Sorensen Group Problem Set
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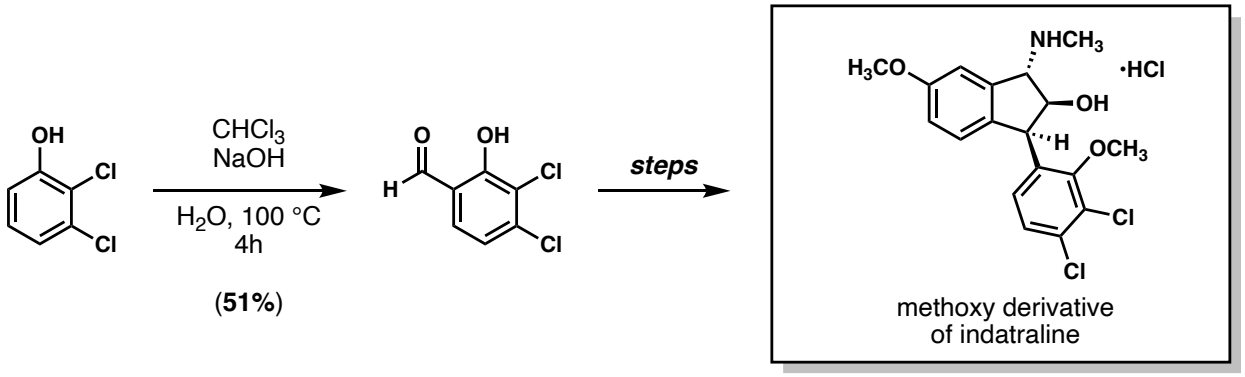
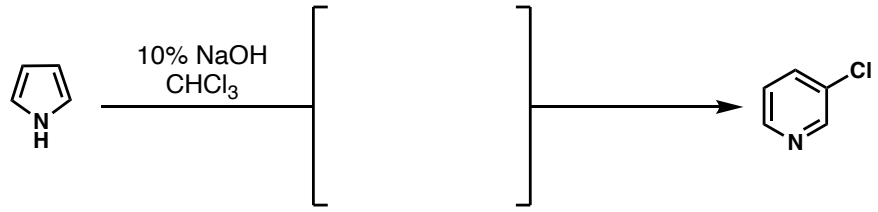
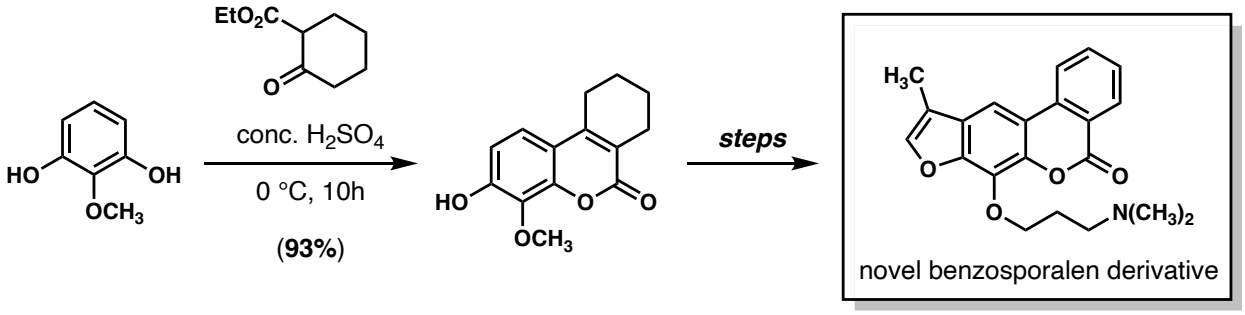
(**1**) Various methods for the formylation of aromatic compounds are known and utilized in either method development or total syntheses. These methods include the well-known Gattermann reaction, the Vilsmeier-Haack reaction and the Duff reaction. However, in 1876 two German chemists discovered yet another formylation strategy employing chloroform as the key reagent to arrive at the desired formylation products. What is the name of this transformation? Propose a mechanism for the reactions below. (*Ber. Dtsch. Chem. Ges.* **1876**, *9*, 423-424.)



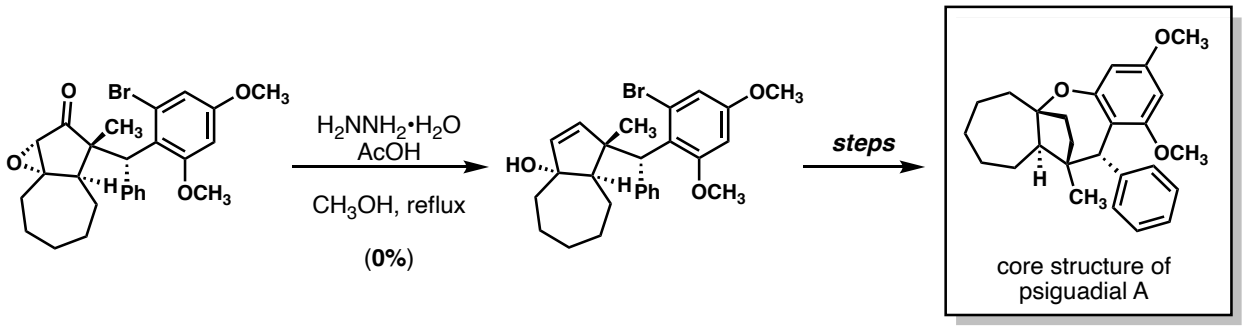
Bonus: provide a mechanism to show how pyrrole can be converted to 3-chloropyridine.



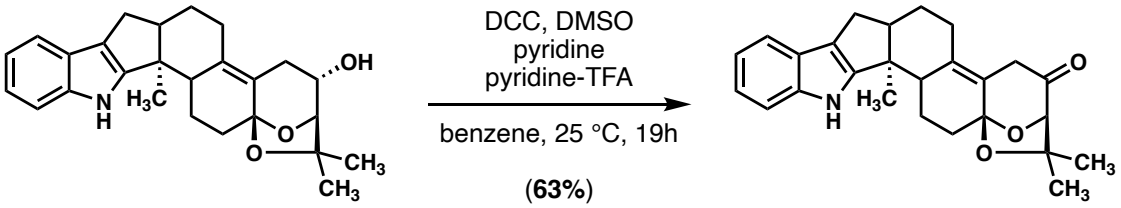
(**2**) Yet another fundamentally important named reaction was discovered in Germany in 1883, which allows for the facile construction of coumarin based organic compounds. The synthetic utility of this method was demonstrated in the research team of L.D. Via. Using this method, they were able to construct various photochemotherapy agents for use in PUVA therapy. What is the name of this transformation? Propose a mechanism for the reaction below. (*Ber. Dtsch. Chem. Ges.* **1883**, *16*, 2119-2128).

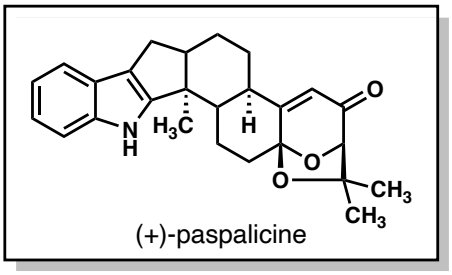


(**3**) During my PhD studies in the Chain lab at the University of Delaware, I was working towards the first total synthesis of psiguadial A. Psiguadial A was of particular interest to us not only due to its complex structure but also because of its biological activity in the HepG2 cell line (IC_{50} = 61 nM). We envisioned the transformation below, however after nearly 8 months of trial and error, no desired product was observed. What is the name of this transformation? Propose a mechanism for the reaction below. (*J. Org. Chem.* **1961**, *26*, 3615-3616).



(**4**) Various protocols to oxidize primary and secondary alcohols exist, however when a substrate is sensitive towards PCC and PDC conditions a milder protocol must be employed. This protocol was discovered in 1963 and allows for the oxidation of sensitive alcohols under mildly acidic conditions. This was shown in the endgame strategy for the total synthesis of (+)-paspalicine from the A. B. Smith lab. What is the name of this transformation? Propose a mechanism for the reaction below. (*J. Am. Chem. Soc.* **1963**, *85*, 3027-3028).





(+)-paspalicine

(**5**) The following reaction was discovered in Germany in 1880 and is an example of an interesting rearrangement under polar acidic conditions. Interestingly when ^{18}O-labeled water is used the product is also labeled. When one N in the starting material is selectively labeled with ^{15}N, the label is found to be randomly distributed in the product. What is the name of this transformation? Propose a mechanism for the reaction below. (*Chem. Ber.* **1880**, *13*, 525).