Honors Cup Synthetic Proposal

Section: 231
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Title: Synthesizing Vanillin

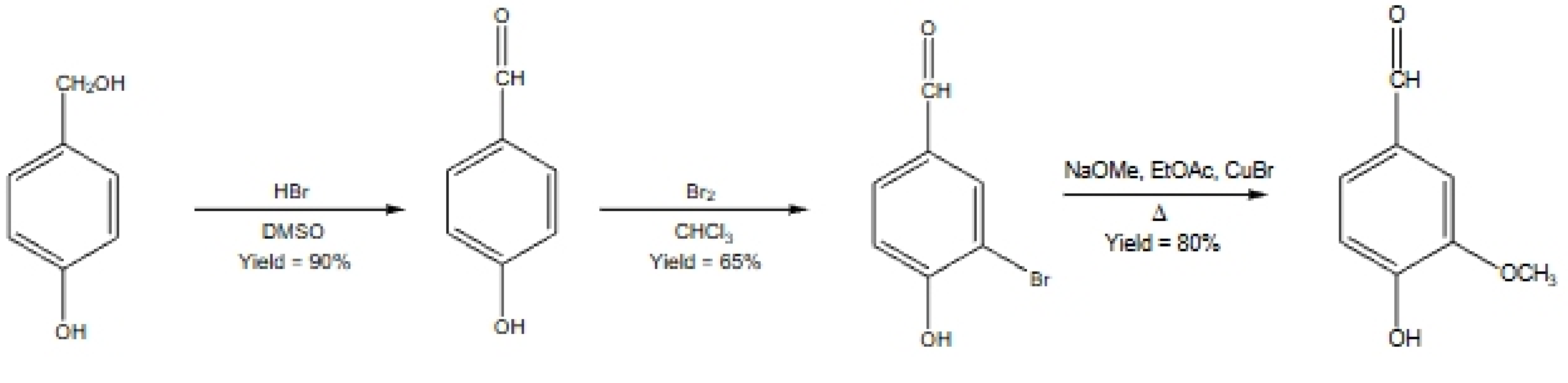
Introduction: (what makes your target interesting?)

The vanilla bean is a long, thin pod produced from the orchid *vanilla planifolia*. Its sweet aromatic scent and characteristic as an aphrodisiac made it a rare treat for royalty. The Aztecs used vanilla to flavor their cocoa drink xocolatl, and today we use it to add flavor to chocolates as well as ice cream and pharmaceutical products. The vanilla bean is still relatively expensive and its production is very time-consuming compared to vanillin, an extract of the vanilla bean. Vanillin costs only $15 a kg compared to $82 a kg of vanilla bean. Also, vanilla orchid blossoms open only for a couple of hours one day a year. After that, they must be hand-pollinated, hand-picked, and cured. The process of collecting natural vanilla takes many, many months. The product, the thin coat with a white, powdery coating called vanillin found on the bean, is what we hope to produce synthetically and much more quickly in our experiment.

Due to the setbacks of natural vanilla, the world demands vanillin at about 3000 tons per year. Vanillin is a very important aspect of food, medicine, and culture, and is a fine chemical for investigation.

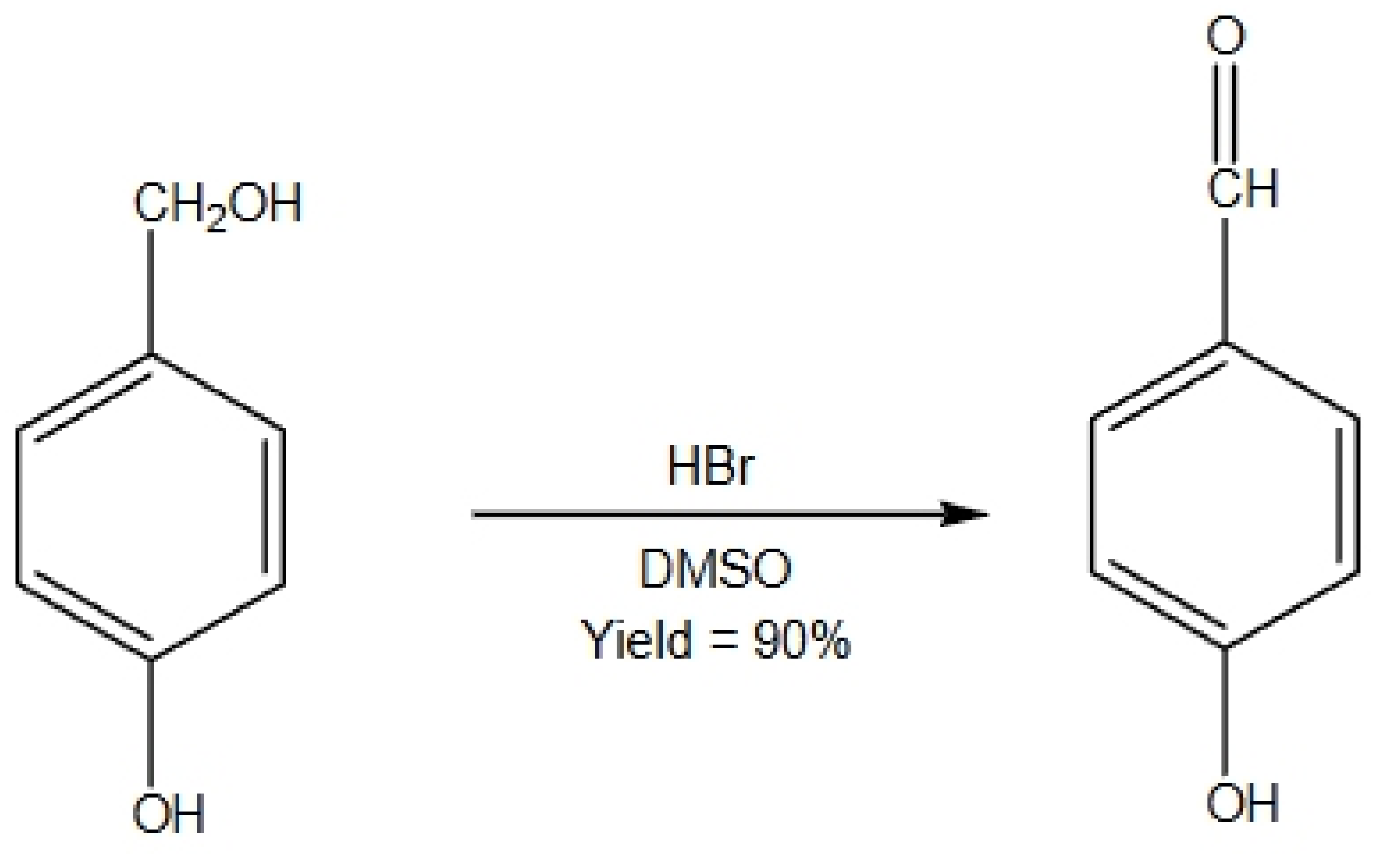
The more common synthesis of vanillin uses a Reimer-Tiemann reaction with guaiacol as a reactant. Though the reaction yields an 85% yield of vanillin, it also forms ortho-vanillin as a sub-product. Ortho-vanillin is a toxic substance. It is difficult and not ideal for the food industry to separate vanillin from the mixture of the product in its purest form. So instead of using guaiacol as a starting material, we will be using a para-molecule in our reaction so that no ortho product will be formed.

Overall synthetic reaction scheme: (a Chemdraw or similar drawing of all three steps)



Step 1

Synthetic transformation 1: (Chemdraw picture of first transformation)



4-hydroxybenzyl

4-hydroxybenzaldehyde

Experimental 1 (notes if this transformation is not exactly the one reported in literature (e.g. on a different scale) and how it was modified):

0.871g of 4-hydroxybenzyl alcohol was mixed with 7.82 mL of DMSO and 0.235 mL of HBr(48%) and stirred in an oil bath at 100°C for 3 hours. 10 mL of brine was added to the reaction mixture followed by extraction with 40 mL of diethyl ether. The ether layer was washed with brine (20 mL). Ether in the mixture was evaporated and the subsequent solution was distilled to produce around 0.771 g of 4-hydroxybenzaldehyde. (note: boiling point of 4-hydroxybenzaldehyde is 117-119°C)

The ideal yield is 95% but the expected yield for this experiment was reduced to 90% to allow room for error

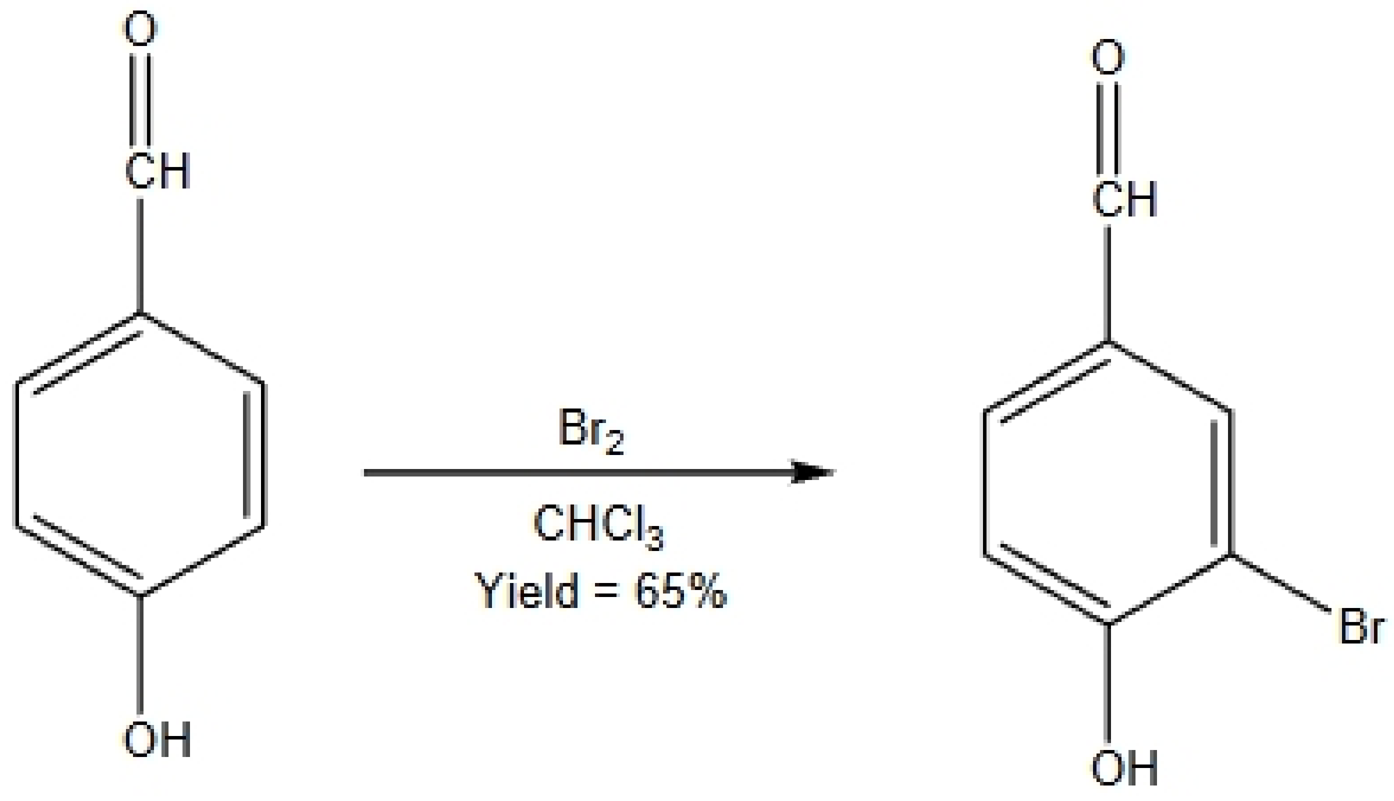
Expected yield: 90% 0.771g

Safety, disposal and green issues:

Hydrobromic acid is a corrosive material, and must always be handled with care. Wear gloves and goggles whenever hydrobromic acid is handled.

Step 2

Synthetic transformation 2: (Chemdraw picture of second transformation)



4-hydroxybenzaldehyde 3-bromo-4-hydroxybenzaldehyde

Experimental 2 (notes if this transformation is not exactly the one reported in literature (e.g. on a different scale) and how it was modified):

3.02 g of Br_2 was dissolved in 30 mL of methanol. The mixture was cooled for 10 mins by swirling in an ice/water bath. 4-hydroxybenzaldehyde obtained from the previous synthesis step was added to the cold Br_2 solution slowly with swirling. After 30 seconds, the reaction was quenched with 15ml of 5% aqueous sodium bisulfite and swirled. The aqueous mixture was extracted with 100 mL diethyl ether. The solution was dried over sodium sulfate. Using rotary evaporation, around 0.699 g of the pink solid 3-bromo-4-hydroxybenzaldehyde was yielded.

Expected yield: 65% 0.699g

Safety, disposal and green issues:

2.5M bromine solutions are extremely caustic and the vapors are dangerous as well. Bromine solution should be handled in the hood as much as possible.

Step 3

Synthetic transformation 3: (Chemdraw picture of third transformation)