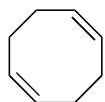
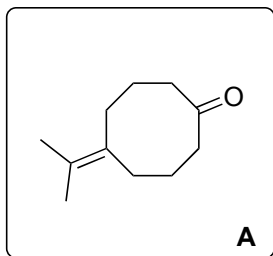


α -Ketenyl Radical Intermediates in the Synthesis of Propellanes. A Formal Synthesis of Modhephene

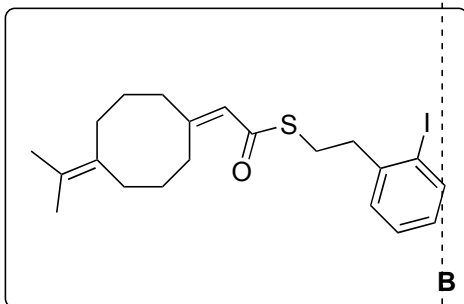
Benoit De Boeck and Gerald Pattenden
Tet. Lett. **1988**, 39, 6975 – 6978.



1-4



7-12



see next page



- 1) $\text{BH}_3 \cdot \text{THF}$, then NaOH , H_2O_2
- 2) TBSCl (1 eq), imidazole, CH_2Cl_2
- 3) TPAP cat., NMO, CH_2Cl_2
- 4) $\text{TiCl}_3 \cdot \text{AlCl}_3$, Li, then add product from reaction 3) and acetone, Δ

Step 4: Name Reaction? Mechanism?

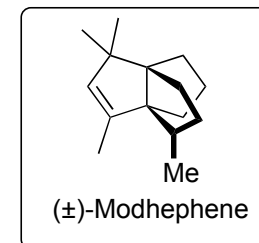
see below

- 7) 40% HF , $\text{H}_2\text{O}-\text{CH}_3\text{CN}$
- 8) Swern
- 9) $\text{Me}_3\text{SiCH}_2\text{CO}_2\text{Et}$, LDA
- 10) 1M NaOH
- 11) 2-(*o*-iodophenyl) $\text{CH}_2\text{CH}_2\text{SH}$, DCC, DMAP, CH_2Cl_2
- 12) Bu_3SnH , AIBN, benzene, Δ

Step 9: Discuss the mechanism of the reaction, advantages and disadvantages compared to other methods. **see below**

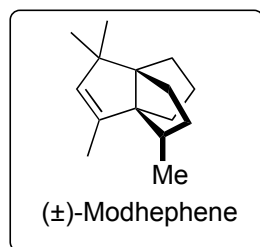
Step 12: Mechanism?

see below



13-20

- 13) NaH, MeOCHO
- 14) TsN₃, Et₂NH
- 15) CuSO₄, toluene, Δ
- 16) *t*-BuLi, CO₂, *then* CH₂N₂
- 17) Me₂CuLi
- 18) MeI, KO*t*-Bu, *then* LiI, collidine
- 19) LiAlH₄
- 20) Martin's Sulfurane



Step 15: Hint: a new ring is formed in this step

Step 17: Mechanism? Rationalize and explain the synthetic utility of this type of strategy and discuss how it could be extended other types of reactions.

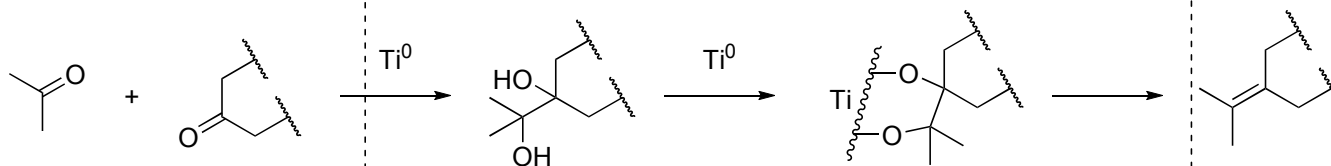
see below

Step 20: Structure of Martin's Sulfurane? What are other reagents that you could use for this transformations?

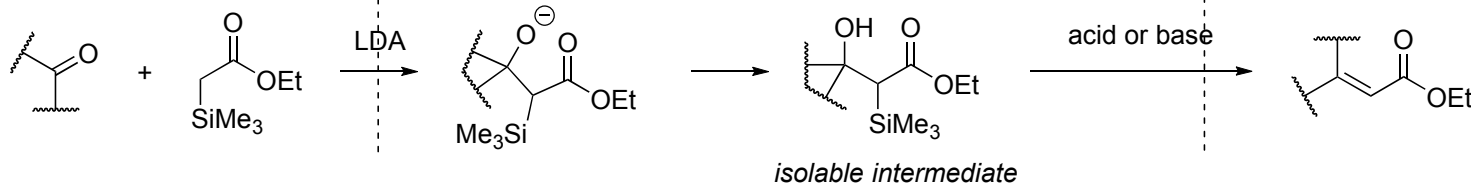
see below

Step 4: McMurry coupling <https://pubs.acs.org/doi/pdf/10.1021/jo00411a002>

Active titanium metal generated by reduction of TiCl₃ by alkaline metal; reaction occurs on the surface of the active titanium particle



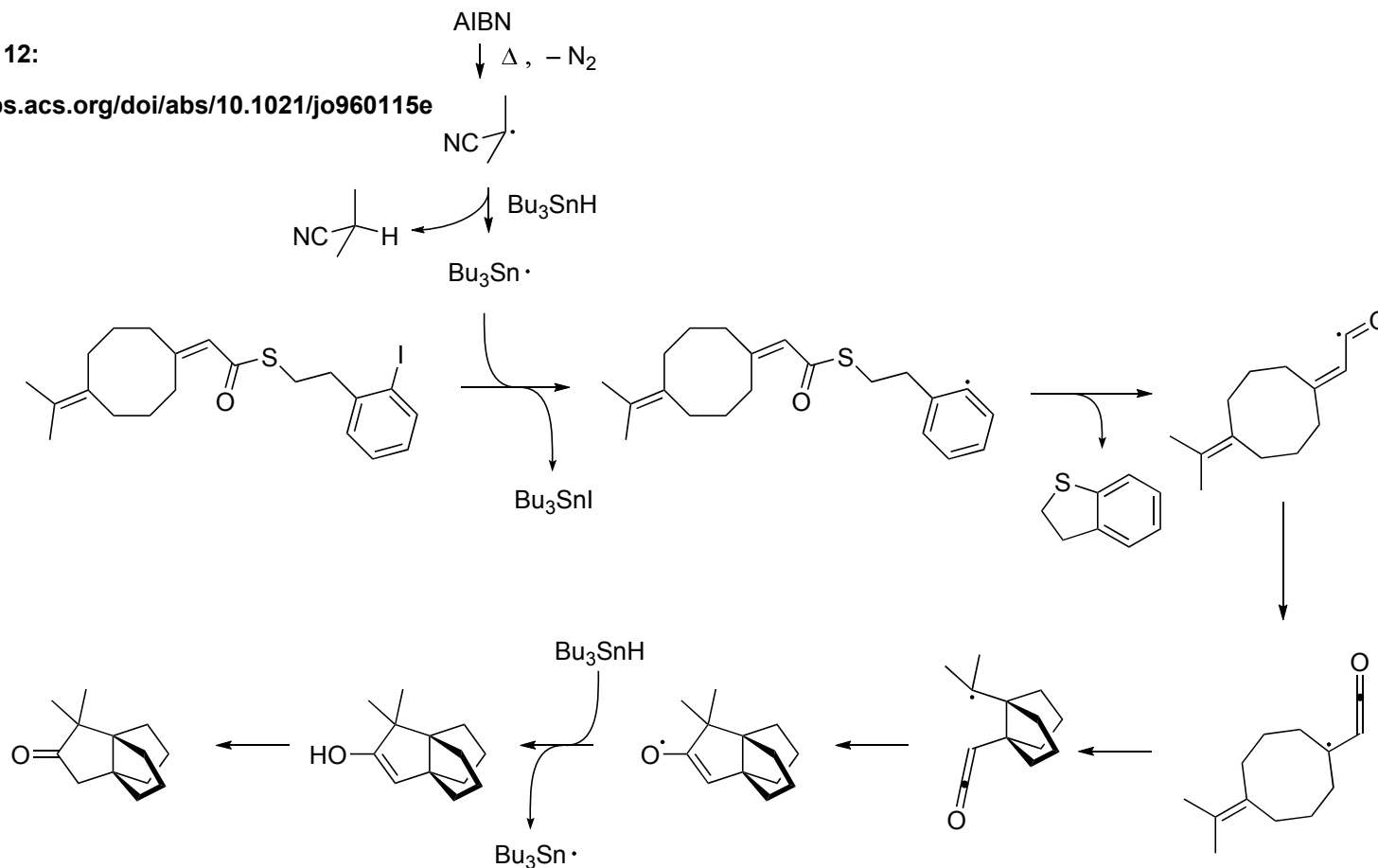
Step 9: Peterson Olefination <http://pubs.rsc.org/en/content/articlehtml/2002/cs/a908402i>



base gives Z- isomer
predominantly
acid conditions favor E-
isomer; byproducts easier
to remove than in
standard Wittig reaction

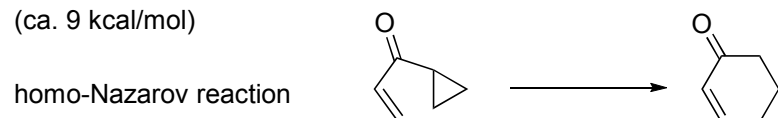
Step 12:

<https://pubs.acs.org/doi/abs/10.1021/jo960115e>

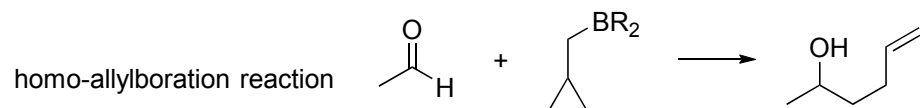


Step 17: alpha-keto cyclopropane ring-opening by cuprate; formally, a 1,5-addition that would require polarity reversal.

cyclopropane as enabling group due to ring strain (28 kcal/mol) that substantially weakens the C-C bond, also due to torsional strain (ca. 9 kcal/mol)



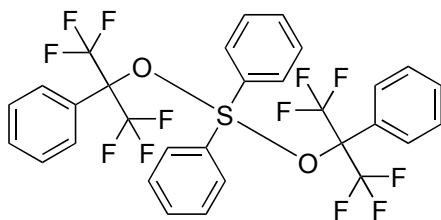
<https://pubs.acs.org/doi/abs/10.1021/ol802970g>



<https://pubs.acs.org/doi/abs/10.1021/ja2048682>

Step 20:

Martin's sulfurane



Burgess reagent

