③ Rearrangements :-

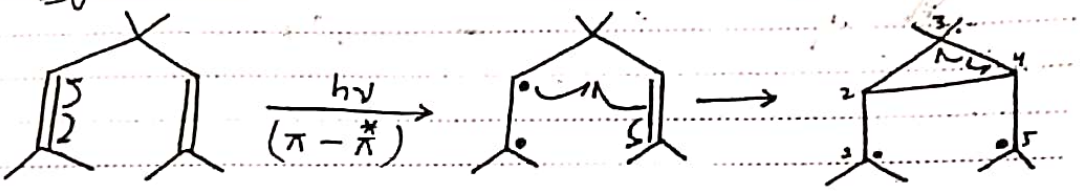
These includes :-

Rearrangement of : 1,4-Pentadiene ( )

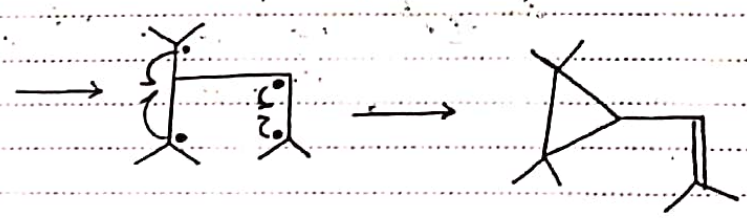
Di-π-methane rearrangement :-

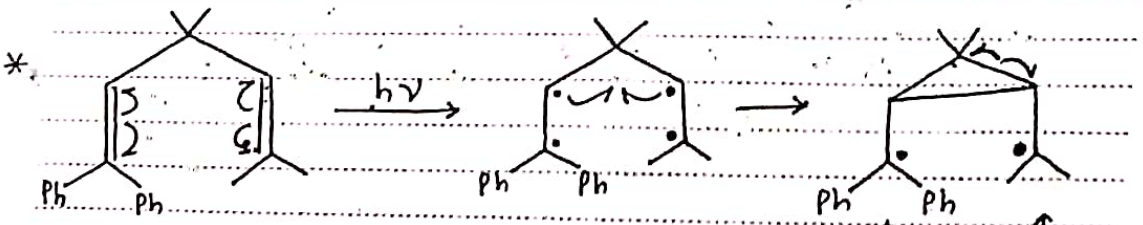
The most common photochemical reactions of 1,4-pentadiene is the di-π-methane rearrangement in which the substrate is converted into a vinyl cyclopropane ( ).

E.g.



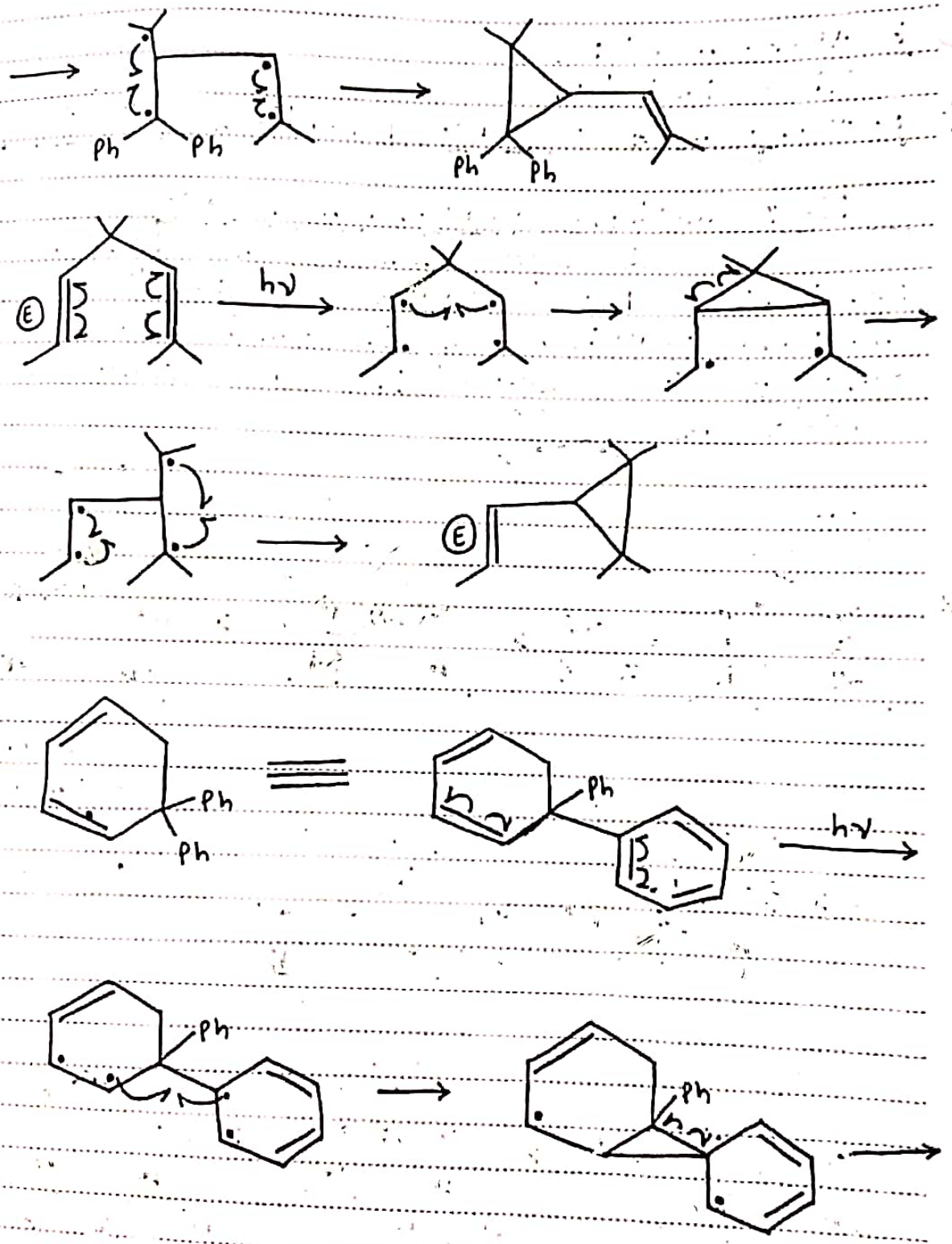
1,5-Diradical intermediate.





More stable radical (gives △)

Less stable radical (gives =)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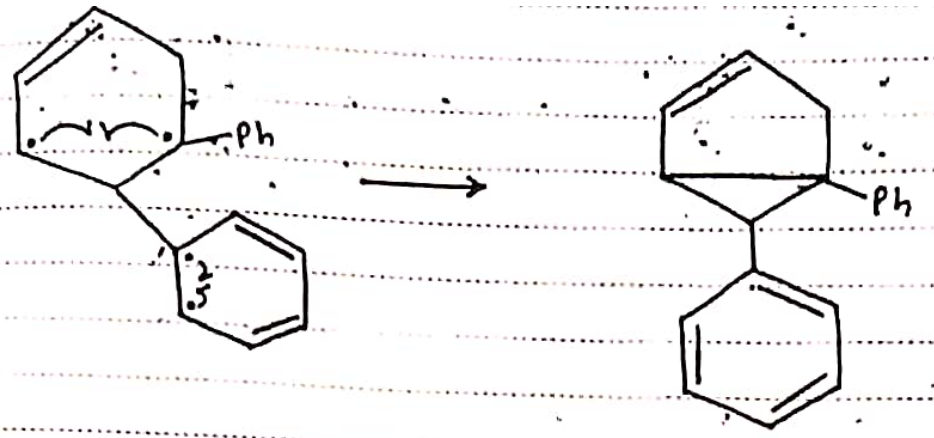

Oxo-Di-π methane rearrangement :-

This rearrangement occurs in such type of compounds in which the carbonyl carbon and double bond are separated by one saturated carbon. In final step, the carbonyl group regenerates.

E.g.

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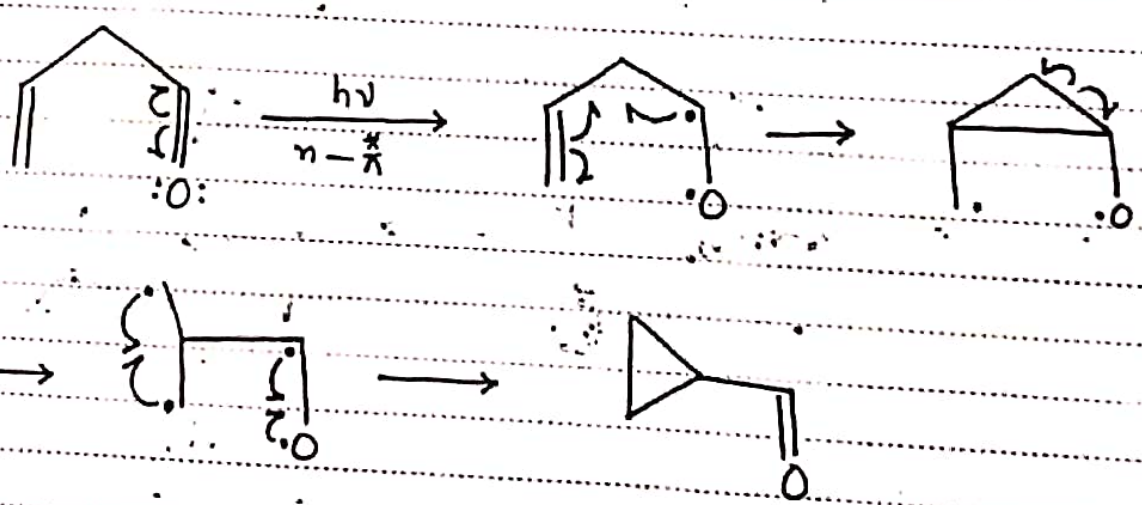

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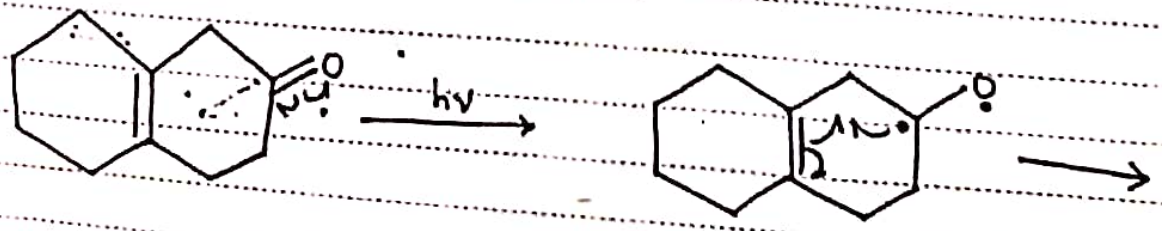

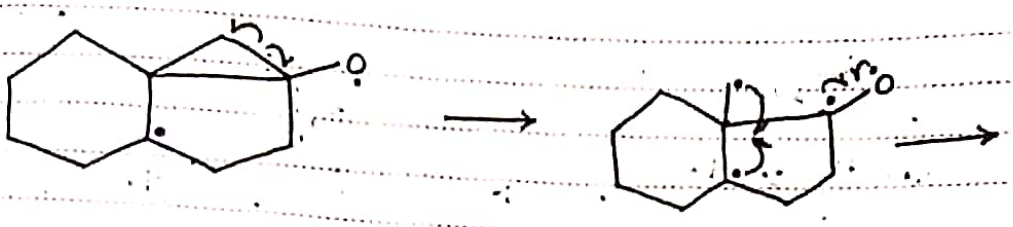

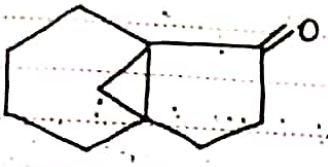

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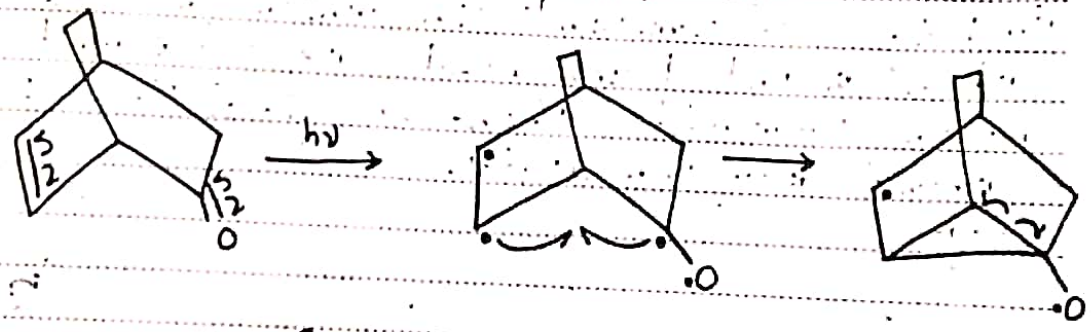

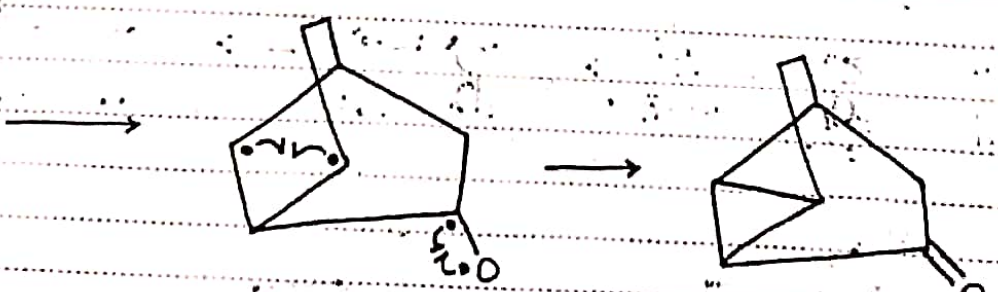

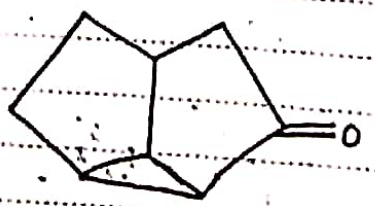

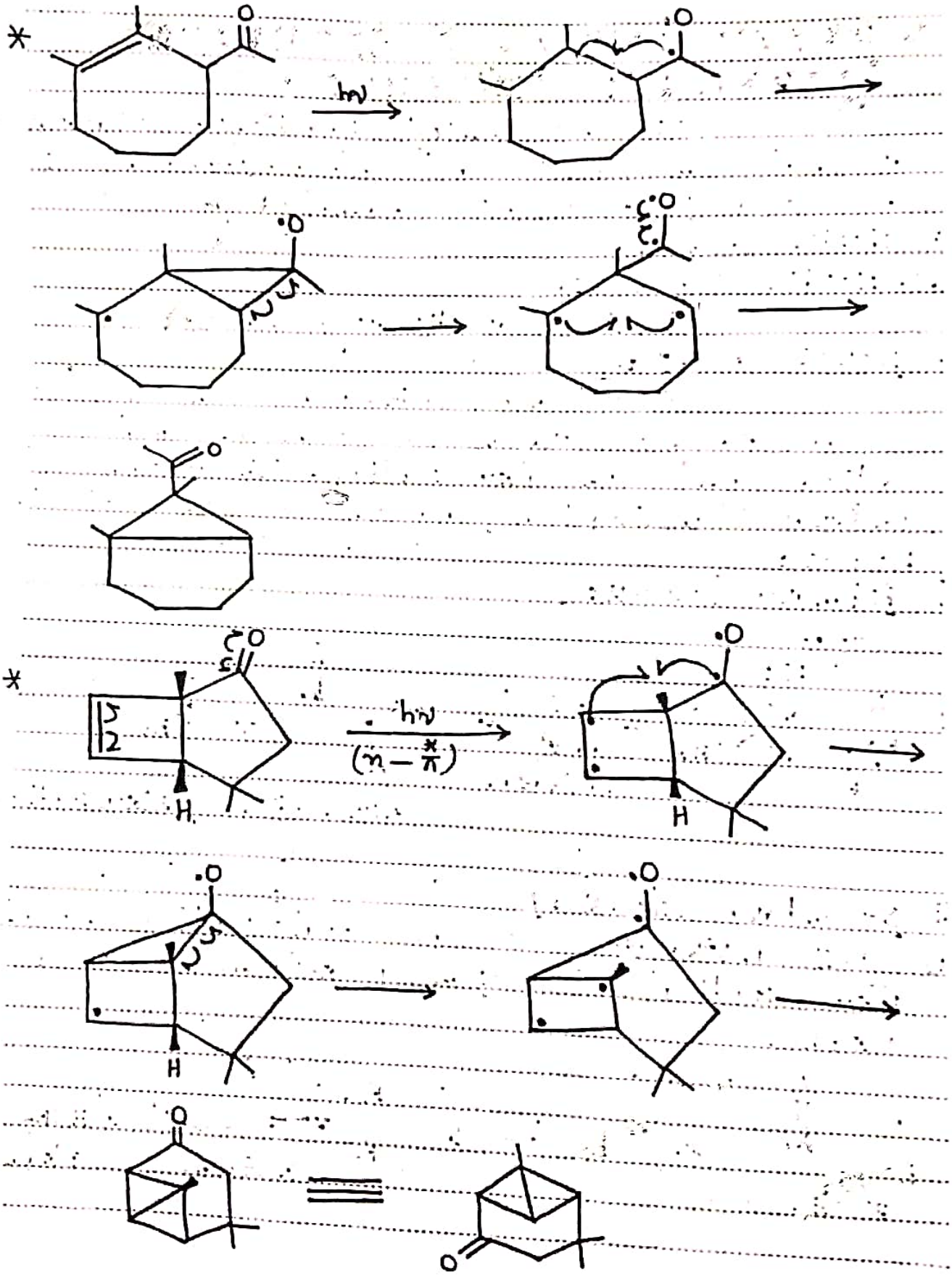
hν
hν
(π − π*)