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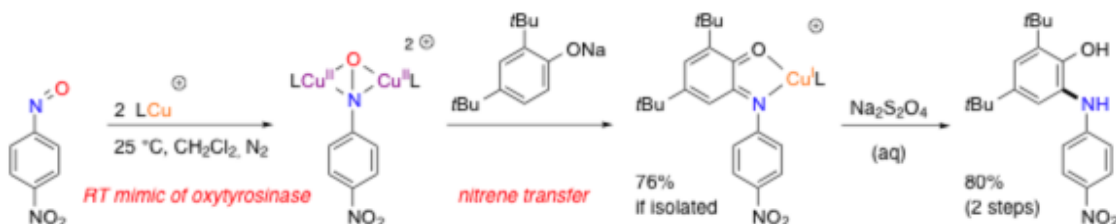
OR09 – Biomimetic Nitrene Transfer from Nitrosoarenes to Phenols

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The formation of dopaquinone during melanogenesis, catalyzed by the ubiquitous enzyme tyrosinase, involves the oxygenation of a phenolic C–H bond via a side-on peroxodicopper(II) species made by reaction between Cu(I) and O₂ at 25 °C. Performing model Cu(I)/O₂ reactions in solution, however, leads to complexes that are thermally unstable (–80 °C) and difficult to study. By substituting O₂ for isoelectronic nitrosoaryl compounds (Ar–N=O), the chemistry is similar but the ensuing Cu/nitrosoaryl complexes are stable at room temperature, and are thus more easily characterized and used.¹ Upon reaction with a phenolate, nitrene transfer occurs cleanly to yield a Cu-iminoquinone complex, which releases an aminophenol under reductive work-up (Scheme).² This reaction is analogous to the formation of quinones in Cu/O₂ chemistry, and comparison with our mechanism of the catalytic aerobic *ortho*-oxygenation of phenols³ provides hints on how to further develop this one-step C–H bond amination.



References

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3. Askari, M. S.; Esguerra, K. V. N.; Lumb, J.-P.; Ottenwaelder, X. *Inorg. Chem.* **2015**, 54, 8665.