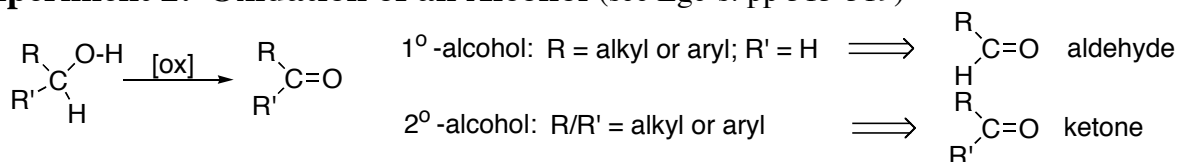
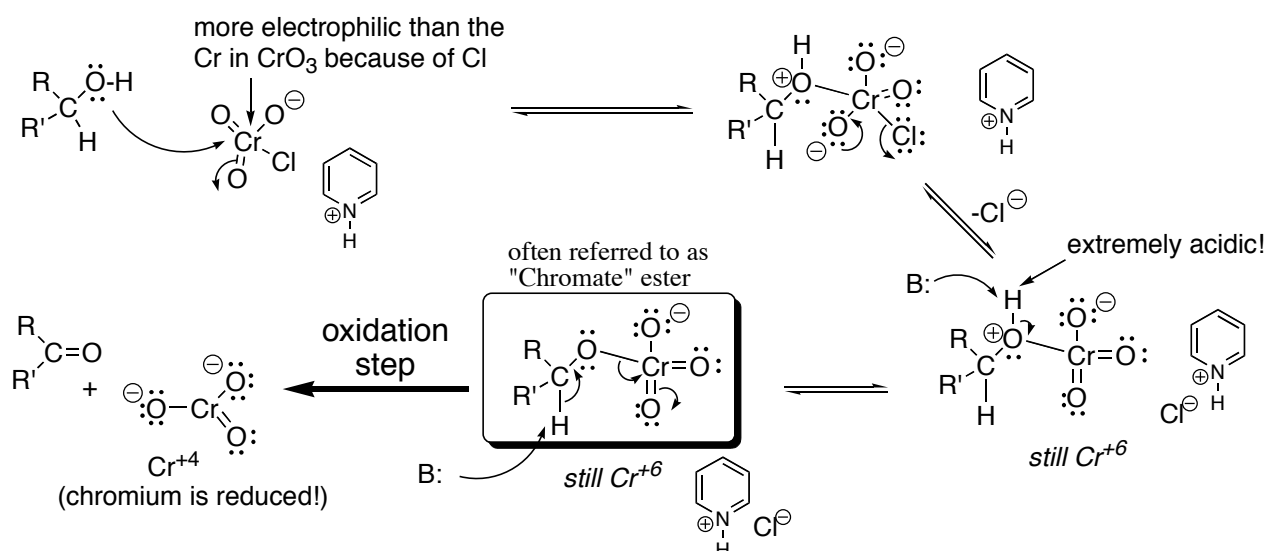


**Experiment 2. Oxidation of an Alcohol** (see Ege's: pp 515-519)

• A number of chromium (VI)-based reagents have been developed for the oxidation of alcohols, e.g., Jones' reagent [ $\text{CrO}_3/\text{H}_2\text{SO}_4/\text{acetone}/\text{water}$ ]. The oxidation of a primary alcohol by the use of the Jones' reagent results in the formation of mostly a carboxylic acid.

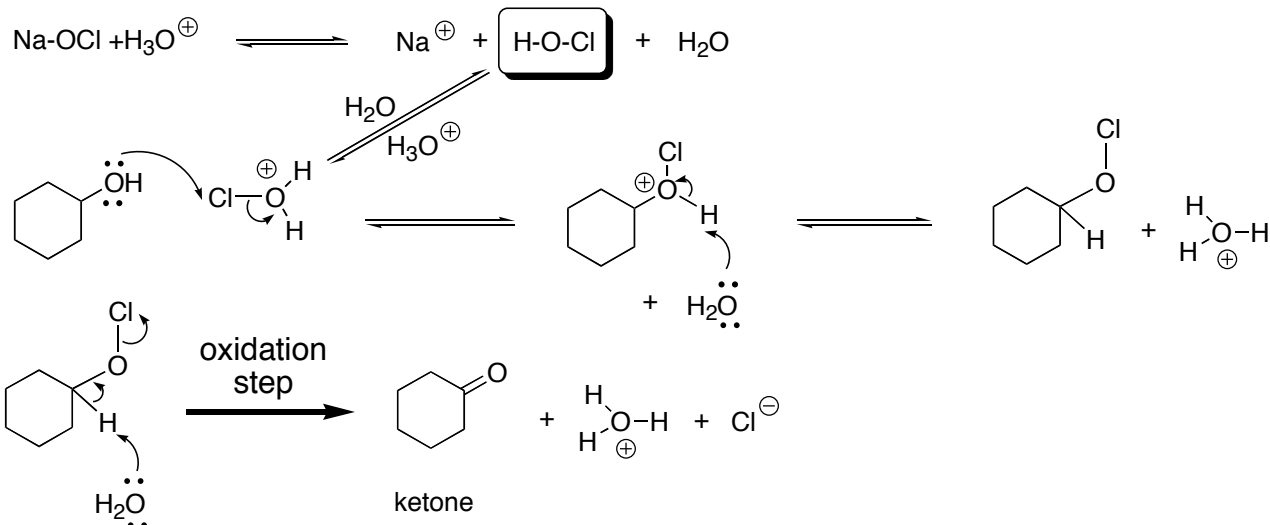
• Pyridinium chlorochromate (abbreviated as PCC; developed in 1975 by E. J. Corey) is one of the mildest and yet highly versatile reagents used for the oxidation of alcohols. With this reagent, the oxidation of a primary alcohol cleanly produces the corresponding aldehyde.

Mechanism of the PCC oxidation of an alcohol:



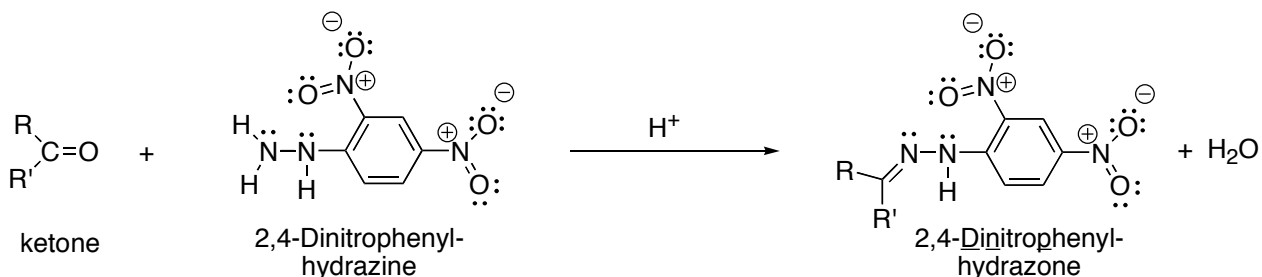
• Due to the suspected toxicity of Cr(VI)-based reagents, a number of alternate reagents have been developed. Oxidation of secondary alcohols can be efficiently achieved using much environmentally safer reagents such as a 5.25% (0.75M) sodium hypochlorite ( $\text{NaOCl}$ ) solution available in the grocery store as household bleach.

Mechanism of the oxidation with bleach:



**Notes for experimental procedures:**

1. The TLC spot of neither any of the alcohol we use nor the ketone product could be visible under the 254 nm UV lamp. Use the vanillin stain (this stain contains vanillin and conc. sulfuric acid in ethanol). After developing the spots, evaporate off the solvent from the plate and strongly heat the plate on a heater.
2. The ketone product is to be collected by the steam distillation.
3. The distillate obtained is to be extracted with ether.
4. Make the 2,4-DNP [2,4-dinitrophenylhydrazone] derivative of the ketone product and recrystallize the 2,4-DNP derivative from methanol (obtain the mp data as well as IR).

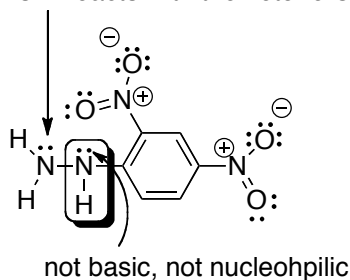


2,4-DNP derivative: usually highly crystalline and sharp melting solids

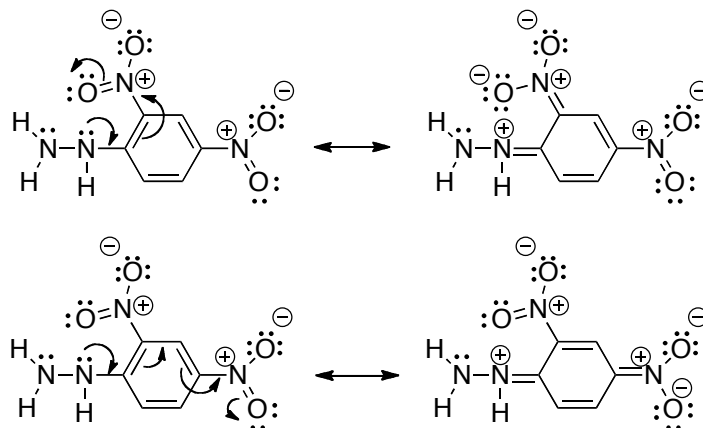
Mechanism of the 2,4-DNP formation:

See Ege's book (pp 575-576). Please note the mechanism for the formation of 2,4-DNP is essentially identical with that described for the formation of oximes. Simply replace the OH in the oxime formation with NHAr in the 2,4-DNP formation [Ar = 2,4-dinitrophenyl].

This N reacts with the ketone C=O!



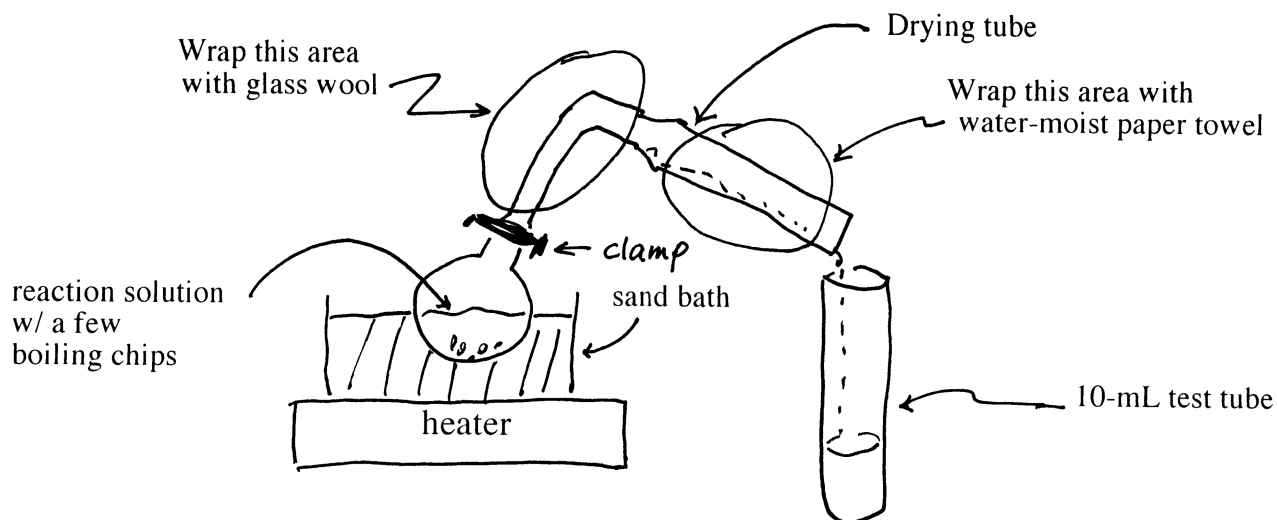
The internal NH lone pair electron is delocalized throughout the aromatic pi system and two nitro groups by extensive resonance.



Topic: Experiment 2 page 3 of 3.

**Steam distillation setup** [see: textbook, pp 141-150 (distillation) and 153-155 (steam distillation)].

Modified setup for this experiment:

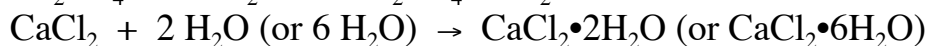
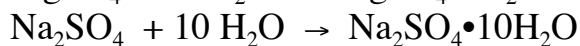
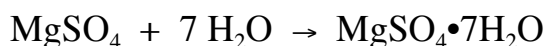


**Extraction procedure** [see: textbook, pp 128-137 (extraction) and 137-140 (drying)]

- The organic layer (i.e., ether in this case) used for extraction from an aqueous solution contains about 2%! of water in it. Thus, this organic layer needs to be dried.
- The organic layer is next washed with a roughly equal volume of *brine* (saturated aqueous NaCl). Brine is highly ionic, thus expelling non-ionic organic compounds/solvents out of the aqueous layer (i.e., brine).

“brine and water-immiscible organic solvents separate better → *drier* organic layer”

- The brine washed organic layer still contains a trace amount of water. In order to further remove water in the organic layer, an inorganic drying agent, for example, anhydrous  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$ , or  $\text{CaCl}_2$ , is used by taking advantage of the following chemical reactions with water.



These are semi-transparent crystalline water-containing inorganic salts. Water molecules are not simply adsorbed on the surface of these inorganics. These water molecules are ligands and are part of their crystalline structures.

- Remove the drying agent by gravity filtration and evaporate the organic solvent from the filtrate.