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

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1-4

1) BH_3•THF, *then* NaOH, H_2O_2
2) TBSCl (1 eq), imidazole, CH_2Cl_2
3) TPAP cat., NMO, CH_2Cl_2
4) $TiCl_3$•$AlCl_3$, Li, *then* add product from reaction 3) and acetone, Δ

Step 4: Name Reaction? Mechanism?

A

7) 40% HF, H_2O-CH_3CN
8) Swern
9) $Me_3SiCH_2CO_2Et$, LDA
10) 1M NaOH
11)(*o*-iodophenyl)CH_2CH_2SH, DCC, DMAP, CH_2Cl_2
12) Bu_3SnH, AIBN, benzene, Δ

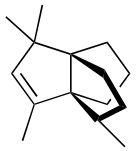
Step 9: Discuss the mechanism of the reaction, advanages and disadvantages compared to other methods.

Step 12: Mechanism?

7-12

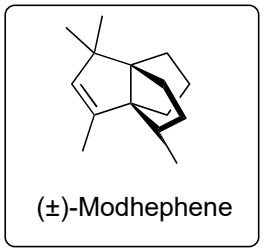
B

see next page



(±)-Modhephene

13-20



(±)-Modhephene

13) NaH, MeOCHO
14) TsN_3, Et_2NH
15) $CuSO_4$, toluene, Δ
16) *t*-BuLi, CO_2, *then* CH_2N_2
17) Me_2CuLi
18) MeI, KO*t*-Bu, *then* LiI, collidine
19) $LiAlH_4$
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 to other types of reactions.

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