

Oxidation of Benzoin to Benzil

Purpose:

A solution of benzoin was oxidized to the diketone product benzil using bleach as an oxidizing agent and Stark's catalyst. The reaction was monitored using thin layer chromatography (TLC) and the product was separated using liquid-liquid extraction. Then, the product was analyzed with ^1H NMR and IR spectral analysis. The bleach oxidation pathway is an easy pathway that can be used to oxidize many compounds for organic chemists. Specifically, the product, benzil, is a starting material used in the synthesis of larger organic compounds. TLC was important to determine when the reaction was complete to insure the purity of the product. Liquid-liquid extraction was important in isolating the product for further spectral analysis (2).

Results, Discussion, and Conclusions:

The reaction observed in this experiment was an oxidation reaction with hypochlorous acid. Hypochlorous acid protonates the alcohol group on benzoin, creating a good leaving group, water, which is kicked out via an $\text{S}_{\text{n}}2$ Reaction with hypochlorite anion as the nucleophile. The final product is produced when a base deprotonates on the geminal carbon, allowing chlorine to leave and the oxygen to form a double bond (3).

TLC was extremely successful in monitoring the reaction to determine when the reaction reached completion. By taking a sample of the organic layer in the reaction and spotting it on the TLC plate, a product spot, benzil, and a reactant spot, benzoin, could be observed. The benzil spot moved significantly further than the reactant spot because its two ketone groups are less polar than the one ketone and one alcohol group of benzoin. Darker benzil spots and lighter

benzoin spots were observed in each subsequent TLC. Eventually, the benzoin spot was completely absent, meaning the reaction indeed went to completion.

Extraction was used as the work-up of the reaction. The addition of a strong base served to remove most of the hypochlorous acid from the aqueous solution as well as deprotonate any remaining starting material, drawing it from the organic layer into the aqueous layer and allowing it to be separated from the product. The organic layer was washed with water to remove any inorganic impurities and saturated sodium chloride to disrupt any emulsions and extracting water that may have dissolved in the organic layer. The success of these extraction steps is questionable due to the impurities observed in spectral analysis of the product (2).

After the product was isolated, it was analyzed with ^1H NMR analysis. The aromatic peaks of the spectrum accurately reflect the expected peaks for benzil, with one doublet shifted at 7.9 ppm and an integration value of 4 and a multiplet with a chemical shift of 7.5 ppm and an integration value of 6.87. The smaller peak represents the 4 equivalent ortho positioned hydrogens on the symmetric benzil molecule. They are shifted further downfield because of their proximity to the electron withdrawing ketone functional groups. The multiplet represents the other 6 hydrogens on the two aromatic rings. They have relatively the same chemical shift because they are both far away from any functional group and split each other into a complex multiplet. The integration value for this peak is expected to be 6, but the observed integration value is slightly higher, at 6.87. This higher integration value could be due to the existence unreacted reactant in the product mixture, which may have added additional hydrogens observed in the aromatic region. Three other impurities were observed in the spectrum. The first is a large, broad peak preceded by a smaller peak in the range of 0.8-1.5 ppm. This peak is Stark's catalyst,

which remained in the organic layer following the extraction procedure. Even though only 1 or 2 drops of the catalyst were used, the catalyst contains a large number of hydrogens because of the long carbon chains branching of the nitrogen in the structure of the molecule. Therefore the integration value for the peak is extremely high, resulting in a large peak (1). There is also a broad, small singlet at the chemical shift of 3.3 ppm. This peak probably represents unreacted starting material since the broad shape and downfield chemical shift reflects an alcohol peak that exists in the benzoin molecule. The final impurity is a sharp singlet at 7.2 ppm, just prior to the two aromatic peaks. This peak is probably from chloroform in the product that may have formed from leftover hypochlorous acid.

Due to the oily product, no IR analysis could be performed. However, IR analysis on the product of a separate reaction also accurately reflected the benzil product. The IR spectrum shows a strong peak at 1675.6 cm^{-1} , which is indicative of the conjugated C=O bond of the ketone groups. There is also a small peak at 2927.33 cm^{-1} , which represents the aromatic C-H bonds in the two aromatic rings of benzil. Finally, there is a medium sized peak at 1592.89 cm^{-1} , which represents the aromatic C=C bonds. Since there is no broad peak in the $3600\text{-}3200\text{ cm}^{-1}$ range, there was no O-H functional group in this product. Therefore the reactant benzoin was not present and the product had to contain benzil (4).

The percent yield of the reaction was calculated to be 18.6%, which assumed all of the benzoin completely reacted to form benzil. This assumption is appropriate because at the end of the reaction no benzoin spot was observed in the TLC plate. The low percent yield was likely due to a variety of sources of error following the conclusion of the reaction. Overambitious use of the separatory funnel such as attempting to separate all of the aqueous layer with each wash

could have resulted in some of the organic layer containing the product being drained out and lost, therefore decreasing the percent yield. Additionally, several mistakes may have been made in the drying step with the nitrogen stream. First, while attempting to clamp the scintillation vial containing the product in the warm water bath, the scintillation vial slipped and dropped into the warm water bath vertically. Some liquid inside may have escaped into the water bath, therefore decreasing the percent yield. When the nitrogen gas was turned on, it was accidentally turned on too quickly, resulting in a strong stream splashing out some of the liquid in the scintillation vial, also likely causing the loss of some of the product (2).

The experiment performed yielded benzil as the product of an oxidation reaction between benzoin and hypochlorous acid. By using TLC, the reaction was monitored and stopped at completion. Extraction with a strong base was then used in order to isolate the product. ^1H NMR analysis showed a multitude of impurities in the final product, so the experiment was certainly not fully successful. More care needed to be put into the extraction steps to ensure maximum percent yield and product purity. The experiment could have been improved by improving the procedure for evaporation of the ethyl acetate solvent under a nitrogen stream. The mistakes made in this step probably resulted in the loss of most of the product (2).

Experimental:

Benzoin (250 mg, 1.178 mmol) was dissolved in 10 mL of ethyl acetate. Then, 6% sodium hypochlorite (10 mL) was added to the reaction mixture. A TLC plate was made and developed to observe the starting composition of the reaction mixture. The TLC plate consisted of 3 lanes. Lane 1 consisted of a benzoin standard that was made by dissolving 5 mg of benzoin in 2 mL of dichloromethane. Stark's Catalyst (2 drops) was added to the mixture to begin the

reaction. Every 15 minutes, the stirring was stopped and a new TLC plate was developed. This process was repeated until no reactant spot was observed on the TLC plate. The reaction was then worked up using extraction with sodium hydroxide. The reaction mixture was added to a separatory funnel and both layers were drained into separate beakers. Next, the aqueous layer was washed with 10 mL of ethyl acetate and the organic layers were combined. After, the organic layer was extracted with 1M aqueous sodium hydroxide (2 x 10 mL), distilled water (2 x 10 mL), and saturated sodium chloride solution (1 x 10 mL). Finally the organic layer was dried over anhydrous sodium sulfate. The solid product was obtained after decanting the solution off of the sodium sulfate drying the ethyl acetate with a stream of nitrogen and warm water bath. ¹H NMR (60 MHz, deuterated chloroform) **6**: 7.4-7.7 (m, 7H), 7.8-8.1 (d, 4H). IR of product of separate reaction ν_{max} (cm⁻¹) 3416.60, 2927.30, 1675.6, 1592.89, 1578.24. No IR was performed on product of this specific reaction due to improper product form.

References

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