Iodoform Test

Functional Group(s): methyl ketones, some alcohols
Known(s): 1-butanol; 2-butanol, tert-butanol, phenol, decene

Procedure
Set up a test tube rack containing six, small (12 mm x 75 mm) test tubes. Label the test tubes 1-6. In test tube #1, dissolve ~10mg of a solid unknown or 4 drops of a liquid unknown in 1.5 ml of dioxane. In test tubes #2-6, dissolve the knowns in ~1.5 ml of dioxane. Vortex the tubes for ~30 seconds. Add .5ml of 10% NaOH to each tube and vortex again for 30-40 seconds. Add ~1ml of the iodoform reagent to each tube and heat the tubes (clamp them!) in a hot water bath for 2 minutes. If the dark color (the iodoform reagent is dark) is dissipated after heating for 2 minutes, add additional iodoform reagent, 5-7 drops at a time, until the dark color remains after heating for 2 minutes. Add 1.5 ml of distilled water to each tube and allow them to stand for ~15 minutes. Observe each tube for the formation of a precipitate. Compare results from the unknown with the results from the known compounds.

Results
The formation of a yellow, foul-smelling precipitate indicates the presence of a methyl ketone, acetaldehyde or compounds (some alcohols) that can be oxidized to a methyl ketone.

Theory
The iodoform reagent is a mixture of iodine (I₂) and potassium iodide (KI). Reaction of a methylketone with strong base promotes the formation of an enolate which reacts with the electrophilic I₂ to generate an α-iodomethylketone. Addition of two more equivalents of base and I₂ lead to formation of the α-triiodoketone. Hydroxide ion then reacts with the carbonyl carbon of the ketone in a nucleophilic acyl substitution, liberating iodoform (CHI₃) from the reaction mixture. Iodoform is not soluble in the reaction conditions and precipitates, indicating the reaction has occurred.

Only methyl ketones (not other types of ketones) can undergo the iodoform reaction because only methyl ketones have three H atoms on the a carbon which are necessary to form the iodoform product. Acetaldehyde has an α-methyl group which behaves the same as methylketones. Alcohols that upon oxidation form methyl ketones will also undergo this reaction.