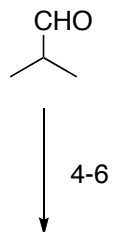
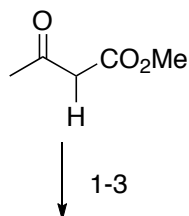


# Intramolecular Photocycloaddition-Cyclobutane Fragmentation: Total Synthesis of ( $\pm$ )-Silphinene

Michael T. Crimmins and S. Wayne Mascarella

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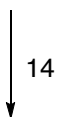
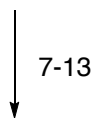
- 1)  $\text{CH}(\text{OMe})_3$ ,  $\text{H}_2\text{SO}_4$
- 2)  $h\nu$ , NBS,  $(\text{PhCO}_2)_2$ ,  $\text{CCl}_4$ , reflux
- 3) NaI

1) What is the pka of the indicated H?

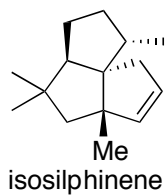
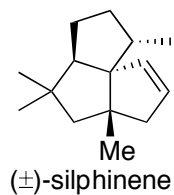
- 4) allyl alcohol, TsOH, p-cymene, reflux
- 5)  $\text{PdCl}_2$ , CuCl,  $\text{O}_2$ , DMF/ $\text{H}_2\text{O}$
- 6) KOH 50 °C

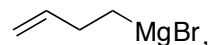
5) What is the name of this reaction and mechanism?

**B**



↓  
15-18

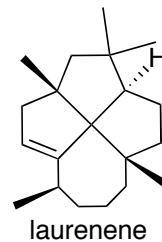


- 7)  $\text{Bu}_3\text{PCuI}$ , THF,   $\text{MgBr}$ , then **A**, HMPA
- 8) 30%  $\text{HClO}_4$ ,  $\text{CH}_2\text{Cl}_2$
- 9)  $\text{NaOMe}$ ,  $\text{MeOH}$ ,  $0^\circ\text{C}$
- 10)  $\text{Me}_2\text{CuLi}$ ,  $\text{Et}_2\text{O}$ ,  $0^\circ\text{C}$
- 11)  $\text{LiCl}$ ,  $\text{DMSO}/\text{H}_2\text{O}$ ,  $145^\circ\text{C}$  to rt
- 12) **ETSA**,  $\text{Bu}_4\text{NF}$ , THF
- 13) Saegusa Oxidation



- 14)  $h\nu$ , rt

- 15)  $\text{TMSCl}$ ,  $\text{NaI}$ ,  $\text{MeCN}$ ,  $80^\circ\text{C}$
- 16)  $\text{Bu}_3\text{SnH}$ ,  $\text{PhH}$ ,  $90^\circ\text{C}$
- 17)  $\text{LDA}$ ,  $(\text{EtO})_2\text{POCl}$ ,  $\text{tBuOH}/\text{THF}$ ,  $-78^\circ\text{C}$
- 18)  $\text{Li}$ ,  $\text{MeNH}_2$ ,  $40^\circ\text{C}$



12) Other alkyl amines tried gave inferior regioselectivity. Why might this combination lead to 96:4 isomer formation?

13) What conditions would you use to perform this transformation?

18) 4.5:1 regioselectivity, Can be separated using  $\text{AgNO}_3$  impregnated silica

Bonus Question: The authors suggest a similar strategy can be used for the synthesis of laurenene. How?

