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

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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. We propose a shorter synthesis from the readily available adamantane carboxylic acid. The tetrasubstitution is introduced using free radical acylation of the tertiary carbons. The alkynes can be introduced using a Corey-Fuchs reaction. Scheme 1. Investigation of the methodology is being carried out using the monosubstituted adamantane for simplicity.

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 tetraldehyde 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.

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References