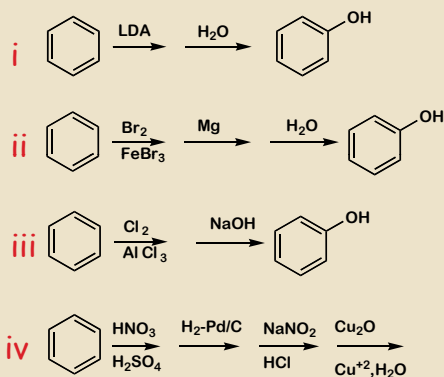


Give a synthesis of phenol from benzene.

How many of these would work?

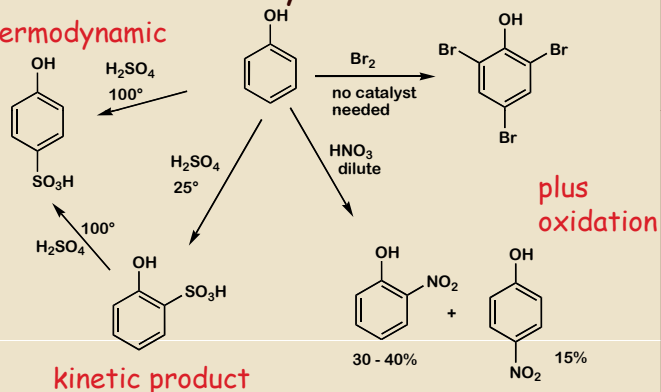
- A 0
- B 1
- C 2
- D 3
- E 4



## Electrophilic Aromatic Substitution

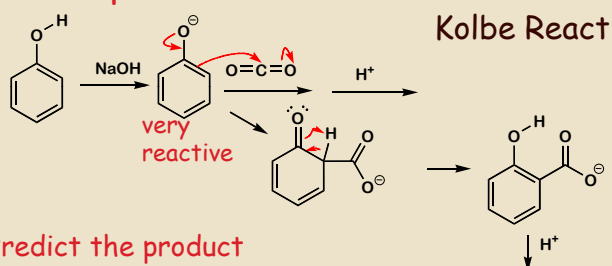
Phenols are very reactive

thermodynamic

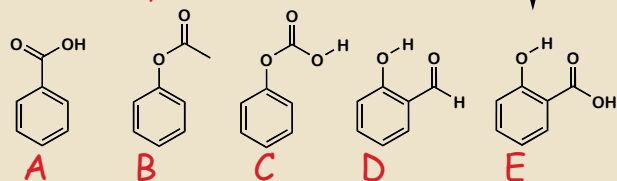


## Electrophilic Aromatic Substitution

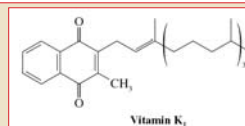
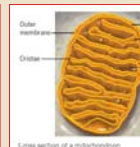
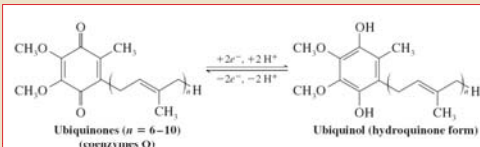
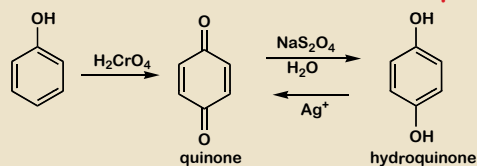
Kolbe Reaction



Predict the product



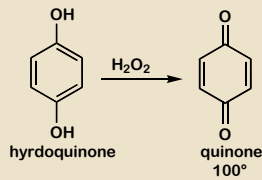
## Phenol can be oxidized to quinone



## Bombardier Beetle

Shoots a stream of hot quinone

The boiling solution is pulsed in shots of several hundred per second



The spray of bombardier beetles contains *p*-benzoquinones (10), compounds well known for their irritant properties (11). A single bombardier beetle can discharge upward of 20 times before depleting its glands (6). The discharges are accompanied by audible detonations, and they have been shown to be potentially deterrent to a number of predators, including ants (6, 12-15).

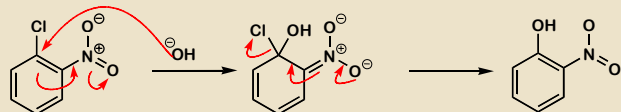
The spray of bombardier beetles is ejected at  $100^\circ\text{C}$  (13). This is because the quinones are generated explosively at the moment of ejection by the mixture of two sets of chemicals ordinarily stored separately in the glands. Each gland consists of two confluent compartments. The larger of these (storage chamber or reservoir) contains hydroquinones and hydrogen peroxide while the smaller one (reaction chamber) contains special enzymes (catalases and peroxidases). To activate the spray, the beetle mixes the contents of the two compartments, causing oxygen to be liberated from hydrogen peroxide and the hydroquinones to be oxidized by the freed oxygen. The oxygen also acts as the propellant, causing the mixture to "pop" out



<http://www.pnas.org/cgi/content/abstract/96/17/9705>

[http://www.youtube.com/watch?v=tpJ3asv3XMY&feature=player\\_embedded](http://www.youtube.com/watch?v=tpJ3asv3XMY&feature=player_embedded)

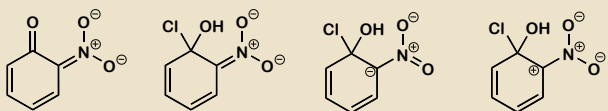




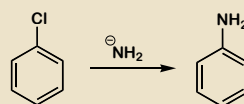
### Substitution Nucleophilic Aromatic $S_NAr$

Only works because of the  $NO_2$  group.

Which of these is the best intermediate?

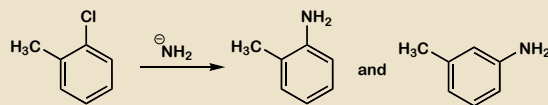


**A**      **B**      **C**      **D**

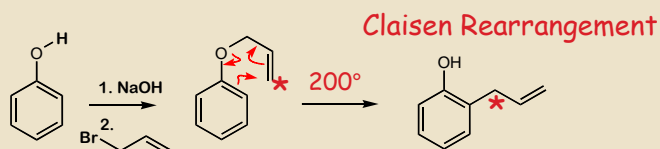
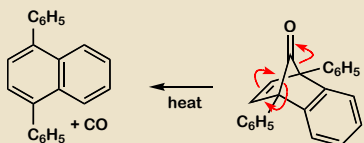
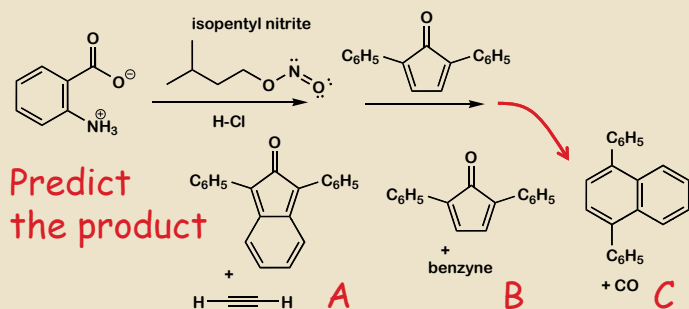
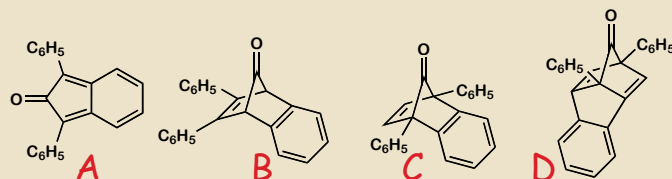
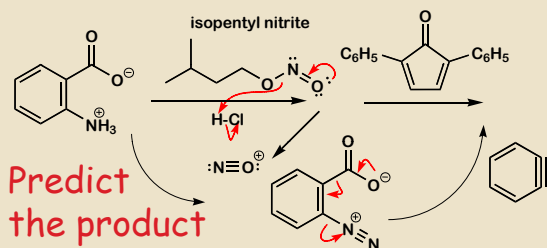
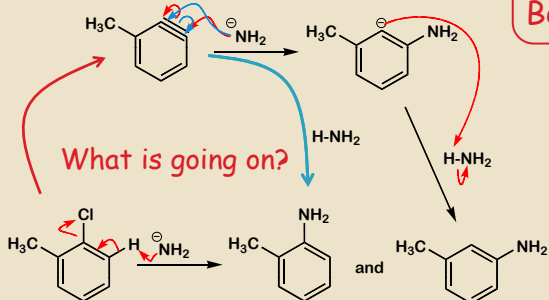
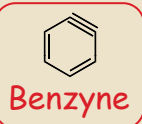


But with a really strong base it appears you don't need a nitro group!

Only works because of the  $NO_2$  group.



### Draw the intermediate



$^{14}C = *$

**Pericyclic Reaction**

**Cyclic flow of electrons**

**Concerted**

keto intermediate "not stable"

