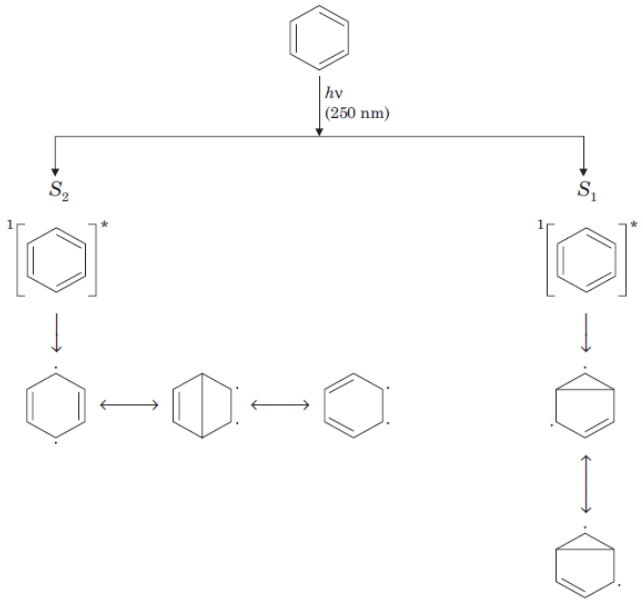
Photochemistry of Aromatic Compounds

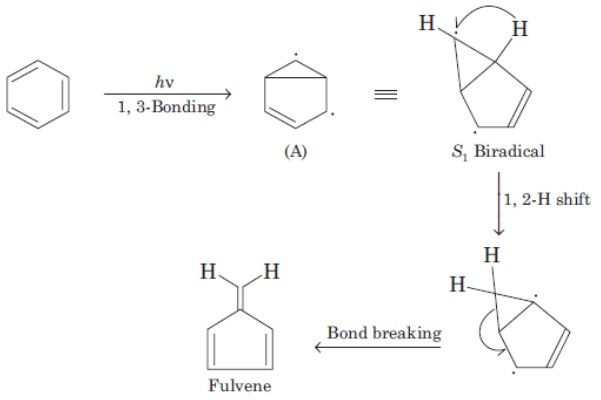
Photorearrangement of benzene and its derivatives, cycloaddition of benzene.

Photoisomerisation of Benzene and Substituted Benzene

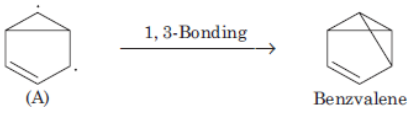
Benzene and substituted benzene undergoes valence isomerisation by irradiation. Selective excitation into *S*1 gives preferentially *meta* and *ortho* product while excitation into *S*2 gives *para* bonded products by valence isomerisation.



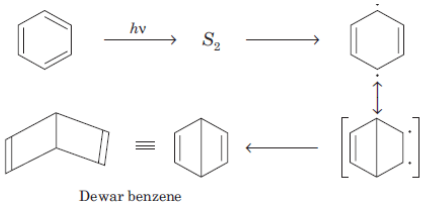
Irradiation of liquid benzene under nitrogen at 254 nm causes excitation to *S*1 state and the products, benzvalene and fulvene are formed *via* 1, 3-biradical.



Formation of benzvalene can take place as follows:

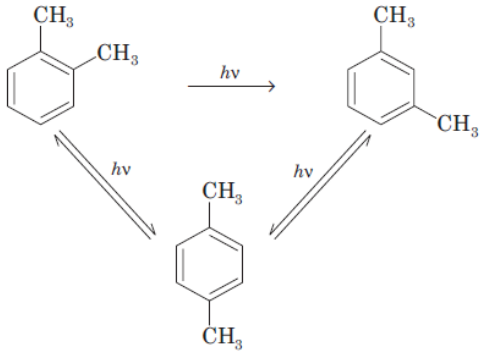


Dewar benzene is formed *via* S_2 state upon short wavelength irradiation (205 nm).



Monocyclic aromatic compounds undergo remarkable photochemical rearrangements.

For example, *o*-xylene on irradiation gives mixture of *o, m* and *p*-xylenes.



Conversion of *o*-xylene into *m*-xylene and *m*-xylene into *p*-xylene is due to 1, 2-alkyl group shift. Similarly conversion of *o*-xylene into *p*-xylene and *vice-versa* is due to the 1,3-alkyl group shift.

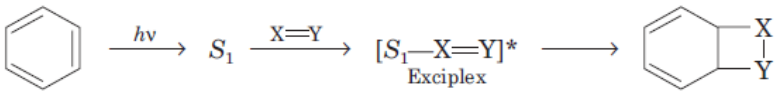
Photoaddition of Alkenes:

Benzene and its derivatives in the S_1 state undergo cycloaddition reactions with various π (*pi*) systems, specially alkenes, alkynes and dienes. The T_1 state of aromatic compounds does not give cycloaddition reactions because the T_1 state of aromatic compounds is quenched by the transfer of excitation energy to the alkene.

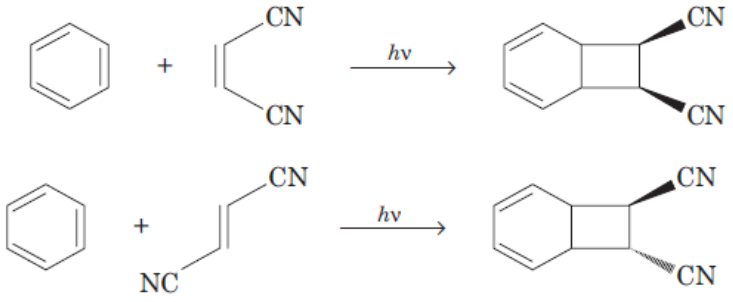
Three different modes of cycloaddition reactions have been observed: 1, 2 or *ortho*, 1, 3 or *meta* and 1, 4 or *para*.

1, 2-addition reactions:

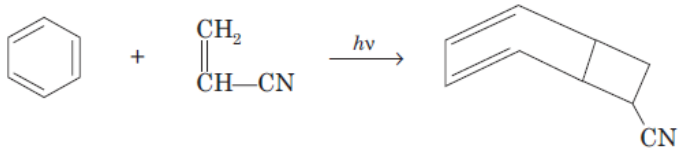
Electron poor alkenes (alkenes having electron withdrawing groups) give 1, 2-addition reaction with arenes in addition to some 1, 4 products. The *para* product is the secondary product. The formation of the *ortho* product is generally favoured by donor-acceptor interaction. The more polar the interactions (charge-transfer) in the exciplex, the longer the proportion of *ortho* and *para* cycloadditions



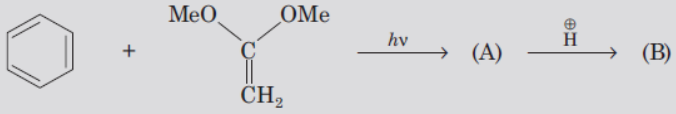
The 1, 2-cycloaddition reactions are concerted reactions. The photocycloaddition of *cis* and *trans*-2-butene to benzene in the liquid phase gives the 1, 2-adduct stereospecifically showing that the reaction is concerted reaction. This also confirmed that the product formation is taking place *via* formation of exciplex.

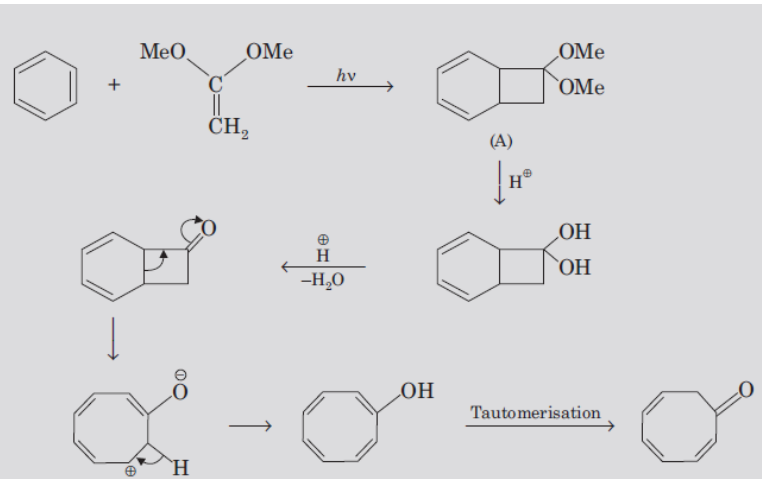


Thus benzene and its derivatives generally forms charge transfer complexes (exciplexes) with dienophiles, and, upon irradiation, gives *ortho*-cycloaddition adducts. The adduct is usually with *exo* orientation.



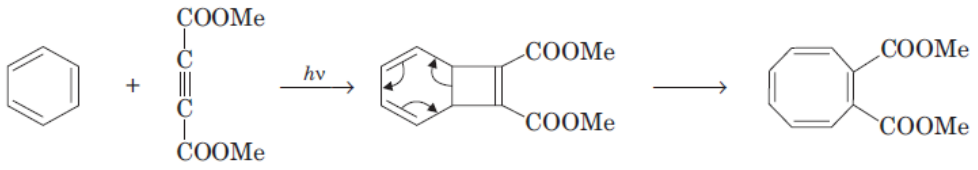
Complete the following sequence of reaction:



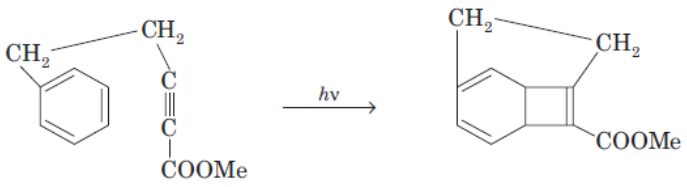


Electrocyclic ring opening is also possible in some adducts to form substituted cyclooctatetraenes

(i)

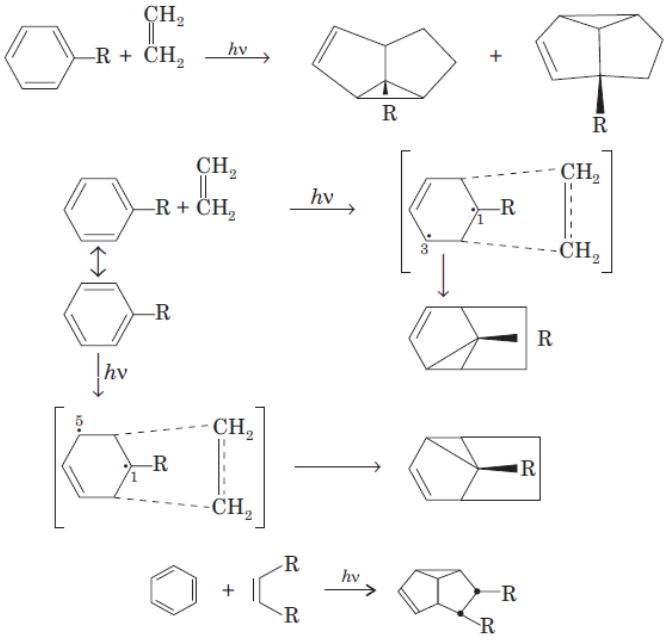


(ii)



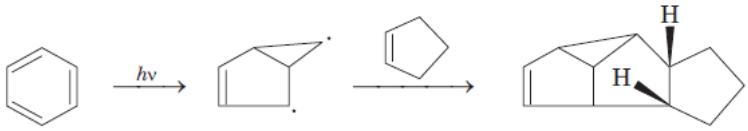
1,3 –Photoaddition of Benzene:

This process leads to tricyclic system in which an olefinic double bond has added across the *meta*-positions of a benzene ring.



The reaction seems to be restricted to double bonds bearing only alkyl substituents such as 2-butene, norbornene, allene and cyclobutene. It occurs with 254 nm light in both gas phase and liquid phase. It is stereospecific and it involves singlet excited benzene. It is known that neither fulvene nor benzvalene is a precursor. Product formation takes place via formation of prefulvene biradical.

In 1, 3-cycloaddition reaction, *endo* product is the major product.



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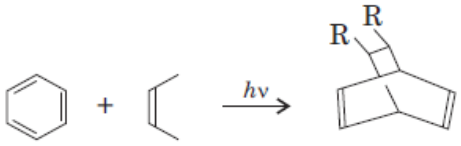
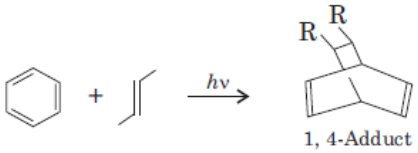
1,4-Photoaddition of benzene:

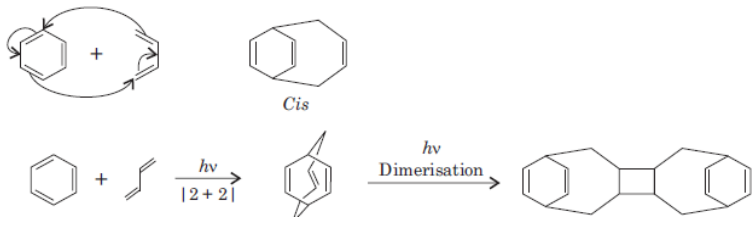
In this reaction olefinic double bond has added across the *para*-positions of a benzene ring.



The reaction is concerted and therefore stereospecific and it involves singlet excited state benzene. The reaction is similar to Diels-Alder reaction because benzene behaves as diene in this case.

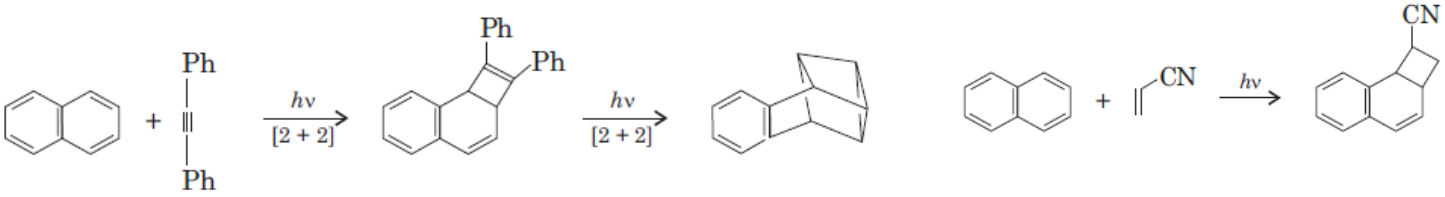


Butadiene also gives [4 + 4] cycloaddition reaction with benzene and reaction is stereospecific.

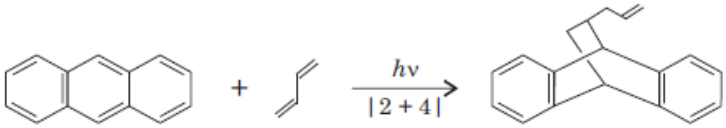


The photoaddition of olefinic systems is not restricted to benzene and its simple homologues. Analogous process occur with condensed aromatics such as naphthalene, phenanthrene or anthracene. In the case of anthracene the cycloaddition is [4 + 2] while in case of phenanthrene and naphthalene it is [2 + 2].

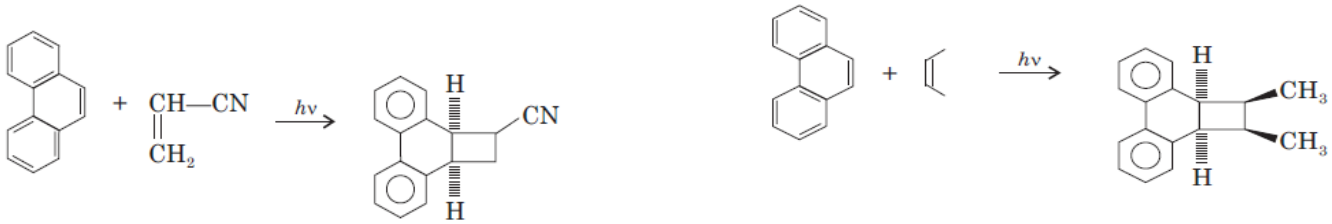
Naphthalene



Anthracene



Phenanthrene



AROMATIC PHOTOSUBSTITUTION

Light-induced substitution in the aromatic compounds can occur either on a ring carbon atom or on an atom of a substituent. These substitution reactions can proceed by heterolytic or radical mechanism.

The most common reactions are the heterolytic substitutions which can be classified into two categories:

(i) Type A: In these reactions the orientation rules are different from those obtaining in the ground state.

i) Photonucleophilic Substitution ii) Photoelectrophilic Substitution

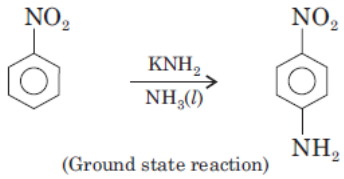
(*ii*) Type B: In these reactions the orientation rules are the same as in the ground state but the process is accelerated by light absorption.

i) Radical Substitutions

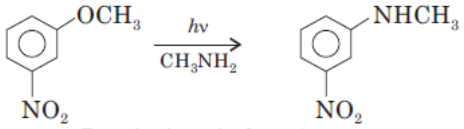
Type A substitutions

i) ***Photonucleophilic Substitution:***

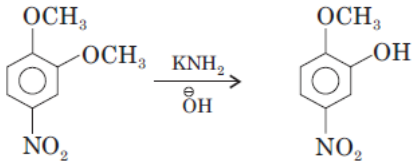
Nitro group is activating group and *ortho* and *para* directing group for nucleophilic substitution reactions in the ground state. In the presence of light (*i.e.,* in the excited state) the nitro group is *m*-directing group.



(Ground state reaction)



(Reaction in excited state)



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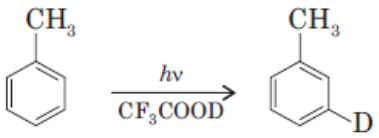
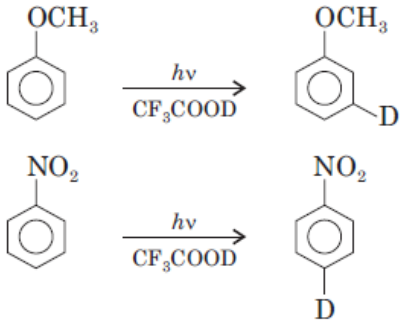
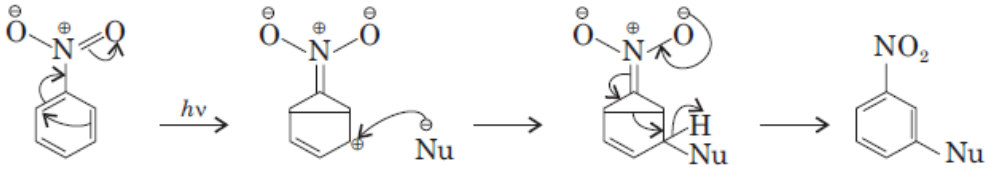
ii)Photoelectrophilic Substitution:

On irradiation in the presence of CF_3COOD, toluene gives mainly *m*- deuterio toluene instead of *o*-and *p*-derivatives.

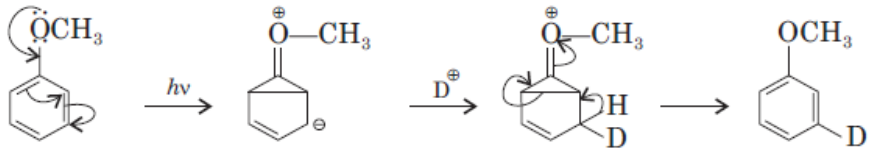


Anisole also gives *m*-derivative whereas nitrobenzene gives *p*-derivative.





Mechanism of photonucleophilic substitution

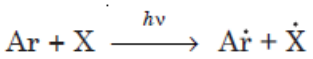


Mechanism of photoelectrophilic substitution

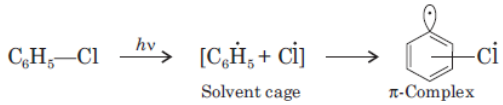
Type B substitutions

i) Radical Substitutions:

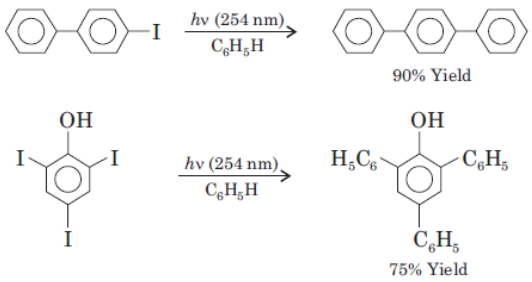
Haloaromatic compounds on irradiation undergo homolysis in ground state to produce radicals which then give rise to products by well-established thermal pathway.



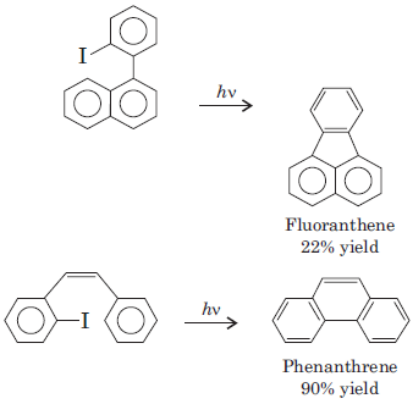
However,when chlorobenzene is excited in the liquid phase, the Ph• and Cl • radicals seems to recombine within the solvent cage generating transient π-chlorobenzene, and isomer of chlorobenzene in which the chlorine atom forms a π complex with phenyl radical.



Halogen atom of π complex is more selective than halogen free radical. The light-induced homolysis of aryl-halogen bonds has important synthetic implications. Irradiation of lodinated aromatics in benzene often gives the phenylated aromatic in high yield.



Intermolecular reactions of this type can be used for the preparation of polynuclear aromatic compounds.



Similar reaction is also given by iodoacetylenes.