

Experiment 5: Benzylidene Acetals as a Protecting Groups for Sugars

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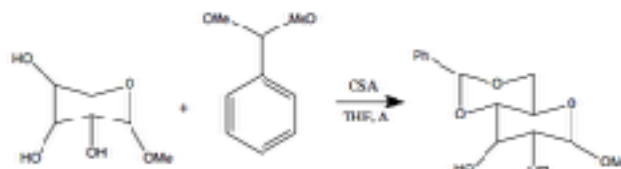
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Lab section: 2

TA: Spencer Pitre

CHM 2123

Introduction



In this experiment, a benzylidene acetal is created at the C4 and C6 alcohol of glucose creating a “protected” glucose. This means the reactivity of the two alcohols is blocked which allows reactivity in other positions. The reaction is done by dissolving Methyl- α -D-glucopyranoside into THF and adding benzaldehyde dimethyl acetal and 10-camphorsulfonic acid. This combination is heated at reflux for about an hour. A TLC plate is prepared using dissolved Methyl- α -D-glucopyranoside and the heated solution at reflux to see if the reaction is complete. Once the reaction is complete the solution is cooled and trimethylamine is added to neutralize the solution. Then the organic phase is diluted using ethyl acetate and separated using a separatory funnel and Na_2SO_4 is added to dry the organic phase. It is then filtered using a gravity filter and ethyl acetate is evaporated using a steam bath. The remaining contents are dissolved and hexanes are added to perform a precipitate which is isolated using a vacuum filter. A second TLC is then prepared using the product dissolved in THF, the mother liquor, and glucose dissolved in water to access if the final product is pure.

For part B of this experiment the accuracy of the Benedict's test for reducing sugars is tested. There is one test tube containing sucrose is dissolved water, a second containing glucose is dissolved in water, a third containing milk, and a fourth containing diet coke. Benedict's solution is added to each test tube and they are placed in a steam bath for about 5 minutes and observations are recorded and used to determine which test tubes contained reducing sugars. HCl is added to the dissolved sucrose and observations are recorded.

Mechanism

On attached page

Table of Reagents

| Name | Molar Mass (g/mol) | Quantity (g or mL) | Density (g/mL) | Number of moles (mol) | Equivalents |
|-------------------------------------|--------------------|--------------------|----------------|-----------------------|-------------|
| Methyl- α -D-glucopyranoside | 194.18 | 0.5g | | 0.0026 | 1.0 |
| benzaldehyde dimethyl acetal | 152.19 | 0.7mL | 1.014 | 0.0047 | 1.8 |

| | | | | | |
|-------------------------|--------|-------|-------|---------|------|
| 10-camphorsulfonic acid | 232.30 | 0.10g | | 0.00043 | 0.15 |
| THF | 72.11 | 10mL | 0.889 | | |

Procedure

Refer to CHM2123 lab manual pages 68-69.

Modifications: Part A step 3: heated at reflux for 60 minutes.

Observations

Part A:

- After reflux was performed there was a solid in the solution still
- the final product was white and had a texture similar to clay

Part B:

- glucose is a fine white crystal
- sucrose is a white crystal
- milk fist turned a brown-yellow colour then turned bright orange and chunky
- glucose turned orange then later turned dark red and formed precipitates
- no initial change for sucrose
- once HCl was added to sucrose it quickly formed yellow bubbled and left a yellow layer on top
- diet coke turned slightly green initially and then no change.

Results

Part A:

Ended up with 0.70g of product

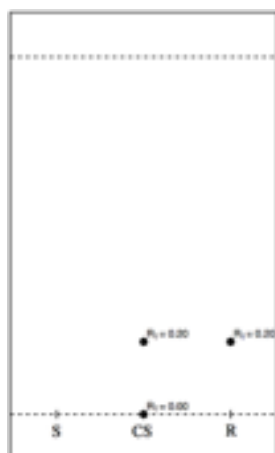
% yield = $0.70\text{g} / (0.0026\text{mol} \times 228.29\text{g/mol}) \times 100 = 117\%$

Part B: According to Benedict's test for reducing sugars, the following are reducing sugars:

- milk
- glucose

TLC Plates

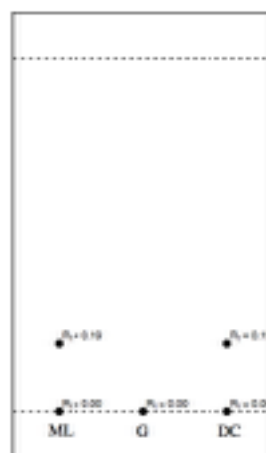
Solvent System: 3:7 hexanes : ethyl acetate



S: Methyl- α -D-glucopyranoside
 CS: Co-spot
 R: Reflux

Rf of CS = 5cm / 1cm
 Rf of CS_{upper} = 0.20

Rf of R = 0.20



ML: Mother liquor
 G: Glucose and water
 DC: Dissolved Crystals

Rf of ML = 4.7cm/0.9cm
 Rf of ML_{upper} = 0.19

Rf of DC_{upper} = 0.19

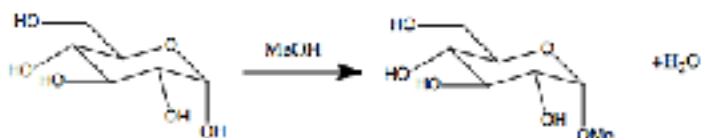
Discussion

In this lab, a benzylidene acetal was created using Methyl- α -D-glucopyranoside dissolved into THF and adding benzaldehyde dimethyl acetal and 10-camphorsulfonic acid. The solution was heated at reflux for an hour and a TLC plate was prepared with a lane for Methyl- α -D-glucopyranoside dissolved, the solution after heated at reflux for an hour, and a co-spot. The TLC was dipped in a methanolic solution of sulphuric acid to make the spots visible. The TLC showed 2 spots in the co-spot lane, 1 with a Rf value of 0 and the other with an Rf value of 0.2. A spot was also visible in the lane with the solution heated at reflux with an Rf value of 0.2. These spots show that the heated solution still contains a small amount of starting material but the reaction is completed and the experiment can be continued. The solution was cooled and a few drops of trimethylamine was added to neutralize the solution. The organic layer is then separated using a separatory funnel and Na_2SO_4 is added to remove excess water in the solution. The solution was placed in a steam bath to evaporate the ethyl acetate and a small amount of solution remained that was thick and a white residue stuck to the edges of the erlenmeyer flask. The contents of the flask were dissolved in dichloromethane and hexanes were slowly added to force out polar molecules and a precipitate formed. The product was filtered leaving us with 0.70g of product leaving us with a percent yield of 117%. The percent is over 100% because the product was not completely dried when the mass was measured therefore the product weighed too much. The second TLC was performed using a lane containing mother liquor, a lane containing glucose dissolved in water and a lane containing the product dissolved in acetone. The TLC shows a spot with an Rf value of 0 at the bottom of each lane, there is also a spot with the Rf value 0.19 in both the lane containing the mother liquor and the lane containing the dissolved final product which shows that the final product is not pure which could also be why a percent yield over 100% was obtained.

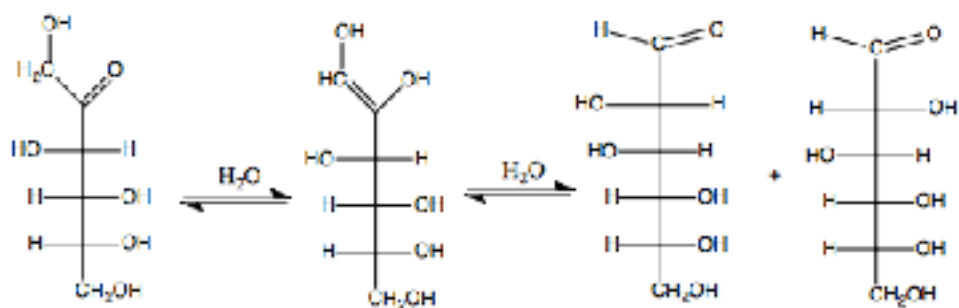
For part B of this experiment we determined if several solutions were reducing sugars or non-reducing sugars based on Benedict's test for reducing agents. According to this test, when Benedict's solution is added to a solution and the solution is heated it will turn green, to yellow, to orange, to brick red due to the increasing concentration of reducing sugar. The experiment had four test tubes, one test tube containing sucrose dissolved in water, a second containing glucose dissolved in water, a third containing milk, and a fourth containing diet coke. Once Benedict's solution was added and they were heated for 5 minutes there was no change recorded for sucrose dissolved in water, the diet coke turned slightly green due to the blue colour of the Benedict's solution mixing with the food colouring of the coke, glucose dissolved in water turned to a dark brick colour, and milk also turned to a dark orange. This shows that milk and glucose are reducing sugars and diet coke and sucrose contain non-reducing sugars. HCl was added to the sucrose dissolved in water and yellow bubbles formed rapidly and a layer of yellow solution remained on top of the clear sucrose solution. The HCl breaks the glycosidic bond in sucrose resulting in the sugars glucose and fructose which are both reducing sugars so once HCl is neutralized the Benedict's test would show this solution turn brick red.

Questions

1. Cellulose is the polymer of beta glucose where units are joined by 1,4- glycosidic bonds and starch is the polymer of alpha glucose where units are joined by 1,4- glycosidic bonds.
- 2.



3.



Fructose has a $-CO-CH_2OH$ group which reacts with H_2O to produce $-CH(OH)-CHO$ and because of the $-CHO$ group it behaves like a reducing sugar.

4. Benedict's test can give false positives when the food sample contains other reducing compounds, for example ascorbates and lactose.

Mechanism

