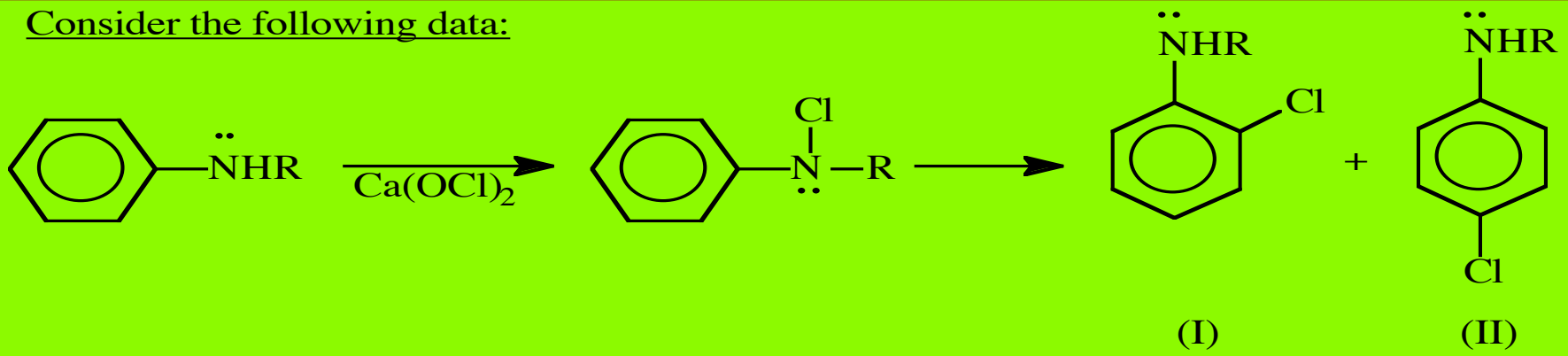
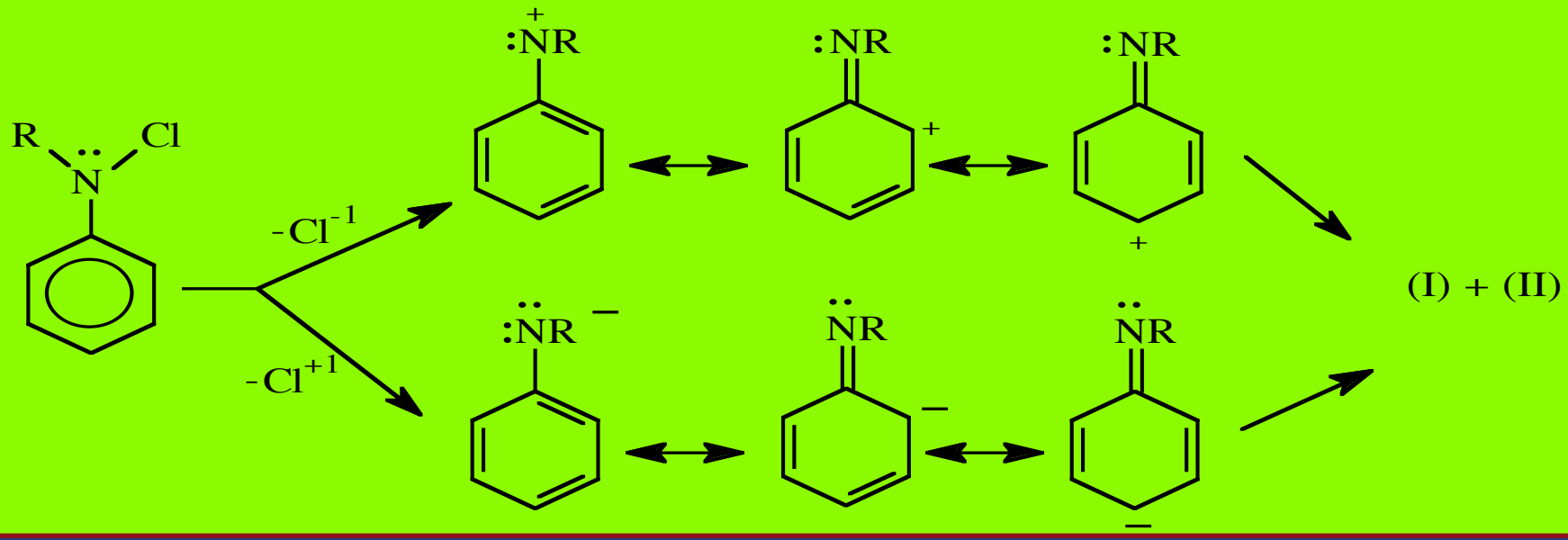
Carbocation Analogues: Nitrenium ions?

Consider the following data:



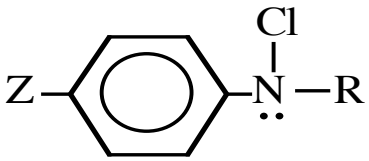
(I) (II)

Possible Mechanistic Pathways:



Evidence to support the existence of nitrenium ions

Study of rearrangement run with para-substituted N-chloroanilines:

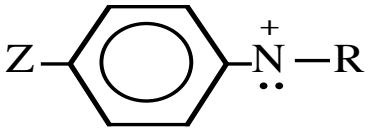


where Z = CH_3, F, H, Cl, and CN

Observation:

The rearrangement is associated with a **negative rho** value indicative of a reaction favored by electron donating benzene ring substituents.

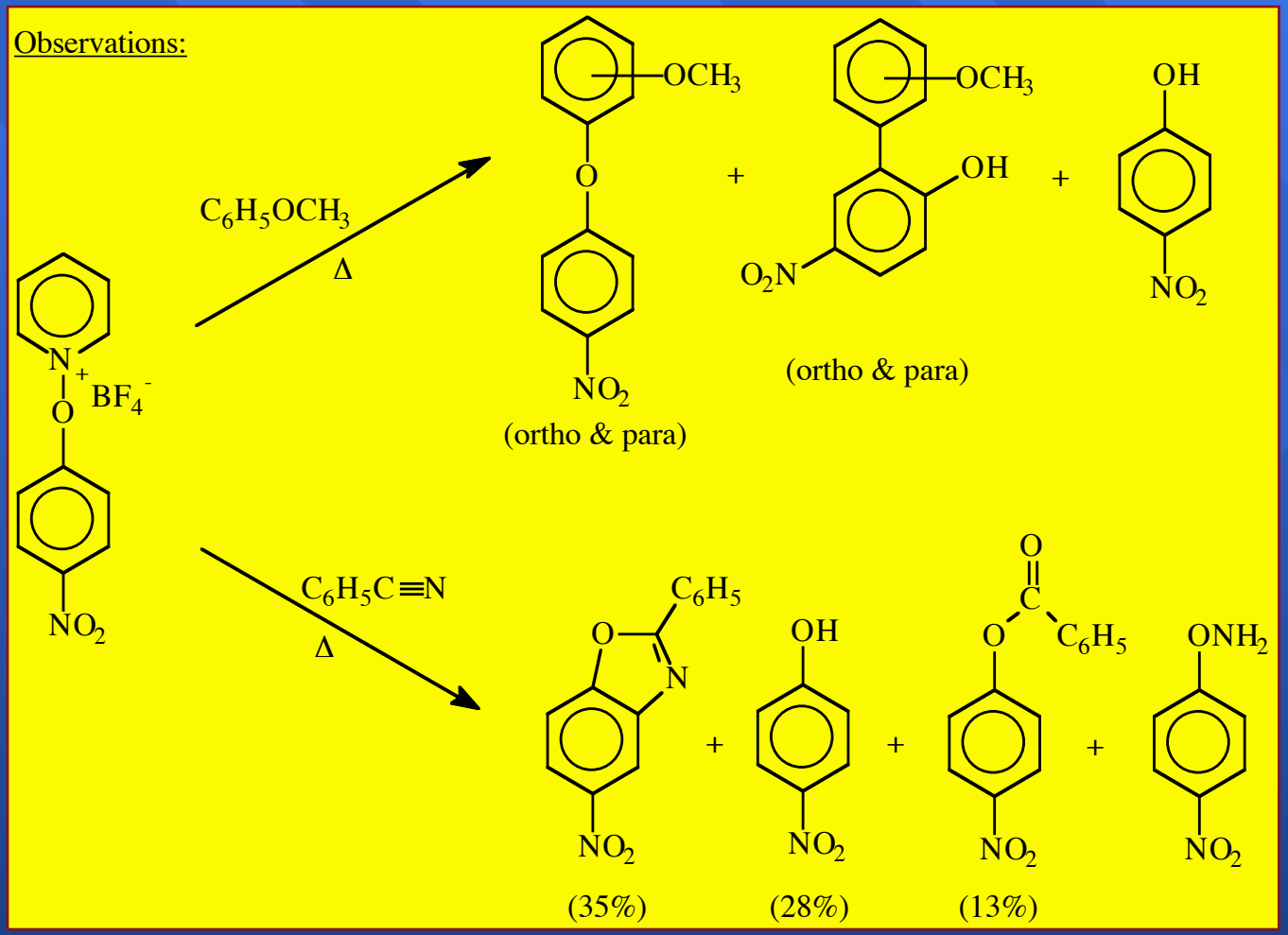
Conclusion:



intermediates take part in the rearrangement.

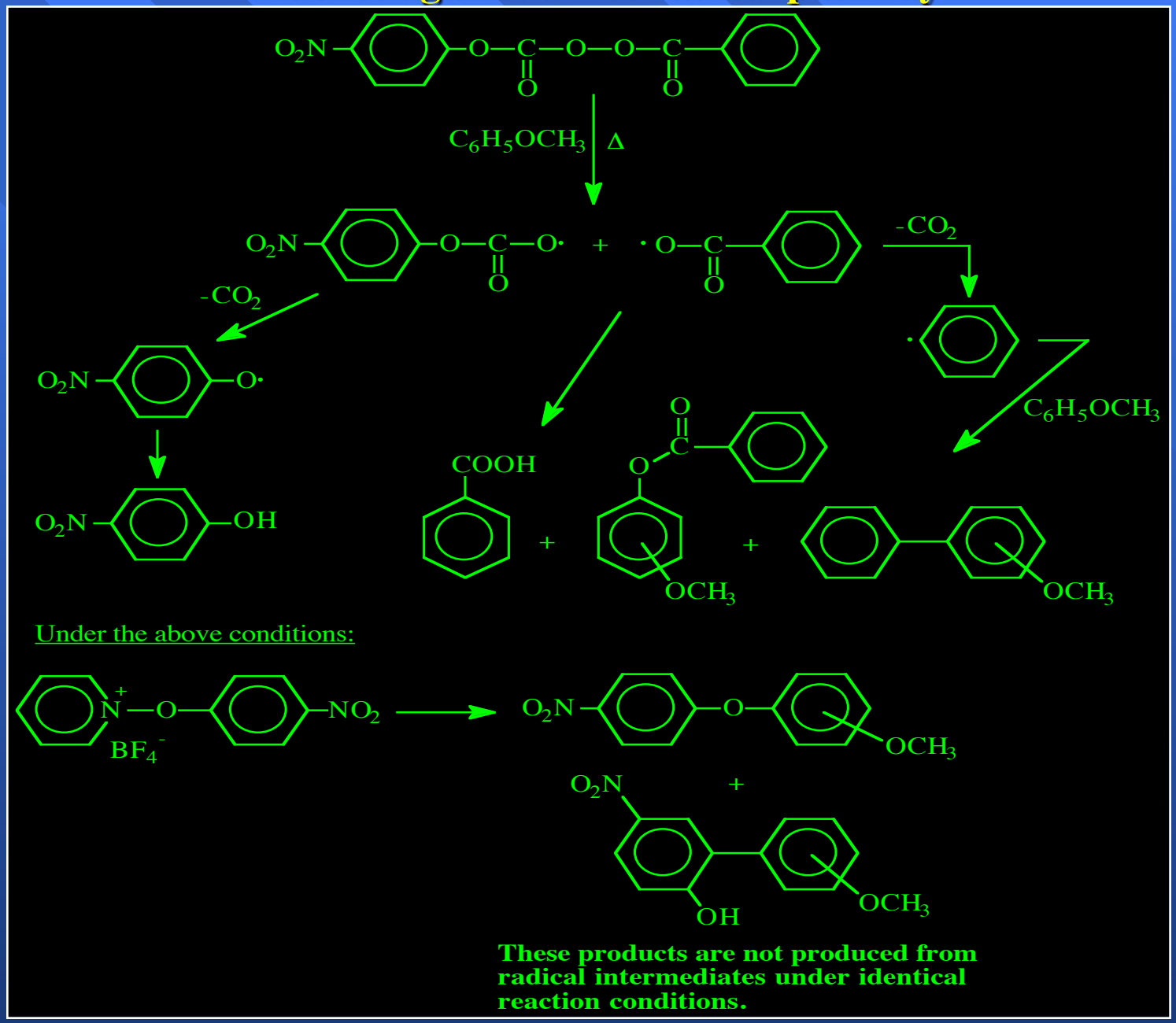
Carbocation Analogues

Oxenium ions?



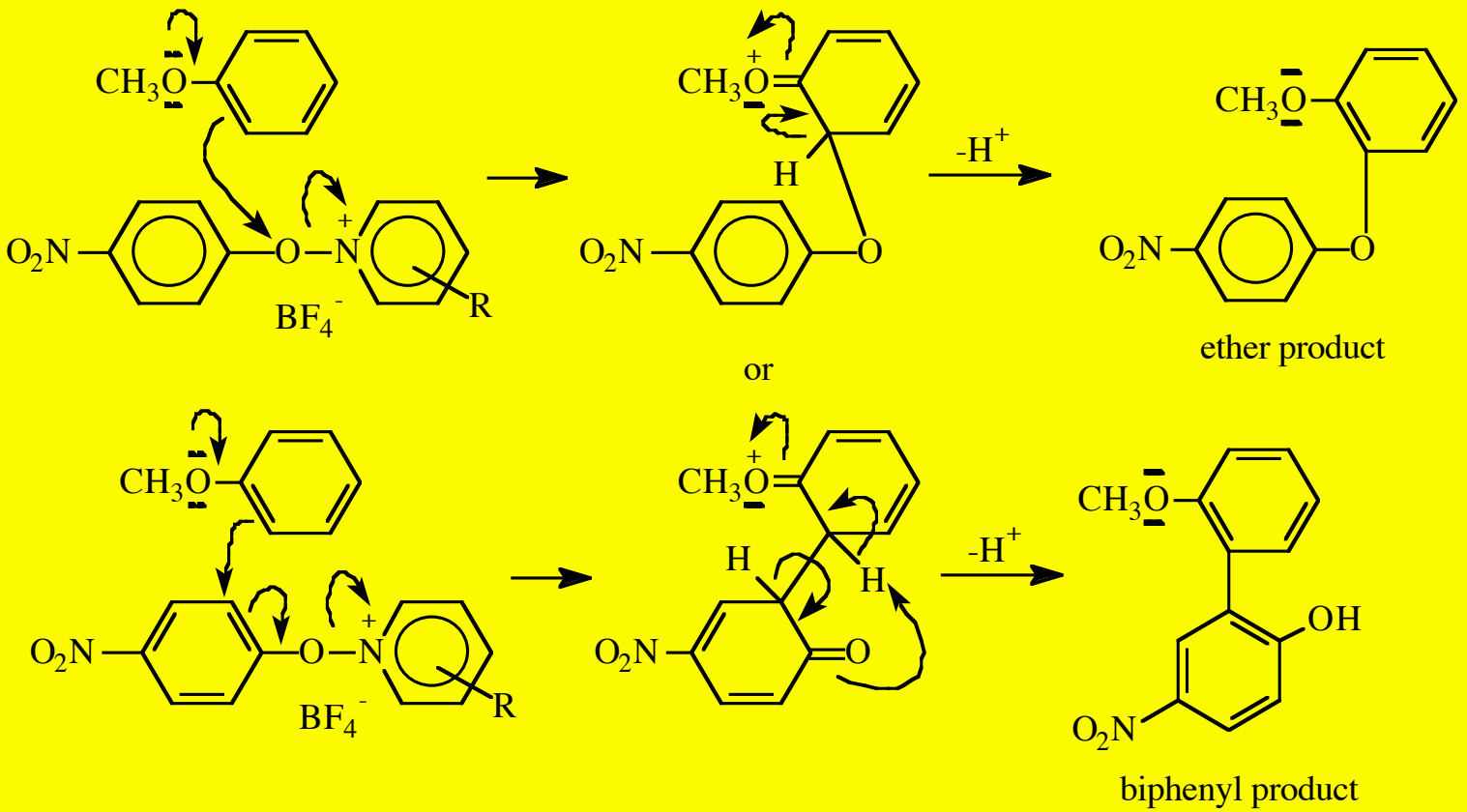
Relevant Facts (I)

Evidence against a free radical pathway



Relevant Facts (II)

Evidence against a concerted pathway

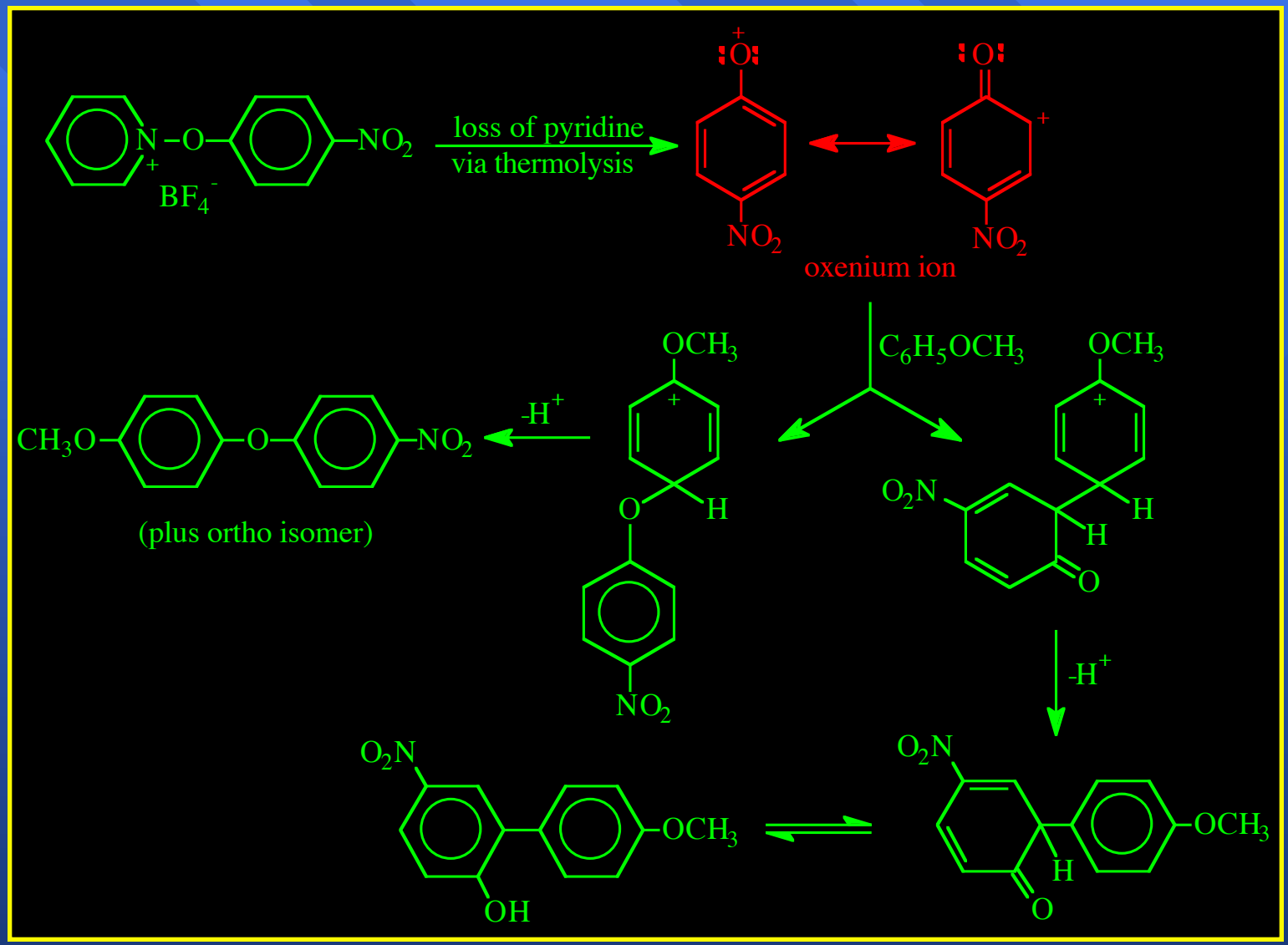


In a concerted pathway, the pyridine ring substituent would be expected to affect the leaving ability of the pyridine group and thereby have an impact on the ratio of ether:biphenyl products.

Observation: For R = 4-methyl, 4-methoxy, 4-phenyl, and 2-hydroxy, a constant ratio of ortho to para diphenyl ethers (28%:72%) was obtained. A constant ratio of ortho to para biphenyl products (75%:25%) was obtained.

Conclusion : The evidence suggests that attack is independent of the pyridine ring R-substituent, a fact contrary to what one would expect for a concerted mechanism.

A plausible explanation involving the intermediacy of Oxenium ions



A plausible explanation involving the intermediacy of Oxenium ions cont'd.