4 Membered Rings

1. cyclobutanes & cyclobutenes
2. oxatanes

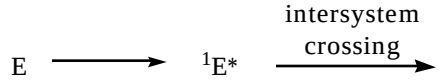
Cyclobutanes

- [2+2] cycloadditions

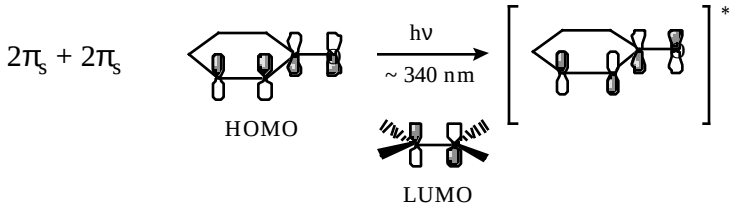
  - photochemical cycloadditions ($2\pi_s + 2\pi_s$)

  Acc. Chem. Res. **1968**, *1*, 50; *Synthesis* **1970**, 287; *Acc. Chem. Res.* **1971**, *4*, 41; *Organic Photochemistry* **1981**, *5*, 123; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 820; *Acc. Chem. Res.* **1982**, *15*, 135; *Organic Photochemistry* **1989**, *10*, 1 *Organic Reactions* **1993**, *44*, 297

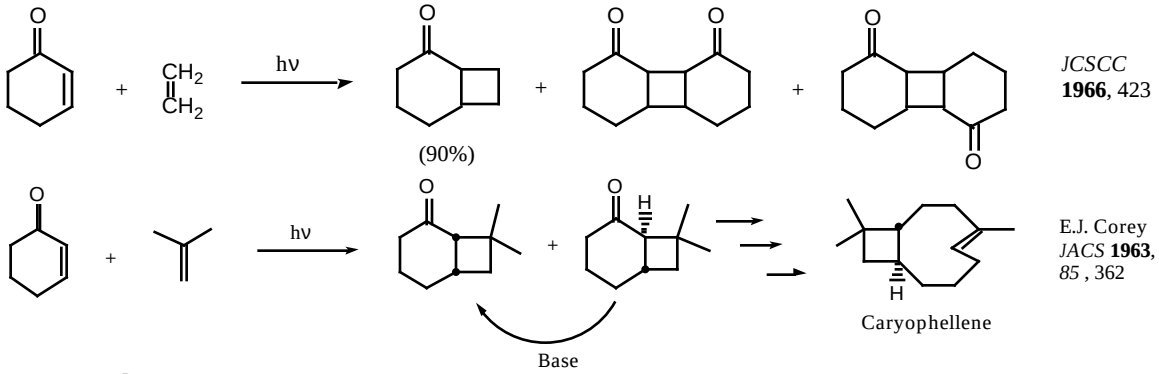
  - for synthetic purposes, cyclic α,β-unsaturated carbonyl are the most useful.



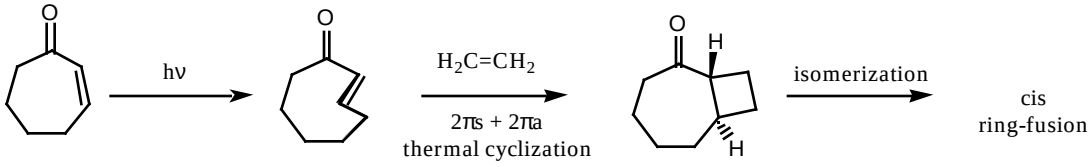
  - symmetry requirements

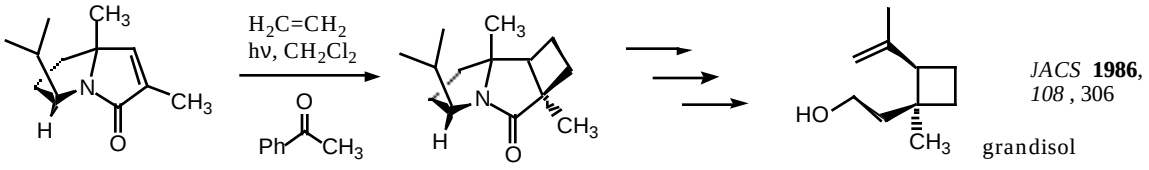


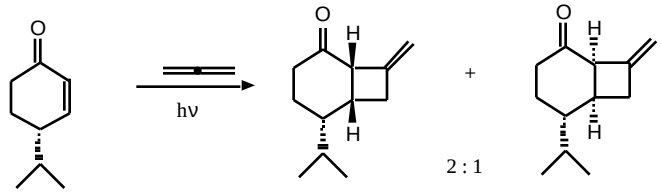
  - enones with olefins



Hot Ground State?

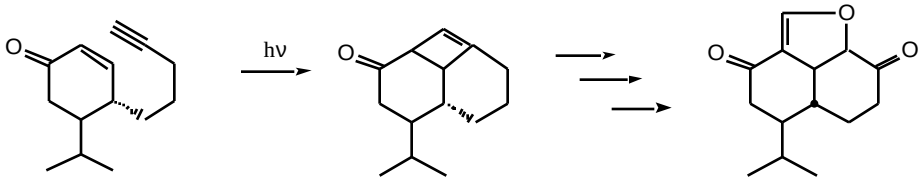






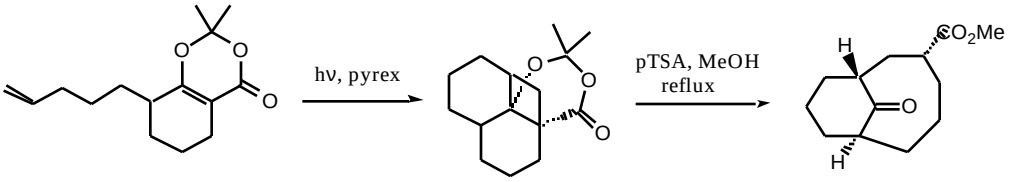
JACS **1984**
106 , 4038

- enones with acetylenes

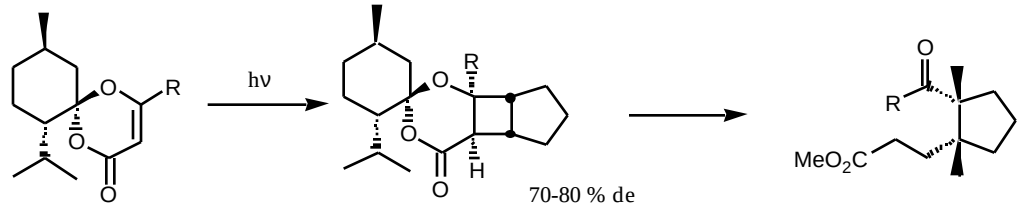


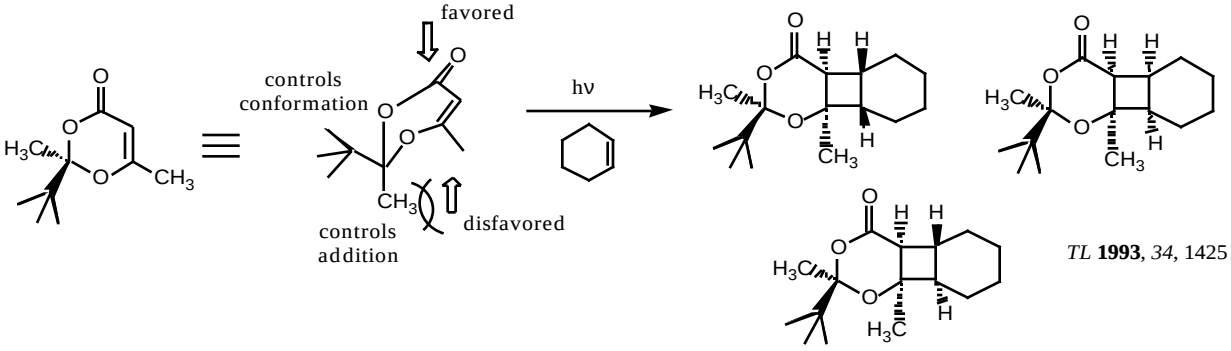
JACS **1982**
104, 5070

- DeMayo Reaction



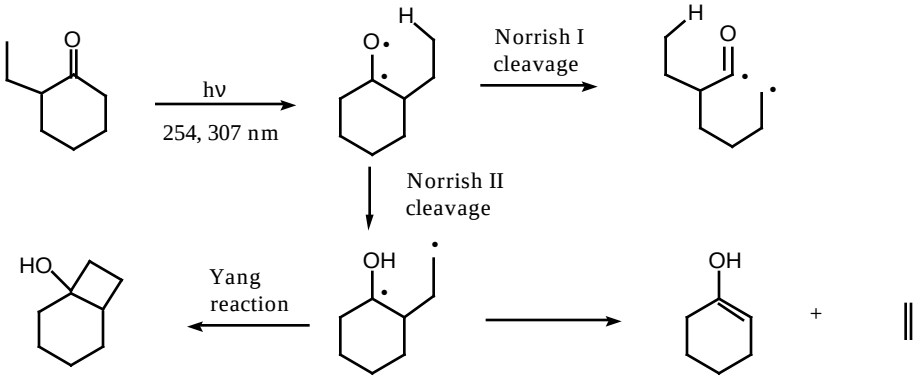
JACS **1986**,
108 , 6425





TL **1993**, *34*, 1425

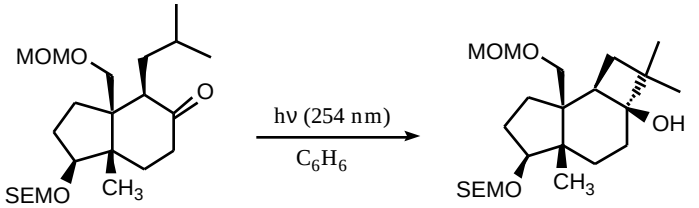
- Photochemistry of Ketones (Norrish Type I and II reactions)



- filtering photchemical reaction to prevent Norrish reactions

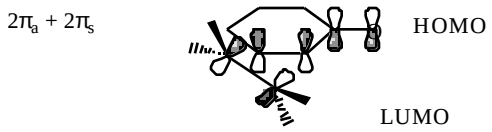
quartz	180 nm
Vycor	200 nm
Pyrex	280 nm
Uranium glass	320 nm

- Yang Reaction

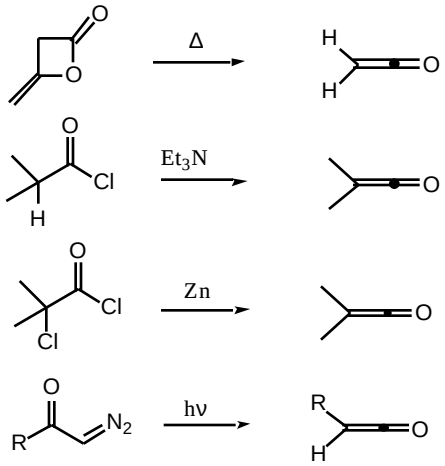


JACS **1987**, *109* , 3017

- thermal cycloadditons ($2\pi_a + 2\pi_s$)
  - symmetry requirements

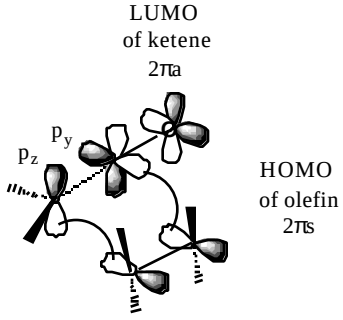


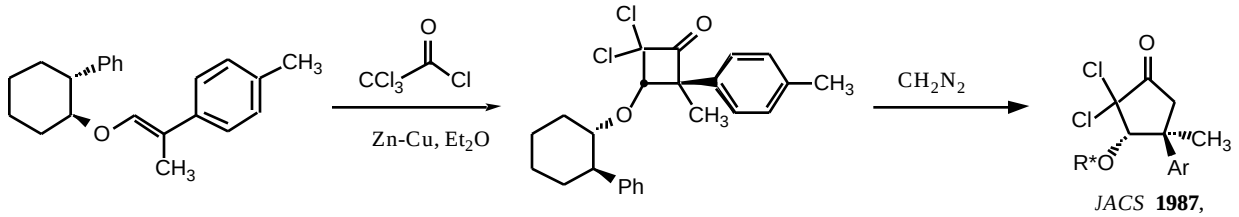
  - ketenes



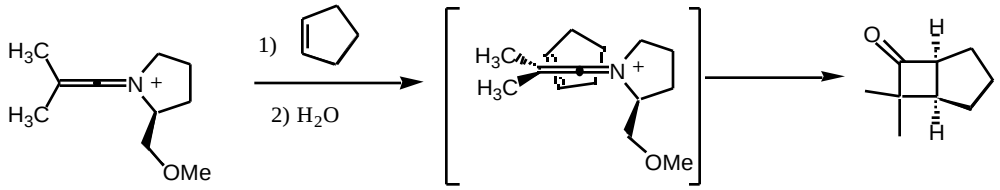
- thermal cyclization of ketene with olefins

Tetrahedron **1986**, *42*, 2587; **1981**, *37*, 2949; *Organic Reactions* **1994**, *45*, 159.



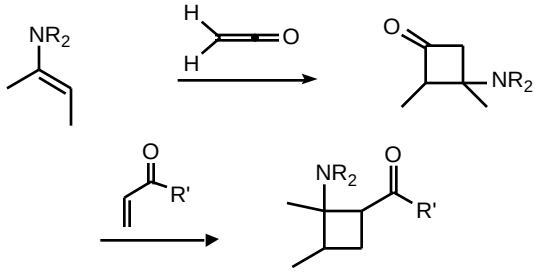


JACS **1987**, *109* , 4753

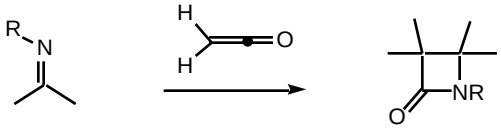


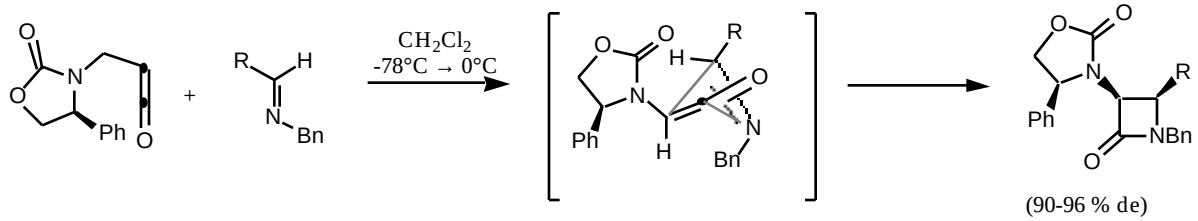
JACS **1982**, *104*, 2920

-reaction of ketene with enamines



- reaction of ketene with imines to give β-lactams (Staudinger Reaction)

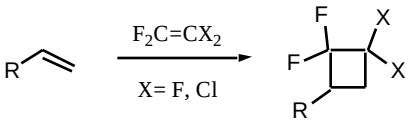




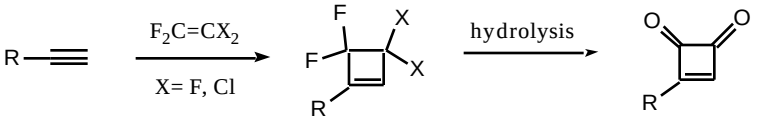
(90-96 % de)

- reaction of difluorodihaloethylene with olefins

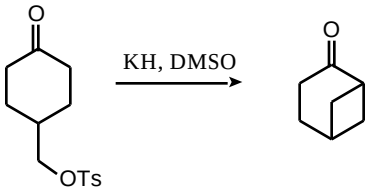
Organic Reactions **1962**, *12*, 1



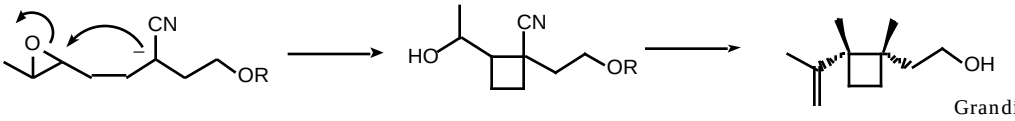
- reaction of difluorodihaloethylene with acetylenes- biradical mechanism



- S_N2 Reaction



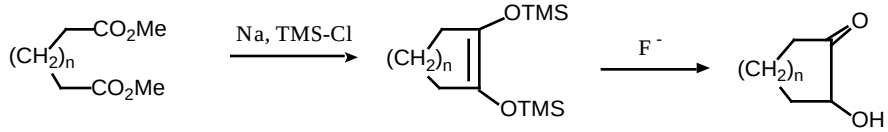
JACS **1980**, *102* , 1404

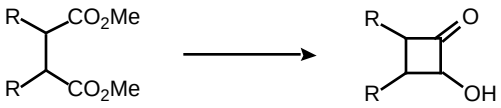


JACS **1974**, 96, 5268, 5272

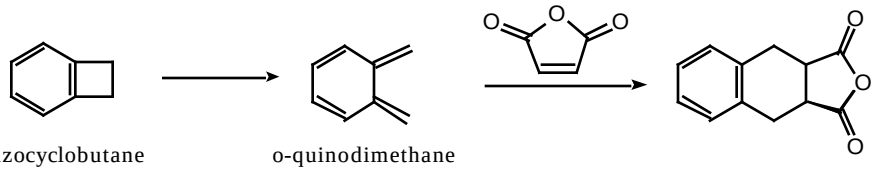
Grandisol

- acyloin reaction *Organic Reactions* **1976**, *23*, 259



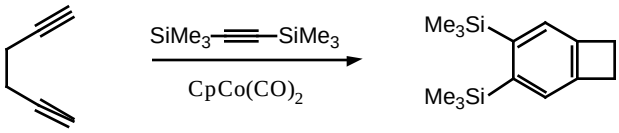


- benzocyclobutanes *ACIEE* **1984**, *23*, 539; *Synthesis* **1978**, 793

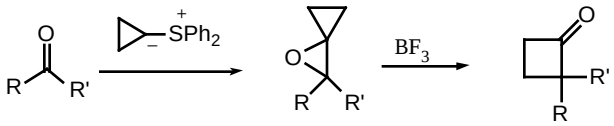


benzocyclobutane o-quinodimethane

- cyclotrimerization of 1,5-diyenes with an acetylenes

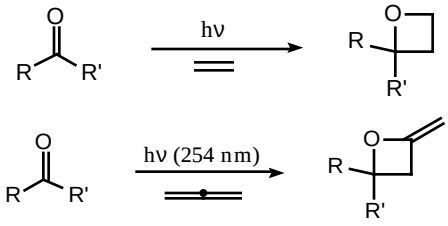


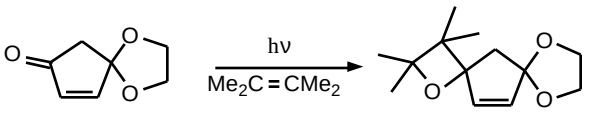
- sulfur ylides



Oxatanes *Organic Photochemistry* **1981**, *5*, 1

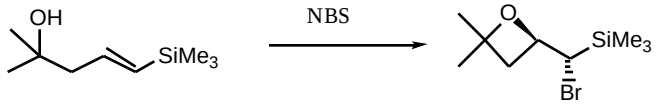
- [2+2] cycloaddition (Paterno-Buchi Reaction)



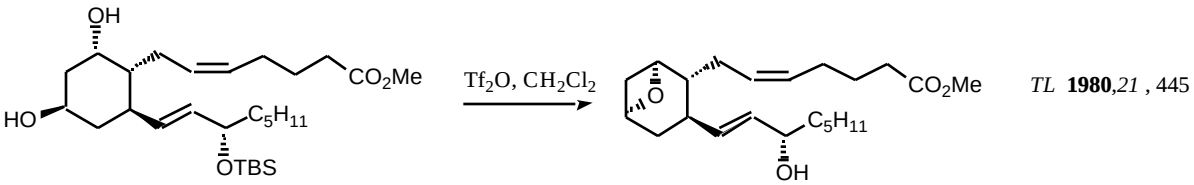


TL **1975** 1001

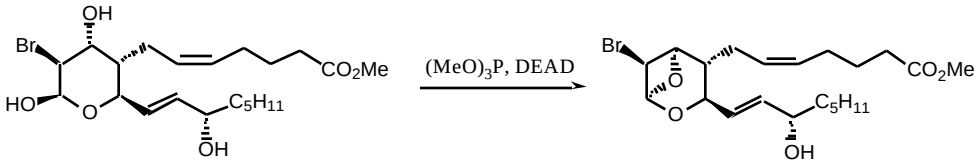
- S_N2 reaction



JCSCC **1979**, 421

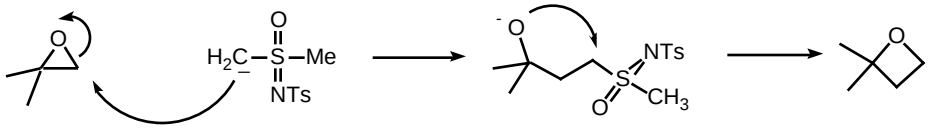


TL **1980**,*21* , 445



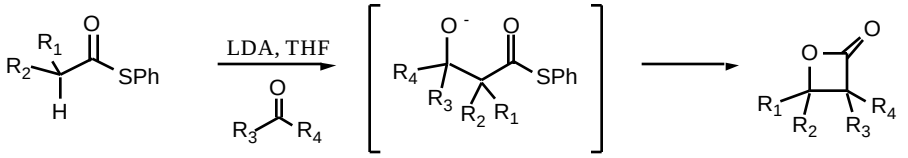
JACS **1984**, *107* , 6372

- sulfur ylides

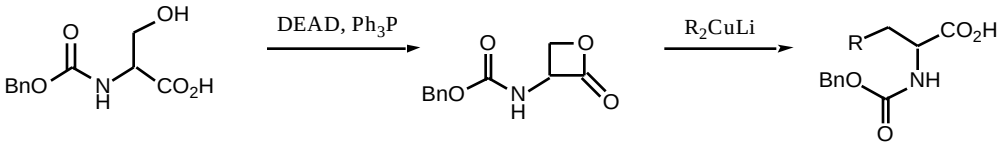


JACS **1979**, *101* , 6135

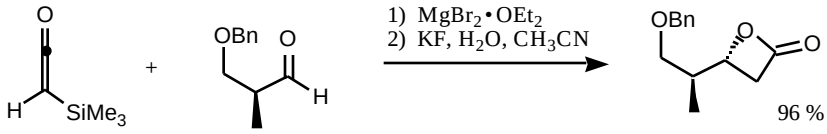
β-*Lactones*



JOC **1991**, *56* , 1176



JACS **1987**, *109* , 4649



TL **1995**, *36*, 4159

96 % de