

Honors Cup Synthetic Proposal

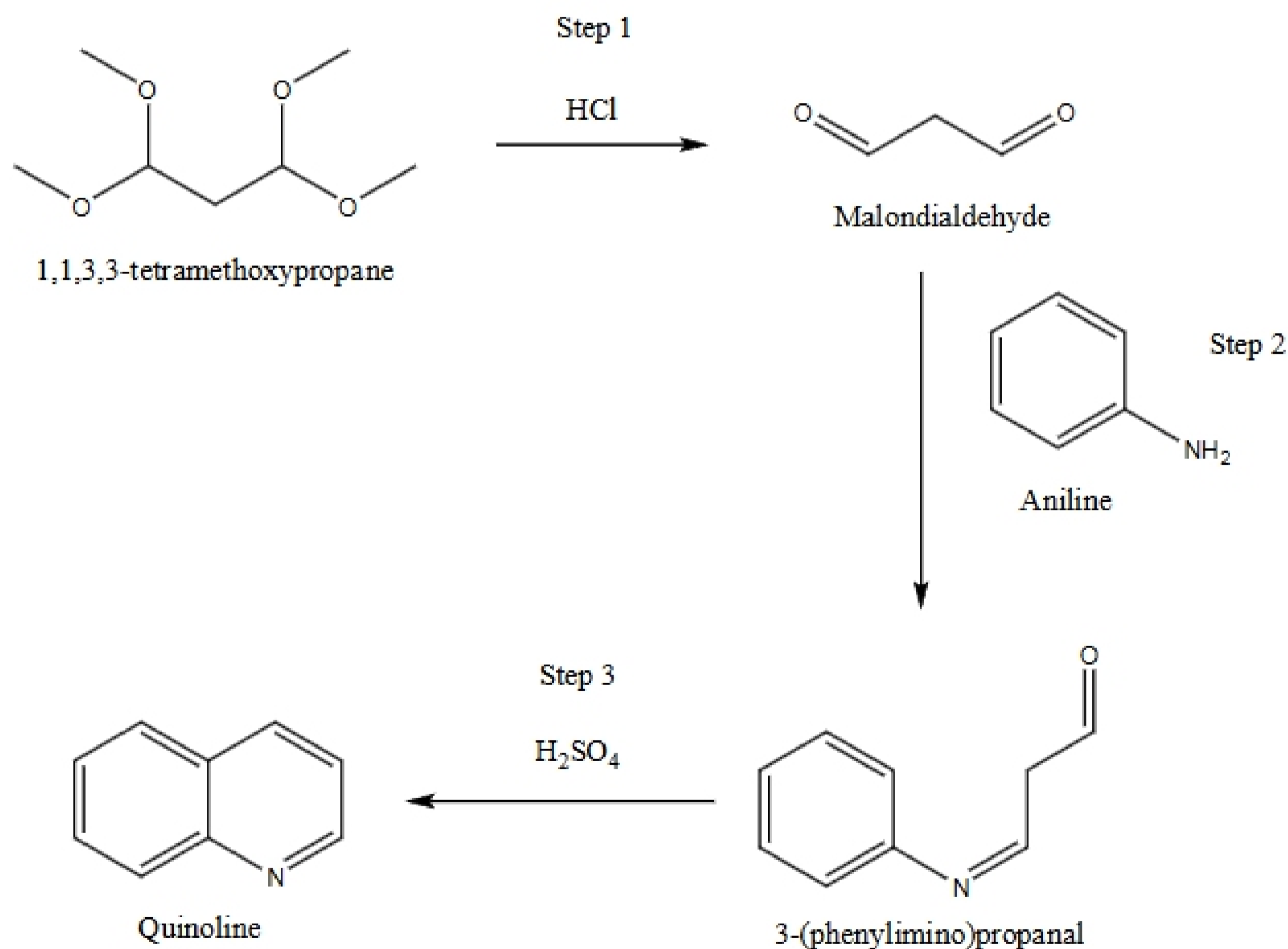
Section: 270-IV

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Title: Synthesis of Quinoline from 1,1,3,3-Tetramethoxypropane

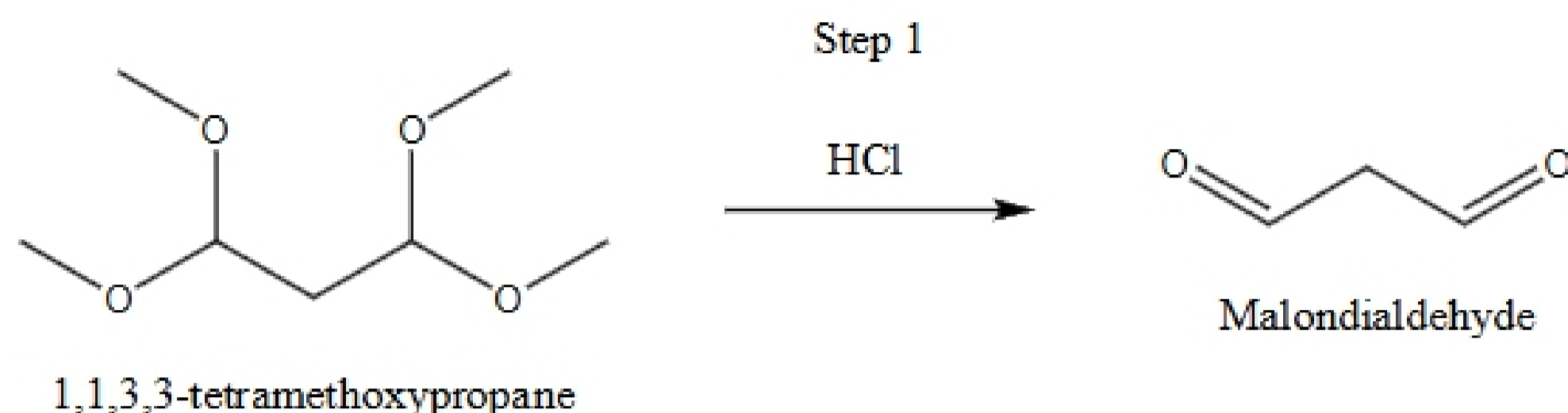
Introduction: Quinoline is used mainly as an intermediate in the manufacture of other products. Quinoline is also used as a catalyst, a preservative for anatomical specimens, and a corrosion inhibitor. Additionally it is also valuable the manufacture of dyes, polymers and agricultural chemicals and as a solvent for resins and terpenes. It is best known to students as a theoretical poison catalyst that prevents a carbon triple bond from being saturated by hydrogen, causing the reaction to rather stop at a carbon-carbon double bond. It is primarily extracted from coal tar, though through a somewhat expensive and not too reliable process. Quinoline is commonly produced by organic chemists through synthesis so as to create a readily available source of quinoline. The Combes reaction, carried out here in the second and third steps, was first documented in the late 1880s as an efficient model for the synthesis of the molecule.

Overall synthetic reaction scheme:



Step 1

Synthetic transformation 1:



Experimental 1:

The transformation of malondialdehyde is performed nearly as detailed in the cited articles. The articles did not include any particular amounts of 1,1,3,3-tetramethoxypropane or HCl so amounts have been created to fit our purposes. There is also no explicit mention of a percent yield, but the reaction is extremely favorable, rapidly occurs, and is implied to have 100% yield. Any non-reaction should be considered negligible. The reaction produces 4 molecules of methanol for every molecule of malondialdehyde. A procedure to separate the two compounds was never discussed, but can easily be performed through exploitation of differing boiling points.

10 mL of 1,1,3,3-tetramethoxypropane was placed into a beaker and 5 mL of .01 M hydrochloric acid added. The reaction was allowed to take place for 30 seconds. The resulting solution was heated on a hot plate to 65 degrees Celsius under the hood. Once the solution reached this temperature, the byproducts of the reaction, methanol and HCl, will have boiled off leaving pure malondialdehyde.

Expected yield: 100 % 9.97g malondialdehyde

Safety, disposal and green issues 1:

A lab apron, goggles, and gloves are required for all stages of step 1.

Although an excess of malondialdehyde was produced, wasting chemicals and not following environmentally friendly protocol, this was necessary in order for the reaction to be completed on a realistically large scale.

1,1,3,3-tetramethoxypropane is flammable and in case of contact with eyes, rinse immediately with plenty of water and seek medical advice. It can be disposed of in the liquid organic waste bucket.

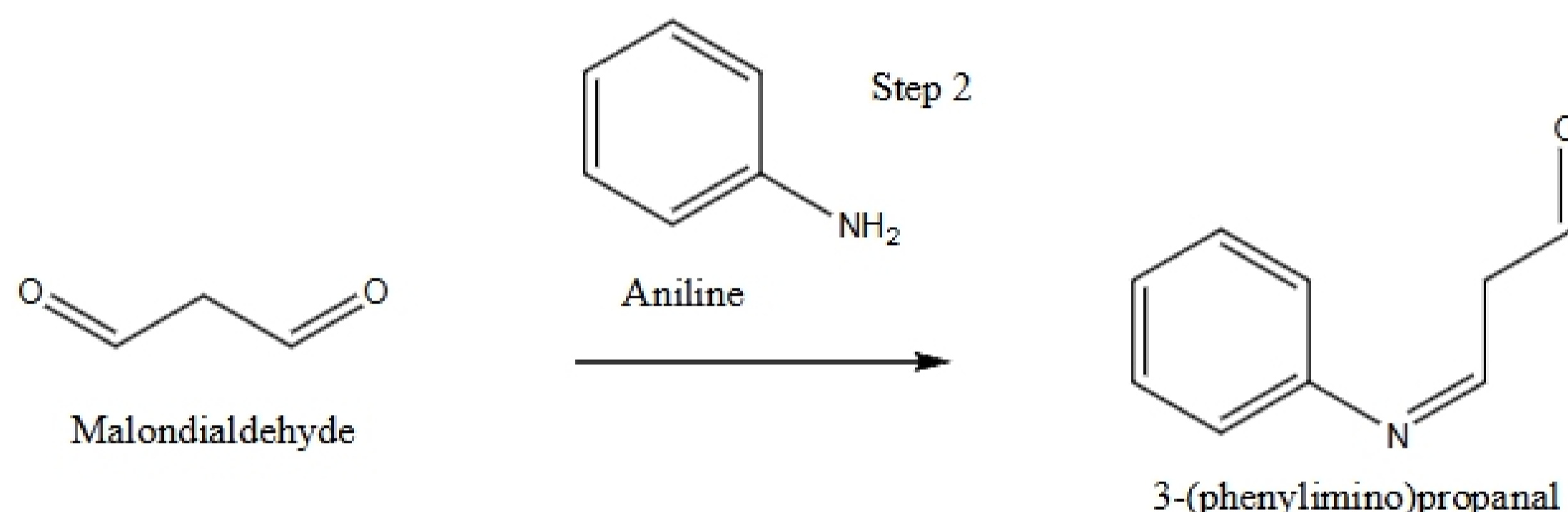
Methanol is highly flammable, and extremely toxic upon inhalation, ingestion, or skin absorption. Methanol must be boiled off under the hood, with ventilation on. This can be disposed of in the liquid organic waste bucket.

Hydrochloric Acid is corrosive and flammable. Inhalation or ingestion can cause serious injury, and exposure to skin and eyes can cause severe damage. The catalytic amount of HCl used must be boiled off under the hood with ventilation on. There is no need for disposal as this byproduct will be boiled off.

Malondialdehyde is harmful by inhalation, ingestion, and can cause eye and skin irritation. Dispose of this chemical in the liquid organic waste bucket.

Step 2

Synthetic transformation 2:



Experimental 2:

The procedure was modified primarily by substituting aniline for p-toluidine (the reactant used in the article), a substituted aniline with a methyl group para to the nitrogen attached to the benzene ring. This modification was considered minor and was assumed to have a negligible effect on the outcome and overall effectiveness of the reaction. The second change made was to adjust the ratio of reactants outlined by the article. Instead of 1: 1.1 malondialdehyde : aniline mol ratio, a 1:1 ratio was adopted. This was because the journal's quantities were designed to ensure completion and their experiment was not affected by the presence of excess reactant. However, since the two chemicals react in a 1:1 ratio, following the journal's procedure would create excess aniline that might affect the following steps of this experiment and thus was not followed. The last modification carried out was to decrease the amounts of the reactants, since the desired yield of the final product was only 0.5 grams.

7.9032 g malondialdehyde were combined with 5 mL aniline in a 25 mL round bottomed beaker and heated to a light boil under reflux for 1.5 hours. 20 mL water were added and the mixture was thoroughly shaken. 20 mL benzene was added and the organic layer was separated. Another 20 mL of water was added organic layer extracted again. Solution was dried over anhydrous