1,3,5,7-Tetraethynyladamantane: An Alternate Synthesis

James Cummings Dr. Carolyn Weinreb
Department of Chemistry, Saint Anselm College
100 Saint Anselm Drive, Manchester NH

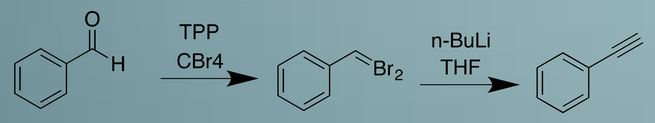
Abstract

An improved synthesis of 1,3,5,7-tetraethynyladamantane is being investigated. As a starting point, 1-ethynyladamantane is the model system being used. This research goal has been to synthesize each step in better yields while striving towards the alkyne. Both the monosubstituted and tetrasubstituted were synthesized to the dibromoolefin and were characterized with a yield of 45% and 64% respectively. ^{1}H NMR indicates the dibromoalkene with a chemical shift of 3.2ppm and the disappearance of the IR/^{1}H NMR peak at 1723cm^{-1} 9.3ppm, respectively, also indicates the presence of the alkene. The last step, elimination, is currently being investigated to complete the synthetic pathway.

Introduction

Functionalized 3D molecules, such as 1,3,5,7-tetraethynyladamantane are desirable as a building block for 3-dimensional networks. The published synthesis is 8 steps with an 11% yield[1]. Our synthesis is 2 fewer steps, with the key step being the photochemical addition of the carbomethoxy esters to the tertiary carbons of the adamantane. The esters can be converted to the alkyne through reduction, oxidation, and a Corey-Fuch's elimination. To insure the success of the synthesis, the monosubstituted adamantane was used as a model system.

Corey Fuch's Reaction

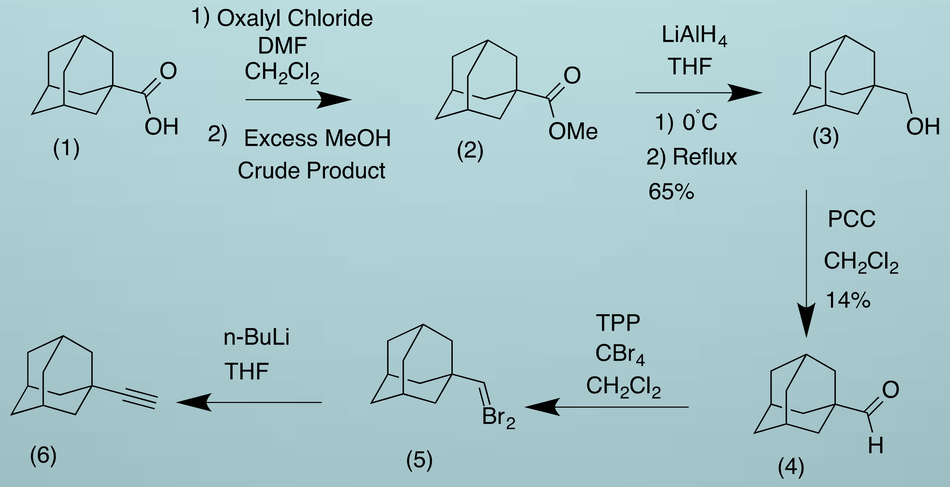


- Initially, phenylacetylene was synthesized from benzaldehyde to trouble shoot the reaction.
- This research was directed at using the Corey Fuch's Reaction to convert an aldehyde to an alkyne.

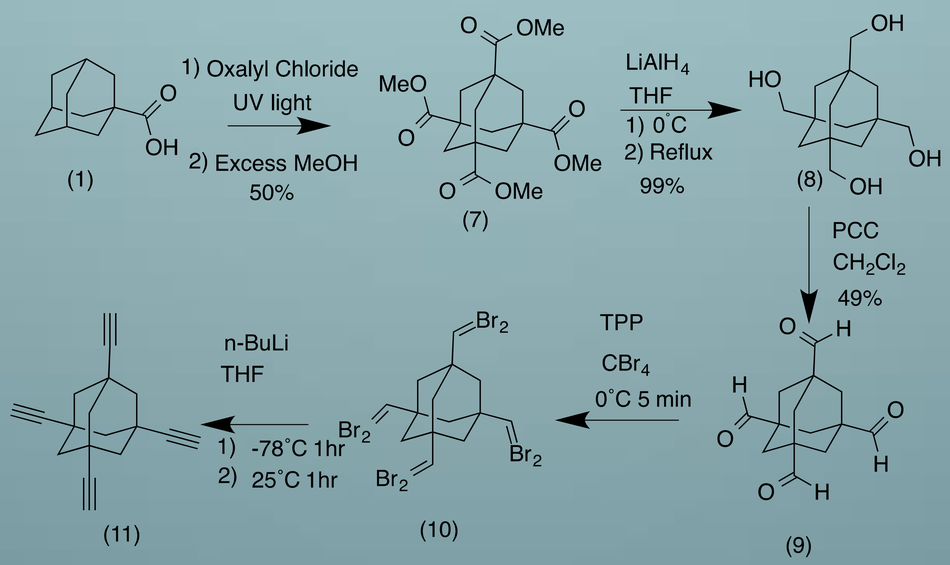
Reference

1. Nakazaki, M.; Naemura, K.; Hokura, Y., Synthesis of (+)-1,3,5,7-tetrakis[2-(1S,3S,5R,6S,8R,10R)-D3-trishomocubanylbuta-1,3-diynyl] adamantane. *Journal of the Chemical Society, Chemical Communications* **1982,** (21), 1245-1246.
2. Corey, E. J.; Fuchs, P. L., A Synthetic Method for Formyl Ethynyl Conversion. *Tetrahedron Letters* **1972,** *36*, 4.

Scheme 1: Synthetic Pathway 1-Ethynyladamantane



Scheme 2: Synthetic Pathway for 1,3,5,7-Tetraethynyladamantane



Results and Discussion

- Adamantanecarbaldehyde was synthesized with a yield of 14%.
- The photochemical reaction to generate the tetrasubstituted adamantane proceeded with a 50% yield and with a conversion to an aldehyde, a 49% yield.
- Once the aldehydes were characterized, formation of the alkyne via a Corey-Fuch's reaction was investigated.
- Both the monosubstituted and tetrasubstituted dibromoalkene were characterized by ^{1}H NMR, showing the proton next to the two bromines at 3.2ppm.
- The disappearing of the IR and ^{1}H NMR peak of 1723cm^{-1} and 9.3ppm indicates the aldehyde was not present.
- The monsubstituted resulted in a 45% yield while the tetrasubstituted a 64% yield.

Conclusion

- The photochemical reaction is a valid method for functionalizing the adamantane at all four tertiary centers.
- Further optimization of the reaction conditions should lead to increasing yields.
- The dibromoolefins were isolated and will be subjected to elimination conditions.

Future Work

Other means of converting an aldehyde to an alkyne are being investigated and will be used in place of the Corey Fuch's Reaction.

Acknowledgements

I would like to thank the Saint Anselm College Chemistry Department, especially Dr. Carolyn Weinreb and Dr. Derk Wierda for all the help, patience, and time.

Funding

This research was funded by NH-INBRE.