

# Improved Synthesis of 1,3,5,7-Tetraethynyladamantane

Joey Pisano & Carolyn Weinreb  
Saint Anselm College Chemistry Department



## Abstract

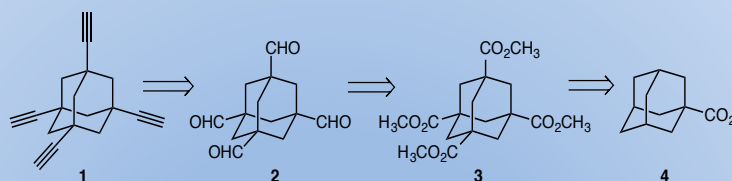
1,3,5,7-Tetraethynyladamantane provides an interesting building block for 3-dimensional networks due to the availability of the alkyne functional groups for coupling reactions. Conversion of the adamantane carboxylic acid to the tetracarbomethoxyadamantane followed by manipulation to the alkynes provides a short efficient synthesis of the desired product. The proposed synthesis is significantly fewer steps than the only other reported synthesis

## Introduction

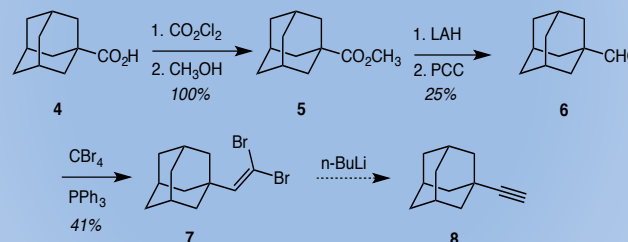
1,3,5,7-Tetraethynyladamantane was synthesized by Nakazaki, et al in 8 steps with an overall 11% yield.<sup>1</sup> We propose a shorter synthesis from the readily available adamantane carboxylic acid. The tetrasubstitution is introduced using free radical acylation of the tertiary carbons.<sup>2</sup> The alkynes can be introduced using a Corey-Fuchs reaction,<sup>3</sup> Scheme 1. Investigation of the methodology is being carried out using the monosubstituted adamantane for simplicity.

## References

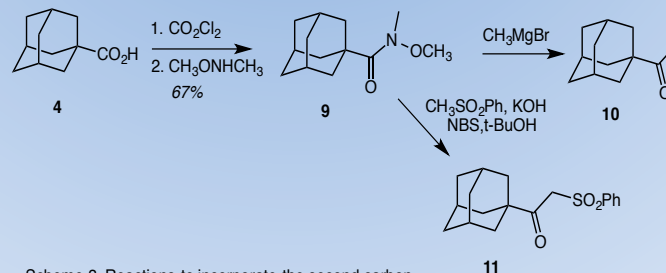
1. Nakazaki, M.; Naemura, K; Hokura, Y. *Journal of the Chemical Society. Chemical Communications* **1982**, (21), 1245-1246.
2. Bashir-Hashemi, A.; Li, J. *Tetrahedron Letters* **1995**, 36, 1233-1236.
3. Corey, E. J.; Fuchs, P. L. *Tetrahedron Letters* **1972**, 13, 3769-3772.



Scheme 1. Retrosynthesis of 1,3,5,7-tetraethynyladamantane **1**.



Scheme 2. Synthesis of 1-ethynyladamantane.



Scheme 3. Reactions to incorporate the second carbon.

## Results & Discussion

- Synthesis of the dibromoalkene **7** was successful, albeit with low yields that can be optimized. Conversion of the dibromide to the alkyne has not been successful.
- To avoid the difficulties in the last step, we decided to introduce the second carbon of the alkyne via a Grignard and with the amide **9**. Unfortunately, no product was formed.
- Synthesis of tetraaldehyde **2** has been successfully completed in an overall 20% yield.

## Conclusion

The method in Scheme 2 continues to show the most promise. The elimination will be attempted using different bases and finally applied to the synthesis of **1**.

## Acknowledgements

Funding for this project was provided by NH-INBRE grant.