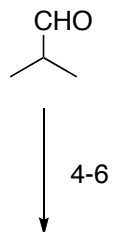
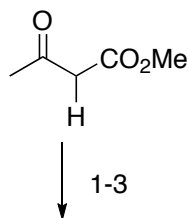


Intramolecular Photocycloaddition-Cyclobutane Fragmentation: Total Synthesis of (±)-Silphinene

Michael T. Crimmins and S. Wayne Mascarella

JACS 1986, 108, 3435-3438



- 1) $\text{CH}(\text{OMe})_3$, H_2SO_4
- 2) $h\nu$, NBS, $(\text{PhCO}_2)_2$, CCl_4 , reflux
- 3) NaI

1) What is the pka of the indicated H?

- 4) allyl alcohol, TsOH, p-cymene, reflux
- 5) PdCl_2 , CuCl, O_2 , DMF/ H_2O
- 6) KOH 50 °C

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

B



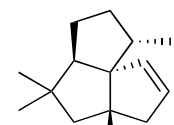
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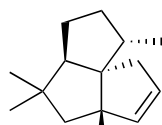
14



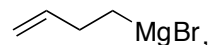
15-18



(±)-silphinene



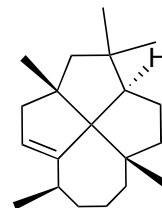
isosilphinene

- 7) Bu_3PCuI , THF,  MgBr , then **A**, HMPA
- 8) 30% HClO_4 , CH_2Cl_2
- 9) NaOMe , MeOH , 0°C
- 10) Me_2CuLi , Et_2O , 0°C
- 11) LiCl , $\text{DMSO}/\text{H}_2\text{O}$, 145°C to rt
- 12) **ETSA**, Bu_4NF , THF
- 13) Saegusa Oxidation



- 14) $h\nu$, rt

- 15) TMSCl , NaI , MeCN , 80°C
- 16) Bu_3SnH , PhH , 90°C
- 17) LDA , $(\text{EtO})_2\text{POCl}$, tBuOH/THF , -78°C
- 18) Li , MeNH_2 , 40°C



laurenene

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?

14) Justify the stereochemistry of the resulting product using Woodward Hoffman rules.

18) 4.5:1 regioselectivity, Can be separated using AgNO_3 impregnated silica

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

