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CHEM 345
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Thiamine-Mediated Benzoin Condensation of Furfural

Reference: Handout; Chemistry lessons: Carbonyl chemistry, oxidation chemistry, carbon skeleton rearrangements; Green lessons: safer and easier to handle reagents and solvents; Bruice pg. 752-753

Purpose: To explore how thiamine affects the formation of furoin from furfural through benzoin condensation reactions

Table of Reagents:

Compounds	MW	Amount	BP (°C)	MP (°C)	Density
Thiamine HCl	337.26 g/mol	0.3 g	-	250 °C	-
Ethanol (EtOH)	46.07 g/mol	3 mL	78.37 °C	-114.1 °C	0.789 g/cm³
Water (H₂O)	18.01 g/mol	-	100 °C	0 °C	1.00 g/cm³
NaOH	39.997 g/mol	8.0 g	1388 °C	318 °C	2.13 g/cm³
Furfural	96.08 g/mol	0.73 mL	162 °C	-37 °C	1.16 g/cm³

Balanced Chemical Equation:
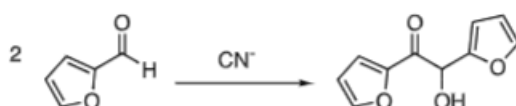
Fig 3. The benzoin-type condensation of furfural

Mechanism:

Thiamine hydrochloride
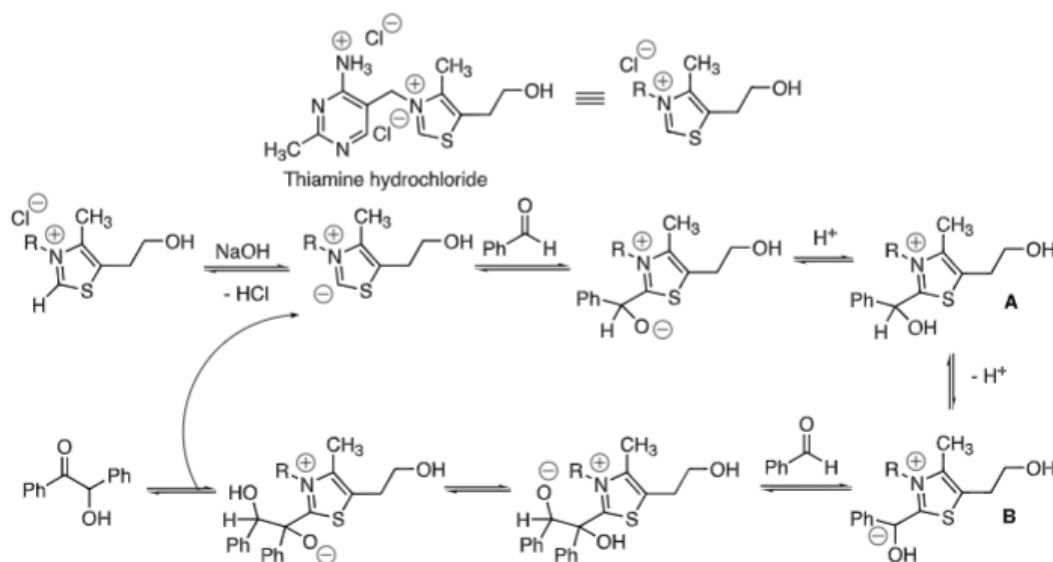
Safety:
➢ Furfural → toxic; Handle with care
➢ Sodium Hydroxide → irritant; Avoid skin & eyes

Experimental Procedures	Data & Observations
Part I: Reaction **1.** Obtain 25 mL round-bottom flask; add stir bar & 0.3 g thiamine HCl in mixture with 0.45 mL water/ 3.0 mL of EtOH ➤ Mixture should be clear/colorless	
2. Dropwise → add 0.9 mL of solution with 8 g of NaOH in 100 mL of water (already provided) ➤ Continue to add NaOH until reaction is pale-yellow; if not, add more NaOH	*Observations:* Mixture started to turn pale yellow
3. Add 0.73 mL of furfural & mix; store in drawer until next lab ➤ BE SURE TO SEAL THE FLASK!!!	
Part II: Workup and Purification **4.** Cool mixture in ice bath; Add water to cooled mixture to drive remainder of product; Isolate using vacuum filtration ➤ Record mass of product	
5. Recrystallize product using the EtOH	
Part III: Characterization **6.** Record yield, melting point, and IR spectrum of the furoin	*True Melting Point:* 135 °C – 137 °C *Product Melting Point:* 137 °C *Product Mass:* 0.58 g

Post-lab Questions:

1.   **a)** Our furoin product was a solid, brownish powder and it melted at 137 °C. The true melting point range of pure furoin is between 135 – 137 °C, which matches our product's melting point signifiying that it is pure furoin, thus it did not experience melting point depression.

b) We collected 0.58 g of the crude product as well as the color of our product was a brownish-powder.

$$\% \, Yield = \frac{Product \; Obtained}{Theoretical \; Yield} \times 100$$

Obtained: 0.58 g   *Color and State:* Solid, Brownish Powder

➢ First, we must obtain the theoretical value of our crude product in grams:

$$0.73 \; mL \; furfural \times \frac{1.16 \; g \; Furfural}{1 \; mL \; Furfural} \times \frac{1 \; mol \; Furfural}{96.08 \; g \; Furfural} \times \frac{1 \; mol \; Furoin}{2 \; mol \; Furfural} \times \frac{192.17 \; g \; Furoin}{1 \; mol \; Furoin}$$

$$= 0.847 \; g \; Furoin$$

➢ Next, we must use the equation above to get our % Yield:

$$\% \; Yield = \frac{0.580 \; g}{0.847 \; g} \times 100 = 68.48\% \; yield$$

➢ *We received a 68.48% yield for our product*
➢ *We received a rather moderately high yield; we did not do the recrystallization step as instructed (cannot calculate the % recovery).*

2.   IR Spectrum of Furoin

3.   **NMR of Fufural and Furoin**

Furfural ¹H NMR

HSP-05-839

Furoin ¹H NMR

HSP-42-682
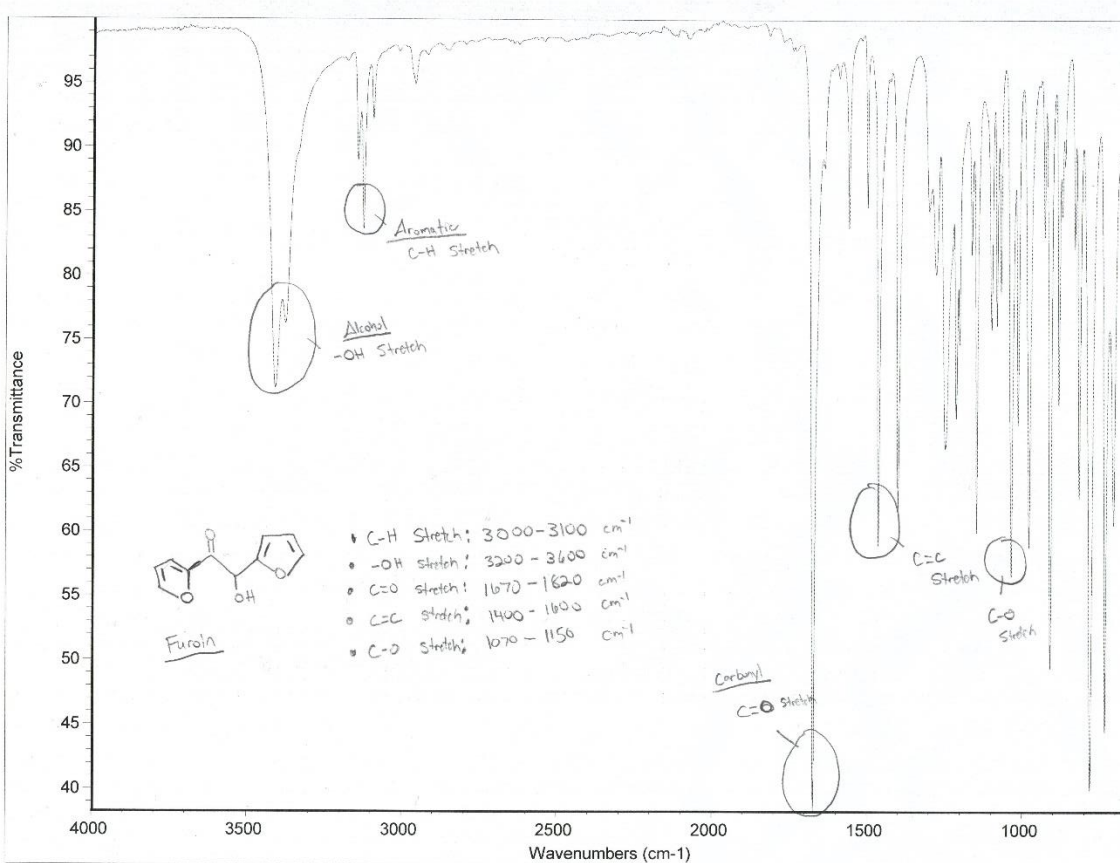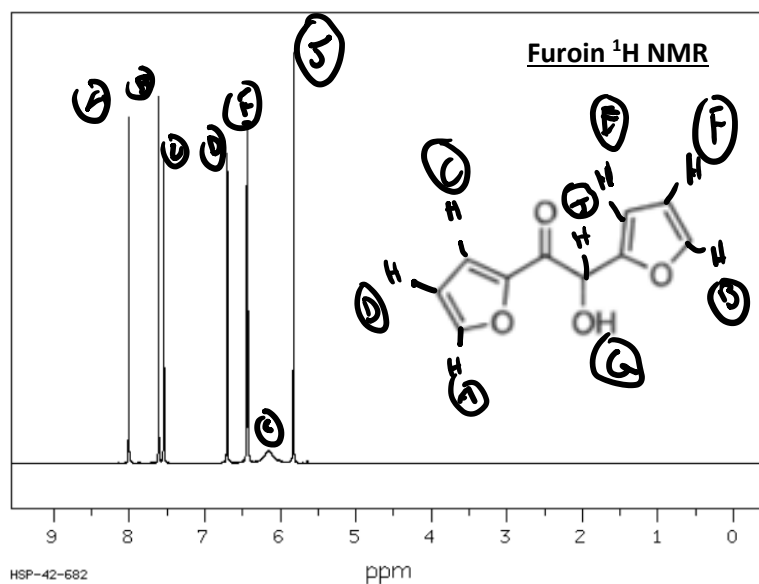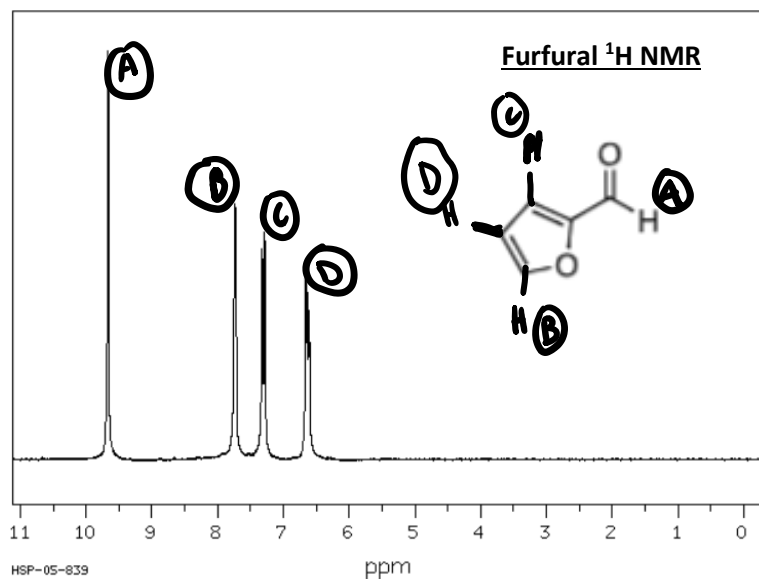
a)   The aldehyde H appears around the 9.8 ppm area on furfural, however, this peak disappears on furoin as the functional group does not exist in furoin.

b)   It is expected for the Hs on the furan ring to be around 7-8 ppm, which is similar to benzene Hs because both satisfy aromatic properties correlating to the common aromatic Hs shown.

c)   The broad peak around 6.2 ppm and the peak around 5.9 ppm attribute to the resonance seen in furoin, but not in furfural.
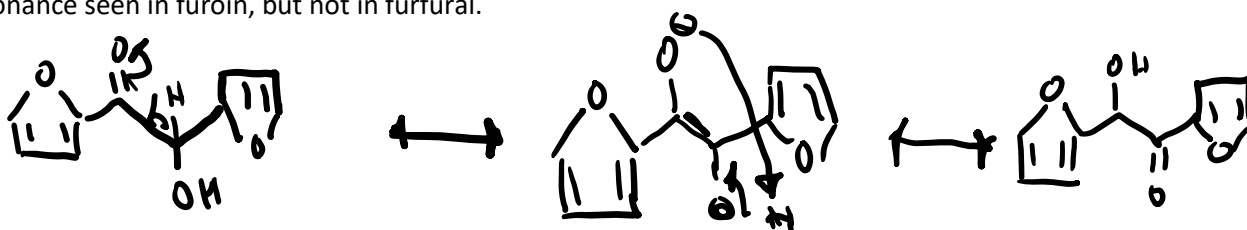
4. $Atom\ Economy = \frac{MW\ of\ products}{MW\ of\ reactants} \times 100$

$Atom\ Economy = \frac{192.15\ g}{2 \times 96.08} \times 100 = 99.99\%\ (100\%)$

5. The compound is chiral, however, is not "optically active" because it is a racemic mixture (50:50 mix of 2 enantiomers). The mixture contains both R and S configuration, which makes it not optically active as one does not dominate the other.

6. My resonance structure supports that the thiazole derivative A is acidic due to the fact that the hydrogen ion (before deprotonation) was the most acidic. However, once the the proton was deprotonated, the ring was stabilized by resonance resulting in carbanion B (charge was moved onto S in the ring).