

Towards the Synthesis of 1,3,5,7-Tetraethynyladamantane

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Abstract

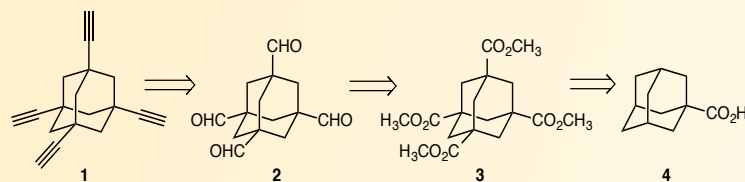
The synthesis of 1-ethynyladamantane from adamantane 1-carboxylic acid was investigated as a model for the total synthesis of 1,3,5,7-tetraethynyladamantane. Three synthetic routes were explored to determine the most efficient pathway for terminal alkyne production. The reaction scheme that proved to be most successful involves a Corey-Fuchs conversion of an aldehyde to the desired alkyne product.¹

Introduction

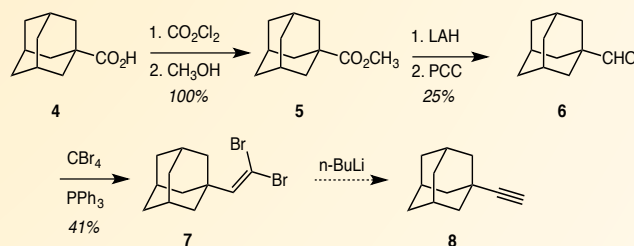
The only known published synthesis of 1,3,5,7-tetraethynyladamantane was performed by Nakazaki in 8 steps with an 18% yield.² The molecule under investigation is a useful building block in the formation of 3-dimensional networks due to the terminal alkyne coupling sites. Tetrasubstitution can be achieved through ultraviolet light induced free radical acylation of the tertiary carbons, shown in Scheme 1.³ For practical purposes, 1-ethynyladamantane was used as a model for the complete synthesis, shown in Schemes 2 and 3.

References

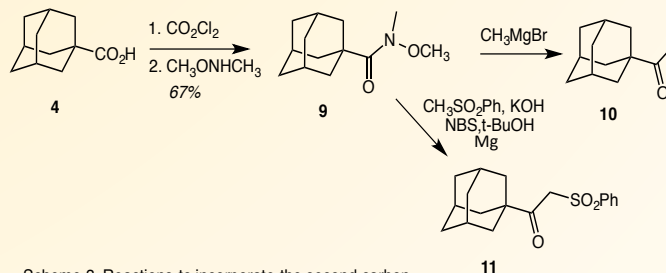
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2. Nakazaki, M.; Naemura, K; Hokura, Y. *Journal of the Chemical Society. Chemical Communications* **1982**, (21), 1245-1246.
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Scheme 1. Retrosynthesis of 1,3,5,7-tetraethynyladamantane **1**.



Scheme 2. Synthesis of 1-ethynyladamantane.



Scheme 3. Reactions to incorporate the second carbon.

Results & Discussion

- Synthesis of **7** was performed successfully but with low yield. Attempts to convert **7** to **8** with *n*-butyllithium and sodium hydride to date has been unsuccessful.
- In Scheme 3, **9** was synthesized with a 67% yield. Efforts to convert to **10** or **11** using Grignard reagents have not resulted in product formation.
- Bromomethylphenyl sulfone was synthesized with a 25% yield to be used in the production of **11**.

Conclusion

The synthesis in Scheme 2, despite not yielding the final product, is the most promising of the three. Further investigation and experimentation is required; however, this is the most reasonable synthesis to attempt to produce **1** by. The next step is to investigate alternative bases to *n*-butyllithium to promote the elimination reaction.

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