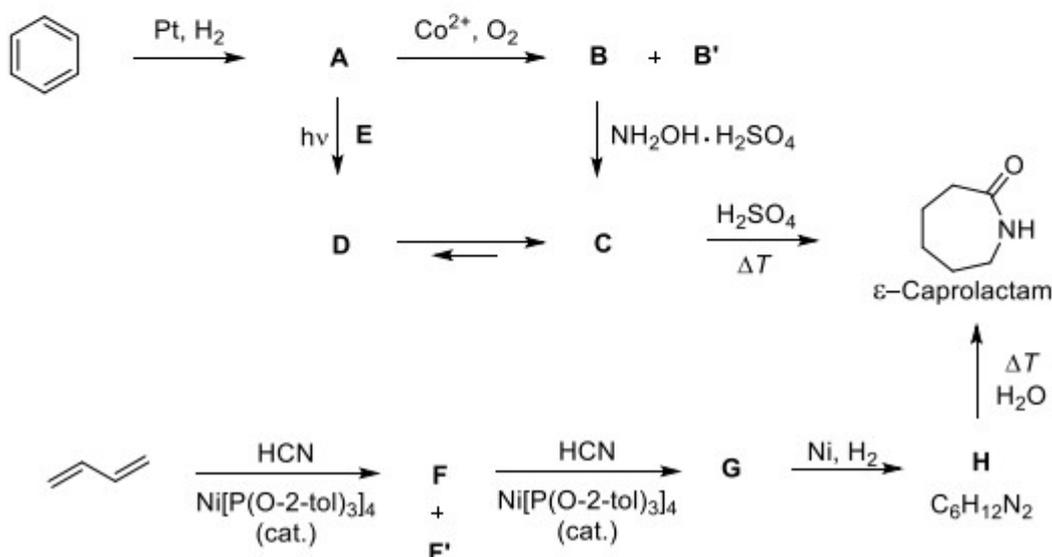


## Problem 25. All roads lead to caprolactam

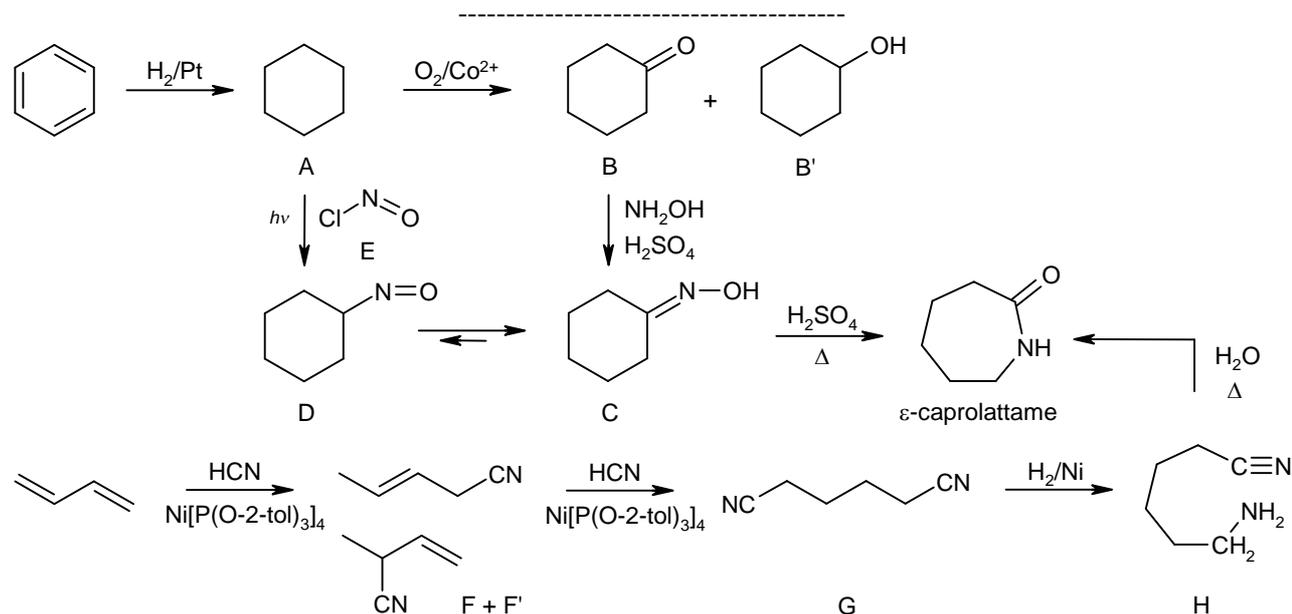
The synthesis of  $\epsilon$ -caprolactam (hexano-6-lactam) starts with benzene, which is converted to compound **A** by exhaustive catalytic hydrogenation and subsequently oxidized by air in the presence of cobalt(II) salts of a fatty acid. First, the desired product **B** has to be separated from the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

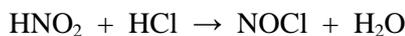
- a) 300 °C, 1 atm
- b) 300 °C, 100 atm
- c) 50 °C, 1 atm
- d) 50 °C, 100 atm

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).

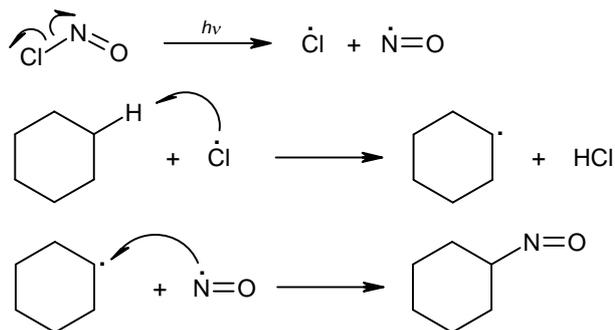
25.3 Write the equation for the formation of compound **E** in the preparation of aqua regia and suggest at least one other way to prepare **E**.



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



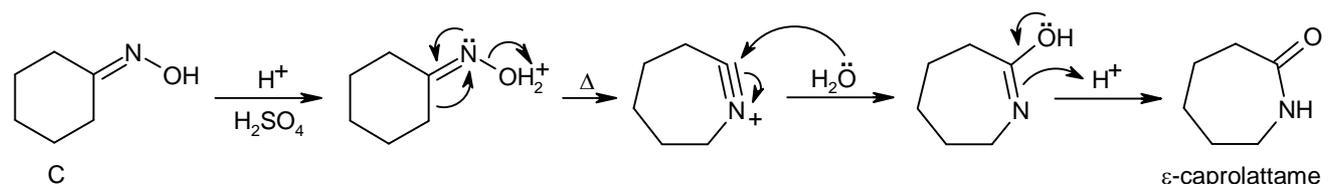
25.4 Suggest the mechanism for the photochemical reaction of **A** with compound **E**.



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  $\epsilon$ -caprolactam. After whom is the reaction named?



Questa reazione è nota come trasposizione di Beckmann