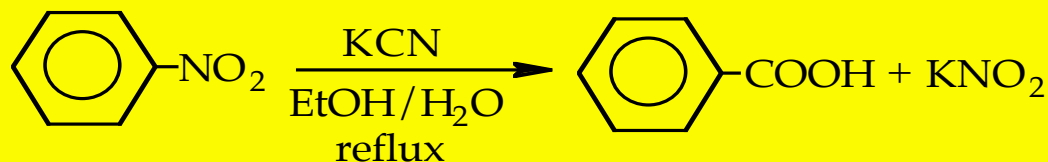


The von Richter Reaction: A Case History

In 1871, von Richter reported the following observations:



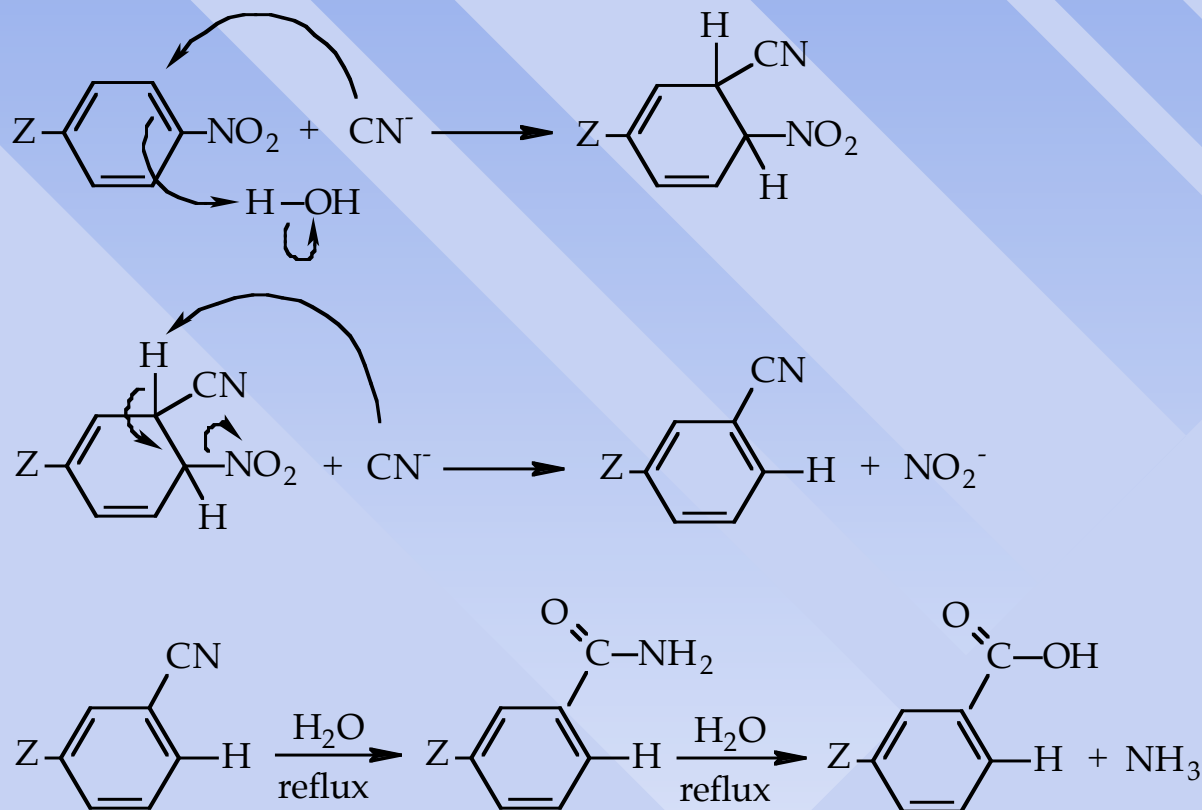
5%-50% yields

Based on the above:

1. Direct displacement of the nitro group is eliminated from consideration.
2. A benzyne intermediate is ruled out. In the case of para-substituted nitrobenzenes, benzyne intermediates would give both meta- and para-substituted benzoic acids.

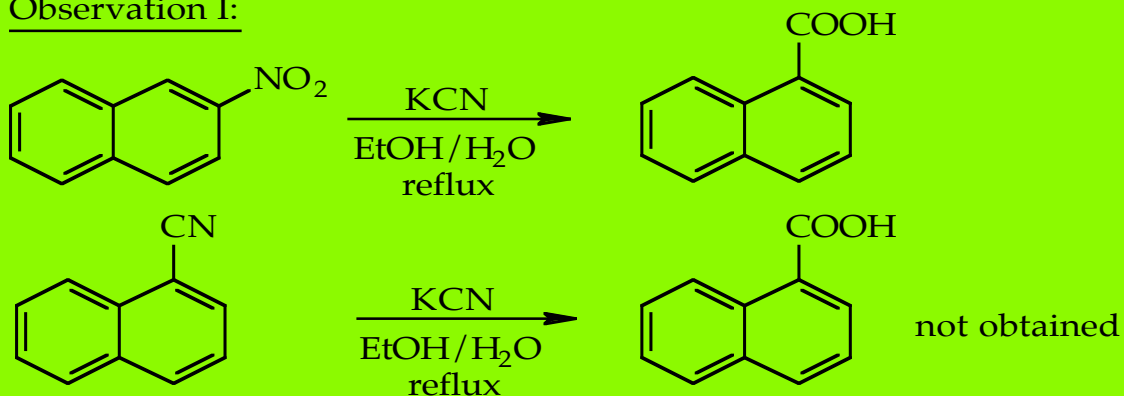
von Richter Reaction: Bunnett Mechanism (1954)

In 1954, Bunnett et al. proposed the following mechanism to account for the known facts pertaining to the von Richter reaction:



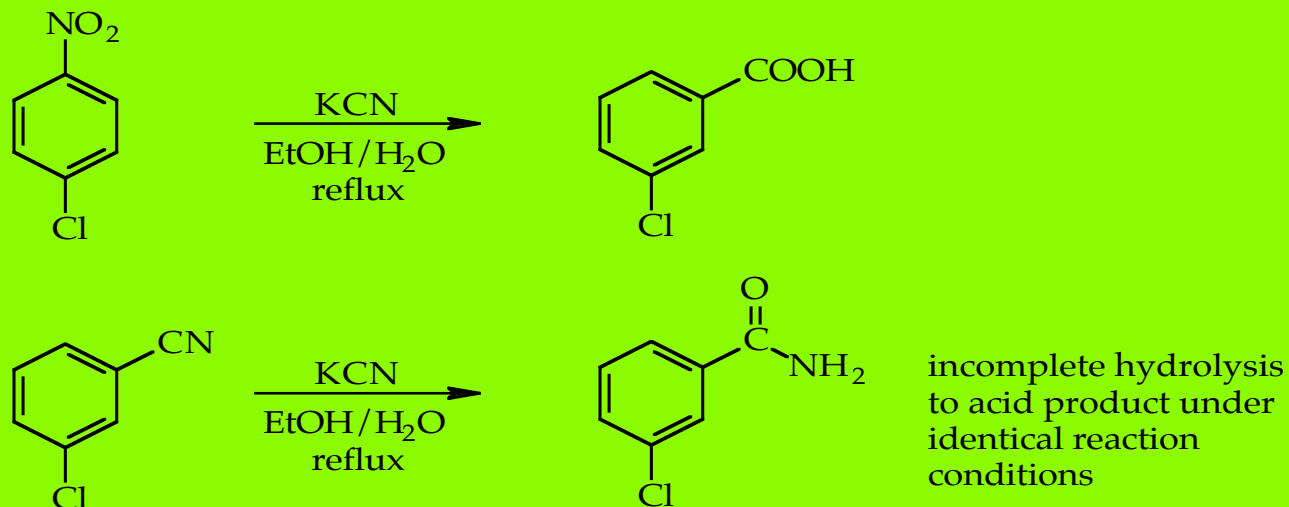
von Richter Reaction: Bunnett Observations (1956)

Observation I:



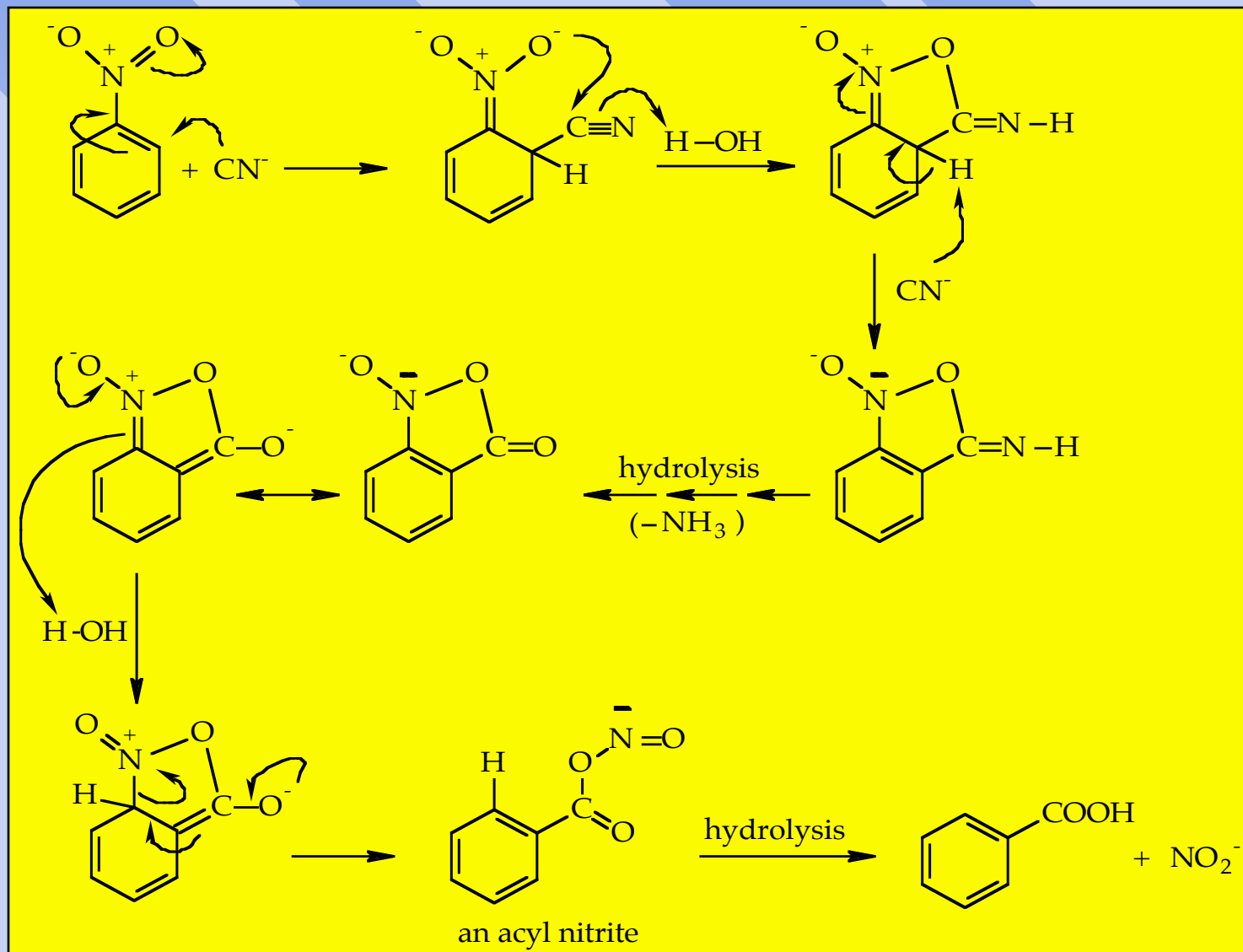
(a presumed intermediate)

Observation II:



Question: What can one conclude from the above observations?

VON RICHTER REACTION: REVISED BUNNETT MECHANISM



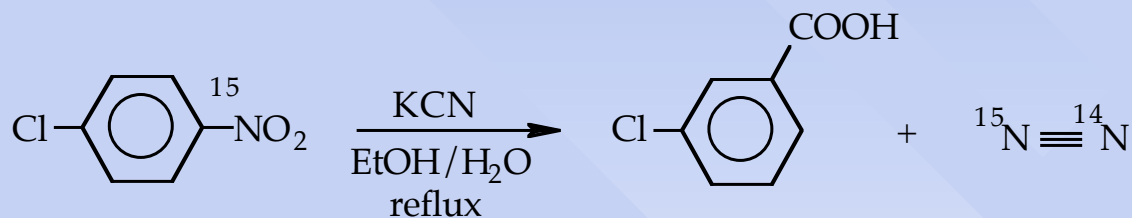
Rosenblum Observations (1960)

Observation I: Instead of nitrite, molecular nitrogen was a by-product of the von Richter reaction. Apparently, in the 1871 von Richter paper, nitrite had never been demonstrated to be a by-product. It had been deduced based on stoichiometry considerations.

Point of Interest: In the revised Bunnett mechanism, ammonia and nitrite are stipulated by-products of the von Richter reaction. Ammonia and nitrite can react to form ammonium nitrite which, upon heating, decomposes to give molecular nitrogen and water.

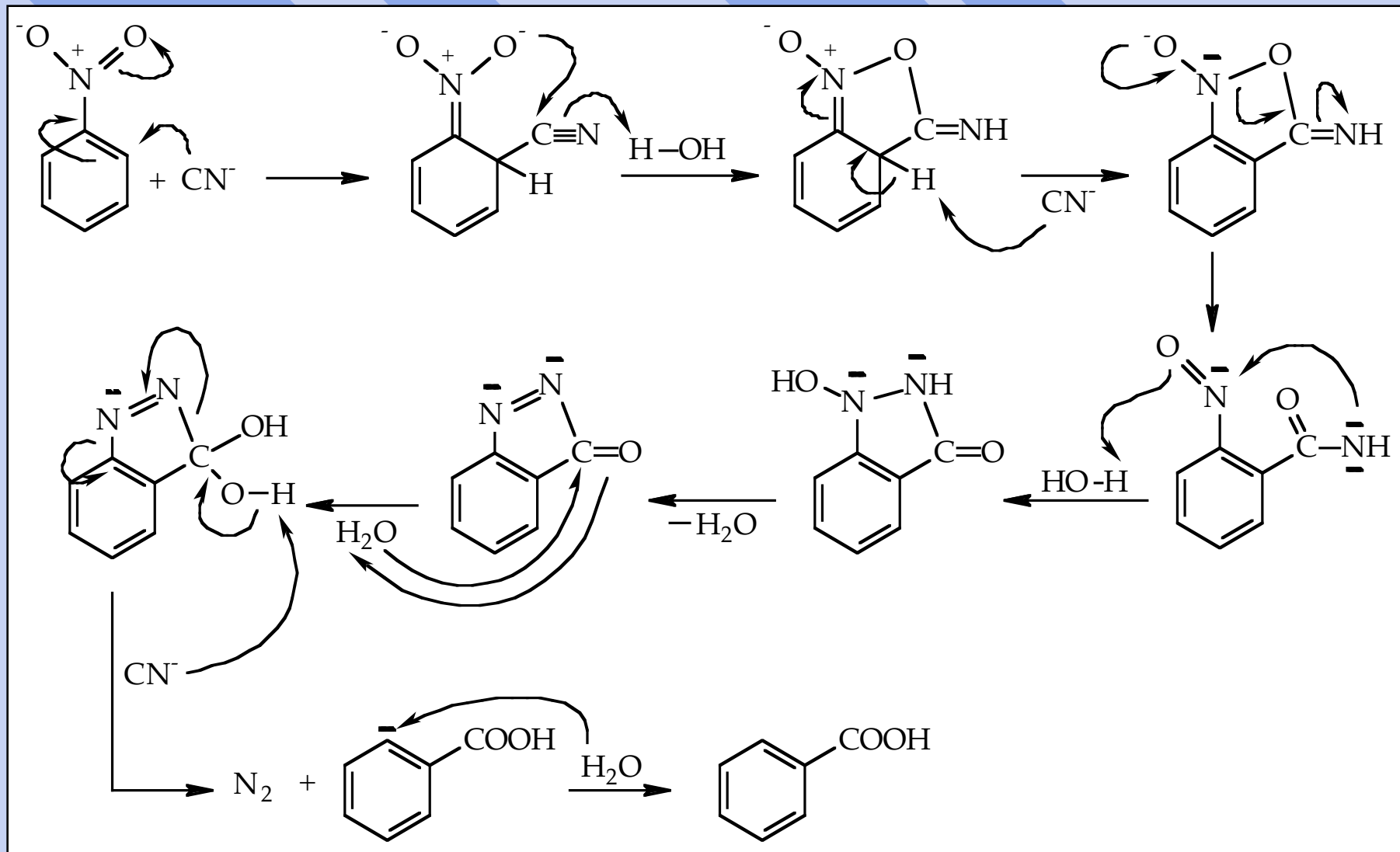
However: Upon addition of $^{15}\text{NH}_3$ to an on-going von Richter reaction, the only molecular nitrogen obtained contained no nitrogen-15! If the revised Bunnett mechanism were correct, the added $^{15}\text{NH}_3$ and the expelled NO_2^- (from the last step) should have produced $^{15}\text{N} \equiv ^{14}\text{N}$.

Observation II:



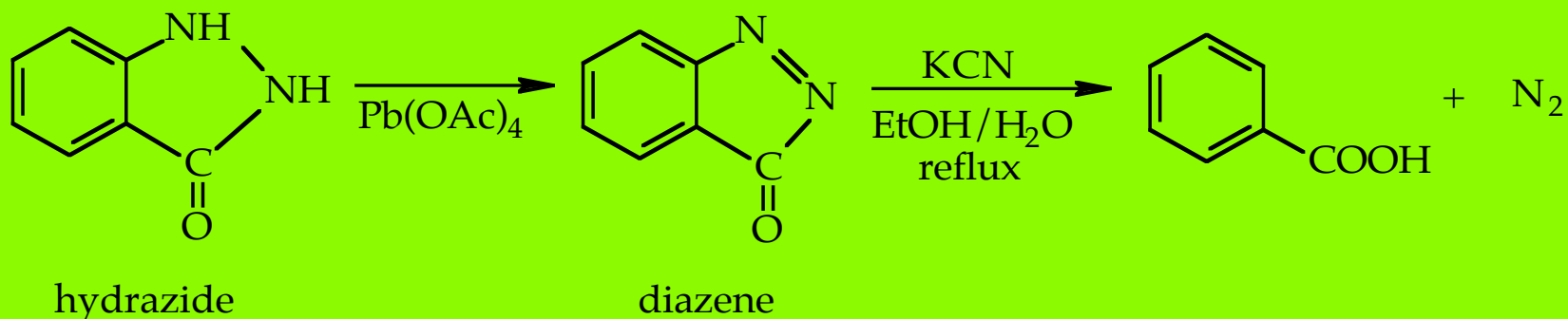
Conclusion: One nitrogen atom must come from the nitro group, and the second must come from the cyano group **intramolecularly!**

Accepted Mechanism for the von Richter Reaction



Supporting Evidence for the Rosenblum Mechanism

Ullman & Bartkus (1962):



Ibne-Rasa & Koubek (1963):

