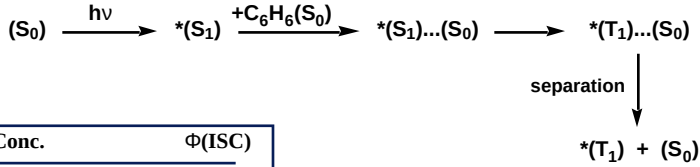
Photochemistry of aromatics:
the short version

- **Rearrangements (including Dewar benzenes)**
- **Electron tranfer**
  - **Sometimes followed by proton transfer and looking like hydrogen abstraction**
- **Addition by solvolysis**
- **Cycloadditions, including dimerizations and intramolecular processes**
- **Nucleophillic attack**

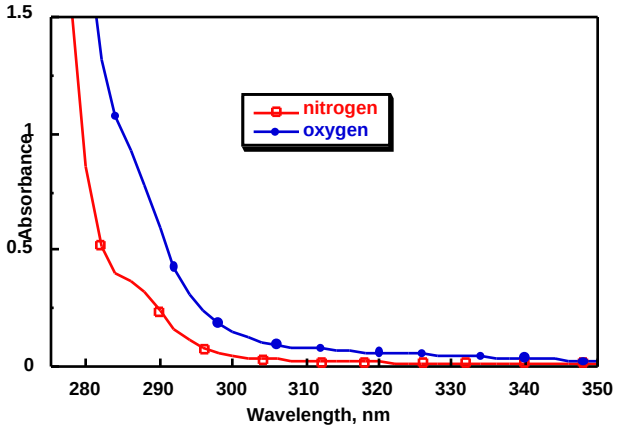
Benzene shows concentration-dependent intersystem crossing



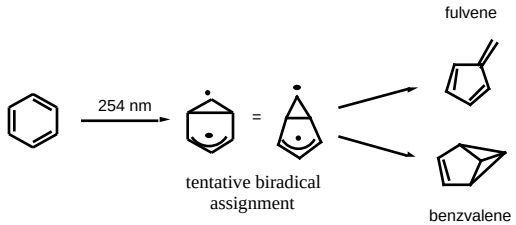
Conc.	Φ(ISC)
0.112 M	0.23
11.2 M (neat)	0.56
(co-solvent = cyclohexane	

Benzene can assist ISC via a S1..So interaction

Benzene undergoes CT interactions with oxygen leading to absorption enhancements



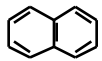
Rearrangements



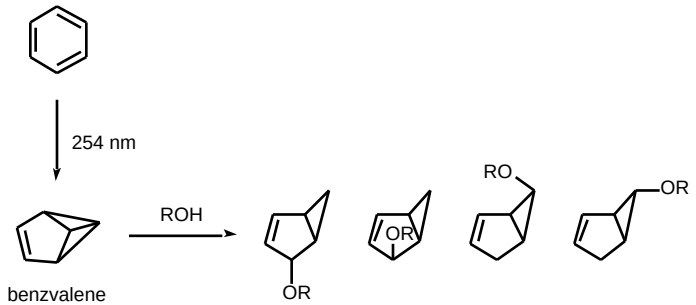
The quantum yield of benzvalene is wavelength dependent, with higher yields at the lower wavelengths.

e.g. at 253 nm $\Phi = 0.016$

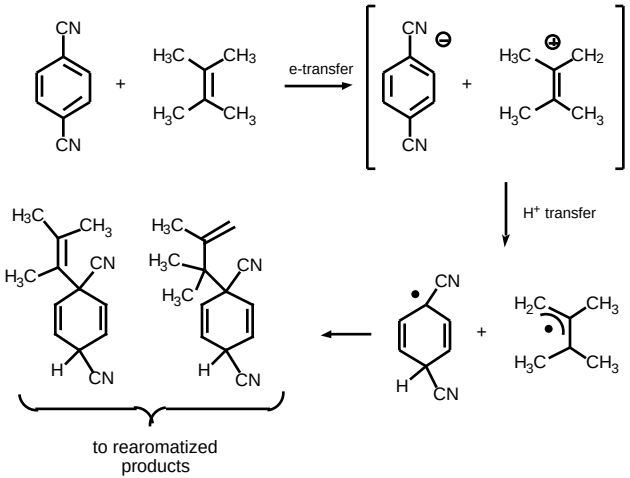
Large S-T gaps are characteristic of the π,π* states of aromatics

	Type	ΔE(S-T)
$CH_2=CH_2$	π,π*	70
	π,π*	40
	π,π*	35
$CH_2C=O$	n,π*	10
$Ph_2C=O$	n,π*	7
		kcal/mol

Addition by solvolysis

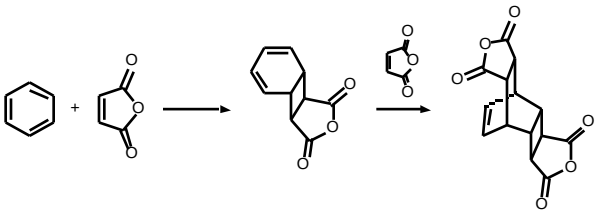


Addition by electron transfer

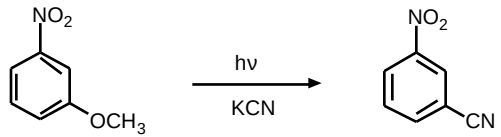


Cycloadditions

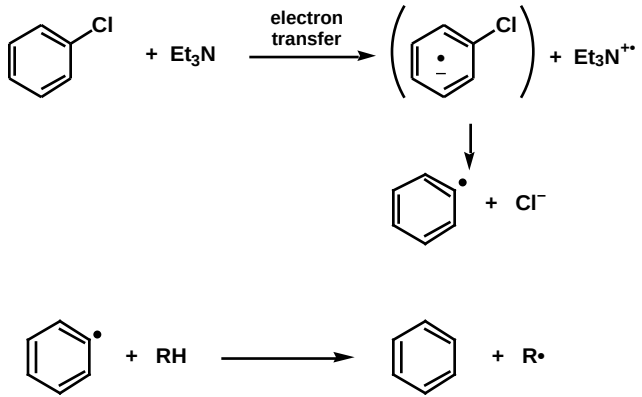
e.g., 2 + 2



Nucleophillic aromatic substitution

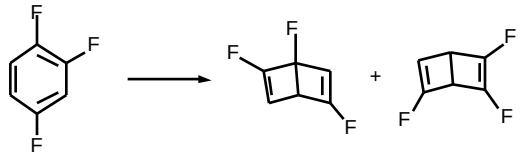


Substitution mediated by electron transfer



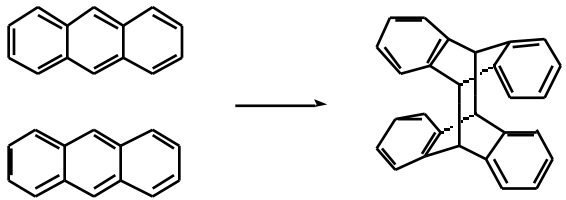
Dewar type isomers favored in the case of fluorinated benzenes

e.g.



Typical quantum yields in the 0.001 range

Dimerization reactions



Intramolecular cyclization