

**B.Sc. Semester-VI  
Group-A / DSE-4  
Organic Synthesis**

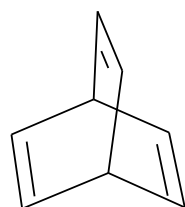
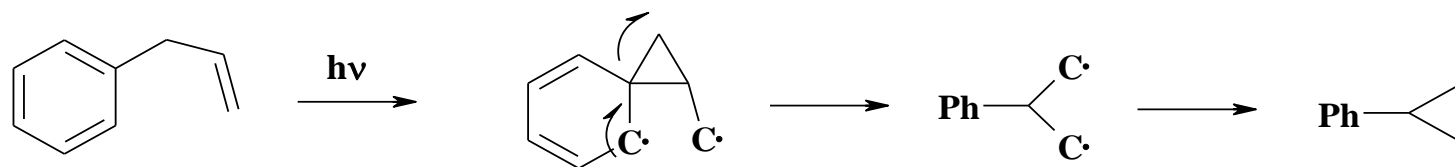
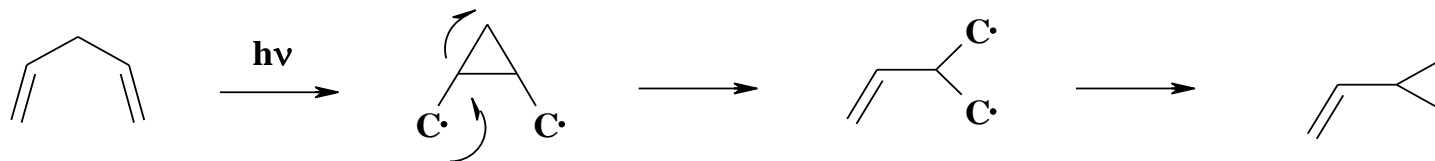


**III. Photochemistry  
9. The Di- $\pi$ -Methane Rearrangement**

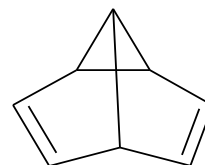


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# The Di- $\pi$ Methane Rearrangement

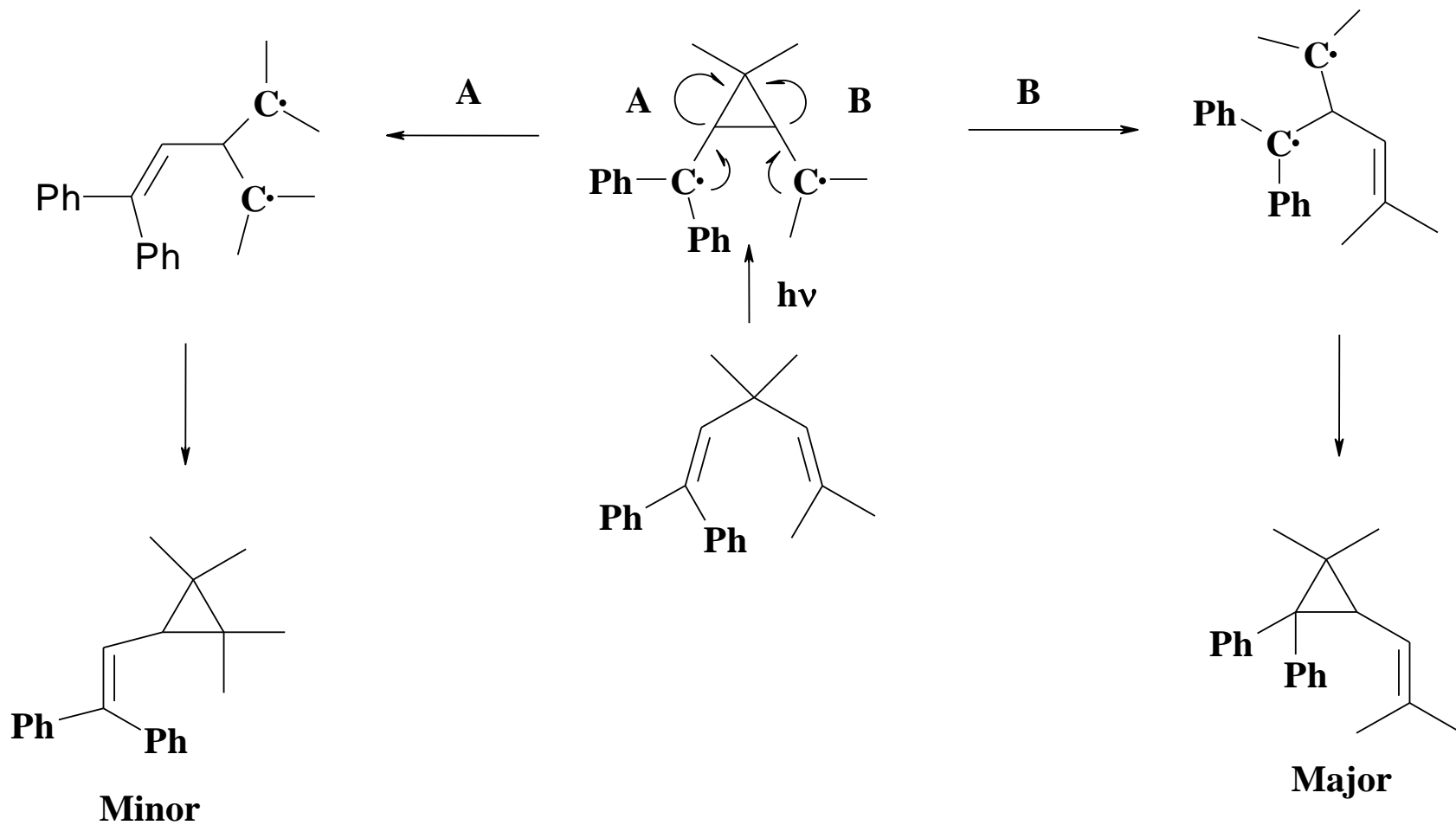


**Barrelene**



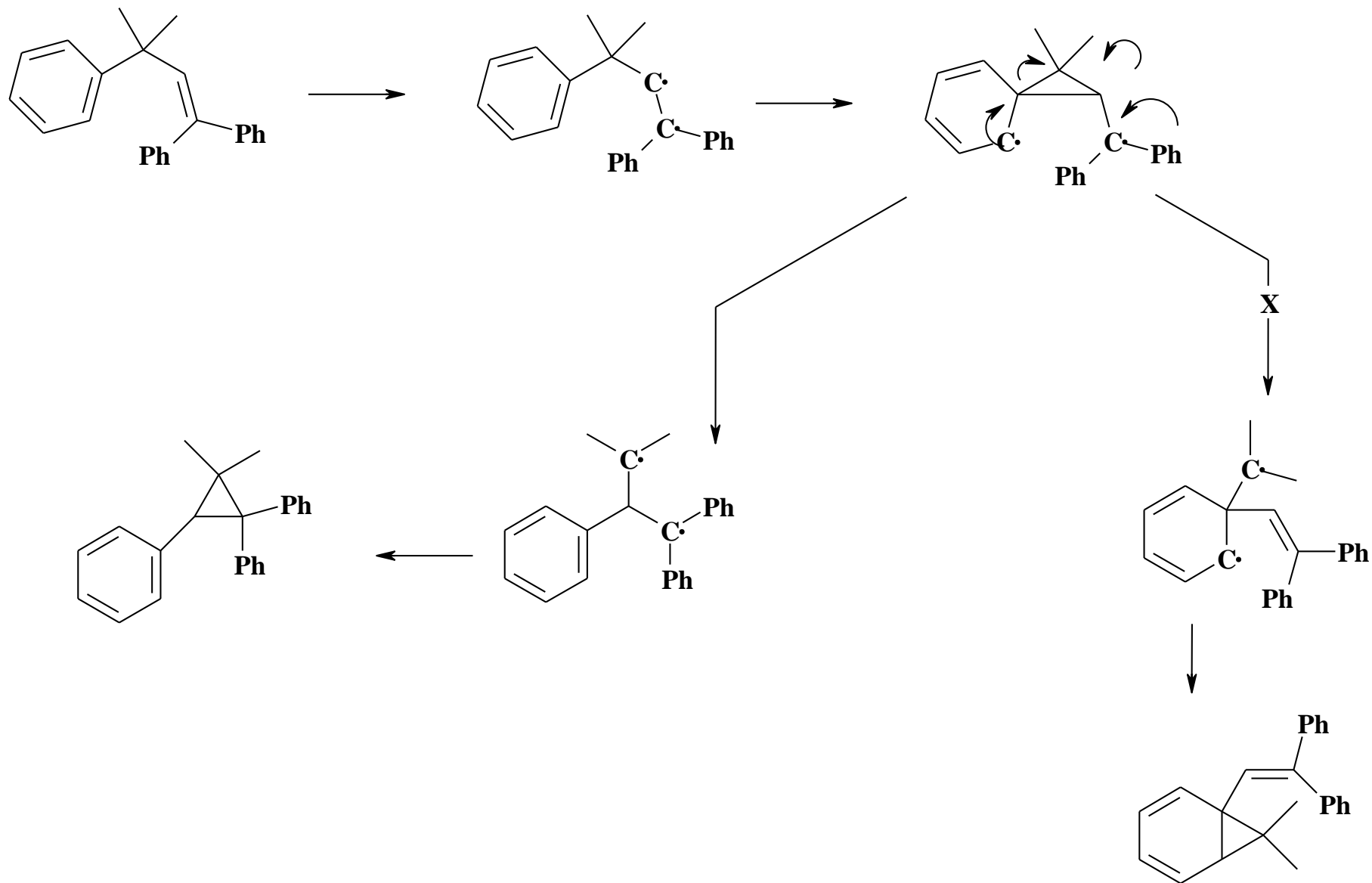
**Semibullvalene**

# Reaction regioselectivity

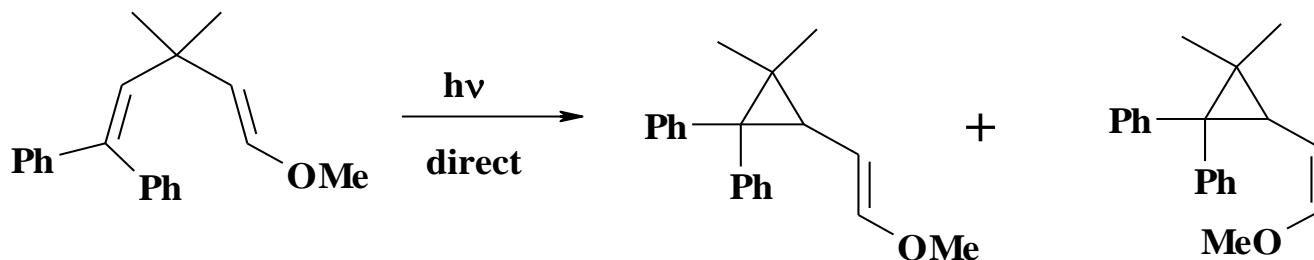
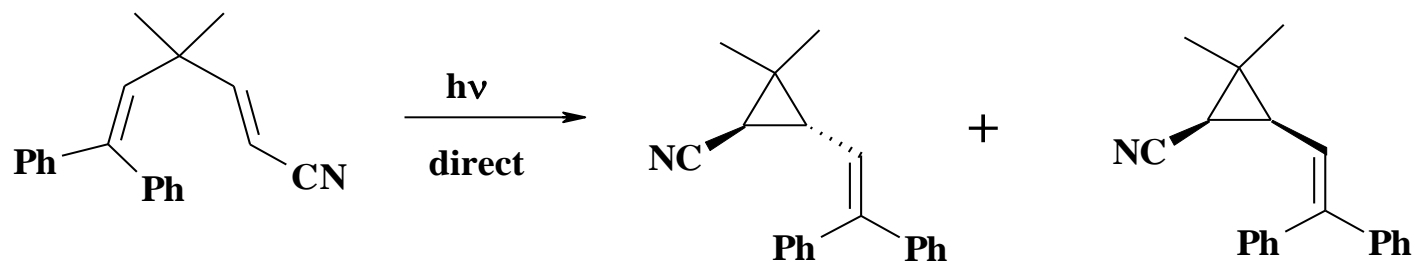


# Stability of benzyhydryl biradical

# More available electron density for ring opening



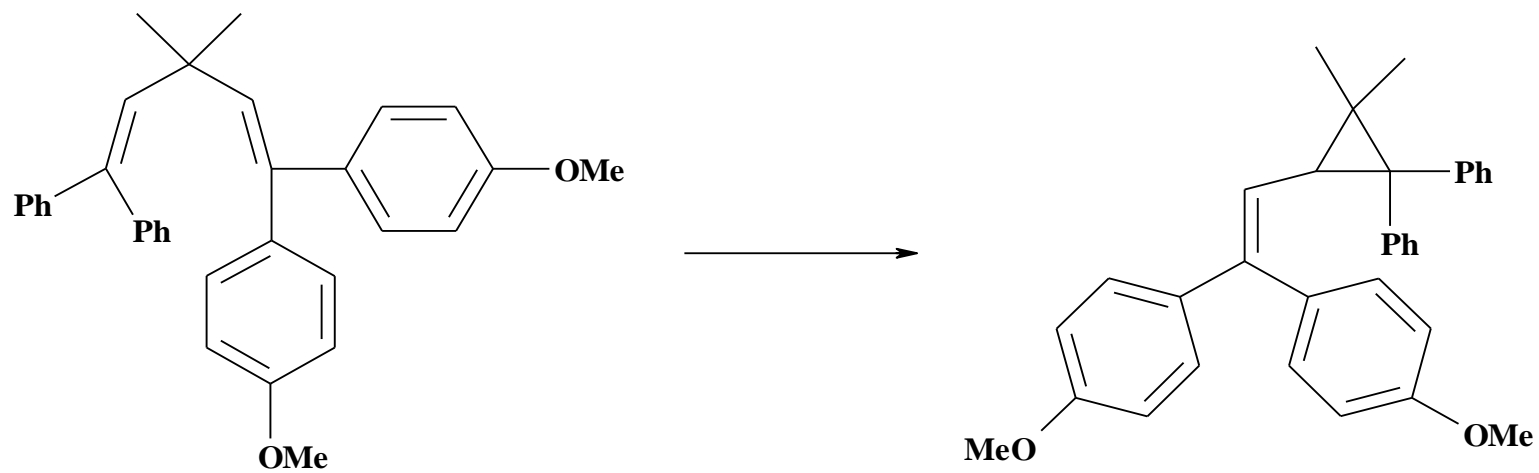
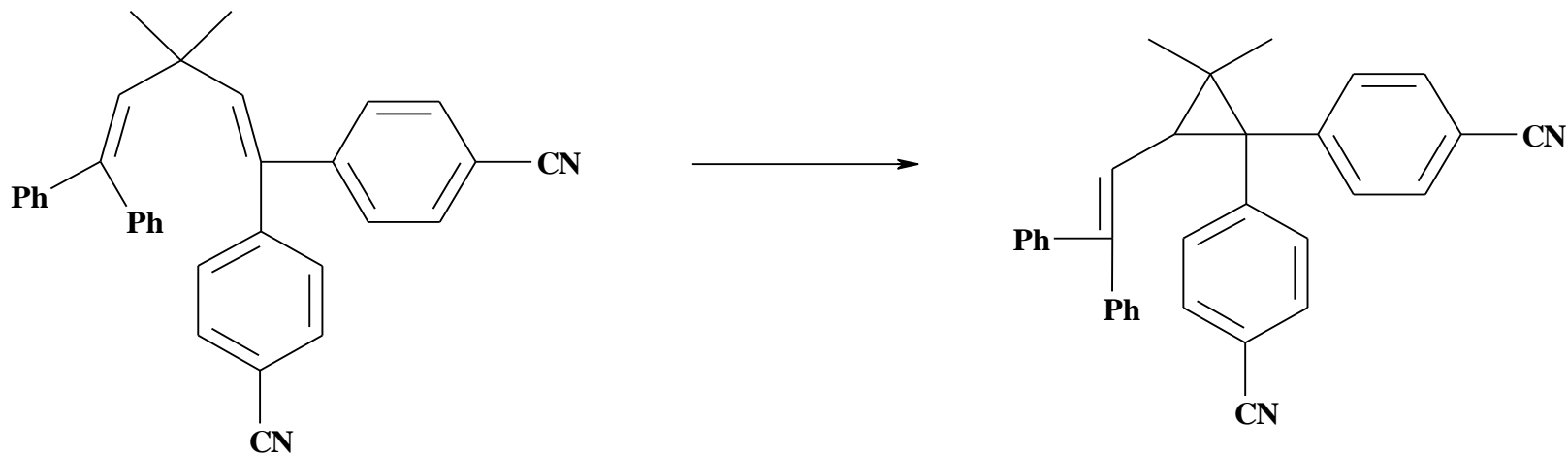
# Electronic factor on regiochemical outcome



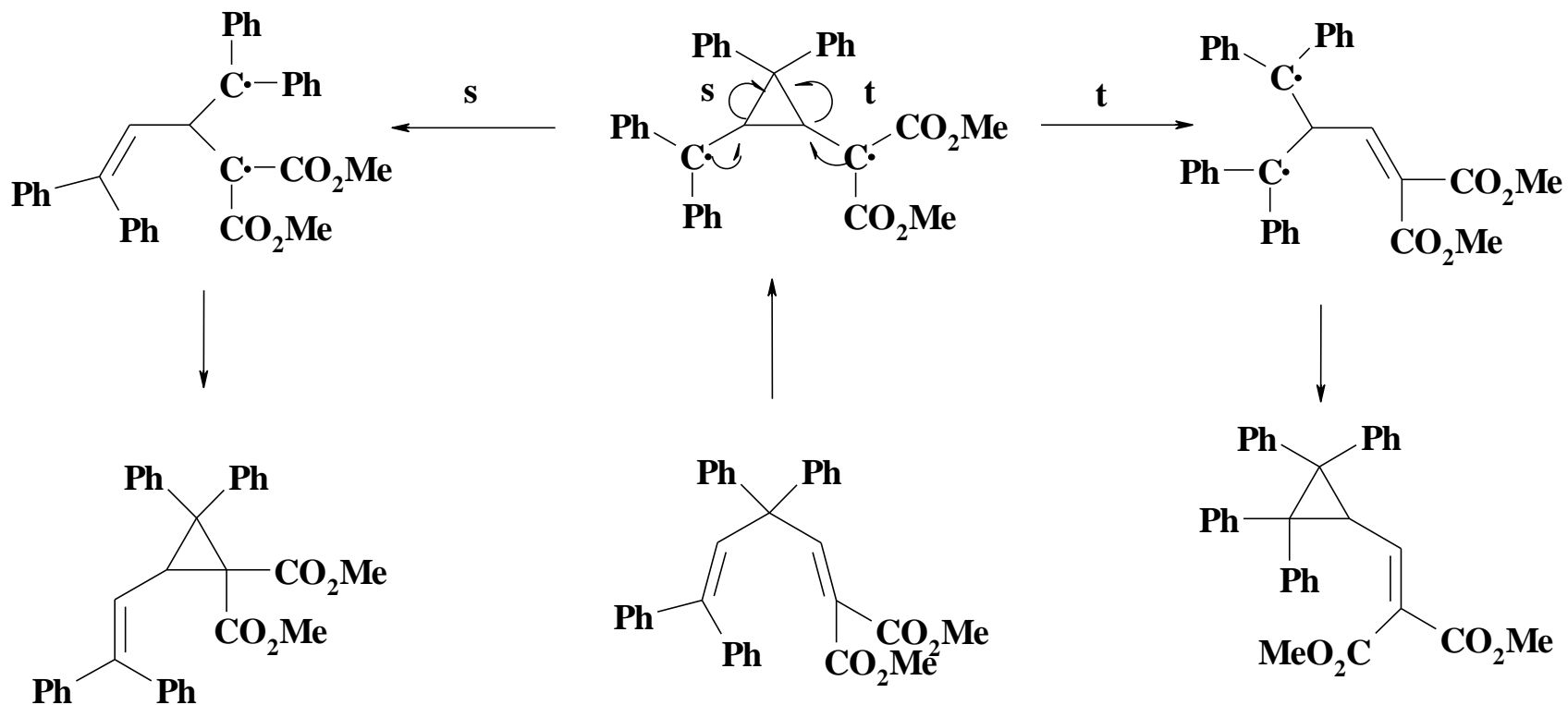
# there is a strong tendency for electron donors to appear on the residual  $\pi$ - bond of the photoproduct

# and for electron withdrawing groups to be found on the product three membered ring

# Reaction regioselectivity

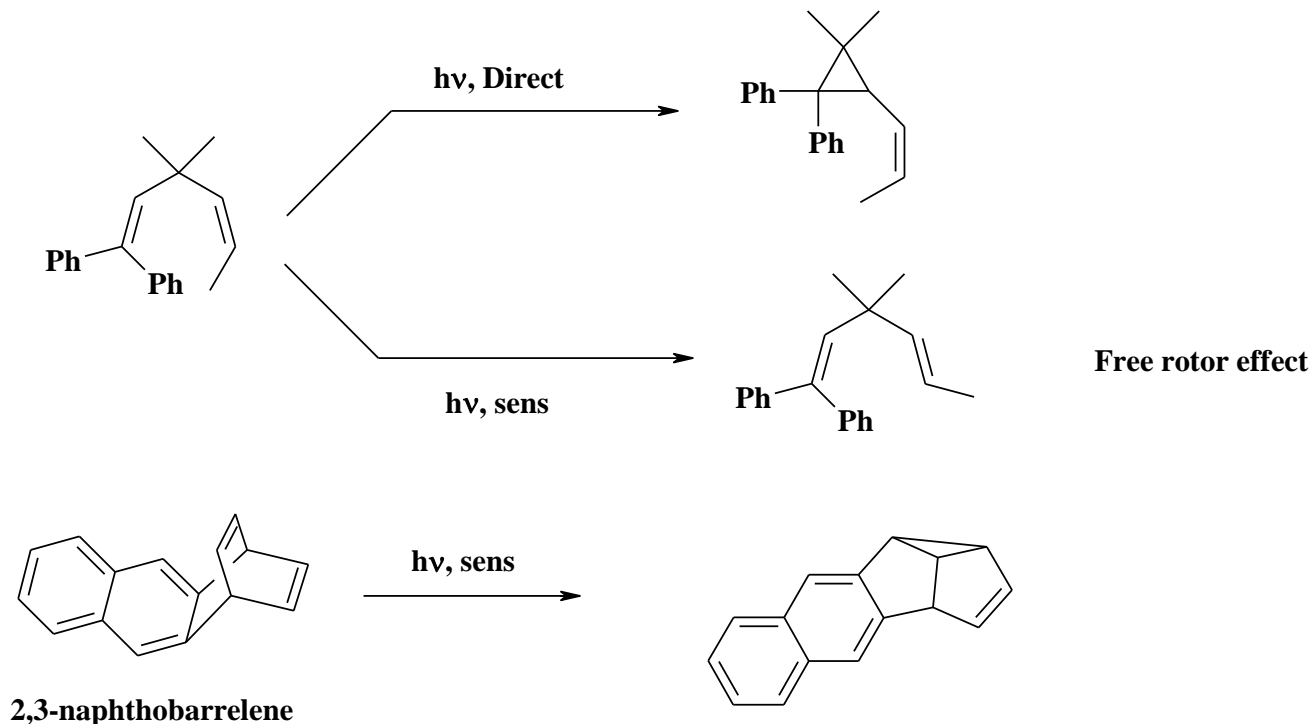


# Multiplicity control of regioselectivity



Large K vs. small K control of excited state selectivity

## Effect of excited state multiplicity on reaction outcome

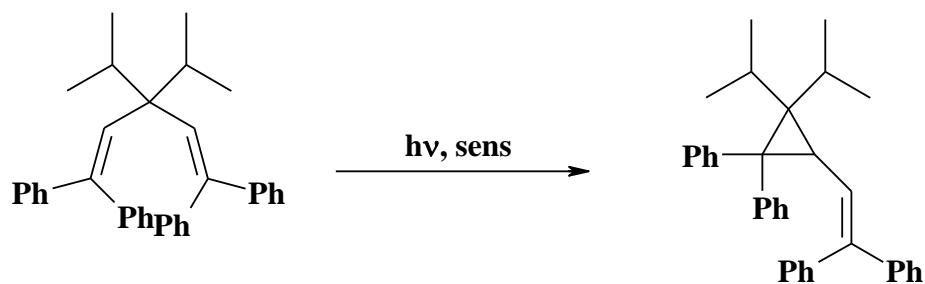


# di- $\pi$ -methane triplets which have double bonds not incorporated in a ring structure or not inhibited from free rotation in some other manner are commonly unreactive.

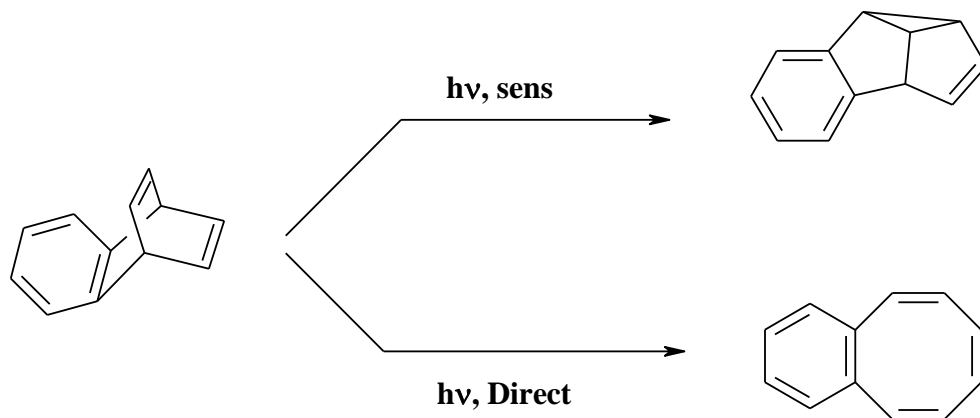
# In contrast cyclic di-enes tend to be perfectly reactive as triplets, and this can be ascribed to their inability to undergo free rotation in the excited state.

# If rate of radiationless conversion of the triplet reactant is slower than the rate of reaction, despite in the presence of free rotor group, triplet reactivity in an acyclic system was observed. Generally in this case free rotation is inhibited by effects such as steric hindrance, so that the triplet may be reactive.

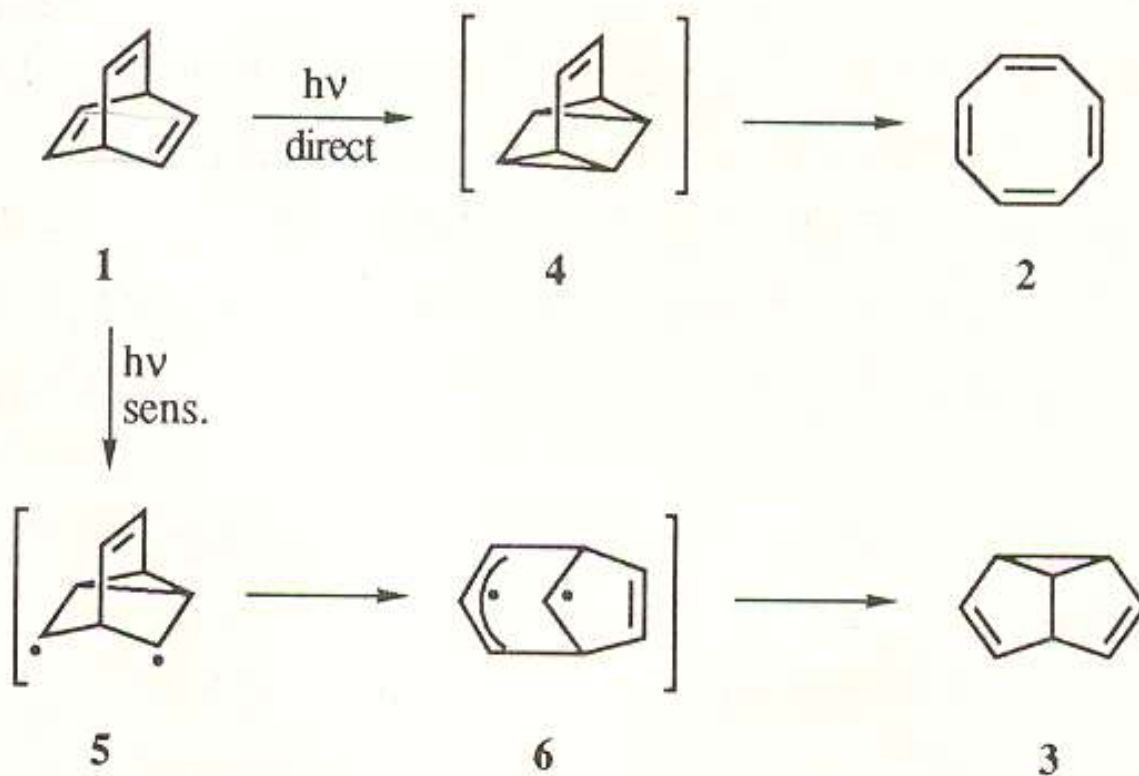


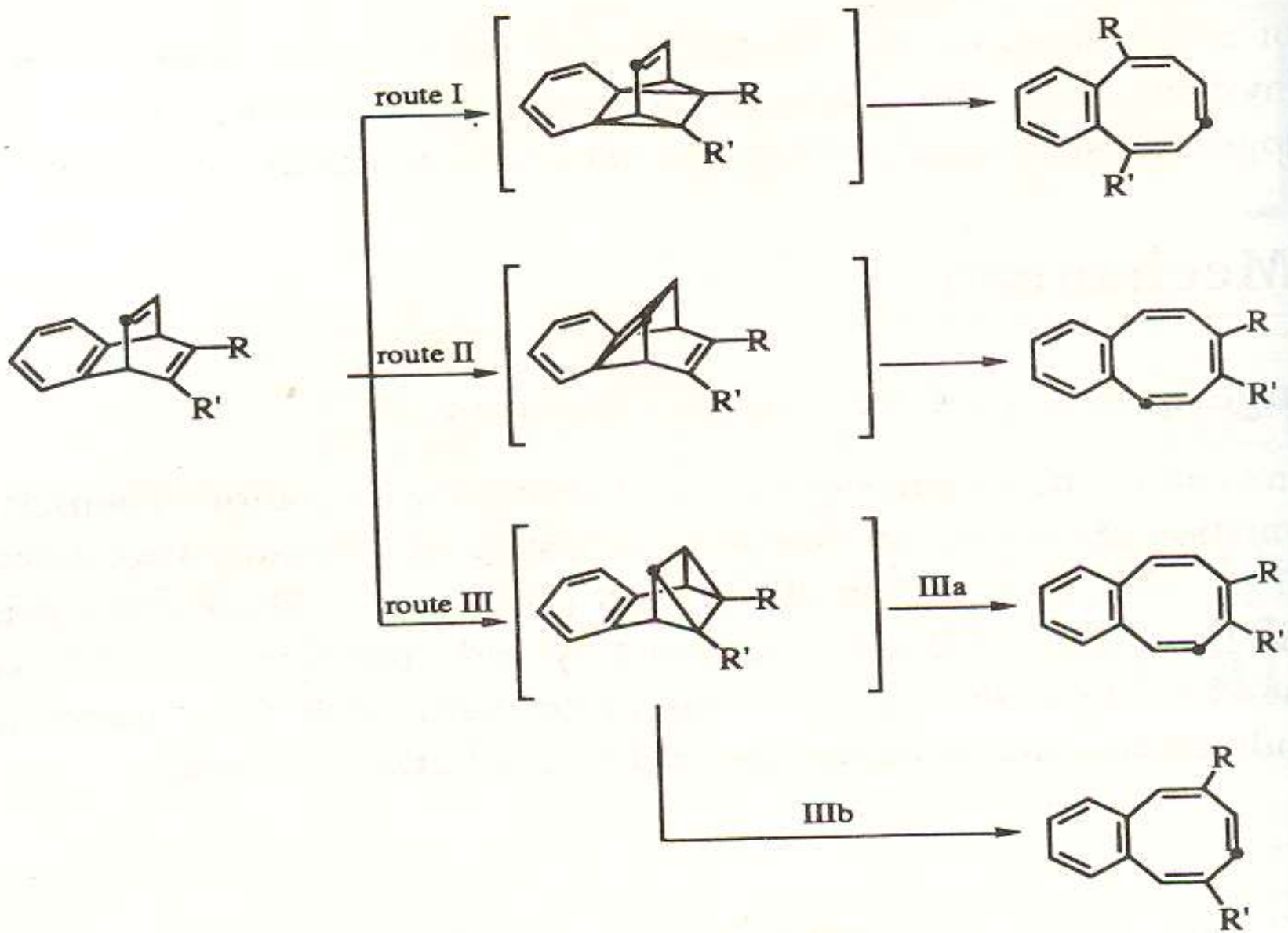


# The original generalization is that cyclic molecules are more likely to react successfully from the triplet excited state via sensitization while acyclic molecule tend to perform better as singlets (obviously in the case of triplet reactivity absence or presence of free rotor is important).

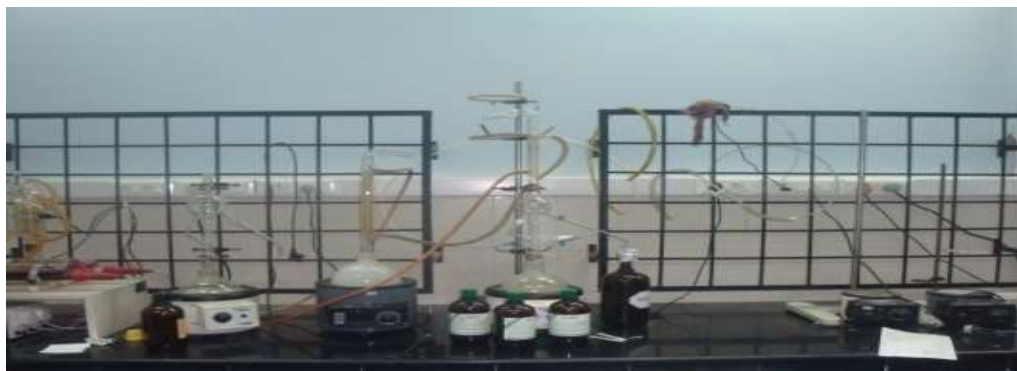


# For many cyclic molecules, direct irradiation with formation of the singlet excited state does not lead to a successful di-p-methane rearrangement. This behaviour arises not because the singlet excited state is incapable of a di-p-methane rearrangement but rather because many cyclic systems have potentially available facile alternative pericyclic process which competes all too successfully.





# Thank You



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