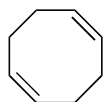
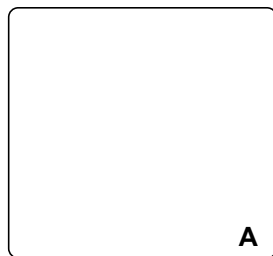


α -Ketenyl Radical Intermediates in the Synthesis of Propellanes. A Formal Synthesis of Modhephene

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



1-4



7-12



see next page

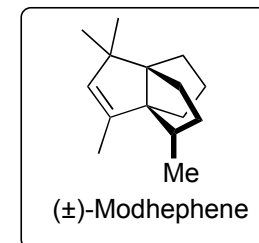
- 1) $\text{BH}_3 \cdot \text{THF}$, then NaOH , H_2O_2
- 2) TBSCl (1 eq), imidazole, CH_2Cl_2
- 3) TPAP cat., NMO, CH_2Cl_2
- 4) $\text{TiCl}_3 \cdot \text{AlCl}_3$, Li, then add product from reaction 3) and acetone, Δ

- 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

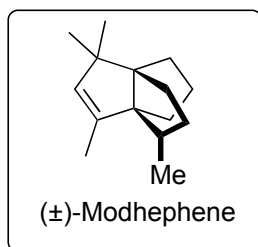
Step 4: Name Reaction? Mechanism?

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

Step 12: Mechanism?



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* Lil, 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.

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