems. One possibility is that the test tube might have been too vertical and some product may have been lost during sublimation. Another possibility could have been that some product was just left in the test tube during the transfer to the watch glass.

Although the overall percent yield was on the lower end of the literature values, all of the spectral data indicates a very successful synthesis and purification of camphor. The \(^1\)H NMR spectrum indicates three methyl groups and approximately seven other hydrogens to correspond to the correct number of hydrogens in camphor. There are no singlets with an integral of one that would appear if there was any of the starting material left in the final product. The IR spectrum confirms the lack of starting material due to the absence of a broad peak around 3000 to 3300 cm\(^{-1}\) that would indicate an alcohol. The peak at 1739 cm\(^{-1}\) indicates the presence of a carbonyl that corresponds to the ketone in camphor. The GC-MS indicated only one compound present in the product. The only peak was at a run time of 13 minutes and had a molecular ion peak of approximately 152 m/z. This peak corresponds to
the molecular weight of camphor, has a 100% composition, and confirms that the final product contained only pure camphor. The melting point of the crude versus the purified products also shows the efficiency of the purification technique used. The melting point for the crude product was between 167-172°C while the melting point for the pure product was 178-184°C. The increase in the melting point of the product indicates an increase in the purity of the sample.

The experiment is an excellent example of the efficiency of the synthesis of camphor in an environmentally friendly way. The experiment also demonstrated the efficiency, ease, and cost effectiveness of sublimation as a means of purification. Finally, during the analysis, an opportunity to explore various means of qualitatively assessing the purity of the compound was provided. GC, GC-MS, $^1$H NMR, IR, and melting point were all used to determine confirm the efficiency of the synthesis and purification of camphor by the oxidation of borneol.

References


Supplemental Information

**Figure 1.** $^1$H NMR of Camphor

**Figure 2.** IR of Camphor

**Figure 3.** GC-MS of Camphor