

M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry



II. Pericyclic Reactions
9. [2+2] Cycloaddition Reaction



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II Pericyclic Reactions 20 Hrs

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1, 3, 5-hexatriene, allyl system, Classification of pericyclic reactions. FMO approach, Woodward-Hoffman correlation diagram method and PMO approach for pericyclic reaction under thermal and photochemical conditions.

Electrocyclic reactions: Conrotatory and disrotatory motion, $4n$ and $(4n+2)$ systems, Cycloaddition reaction: $[2+2]$ and $[4+2]$ cycloaddition reaction, Cycloaddition of ketones, Secondary effects in $[4+2]$ cycloaddition. Stereochemical effects on rate of cycloaddition reaction, Diels-Alder reaction, 1,3-dipolar cycloaddition, Chelotropic reaction, The Nazarov reaction.

Sigmatropic rearrangement: Suprafacial and antarafacial shift involving H and carbon-moieties, Peripatetic cyclopropane bridge, Retention and inversion of configuration, $[3,3]$ -, $[1,5]$ -, $[2,3]$ -, $[4,5]$ -, $[5,5]$ -, and $[9,9]$ -Sigmatropic rearrangements, Claisen rearrangements (including Aza-Claisen, Ireland-Claisen), Cope rearrangements (including Oxy-Cope, Aza-Cope), Sommelet-Hauser rearrangements, Group transfer reaction, Ene reaction, Mislow - Evans rearrangement, Walk rearrangement.

Coverage:

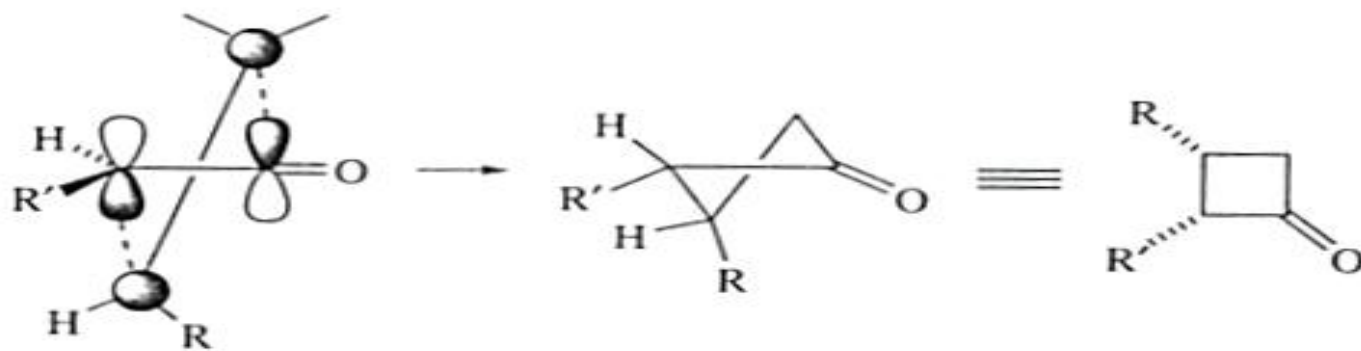
1. $[2+2]$ Cycloaddition of Ketenes
2. $[2+2]$ Cycloaddition of Carbonyl Compounds
3. $[2+2]$ Cycloaddition of Alkenes/Alkynes

[2+2] Cycloaddition of Ketenes

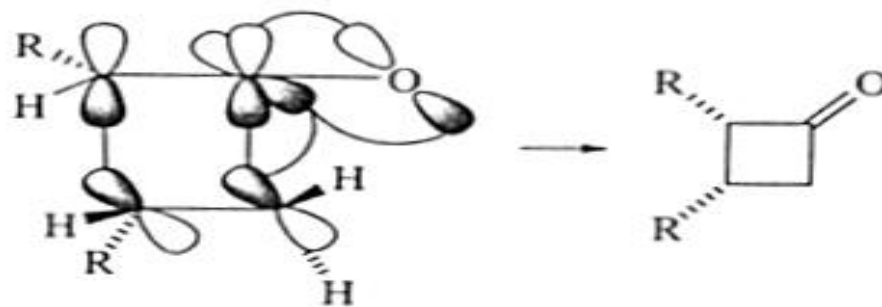
(HOMO-LUMO Approach)



(a)

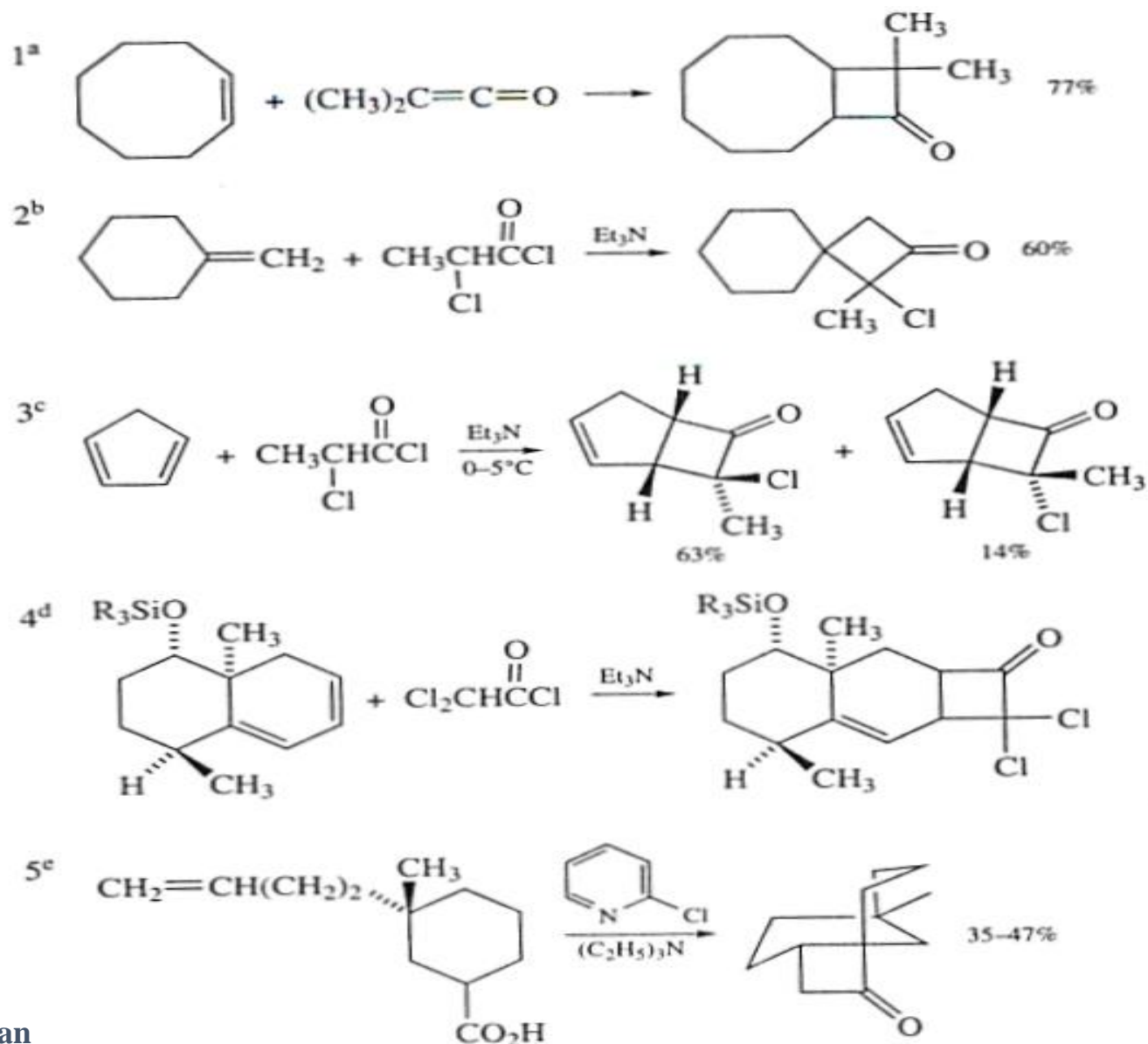


(b)

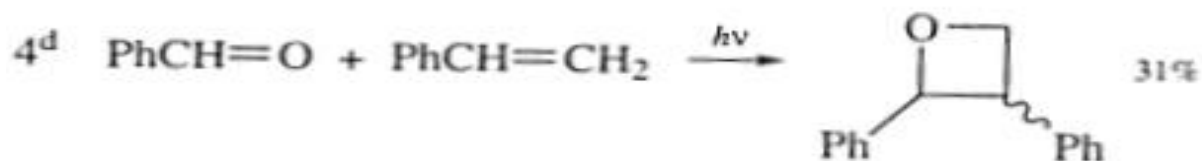
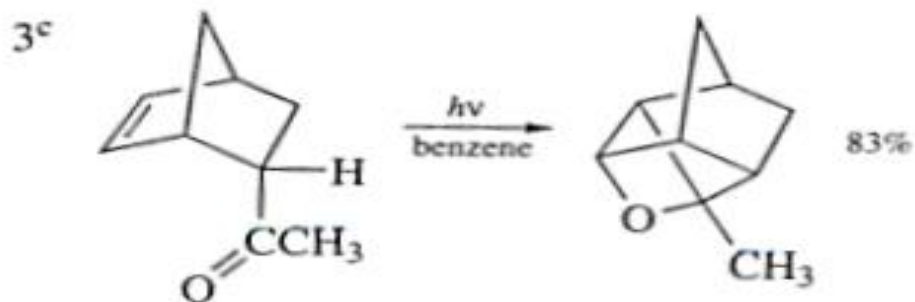
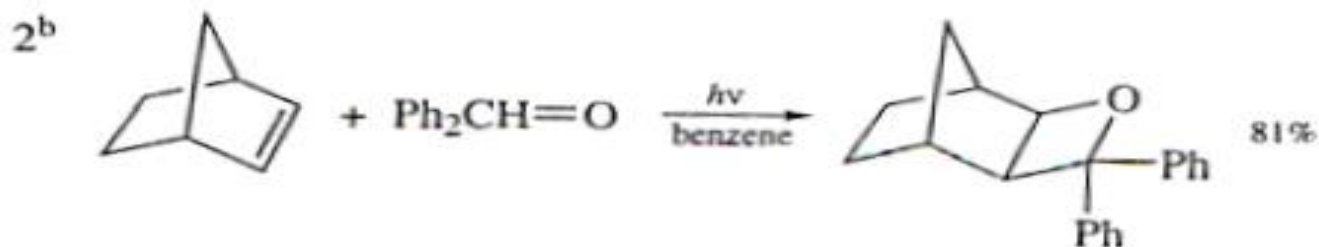
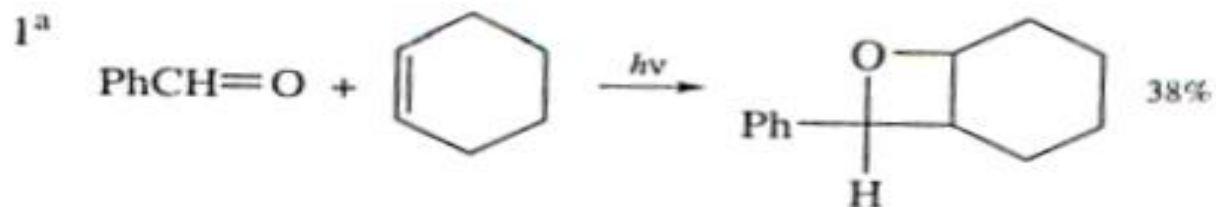


(c)

[2+2] Cycloaddition of Ketenes



[2+2] Cycloaddition of Carbonyl Compounds



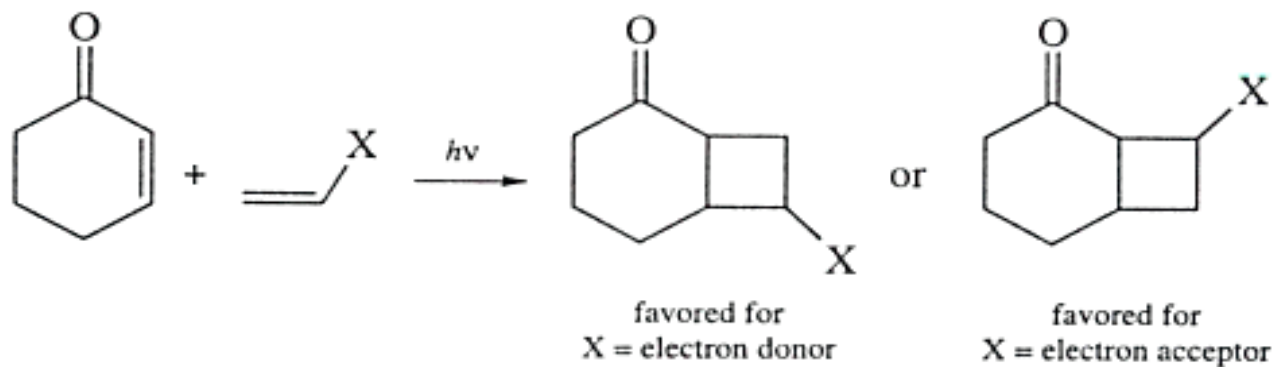
[2+2] Cycloaddition of Alkenes to Form Cyclobutane



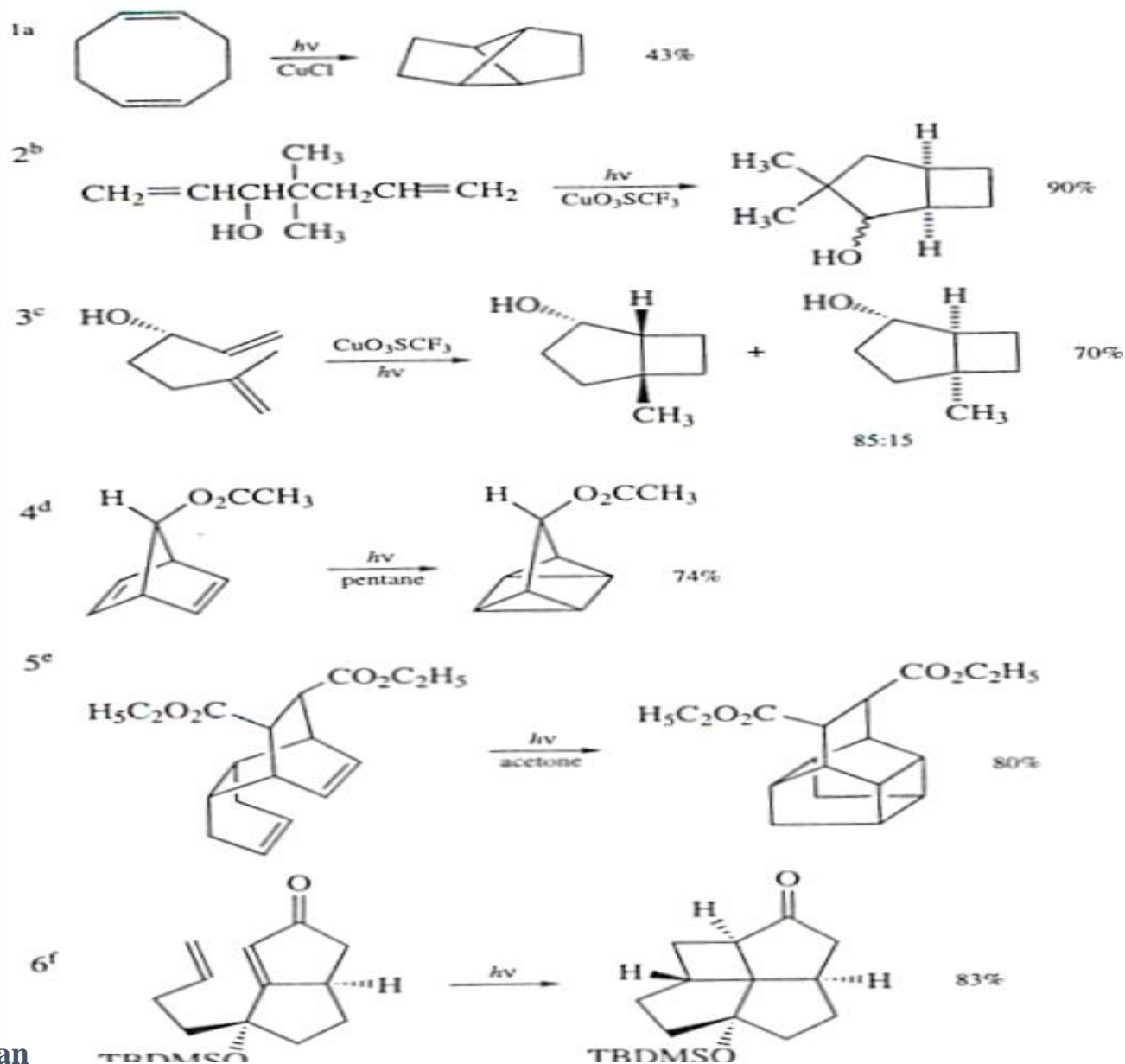
Electron releasing groups = Electron withdrawing groups

Electron releasing groups = -OR, NR_2

Electron withdrawing groups = $-\text{NO}_2$, $-\text{CN}$

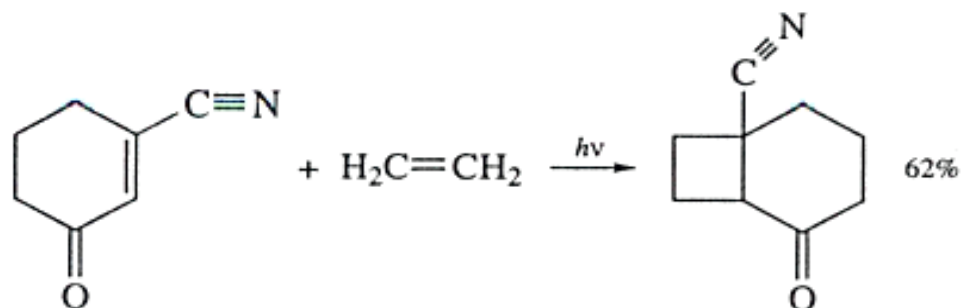


[2+2] Cycloaddition of Alkenes

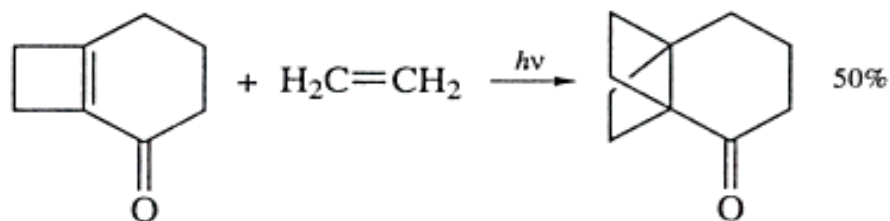


[2+2] Cycloaddition of Alkenes/Alkynes

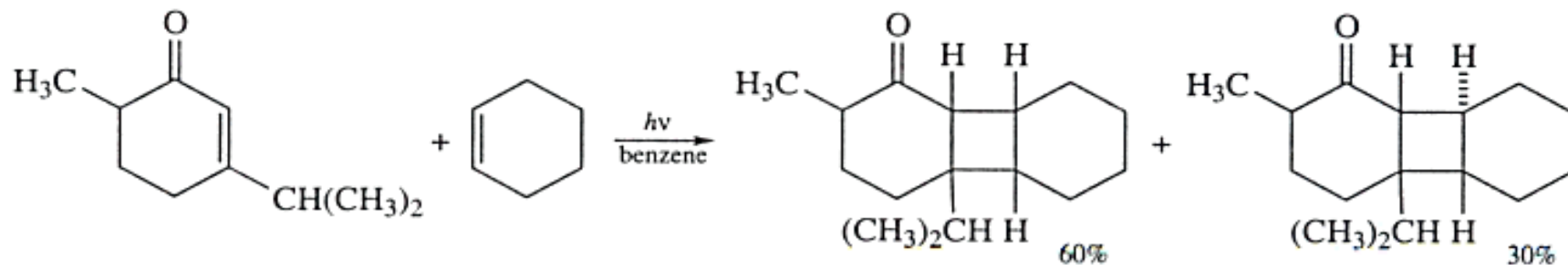
1^a



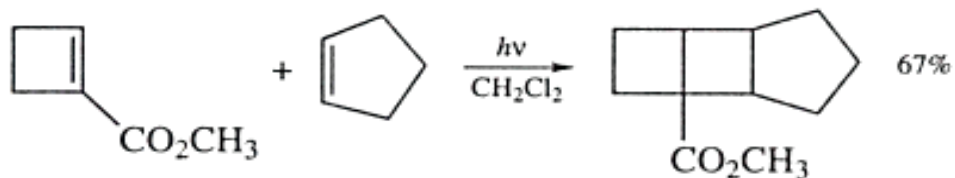
2^b

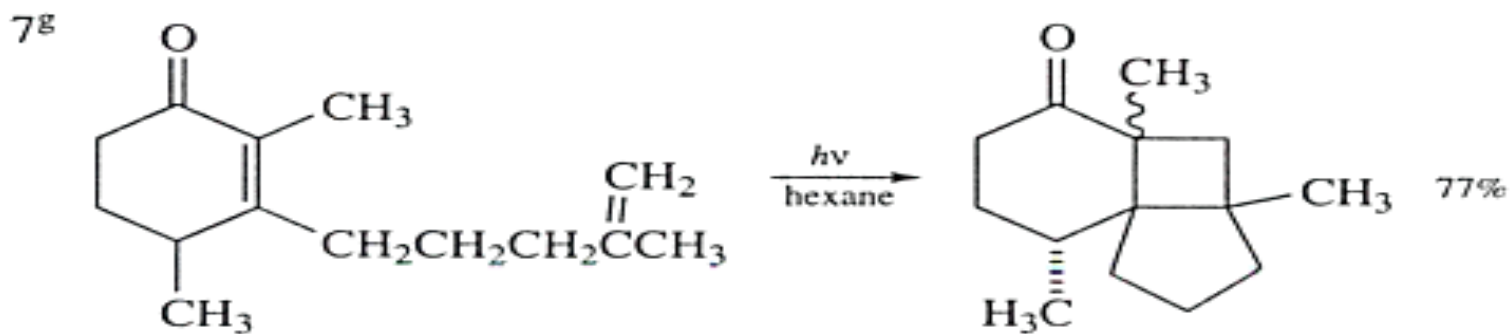
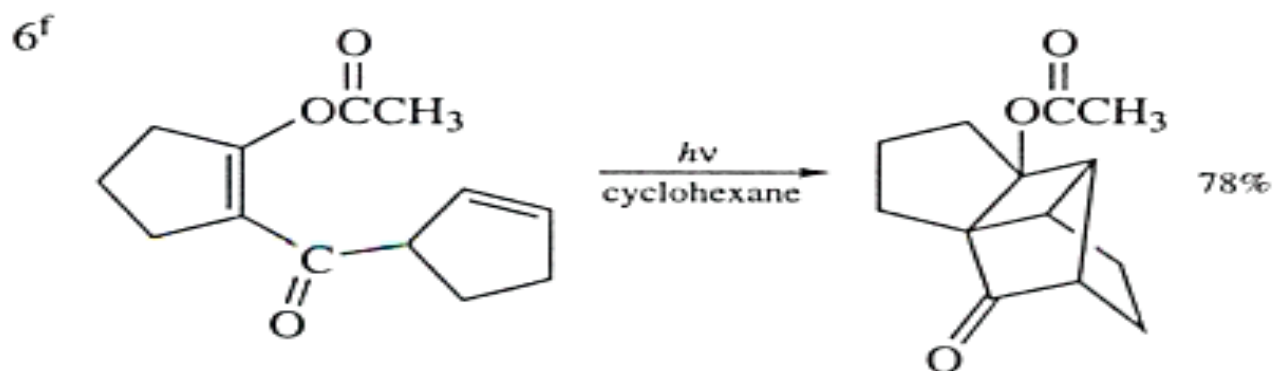
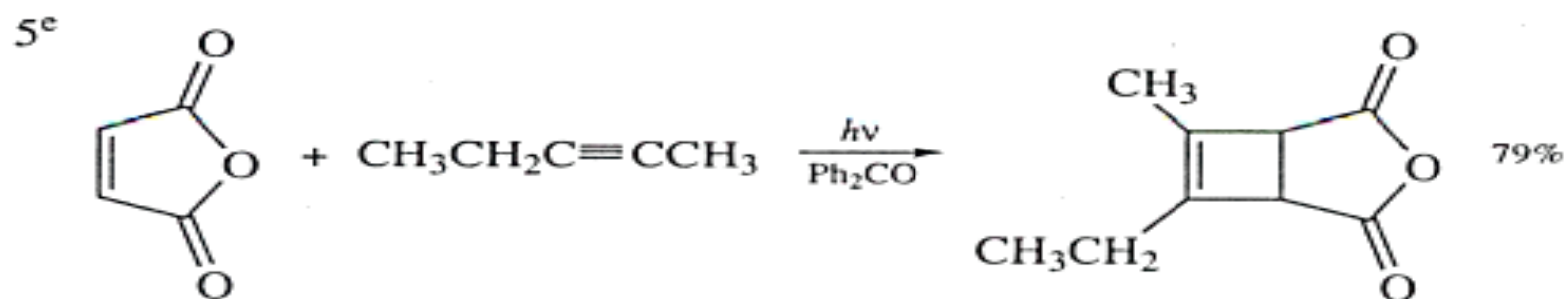


3^c

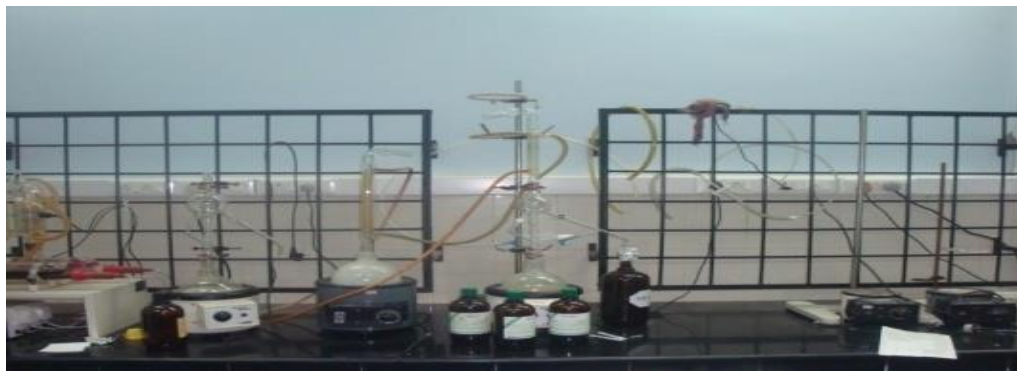


4^d





Thank You



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