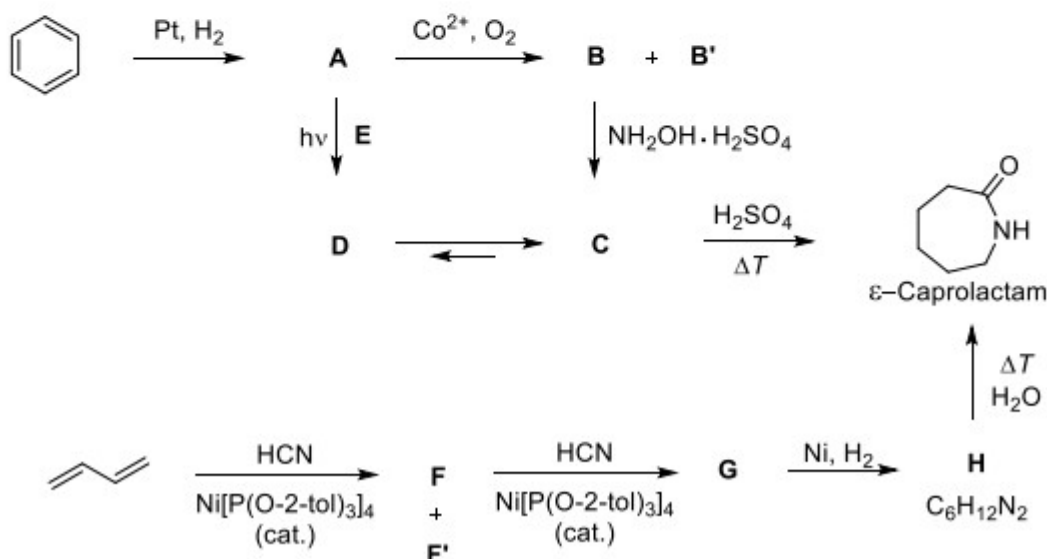


Problem 25. All roads lead to caprolactam

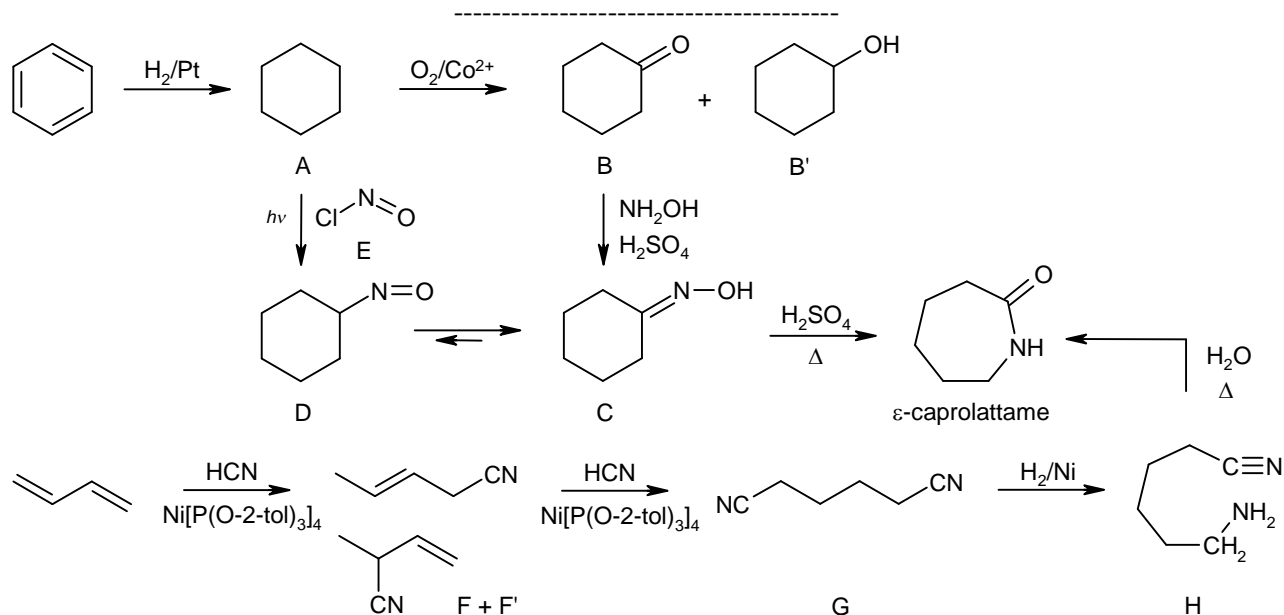
The synthesis of ϵ -caprolactam (hexano-6-lactam) starts with benzene, which is converted to compound **A** by exhaustive catalytic hydrogenation and subsequently oxidized by air in the presence of cobalt(II) salts of a fatty acid. First, the desired product **B** has to be separated from the side product **B'** by fractional distillation. Compound **C** can be obtained by heating **B** with hydroxylamine sulfate and the desired ϵ -caprolactam can be obtained by heating **C** with sulfuric acid.

A modern alternative to this process is the photochemical reaction of compound **A** with orange-coloured gas **E**. Compound **E** contains a chlorine atom and is also formed during the preparation of aqua regia. Compound **D** immediately rearranges to compound **C**.

Caprolactam can also be prepared from buta-1,3-diene by sequential catalytic hydrocyanation with two equivalents of hydrogen cyanide. In the first reaction, in addition to the desired compound, **F**, compound **F'** is formed and has to be separated first. Compound **G**, after partial hydrogenation, provides compound **H**, which is heated in the presence of water in order to give caprolactam.



25.1 Draw the structures of unknown compounds A–H.



25.2 Under which conditions will the equilibrium be most shifted from benzene to compound **A**?

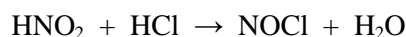
- a) 300 °C, 1 atm
- b) 300 °C, 100 atm
- c) 50 °C, 1 atm
- d) 50 °C, 100 atm

25.2 L'equilibrio della reazione di idrogenazione catalitica è più spostato a destra a temperature più basse in modo da minimizzare il termine $T\Delta S^\circ$ nell'equazione $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ dato che l'entropia della reazione è sfavorevole perchè 4 molecole si fondono per formarne una sola. Inoltre la reazione è più spostata a destra con alte pressioni di idrogeno. La risposta corretta è quindi la d).

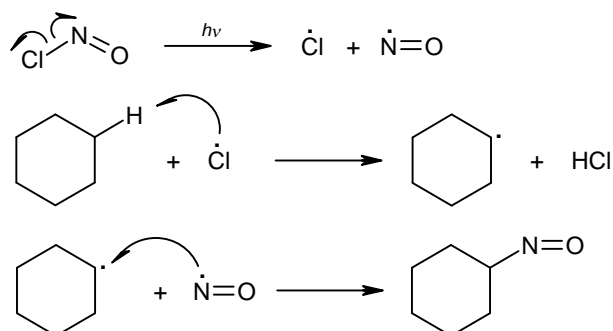
25.3 Write the equation for the formation of compound **E** in the preparation of aqua regia and suggest at least one other way to prepare **E**.



NOCl si può anche preparare per disidratazione dell'acido nitroso con HCl



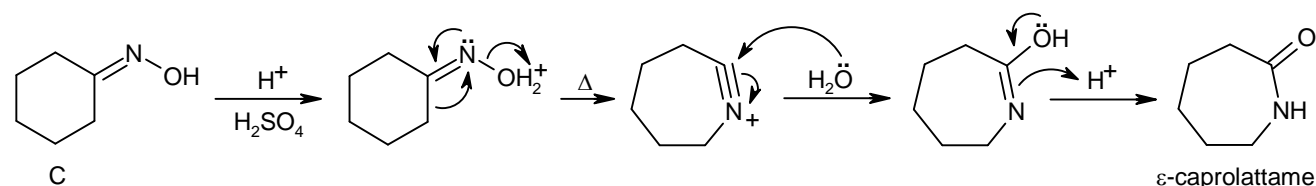
25.4 Suggest the mechanism for the photochemical reaction of **A** with compound **E**.



25.5 What is an approximate wavelength suitable to perform the mentioned photochemical reaction? *Hint: E is not colourless.*

La frequenza adatta a rompere il legame N-Cl in NOCl è quella che viene assorbita dalla molecola nel visibile. Dato che questo gas è arancione, significa che assorbe il colore complementare dell'arancione, quindi tra il blu e il ciano. La frequenza, quindi, deve essere di circa 470 nm, dato che la zona del blu va dai 400 ai 500 nm.

25.6 Suggest a plausible mechanism for the conversion of **C** to ϵ -caprolactam. After whom is the reaction named?



Questa reazione è nota come trasposizione di Beckmann