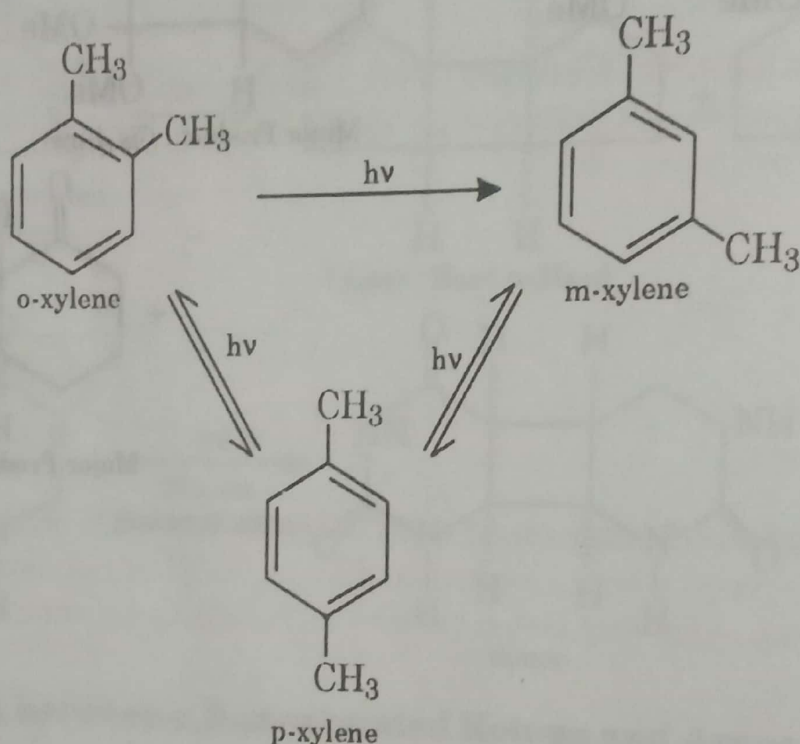


**ISOMERISATIONS**

On irradiation, benzene and its derivatives undergo isomerisation and form new product by reorganization of bond.

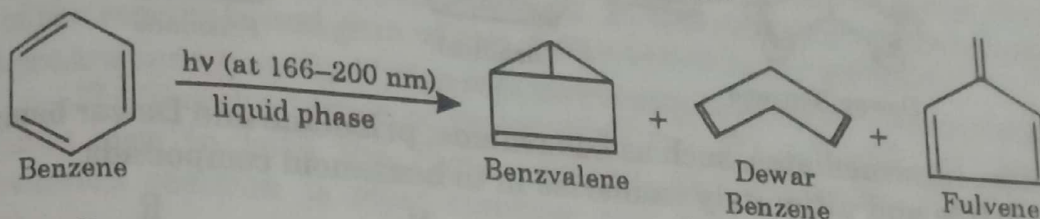
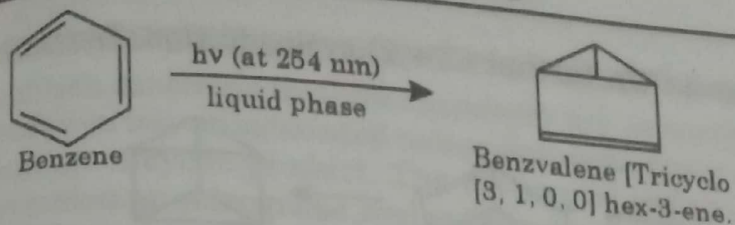
Monocyclic aromatic compounds show remarkable photochemical rearrangements. In presence of light radiations, ortho-xylene gives a mixture of o, m, and p-xylenes.



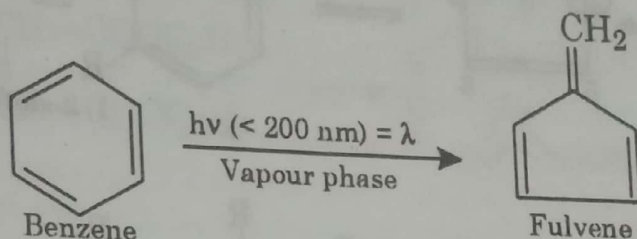
1, 2-alkyl group shift : 1, 2-alkyl group shift takes place by benzvalene as well as prismane intermediates. Conversion of o-xylene into m-xylene, and m-xylene into p-xylene is due to 1, 2-alkyl group shift.

1, 3-alkyl group shift : 1, 3-alkyl group shift takes place only by prismane intermediate. Conversion of o-xylene into p-xylene and p-xylene into o-xylene is due to 1, 3-alkyl group shift.

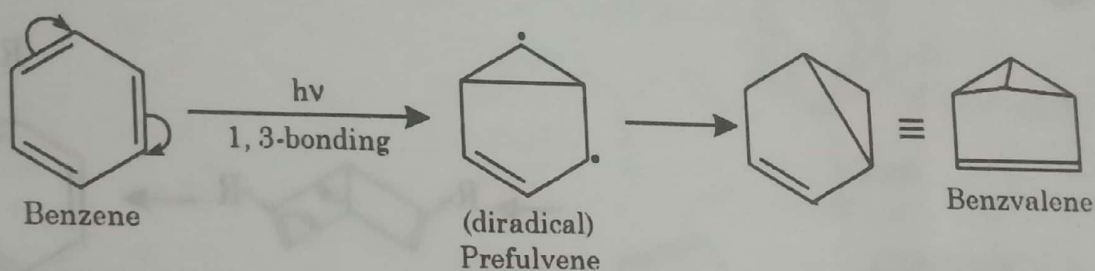
Irradiation of benzene in liquid phase at 254 nm gives benzvalene and at 166-200 nm gives a mixture of three intermediates, namely benzvalene, Dewar benzene and fulvene.



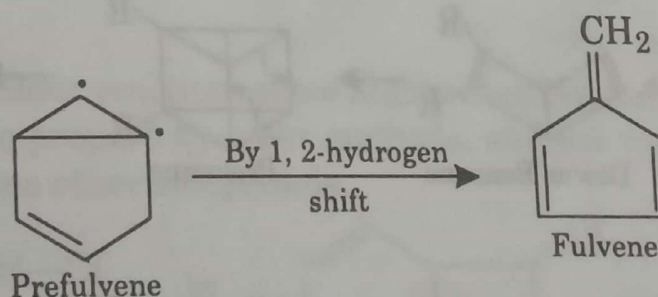
On irradiation at the wavelength < 200 nm, benzene in vapour phase gives only fulvene, as an reaction intermediate.



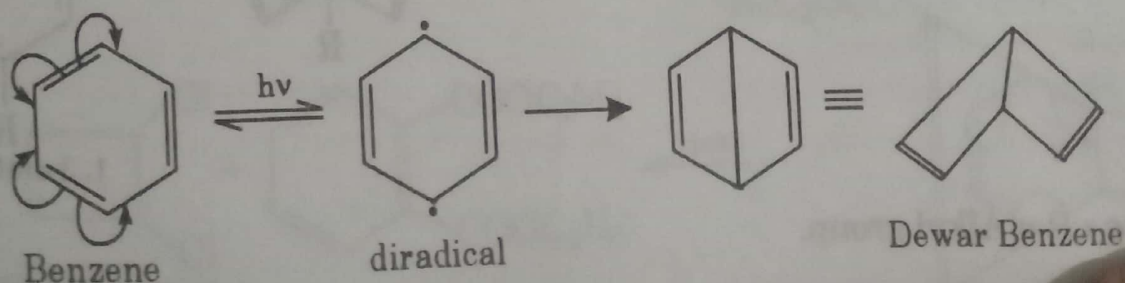
The key intermediate is believed to be a diradical, formed by 1, 3-bonding. Formation of diradical is analogous to the formation of bicyclobutane from photochemically excited butadiene.



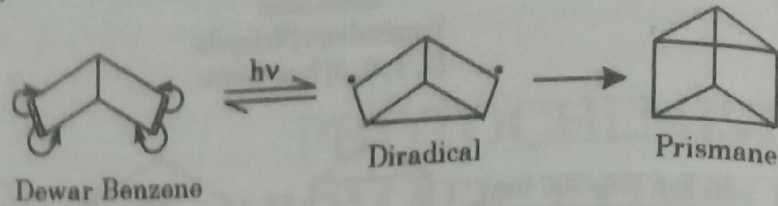
By 1, 2-hydrogen shift and carbon-carbon bond cleavage, prefulvene gives fulvene :



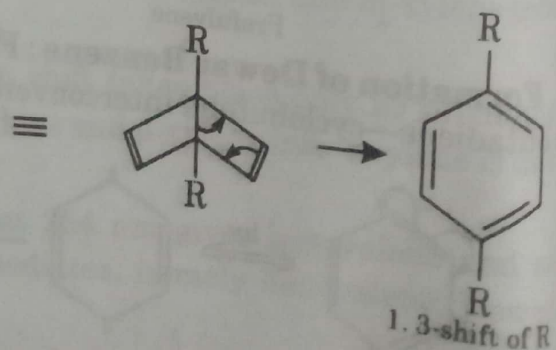
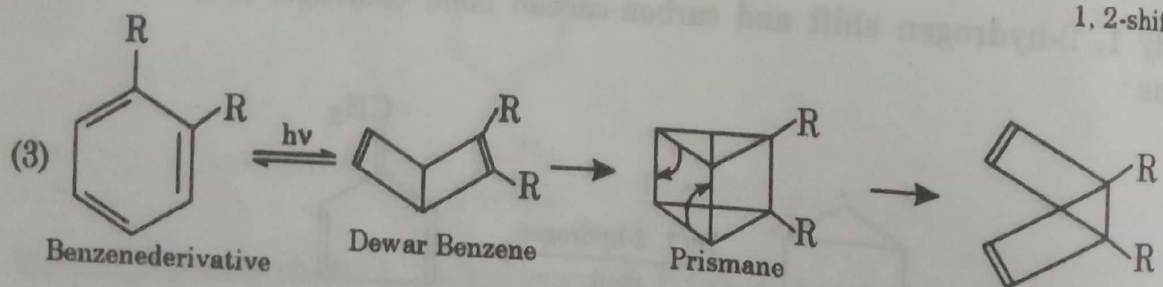
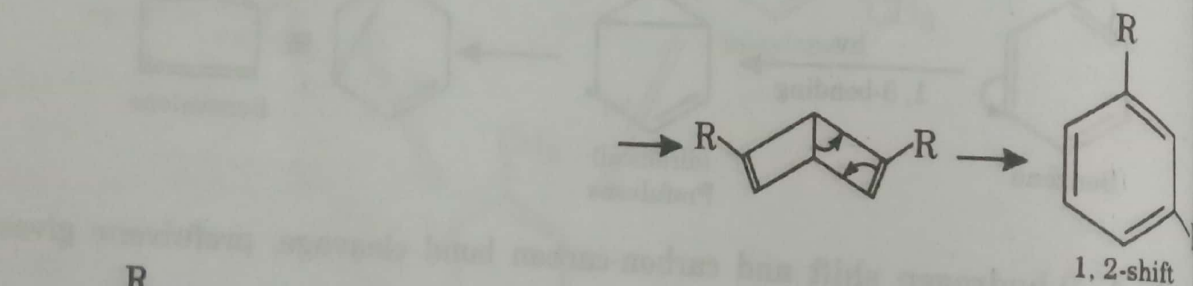
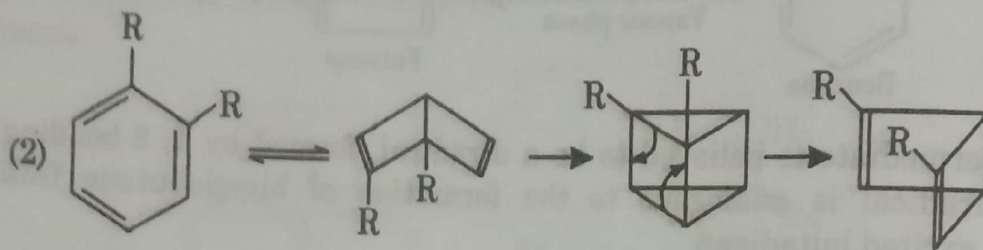
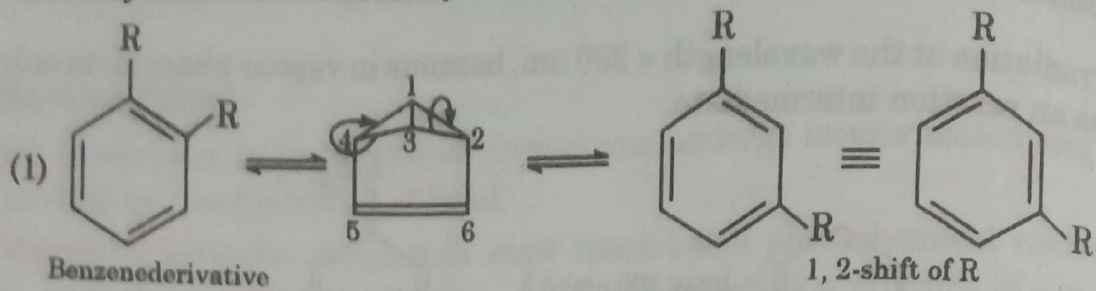
Formation of Dewar Benzene : Formation of Dewar benzene is analogous to the butadiene—cyclobutene interconversion.



Formation of Prismane : On further (2 + 2) cycloaddition, Dewar benzene gives prismane.



All these intermediates, such as benzvalene, prismane and Dewar benzene, are thermally labile and ultimately isomerise into benzenoid compounds.



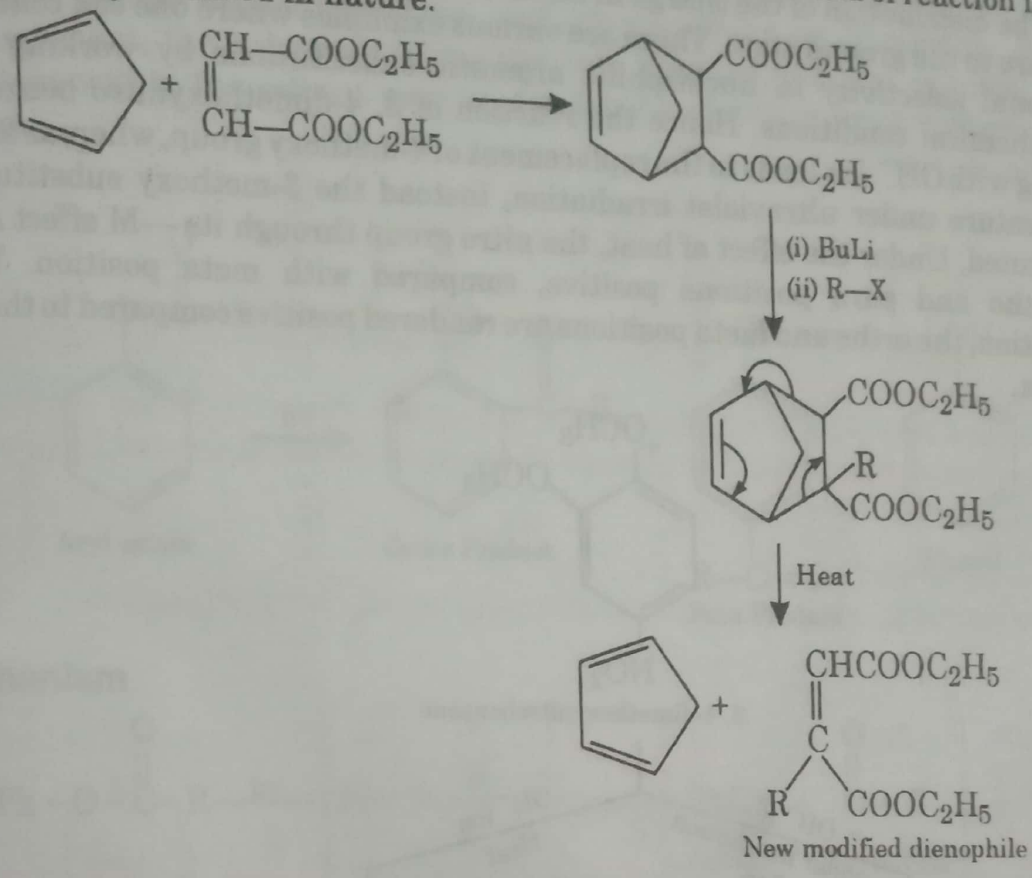
Note : R = Alkyl group.

PHOTOADDITION REACTIONS IN AROMATIC COMPOUNDS

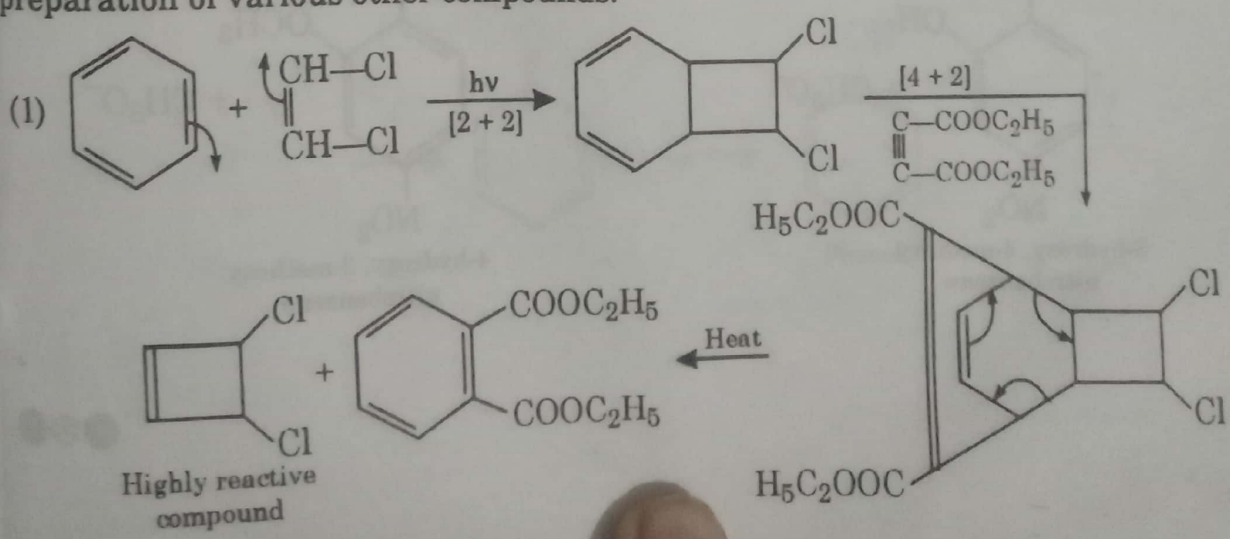
Addition reactions in photochemistry are reversible in nature. These reactions occur between two unsaturated molecules and known as cycloaddition reactions due to formation of cyclic product. The reverse of cycloaddition reactions are called as cycloreversion or retrograde cycloadditions. In this reaction, there is loss of two pi bonds of the reactants and gain of two sigma bonds in the product.

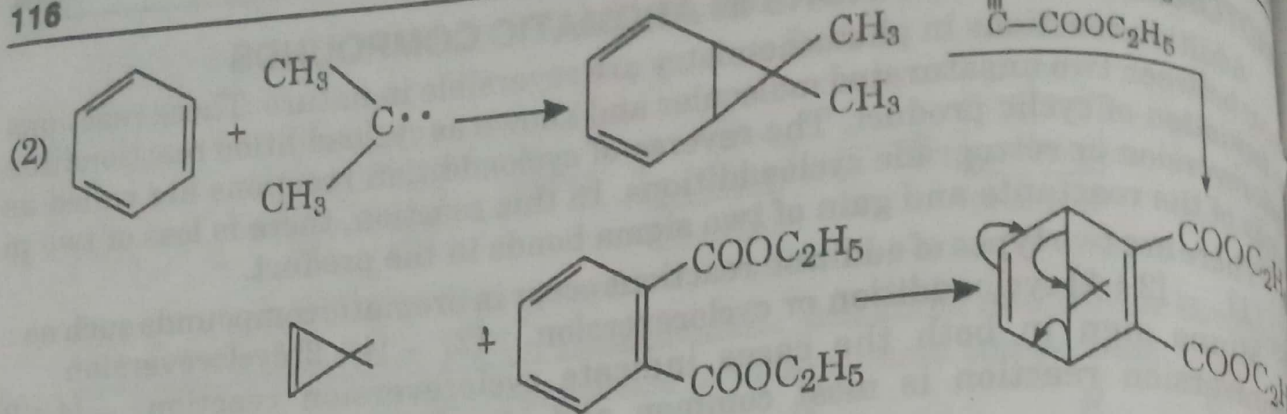
There are two types of addition reactions occur in aromatic compounds such as :
 (1) - [2 + 2] cycloaddition or cycloreversion (2) - [4 + 2] cycloreversion
 Minus sign in both the cases indicate cycloreversion reaction. - [4 + 2] cycloreversion reaction is most common and also known as retro-Diels-Alder reaction.

In retro-Diels-Alder reaction, the adduct obtained at the end of reaction is new and chemically modified in nature.



By retro-Diels-Alder reactions some highly reactive compounds can be formed, which are difficult to prepare by other methods, and are used as a reagent for the preparation of various other compounds.





PHOTOCHEMICAL AROMATIC SUBSTITUTION

The distribution of the charge in an excited species can be entirely different, compare to the ground state. There are various examples where one can control positional selectivity in nucleophilic aromatic substitutions by working under photochemical conditions. Hence the reaction of 3, 4-dimethoxynitro benzene heating with OH^- ion leads to the replacement of 4-methoxy group, whereas at room temperature under ultraviolet irradiation, instead the 3-methoxy substituent is substituted. Under the effect of heat, the nitro group through its $-\text{M}$ effect makes the ortho and para positions positive, compared with meta position. Under irradiation, the ortho and meta positions are rendered positive compared to the para position.

