APPENDIX XV: FUNCTIONAL GROUP CLASSIFICATION TESTS

1. Carbon-Carbon Unsaturation (alkenes and alkynes)

a. Br_2/CCl_4: Add 1 drop (or a small spatula tip) of your sample to approximately 1 ml of 80:20 CCl_4/ethanol in a clean, dry test tube. Then add 5% Br_2 in CCl_4 dropwise to this solution. The disappearance of the bromine color indicates a positive test result.

b. $KMnO_4$: Add 1 drop (or a small spatula tip) of your sample to approximately 1 ml of acetone in a clean test tube. Add 1% aqueous $KMnO_4$ dropwise to this solution. The disappearance of the purple color of $KMnO_4$ and the appearance of a brown solid (MnO_2) constitutes a positive test result.

2. Alcohols

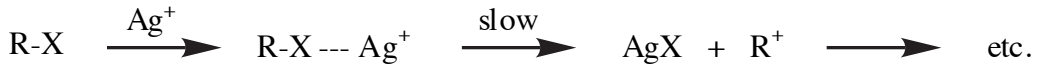
a. H_2CrO_4: Dissolve 1 drop (or a small spatula tip) of your sample in approximately 1 ml of acetone and add 1 drop of the orange-colored CrO_3/H_2SO_4 reagent. The disappearance of the orange color and the formation of a green precipitate within several seconds is a positive test result for 1º and 2º alcohols. 3º alcohols cannot be oxidized, so they will not give a green precipitate. If a negative test result is obtained, add two drops of ethanol to destroy the unreacted H_2CrO_4 and to observe what a positive test result looks like.

3. Halides

a. Beilstein test: Heat the looped end of a copper wire in the hot portion of a burner flame until no green color is imparted to the flame. This process is to clean all copper halides from the surface of the wire. Allow the wire to cool to room temperature and dip it into the compound to be tested. Place the wire into the flame immediately. There will be an initial yellow flame as the organic compound burns, followed by a green flame if the compound contains halogen.

b. Alcoholic $AgNO_3$: Add 1 drop (or a small spatula tip dissolved in a minimum amount of ethanol) of your sample to 2 mL of 2% ethanolic silver nitrate. If no reaction is observed within five minutes, boil the reaction mixture on a steam bath for several minutes. Note the color of any precipitate that forms. Silver chloride is white, silver bromide is pale yellow, and silver iodide is deep yellow.

This test depends on the rapid and quantitative reaction of silver nitrate with halide ion to produce an insoluble silver halide (except for the fluoride). Silver nitrate in aqueous or ethanolic solution gives an immediate precipitate with compounds such as acid halides, which react immediately with water or ethanol to produce halide ion. Many other halogen-containing substances react with silver nitrate to produce an insoluble silver halide. The rate of such reactions is a measure of the reactivity of the substrate in S_N1 reactions. Silver and other heavy metal salts catalyze S_N1 reactions of alkyl halides by complexation with the unshared electrons of the halogen



atom, making the leaving group a metal halide rather than a halide ion. The rate of precipitation of silver halide depends upon the halide (I > Br > Cl) and upon the structure of the alkyl group. Any structural factors which stabilize the electron-deficient carbocation intermediate, R^+, will accelerate the reaction. The expected order of reactivity is: tertiary > benzyl $\simeq$ allyl > secondary > primary > vinyl $\simeq$ aryl.

4. Ketones and Aldehydes

a. 2,4-Dinitrophenylhydrazine: Place approximately 1 ml of the 2,4-dinitrophenylhydrazine reagent in a small test tube. Dissolve 1 drop (or a small spatula tip) of your sample in about 1 ml of ethanol in another test tube and add this solution to the reagent. Mix them thoroughly and observe whether a yellow, orange or red precipitate of the corresponding 2,4-dinitrophenyl-hydrazone is formed. The formation of this precipitate is a positive test result for the carbonyl group of ketones and aldehydes. The color of the 2,4-dinitrophenylhydrazone derivative gives an indication of the carbonyl compound's degree of conjugation. Unconjugated ketones and aldehydes afford yellow precipitates. Moderately conjugated ketones and aldehydes give orange derivatives. Highly conjugated ketones and aldehydes yield red products. If there is any doubt about what a positive test result looks like, repeat the above steps with one drop of the ketone, acetone, as the substrate.

5. Carboxylic Acids

a. $NaHCO_3$: Place approximately 1 ml of 5% sodium bicarbonate solution in a small test tube, warm it on a steam bath, and add 1 drop (or a small spatula tip) of your sample to the solution. Watch for carbon dioxide evolution to occur as the sample dissolves. The evolution of carbon dioxide is a positive test result for carboxylic acids.