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Synthesis of Phosphorus-Based Hemiacetals for Potential Flame Retardants

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Synthesis of Phosphorus-Based Hemiacetals for Potential Flame Retardants



Honors Thesis

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Department: Chemistry

Advisor: Vladimir Benin, Ph.D.

April 2015

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Abstract

Flame retardants which contain a phosphorus moiety attached to a carbohydrate backbone were developed. To synthesize the flame retardants, carbohydrates and polyols were used as the starting materials which occur in nature and are environmentally and toxicologically safe materials. The two target structures include one with a triose substructure and one with a pentose substructure. For both situations, however, multiple steps were taken for the synthesis of the flame retardant, as the carbohydrate needed to be generated into its protected form. The protected carbohydrate then interacted with a dialkyl phosphite, resulting in a phosphorous hemiacetal. This hemiacetal was then deprotected to form the final product, which is the target flame retardant. Ultimately, the goal is to produce a flame retardant which is both safe and effective.

Acknowledgements

I would like to express my gratitude to Dr. Vladimir Benin for the time and effort he contributed. This project could not have been completed without his help and guidance. I would also like to thank the University of Dayton Chemistry Department as well as the University Honors Program for providing me with the resources to achieve our goals. Finally, I appreciate all of my friends, family, and fellow students who have been there to support me throughout this time.



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Introduction

Flame retardants work to limit flammability and in turn, limit any potential damage or hazard that a fire may cause. Limiting flammability is important for various reasons whether it be needed in somebody's home or for commercial uses. Research in flame retardants is a growing area as the search for safer and more efficient structures is ongoing. Worldwide, about 2 million tons of flame retardants are consumed. The consumption of flame retardants, according to a 2012 market study of Townsend, continues to increase at a rate of about 4-5% this year, with North America being the continent that consumes the largest volume. As they experience an increase in use and as standards rise, the demand for better options of flame retardants also increases. Figure 1 displays the prevalence of different types of flame retardants that are currently in use:

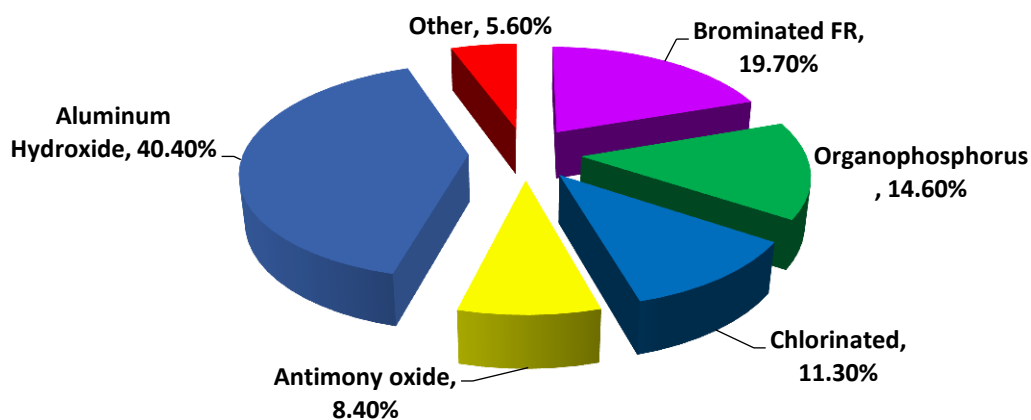


Figure 1. Relative volumes used of different types of flame retardants.

With polyurethane as the largest fuel source in the home, flame retardants are evidently necessary to ensure the safety of people. Polyurethane is a foam polymer that is present in various places such as furniture, mattresses, and carpet floor pads. However, it is an extremely flammable material. Upon being ignited, the foam collapses and eventually liquefies. The liquefied foam creates a “pool fire” which ultimately leads to the rapid spread of flames. In order to prevent this from occurring, flame retardants are necessary for polyurethane to pass existing U.S. regulatory tests.

Commonly, the process that is used in reducing flammability is based on the combustion mechanism, which is shown in Figure 2.

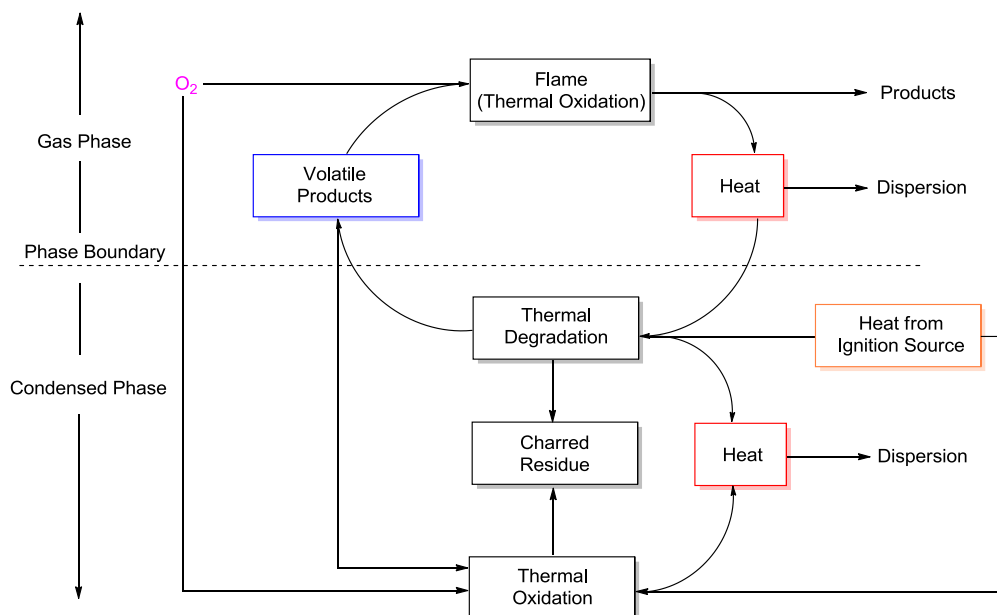


Figure 2. The mechanism of polymer combustion.

Either disturbing this mechanism or redirecting it as combustion occurs can lead to the reduction of flammability. There are two general methods for the introduction of a flame retardant into a polymer material. The first is the addition (or mixing) of a flame retardant compound into an existing polymer. Commonly used phosphorus-based flame retardants of this type are shown below in Figure 3.

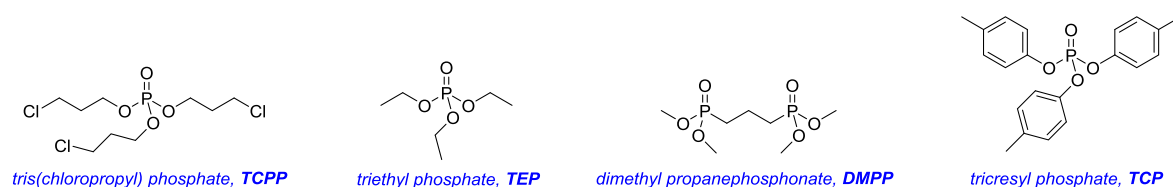


Figure 3. Currently used, common P-based flame retardants for polyurethane of the additive type.

Some disadvantages of this method are seen, particularly with the possibility of the flame retardant leaching out of foam. This can lead to a negative impact on the environment as well as a decrease in fire protection over time. As a result, researchers are looking for potential new flame retardants that can be used in the second method of introduction into a polymer material in order to solve these issues. The second methodology is based on

modifying the polymer so that it has a flame-retardant component incorporated into the chain. Figure 4 displays the formation of polyurethane.

Formation of Polyurethane:

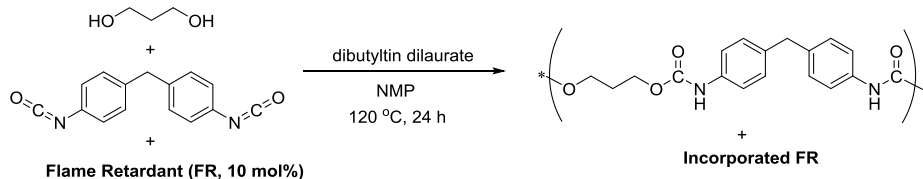


Figure 4. Formation of polyurethane.

As seen, a diol and isocyanate react to form polyurethane. Typically, polyether diols are generated through the use of starters, or initiators. These polyether diols are long chains which are beneficial as they allow for flexibility of the polyurethane polymer, something that is favorable for polyurethane foams used in all types of products such as furniture. This reaction is shown in Figure 5.

**Use of Starters (Initiators)
in the Generation of
Polyether Diols:**

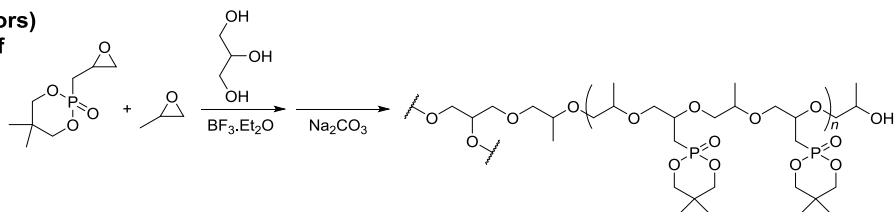


Figure 5. The formation of polyether diols using initiators.

Typical starters include glycerol, shown in Figure 5, as well as trimethylolpropane. In order for a flame retardant to be able to connect to the polymer backbone as a co-polymer component, specific functional groups must be present in the flame retardant. The hydroxyl group is a versatile functional group that is often utilized and present in a variety of structures, including carbohydrates and other polyols. Using this information, an initiator with an incorporated flame retardant appears to be plausible. This would lead to the incorporation of the flame retardant in polyether diols, and ultimately into polyurethane. The possibility of using carbohydrates and polyols to synthesize phosphorous-containing flame retardants is examined in this research.

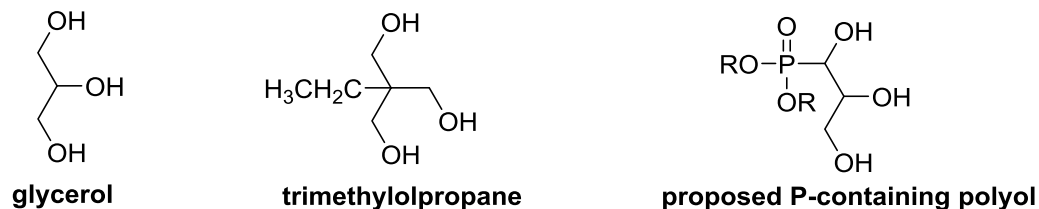


Figure 6. Structures of glycerol, trimethylolpropane, and suggested P-containing polyol.

Phosphorus-based flame retardants are well-known and therefore, a good synthetic target. They are able to act in two phases: the gas phase and the condensed phase. In the gas phase, the combustion reaction is redirected when hydrogen and hydroxyl radicals are replaced by less effective radicals or when they undergo radical recombination to become harmless. This results in a reaction that is much less exothermic, thus slowing down the reaction and preventing the rapid spread of flames. The second and more predominant mode of action is in the condensed phase. In this phase, the phosphorus compounds are well known to impart char formation with a variety of heteroatom-containing polymers (polymers with O or N in their chemical structure). This is proposed to occur via the formation, upon heating, of extensive P – O or P – N networks, yielding thermosets that are difficult to melt. They then serve as protection from fire for the polymer underneath. A suggested pathway for char formation is shown in Figure 7.

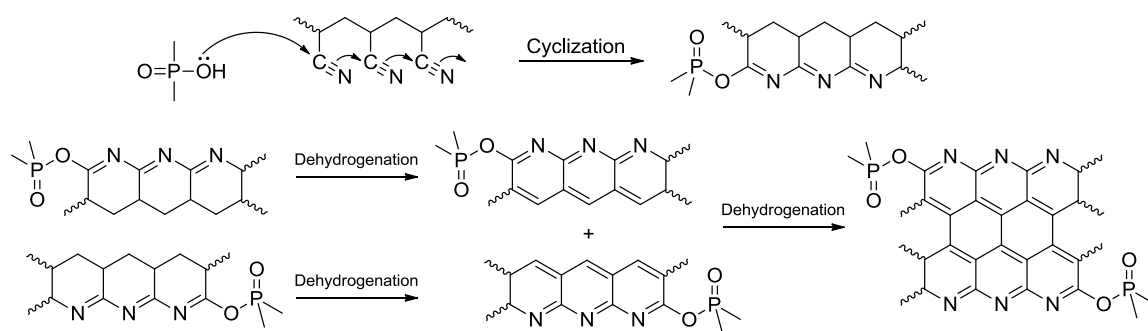


Figure 7. Suggested pathway for char formation in a polymer sample containing a phosphorous-based flame retardant.

As well as cross-linking, char formation is helped in two other ways. First, the promotion of dehydration reactions leads to the formation of char. Secondly, the presence of

phosphorus flame retardants leads to faster decomposition of the polymer and the removal of volatiles, which can be seen in Figure 8.

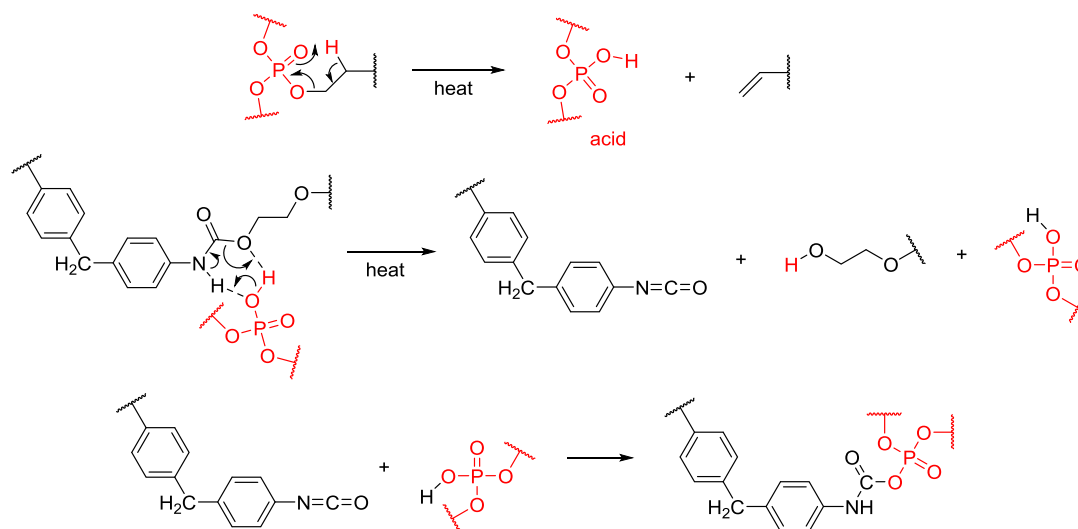
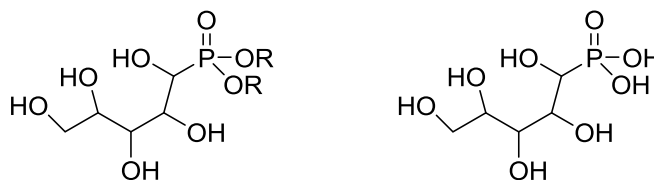


Figure 8. Suggested pathway for the breakdown of polyurethane upon burning, in the presence of an incorporated phosphorus-based flame retardant.

According to this pathway, upon ignition, a polymer containing a phosphorus-based flame retardant first breaks down into phosphoric acid and the remaining polymer chain. This acid then acts as a catalyst and reacts with the chain to break it down further into isocyanate and a diol chain. The isocyanate compound is fairly volatile and evaporates in this process. As more of the volatile portion of the polyurethane continues to be removed, the remaining compound gets closer and closer to its carbon skeleton, which eventually leads to the formation of char and protects the polymer from the fire. Furthermore, the regenerated phosphoric acid reacts with the chain in order to result in cross-linking as discussed above.

The general objective of this project is to prepare and study new phosphorus-based hemiacetals, containing a carbohydrate sub-structure. Target structures are shown in Figure 9:

P-hemiacetals based on a triose substructure:**P-hemiacetals based on a pentose substructure:****Figure 9.** Proposed target structures.

These hemiacetals are then to be incorporated into model polyurethanes which are examined in flammability studies. Specifically, these phosphorus-based hemiacetals will be synthesized using trioses and pentoses as starting materials. Each step's product is then to be analyzed through the use of NMR and elemental analysis. This could eventually be beneficial as these materials are both natural and abundant, potentially leading to an excellent starting material for flame retardants due to these materials likely being both cheaper and safer for the environment than flame retardants currently in use.

Results and Discussion

The preparation of the proposed structures requires multi-step organic synthesis, aimed at the conversion of the carbonyl compound (carbohydrate) to a phosphorous hemiacetal by interaction with a dialkyl phosphite. This project was split into two parts: The synthesis of phosphorus hemiacetals based on a triose substructure and the synthesis of phosphorus hemiacetals based on a pentose substructure.

Synthesis of P-Hemiacetals Based on a Triose Substructure

First, the partially protected mannitol, 1,2:5,6-di-O-isopropylidene-D-mannitol (**1**), was oxidatively cleaved to form two equivalents of protected glyceraldehyde, or 2,2-dimethyl-1,3-dioxolane-4-carbaldehyde (**2**).

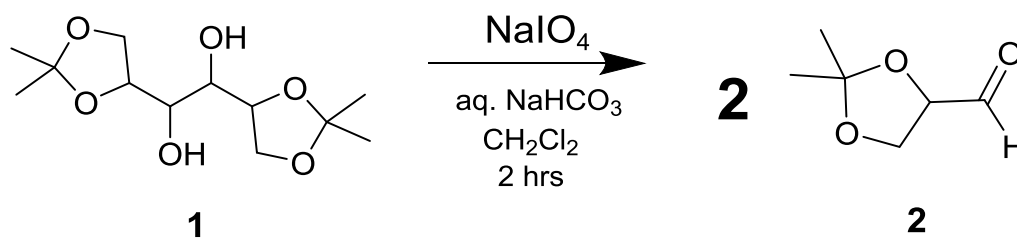


Figure 10. Generation of protected glyceraldehyde from partially protected D-mannitol.

The mechanism for this reaction is shown below in Figure 11.

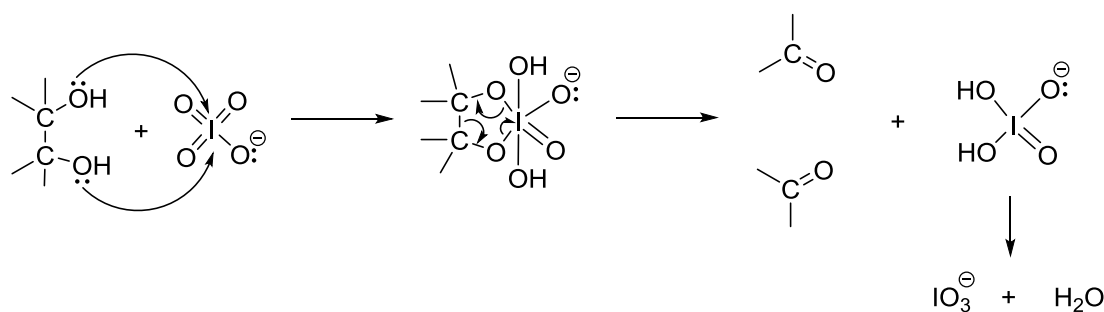


Figure 11. Mechanism for the oxidative cleavage of a diol.

In the second step, the aldehyde was reacted with a dialkylphosphite in the presence of a base to form a phosphorus hemiacetal. Specifically, **2** was reacted with three different dialkylphosphites. The general reaction is shown in Figure 12.

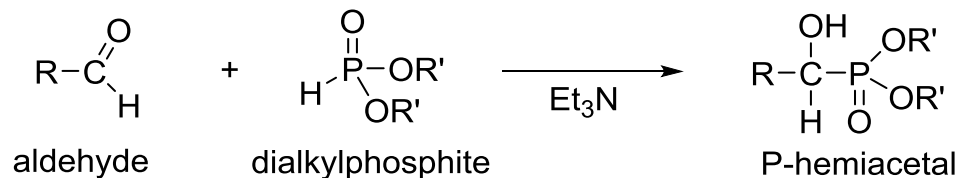


Figure 12. General reaction for the formation of a P-hemiacetal from an aldehyde and a dialkylphosphite

The mechanism for this reaction is shown below in Figure 13.

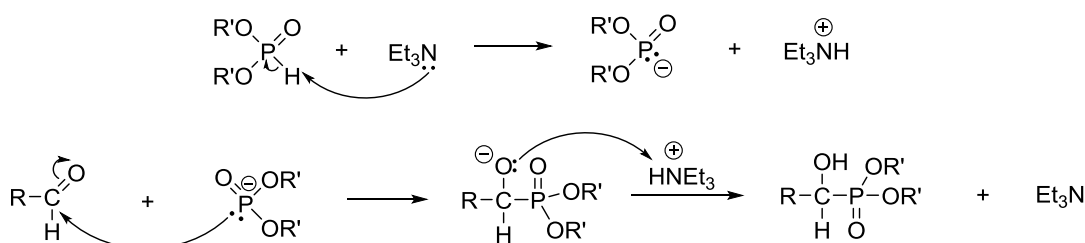


Figure 13. Mechanism for the formation of the P-hemiacetal.

In this reaction, the base that is used, triethylamine, deprotonates the dialkylphosphite to produce an anion. This anion then participates in nucleophilic addition to the carbonyl carbon of the aldehyde, to ultimately produce the desired phosphorus hemiacetal. This reaction was attempted three times, each time with a different dialkylphosphite. The first dialkylphosphite that was used was a cyclic phosphite, forming 2-((2,2-dimethyl-1,3-dioxolan-4-yl)(hydroxy)methyl)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (**3**):

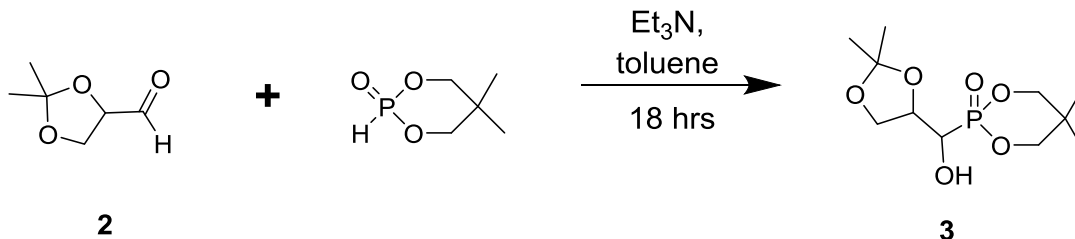


Figure 14. The reaction of protected glyceraldehyde with a cyclic phosphite.

Figures 15 and 16 show the NMR spectra of Compounds 2 and 3, respectively.

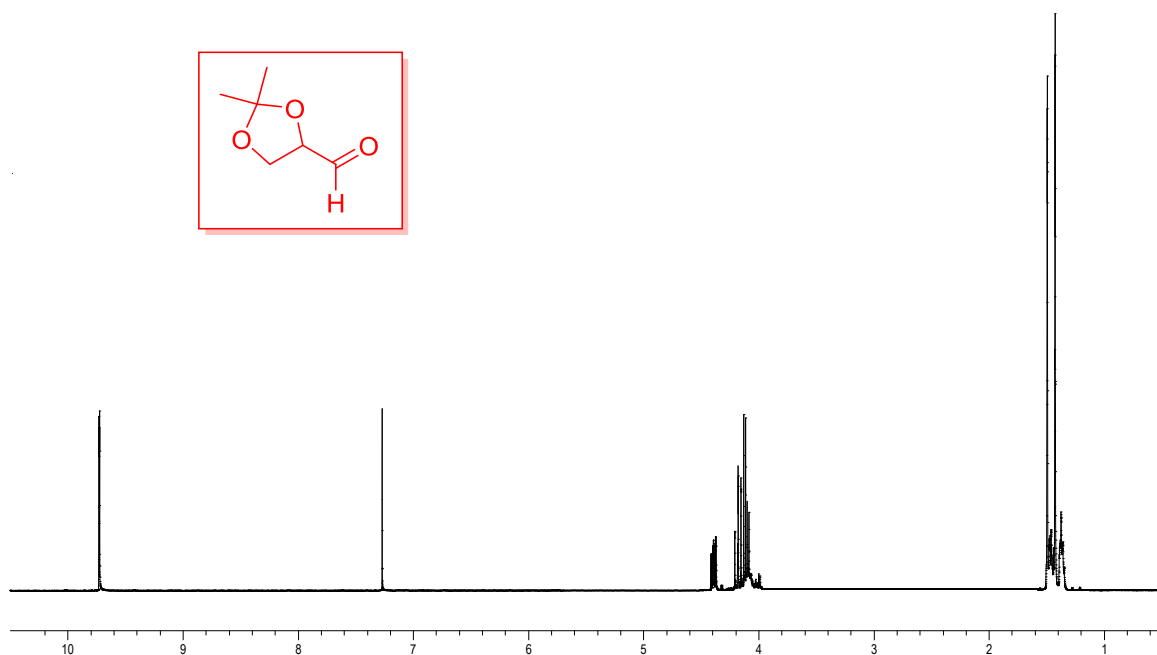


Figure 15. NMR spectrum of Compound 2.

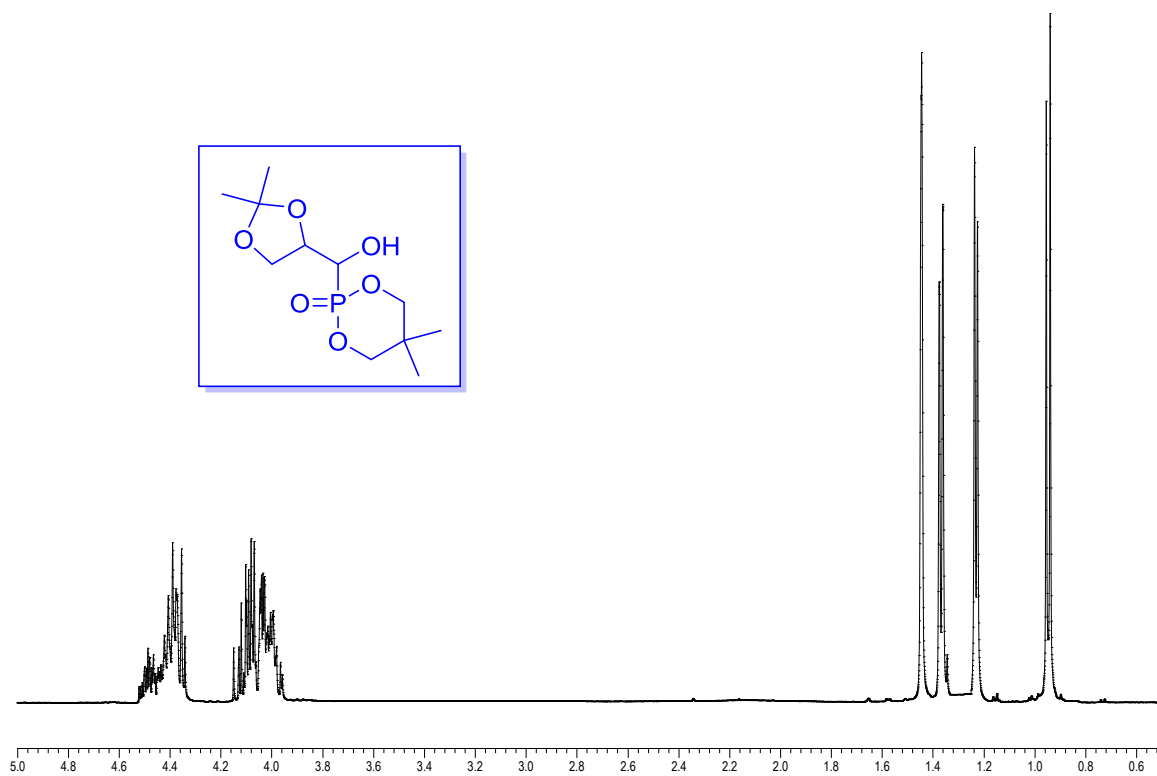


Figure 16. NMR spectrum of Compound 3.

With its distinctive peak at 9.72 ppm, the NMR spectrum in Figure 15 confirms the presence of an aldehyde. This peak is completely absent in the spectrum for Compound **3**, shown in Figure 16, showing that the aldehyde had completely reacted with the cyclic phosphite. Furthermore, due to the addition of a chiral center, the NMR spectrum for Compound **3** does not have peaks that are as distinct as those of the NMR spectrum of Compound **2**. The second dialkylphosphite that was attempted was diphenyl phosphite, forming diphenyl ((2,2-dimethyl-1,3-dioxolan-4-yl)(hydroxy)methyl)phosphonate (**4**):

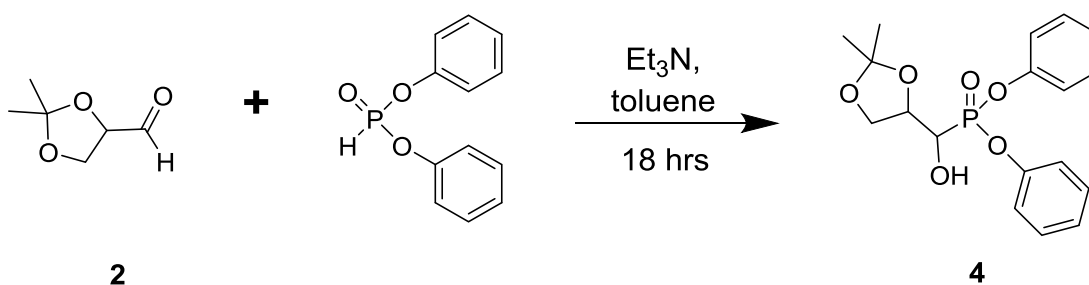


Figure 17. The reaction of protected glyceraldehyde with diphenyl phosphite.

The final dialkylphosphite that was used was diethyl phosphite, forming diethyl ((2,2-dimethyl-1,3-dioxolan-4-yl)(hydroxy)methyl)phosphonate (**5**):

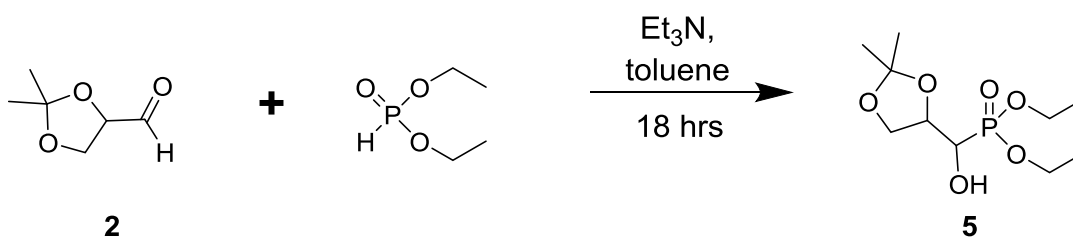


Figure 18. The reaction of protected glyceraldehyde with diethyl phosphite.

Only the reaction forming **3** produced any type of yield. Thus, when this reaction was attempted with the pentose substructure, only the cyclic phosphite was attempted.

The final step with regards to the triose substructure is the de-protection of the phosphorus hemiacetal, forming 5,5-dimethyl-2-(1,2,3-trihydroxypropyl)-1,3,2-dioxaphosphinane 2-oxide (**6**):

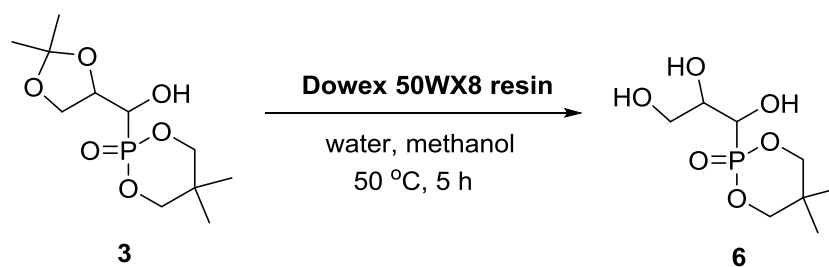


Figure 19. De-protection of the three-carbon phosphorus hemiacetal.

The Dowex resin is a good method for the de-protection because it provides an acid catalyst in a bound form, thus making it easier to separate (via filtration) after the reaction is complete.

Synthesis of P-Hemiacetals Based on a Pentose Substructure

Because the desired diol was not commercially available, the starting material for the synthesis of phosphorus hemiacetals based on a pentose substructure was D-mannitol, or hexane-1,2,3,4,5,6-hexaol (**7**). This had to first be fully protected to form 1,2:3,4:5,6-tri-O-isopropylidene-D-mannitol (**8**):

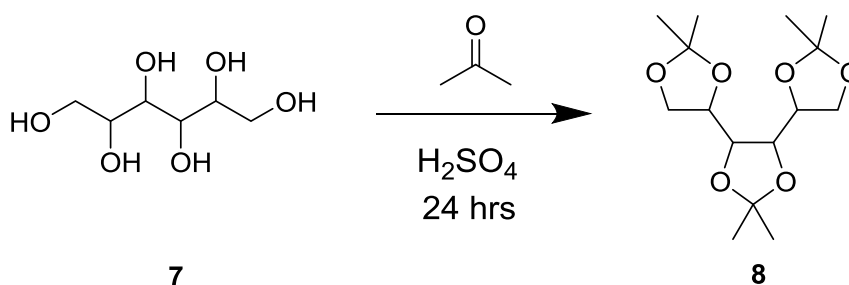


Figure 20. Full protection of D-mannitol.

The mechanism for this step is shown below in Figure 21.

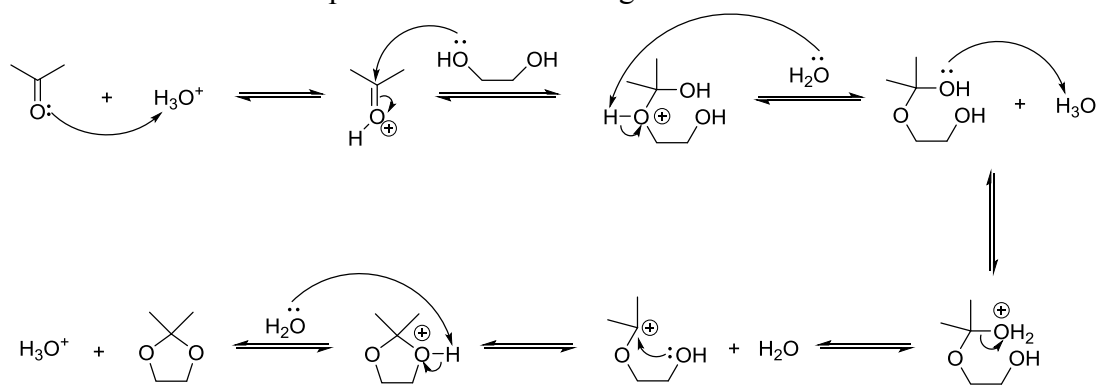


Figure 21. Mechanism for protection and de-protection of a diol.





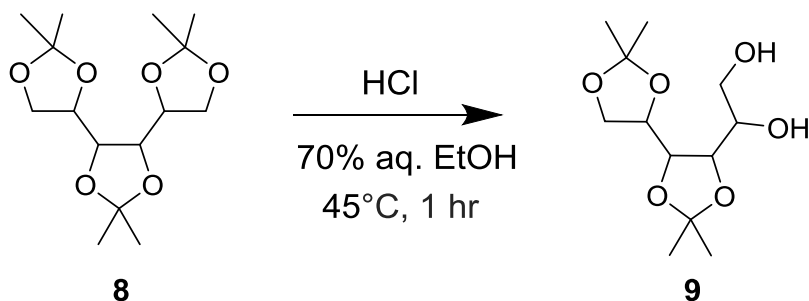



Figure 22. Partial de-protection of fully protected D-mannitol

The protection and de-protection of a compound is a reaction that takes place in equilibrium. Thus, the mechanism shown above in Figure 21 applies for the de-protection step as well, but in the reverse. This step had to be monitored very carefully. If it was allowed to take place for too long, then more of the protected groups would have been de-protected which was not desired. On the other hand, if it was not allowed to react for long enough, there would have been a large amount of reactant still left and very little of the partially de-protected mannitol would have been produced.

Once the desired diol, **9**, was formed, the synthetic protocol followed a scheme essentially the same as that of the triose substructure. The synthesized diol was oxidatively cleaved to form a protected aldehyde with a pentose substructure, 2,2,2',2'-tetramethyl-[4,4'-bi(1,3-dioxolane)]-5-carbaldehyde. This was attempted using two different reactions as shown below in Figure 23:

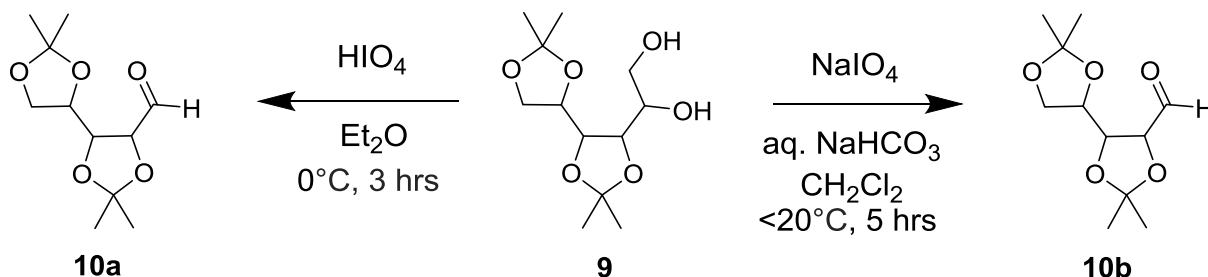
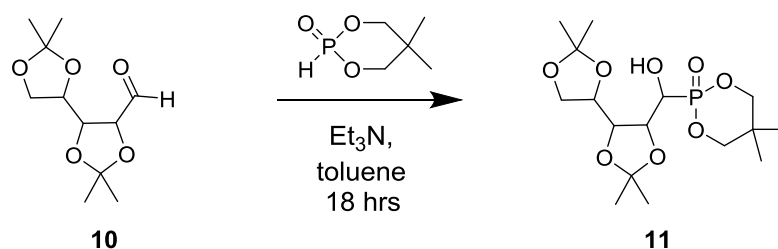


Figure 23. Formation of protected aldehyde from partially protected D-mannitol.

The first reaction of the two that was used was with the periodic acid (HIO_4), while the second that was used was with sodium periodate (NaIO_4). The mechanism for these reactions is the same as that of Figure 11. Then, compound **10** was reacted with the cyclic phosphite to form the phosphorus hemiacetal, 2-(hydroxy(2,2,2',2'-tetramethyl-[4,4'-bi(1,3-dioxolan)]-5-yl)methyl)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (**11**):



Experimental Methods

Synthesis of P-Hemiacetals Based on a Triose Substructure

2,2-Dimethyl-1,3-dioxolane-4-carbaldehyde (2) 1,2:5,6-Di-O-isopropylidene-D-mannitol (2.82 g, 10.74 mmol) was dissolved in methylene chloride (33.17 g, 390.50 mmol, 25 mL). Concentrated aqueous sodium bicarbonate (2.49 g, 29.60 mmol, 1.13 mL) and solid sodium periodate (4.60 g, 21.17 mmol) were added to the mixture which was then stirred at room temperature for 2h. The resultant mixture was separated using methylene chloride (25 mL) and water (50 mL) and the organic layer was retrieved. The organic layer was dried using magnesium sulfate. The dried contents were put through gravity filtration and the product was roto-vapped to remove solvent. Crude residue was left as the desired aldehyde in almost pure form, according to NMR data (24% yield). ^1H NMR (CDCl_3) δ 1.42 (s, 3H), 1.49 (s, 3H), 4.07 – 4.20 (m, 2H), 4.36 – 4.41 (m, 1H), 9.72 (s, 1H).

2-((2,2-Dimethyl-1,3-dioxolan-4-yl)(hydroxy)methyl)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (3) Compound **2** (0.66 g, 5.08 mmol) and cyclic phosphite (0.76 g, 5.08 mmol) were mixed with toluene (6.96 g, 75.54 mmol, 8 mL). Triethylamine (0.26 g, 2.54 mmol, 0.36 mL) was added. This mixture was stirred at room temperature for 18 h. The resultant mixture was vacuum filtered, using hexanes to wash the solid product. Impurities were removed using toluene and a small amount of ethanol for recrystallization. The recrystallized product was the desired phosphorus hemiacetal, according to NMR data (68% yield). ^1H NMR (CDCl_3) δ 0.95 (d, $J = 6.3$ Hz, 3H), 1.23 (d, $J = 6.4$ Hz, 3H), 1.38 (d, $J = 3.0$ Hz, 3H), 1.46 (s, 3H), 4.01 – 4.14 (m, 4H), 4.37 – 4.52 (m, 4H). ^{13}C NMR (CDCl_3) δ 20.8, 22.0, 25.2 (d, $J = 8.0$ Hz), 26.3, 26.8, 32.4 (dd, $J_1 = 3.2$ Hz, $J_2 = 8.0$ Hz), 64.5 (d, $J = 3.6$ Hz), 66.4 (d, $J = 5.0$ Hz), 67.9, 70.0, 72.1, 74.8, 74.9, 75.0, 75.1, 76.6, 77.1, 77.5, 78.0 – 78.1, 78.2. Anal. Calcd. for $\text{C}_{11}\text{H}_{21}\text{O}_6\text{P}$: C, 47.14; H, 7.55. Found: C, 47.16; H, 7.47.

Diphenyl ((2,2-dimethyl-1,3-dioxolan-4-yl)(hydroxy)methyl)phosphonate (4) Compound **2** (0.66 g, 5.08 mmol) and diphenyl phosphite (1.19 g, 5.08 mmol, 0.98 mL) were mixed with toluene (6.96 g, 75.54 mmol, 8 mL). Triethylamine (0.26 g, 2.54 mmol, 0.36 mL) was added. This mixture was stirred at room temperature for 18 h. The resultant mixture was vacuum filtered, using hexanes to wash the solid product. Impurities were

removed using toluene and a small amount of ethanol for recrystallization. No product formed (0% yield).

Diethyl ((2,2-dimethyl-1,3-dioxolan-4-yl)(hydroxy)methyl)phosphonate (5)

Compound **2** (0.56 g, 4.31 mmol) and diphenyl phosphite (0.595 g, 4.31 mmol, 0.56 mL) were mixed with toluene (6.96 g, 75.54 mmol, 8 mL). Triethylamine (0.22 g, 2.16 mmol, 0.30 mL) was added. This mixture was stirred at room temperature for 18 h. The resultant mixture was vacuum filtered, using hexanes to wash the solid product. Impurities were removed using toluene and a small amount of ethanol for recrystallization. No product formed (0% yield).

5,5-Dimethyl-2-(1,2,3-trihydroxypropyl)-1,3,2-dioxaphosphinane 2-oxide (6)

Compound **3** (0.30 g, 1.07 mmol) was suspended in water (7.30 g, 405.56 mmol, 7.3 mL) and allowed to stir at room temperature. Methanol (1.5 mL) was added to increase solubility. Pre-washed Dowex 50WX8 resin (0.73 g) was added. The mixture was heated 50° C and continued to stir for 5 h. The resultant mixture was then gravity filtered to remove the Dowex resin. To isolate the solid final product, the filtrate was roto-vapped. According to NMR data, the desired product was obtained.

Synthesis of P-Hemiacetals Based on a Pentose Substructure

1,2:3,4:5,6-Tri-O-isopropylidene-D-mannitol (8) D-mannitol (41.67 g, 229 mmol) was mixed with acetone (411.3 g, 7.08 mol, 520 mL). Sulfuric acid (7.67 g, 78.00 mmol, 4.17 mL) were added to the mixture. This solution was suspended for 24 h. The solution was neutralized by adding ammonium hydroxide (13.5 g, 385.27 mmol, 15 mL), followed by sodium bicarbonate (26 g, 309.50 mmol). Solid crude product was removed after vacuum filtration and evaporation of the solvent using the roto-vapor (63 g). Impurities were removed *via* recrystallization, dissolving the crude product in 50 mL of acetone. The desired solid product was isolated through vacuum filtration and allowed to dry. NMR data confirmed the presence of the desired product (42% yield). ¹H NMR (CDCl₃) δ 1.36 (s, 6H), 1.40 (s, 6H), 1.43 (s, 6H), 3.94 – 4.21 (m, 8H).

1,2:3,4-Di-O-isopropylidene-D-mannitol (9) A mixture of compound **8** (11.87 g, 39.26 mmol) and 70% aqueous ethanol (270 mL) was treated with HCl (0.84 g, 23.15 mmol, 0.83 mL). This was allowed to stir for 1 h at 45° C. Excess amounts of K₂CO₃

were then added, resulting in an organic and aqueous layer. With the ethanol layer separated, the aqueous layer was extracted using ethyl acetate (100 mL). The collected organic layers were roto-vapped to remove the solvent. The residue was obtained from the flask using cold water. This mixture was then filtered through vacuum filtration. The separated solid was unreacted starting material. The aqueous layer was then extracted twice, each time with ethyl acetate (100 mL). The collected layers were roto-vapped to remove remaining solvent. According to NMR data, the desired diol was the final solid product (29% yield). ^1H NMR (CDCl_3) δ 1.35 – 1.46 (m, 12H), 3.71 – 4.22 (m, 8H).

2,2,2',2'-Tetramethyl-[4,4'-bi(1,3-dioxolane)]-5-carbaldehyde (10a)

Compound **9** (2.45 g, 9.34 mmol) was dissolved in diethyl ether (0.25 M, 37.36 mL) at 0°C . Periodic acid (2.77 g, 12.14 mmol) was added portionwise throughout 20 minutes. The mixture was allowed to stir for 3 h at 0°C . The resultant mixture was filtered through celite and roto-vapped. NMR analysis confirmed the presence of the desired aldehyde.

2,2,2',2'-Tetramethyl-[4,4'-bi(1,3-dioxolane)]-5-carbaldehyde (10b)

Compound **9** (2.99 g, 11.40 mmol) was dissolved in methylene chloride (13.26 mL). This solution was treated with saturated aqueous sodium bicarbonate (0.98 mL). NaIO_4 (4.88 g, 22.80 mmol) was added portionwise for 20 minutes to the solution, which was cooled to 0°C . The mixture was allowed to stir for 5 h at room temperature, below 20°C . Solid Na_2SO_4 was added (1.3 g, 9.15 mmol) and the mixture stirred for another 15 minutes. The mixture was then filtered through vacuum filtration and washed with methylene chloride. This was then roto-vapped to provide the aldehyde, confirmed by NMR data (89% yield). ^1H NMR (CDCl_3) δ 1.35 – 1.48 (m, 12H), 3.97 – 4.40 (m, 4H), 4.42 (d, $J = 1.0\text{ Hz}$, 1H), 9.76 (s, 1H).

2-(Hydroxy(2,2,2',2'-tetramethyl-[4,4'-bi(1,3-dioxolan)]-5-yl)methyl)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (11) Compound **10** (2.32 g, 10.09 mmol) and cyclic phosphite (1.51 g, 10.09 mmol) were mixed with toluene (25 mL).

Triethylamine (0.51 g, 5.05 mmol, 0.70 mL) was added. This mixture was stirred at room temperature for 18 h. The resultant mixture was vacuum filtered, using hexanes to wash the solid product. Impurities were removed using toluene and a small amount of ethanol

for recrystallization. The recrystallized product was the desired phosphorus hemiacetal, according to NMR data (41% yield).

(1,2,3,4,5-Pentahydroxypentyl)phosphonic acid (12) A solution of compound **11** (0.50 g, 1.31 mmol) and 70% aqueous ethanol (9 mL) was treated with HCl (0.03 g, 0.84 mmol, 0.03 mL). This solution was allowed to stir overnight at a temperature of 45° C. The mixture was roto-vapped and placed under a pump to remove the ethanol. Analysis seems to show that compound **12** was synthesized.

5,5-Dimethyl-2-(1,2,3,4,5-pentahydroxypentyl)-1,3,2-dioxaphosphinane 2-oxide (13) Compound **11** (0.41 g, 1.07 mmol) was suspended in water (7.30 g, 405.56 mmol, 7.3 mL) and allowed to stir at room temperature. Methanol (1.5 mL) was added to increase solubility. Pre-washed Dowex 50WX8 resin (0.73 g) was added. The mixture stirred for 5 h at room temperature. The resultant mixture was then gravity filtered to remove the Dowex resin. To isolate the solid final product, the filtrate was roto-vapped. According to NMR data, the desired product was obtained.

Conclusion and Future Directions

- Through the proposed multi-step pathway, phosphorus hemiacetals were prepared, containing a carbohydrate sub-structure, specifically those with triose and pentose substructures.
- NMR and elemental analysis confirmed the structure of these products.
- Testing of the final products for effectiveness as flame retardants is ongoing.

In the future, focus and emphasis should be on the following:

- With regards to the actual synthetic procedure, a complete study needs to be done on the de-protection of the phosphorus hemiacetals in order to ensure that only the desired protected groups are de-protected in the compound.
- With regards to flame retardant testing, the synthesized targets should be utilized in polyurethane preparation in order to conduct flammability studies on these samples.

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