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A scheme of qualitative organic analysis of Ketones.

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Boston University
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Thesis
A SCHEME OF QUALITATIVE ORGANIC ANALYSIS
OF KETONES
Submitted by
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Outline of Contents

I--Introduction----------------------------------------:~~e
II--Outline of Method of Procedure-----------------------6
III--The Ultimate Analysis of Organic Compounds--------10
IV--Methods of Procedure to Detect Ketones-----------12
V--General Physical and Chemical Properties of Ketones--18
VI--Specific and Semi-Specific Tests for Ketones-----21
   Acetone
   Acetophenone
   Benzalacetone
   Benzoin
   Benzophenone
   Camphor
   Ethyl Propyl Ketone
   Methyl Ethyl Ketone
VII--Experimental Procedure for Applying General
   Tests for Detecting Ketones (IV)------------------41
VIII--General Instructions for Applying Specific and
   Semi-Specific Tests for Ketones (VI)-------------44
IX--Condensed Tabular Form for Specific Tests for
   Ketones Group A----------------------------------47
   Group B-----------------------------------------49
   Colorations with Sodium Nitroprusside------------51
X--A Scheme for the Separation of Ketones and Identifi-
   cation of Individual Ketones Group A-------------53
   Group B-----------------------------------------58
XI--Bibliography--------------------------------------62
I---Introduction
I--Introduction

This thesis, suggested by Professor Newell, is a part of a more comprehensive plan to devise a scheme for the detection of common organic compounds. My problem was to check up such tests for ketones as have already been published, to search for group color tests or group precipitants, and to search for sub-groups and individual tests for compounds.

From this material I have finally devised a scheme which is adapted to the use of students in an elementary course in Organic Chemistry.

I have received suggestions from many texts, but I am indebted chiefly to the books of Samuel P. Mulliken and to Professor Newell who has directed my work and has given me valuable assistance.
II---Outline of Method of Procedure
So far as I know, there is at present no comprehensive yet simple plan for the identification of ketones. However, in Mulliken's "A Method for the Identification of Pure Organic Compounds", Volume I, I found a basis for such a scheme.

The tests which Mulliken describes are, in most cases, direct and conclusive; the directions are clear and full; the apparatus used in the tests is of comparative simplicity.

I have found valuable suggestions in W. A. Noyes's "Organic Chemistry for the Laboratory", a book which presents numerous references to the original literature, and also in J. F. Norris's "Experimental Organic Chemistry" and in Matthew Steel's "A Laboratory Manual of Organic Chemistry for Medical Students".

I have consulted Richter's "Organic Chemistry", Volumes I and II, as a reference book for the essential facts and principles on the subject of ketones.

Also, I am indebted to Allen's Commercial Organic Analysis", a nine-volume treatise on the properties and methods of detection of the various organic chemicals and products employed in the arts, manufactures, medicine, etc.

The bibliography at the conclusion of this thesis
contains a complete list of all the texts which I have consulted. In so far as it seemed profitable, I have worked out the analytical methods described in these books, adapted them to my purpose, and, in many cases, elaborated upon the tests.

The ketones with which I have experimented are

Acetone
Acetophenone
Benzalacetone
Benzoin
Benzophenone
Camphor
Ethyl Propyl Ketone
Methyl Ethyl Ketone

In selecting these from the vast number of organic substances as best adapted for a work of this kind, compounds have, as a rule, been excluded which might present some inherent difficulty in being procured or some danger or discomfort on being analyzed.

I have attempted to present the results of my work in a complete, yet direct manner, omitting no test merely because it did not accord strictly with the results of other investigations.

In the selection and order of arrangement of the
several subjects, I have followed this plan:—I have first presented two methods of procedure to be employed in detecting the presence of a ketone; next, I have endeavored to describe briefly the more important general physical and chemical properties of the ketones. Following this is a compilation of "Specific and Semi-Specific Tests for Ketones" arranged according to the individual compounds. Many of these tests are to be found among existing analytical methods; many are original. After some brief directions for applying these general and individual tests, I have collected, classified, and arranged these tests in a condensed tabular form. They are included in two groups: in Group A are to be found the tests for solid ketones having a melting point above 30°C; Group B comprises the tests for those ketones which are liquids or solids melting below 30°C. In conclusion, I have described and outlined a method or scheme of analysis to be employed in the identification of an unknown compound. The bibliography at the end contains a list of all the books to which I am in any way indebted for information and suggestions on the subject of ketones.
III---The Ultimate Analysis of Organic Compounds
III---The Ultimate Analysis of Organic Compounds

Carbon,
Hydrogen,
Sodium Fusion,
Sulphur,
Nitrogen,
Phosphorus,
Iodine,
Bromine,
Chlorine.

This procedure is identical with that described in the thesis of Mr. Edward V. Atwood (1921), entitled "A Scheme of Organic Analysis of Phenolic Compounds and Aldehydes," pages 6 to 11. There is, therefore, no need of repeating the procedure in this thesis.
IV---Methods of Procedure to Detect Ketones.
IV—Methods of Procedure to Detect Ketones.

The test by means of which the presence of a ketone is detected differs according as it is to be applied to solid ketones melting above thirty degrees Centigrade or to liquid ketones and to solid ketones melting below thirty degrees Centigrade. There are two procedures, Procedure A and Procedure B.

Procedure A is to be employed if the compound under examination has a melting point above 30° C.

Procedure B is to be employed if the compound under examination is a liquid or a solid having a melting point not higher than 30° C.

Procedure A:—Hydroxylamine Test.

Fit two dry six-inch test tubes with perforated rubber stoppers, through each of which a meter length of glass gas delivery-tubing 7-8 mm. in internal diameter has been inserted. In the first test tube place 0.04-0.06 gm. of the powdered substance, 0.5 cc. of hydroxylamine hydrochloride solution, and 2 cc. of alcoholic sodium hydroxide solution.

Reagents for this test:—

(1) The hydroxylamine hydrochloride solution is made by dissolving 7.25 gm. of the solid hydroxylamine hydrochloride in 9 cc. of water and diluting this to 35 cc. with strong alcohol.
(2) The alcoholic sodium hydroxide solution is made by dissolving 10 gm. of sodium hydroxide in 20 cc. of hot distilled water and then diluting this to 140 cc. with strong alcohol.

Charge the second test tube which is to be used as a blank experiment in the same manner except that 0.5 cc. of 25 % alcohol is to be substituted for the hydroxylamine solution. Support both tubes by clamps in vertical positions so that their lower extremities may be heated by immersion in a water bath which is at a temperature of 100° C. or in a beaker nearly filled with water already boiling. Allow the solutions to boil up briskly for at least five minutes.

Then cool; dilute each with 10 cc. of cold water and shake vigorously to precipitate out any substances insoluble in dilute aqueous alkali. Filter through double wetted filters, repeating, if necessary, until clear filtrates are obtained. Add one drop of phenolphthalein to each filtrate and then dilute hydrochloric acid, drop by drop, until the red color is just discharged. Again close the mouth of each test tube and shake vigorously. Note whether the solutions remain clear, become turbid, or opaque, or give precipitates.

If the solution from the tube to which hydroxylamine was added gives a precipitate, or becomes opaque after neutralization with acid and shaking, while the solution in the blank experiment remains clear or only becomes slightly tur-
bid, the compound under examination is a ketone. The precipitate in this case consists of an oxime which is soluble in alkali, but not in neutral aqueous solution. A majority of oximes which are precipitated in this test dissolve in an excess of cold dilute hydrochloric acid to clear solutions from which they may be again precipitated by neutralization and shaking.

Procedure B—Phenylhydrazine Test.

If the unknown compound is readily soluble in water, dissolve one drop in 2 cc. of cold water in a dry 6-inch test tube and add 4 drops of a phenylhydrazine solution. (1)

(1) The phenylhydrazine solution is prepared by mixing 0.3 cc. of glacial acetic acid with 7.0 cc. of cold water and adding to the mixture 2 cc. of light colored phenylhydrazine. This will keep five days if not exposed to the light.

If the compound is not soluble in water, substitute for the latter 2 cc. of dilute alcohol (1 volume of strong alcohol to 2 volumes of water). It is not necessary in this case that the substance should dissolve visibly.

Suspending the test tube by its lip between the thumb and forefinger, sway it from side to side with a slow pendulum motion (one or two swings a second) for at least a minute. Vigorous shaking might spoil the test by breaking
up a difficultly soluble substance into minute droplets and forming an opaque emulsion.

If the solution remains clear, stopper the test tube very loosely with a clean cork and stand it upright in a beaker containing a layer of water 2-3 cm. deep. Have the water gently boiling at the moment when the tube is introduced, and continue to heat to 100°C for five minutes. The water in the beaker should not boil actively during this period, for the steam arising then heats the side walls of the test tube to such an extent that the loss of alcohol by evaporation may become too important a factor in the final result and violent bumping may cause emulsion of the original mixture. Whenever this test in hot solution has to be applied a blank experiment must be made at the same time using the same quantities of the substance and solvent, but omitting the phenylhydrazine.

If the solution still remains clear after it has been heated for five minutes, remove it from the waterbath, and, after allowing it to stand 25-30 seconds, carefully observe its degree of transparency and its color. The delay in making this observation is mainly to permit suspended drops of unchanged substance to settle out. The appearance of a precipitate or opacity after 30 seconds may be caused by separation of the original substance from its supersat-
urated solution and without significance.

To test for opacity, hold the test tube in front of and in actual contact with a piece of white paper on which a small cross has been drawn in black ink in lines 1 mm. in width. If the cross cannot be seen through the solution when the position of the test tube is slightly changed, the solution is to be considered "opaque".

An opaque solution shows the presence of a ketone.
V—General Physical and Chemical Properties of Ketones.
V—General Physical and Chemical Properties of Ketones.

The ketones are closely related to the aldehydes and strongly resemble them in chemical behaviour. On reduction they yield secondary alcohols, while oxidation takes place with much more difficulty than with the aldehydes, because here oxidation involves a rupture of the carbon chain.

The ketones are neutral bodies; they range from volatile, ethereal-smelling liquids to crystalline solids. They all possess characteristic odors and tastes and give numerous color reactions. The tests with sodium nitroprusside, concentrated sulphuric acid and concentrated nitric acid, especially, result in distinctive colorations. There is evidence that concentrated nitric acid converts some of the ketones into dinitro-paraffins, though diketones may be formed at the same time if the ketone is suitably constituted. Under the influence of concentrated sulphuric acid, acetone and other ketones having a suitable constitution change into trialkyl benzenes.

The ketones never undergo polymerization. With hydroxylamine they yield ketoximes, with phenylhydrazine they form hydrazones, and with semicarbazide they give semicarbazones. Many of these compounds crystallize definitely and are valuable in the identification of certain ketones. Towards certain reagents like sodium bisulphite many ketones
act like unsaturated compounds. These, like the corresponding aldehyde compounds, can be considered as salts of sulphurous acid esters. These double salts are very suitable for the isolation and purification of the ketones which can be liberated from them by the action of dilute sulphuric acid or a sodium hydroxide solution. A negative result with the alkali bisulphites does not necessarily indicate that the substance is not a ketone.
VI—Specific and Semi-Specific Tests for Ketones.
VI---Specific and Semi-Specific Tests for Ketones.

Acetone

Acetone, CH₃.CO.CH₃, is a colorless liquid of a peculiar, not disagreeable odor, and burning taste. It boils at 57°C, and is miscible in all proportions with water as well as with alcohol and ether; its specific gravity is 0.819.

Benzaldehyde Test--Place in a dry 6-inch test tube 2 drops of the ketone and 0.4 cc. of cold water. Add 0.4 cc. of benzaldehyde and 2.0 cc. of strong alcohol and 0.5 cc. of a 10% aqueous solution of sodium hydroxide. Mix by shaking. Boil gently over a small flame for one minute, counting the time from the moment when the mixture actually boils. (If no precipitate appears, cool, shake vigorously, and proceed.) Filter off the crystals and wash with 2 cc. of cold strong alcohol. Recrystallize from 2 cc. of boiling alcohol. Cool, and, if necessary, shake persistently until crystals appear. Filter, wash with 10 cc. of cold strong alcohol, and dry half an hour or longer at 100°C. In taking the melting point raise the temperature at the rate of about one degree in 20 seconds. The product formed in this test is benzylideacetone (C₆H₅.CH.CH₂)₂CO. It crystallizes in pale yellow, lustrous plates which melt at 111°-112°C. Time--50 minutes.
Sodium Nitroprusside Test—Shake 5 drops of the ketone with 2 cc. of cold water, add 2 drops of a 1% aqueous solution of sodium nitroprusside and 2 drops of sodium hydroxide (1:10). The solution becomes orange. Divide it into two equal portions, "a" and "b". To portion "b" add 3 drops of glacial acetic acid; "b" assumes a red coloration with a tendency to purple. At the end of twenty minutes "a" fades to yellow but the color of "b" still persists.

Time—25 minutes.

Iodoform Test—To about 5 cc. of dilute acetone solution (25% acetone) add 10 drops of 6 N. sodium hydroxide and then, drop by drop, iodine solution (2% potassium iodide solution, with enough iodine to color it yellow) until the liquid becomes yellow. The presence of iodoform may be detected by its odor.

Time—3 minutes.

Salicylic Aldehyde Test—To 10 cc. of dilute acetone solution (20% acetone) add about one gram of solid potassium hydroxide and, before it dissolves, introduce 10 drops of salicylic aldehyde; warm to 70°C. on a water bath. A purple-red ring appears; if the potassium hydroxide is dissolved before the addition of the salicylic aldehyde the liquid becomes yellow, then reddish and finally turns purple-red.

Time—10 minutes.
**Mercuric Chloride Test**—A saturated mercuric chloride solution is precipitated by alcoholic sodium hydroxide. (Directions for the preparation of this reagent will be found under "Procedure A"—IV.) To 5 cc. of this add 1 cc. of the liquid to be tested, shake well, and filter. In the presence of acetone the filtrate contains mercury which may be detected by ammonium sulphide. Time—5 minutes.

**Bisulphite Test**—To 3 cc. of a saturated solution of sodium bisulphite add 2 cc. of the ketone. Crystals will settle out on standing; it may be necessary to let it remain over night.

**Sulphuric Acid Test**—To 5 drops of the ketone add 2 cc. of concentrated sulphuric acid. An orange yellow solution results. Time—2 minutes.

**Test with Sulphuric and Nitric Acids**—Shake 5 drops of the ketone with 2 cc. of concentrated sulphuric acid; then add gradually 2 cc. of concentrated nitric acid. This gives a wine-colored solution. Time—5 minutes.

**Bromine Water Test**—To 5 drops of the ketone add 2 cc. of concentrated nitric acid and 1 cc. of bromine water. The solution is decolorized. Time 5 minutes.
Acetophenone

Acetophenone, CH₃.OO.C₆H₅, is insoluble in water, but soluble in alcohol and in ether. It melts at 20.50°C, boils at 202°C, and has an aromatic odor. It does not combine with sodium bisulphite, but it forms most of the derivatives and condensation products which characterize the ketones.

Phenylhydrazine Test--Place 2 drops of the ketones and 4 drops of phenylhydrazine (see "Procedure B"--IV) in a dry test tube and heat until the mixture begins to boil. Cool, and add 10 drops of glacial acetic acid and 10 cc. of water. Shake vigorously and filter off the crystals. Recrystallize from 12 cc. of boiling 50% alcohol. Allow to cool slowly. Filter; wash with 3 cc. of 50% alcohol. Remove the mother liquor on a porous tile, and then dry 10-15 minutes at 500-600°C in the dark. This must be done consecutively and the melting point determined at once. Acetophenonephenylhydrazone is a rather unstable body and is liable to undergo slight decomposition on drying. It shows signs of softening at 100°C and is completely melted at 103°C.

Time--40 minutes.

Sodium Nitroprusside Test--Shake 5 drops of the ketone with 2 cc. of cold water. Filter through a wet filter and to the
clear solution add 2 drops of a 1% aqueous solution of sodium nitroprusside, and then 2 drops of sodium hydroxide (1:10). The solution is red with a slight tendency to violet-red. Divide it into two portions, "a" and "b", and to portion "b" add 3 drops of glacial acetic acid. This portion changes to a strong blue. At the end of 20 minutes "a" has changed to yellow, "b" has faded one tint. Time--25 minutes.

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Salicylic Aldehyde Test--To 10 cc. of dilute acetophenone solution (20% acetophenone) add 1 gm. of solid potassium hydroxide and 10 drops of salicylic aldehyde. Warm to 70°C on a waterbath. A purple-red ring appears or the entire solution may be colored purple-red. Time--10 minutes.

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Concentrated Sulphuric Acid Test--To 5 drops of the ketone add 2 cc. of concentrated sulphuric acid. A brown viscous liquid results. Time--3 minutes.

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Concentrated Nitric Acid Test--To 5 drops of the ketone add 2 cc. of concentrated nitric acid. The solution is colored yellow. Time--3 minutes.
Test with Concentrated Sulphuric and Nitric Acids.—Shake 5 drops of the ketone with 2 cc. of concentrated sulphuric acid; then add gradually, 2 cc. of concentrated nitric acid. This gives a brown viscous solution. Time—5 minutes.

Bromine Water Test.—To 5 drops of the ketone add 2 cc. of concentrated nitric acid and 1 cc. of bromine water. This is decolorized. Time—5 minutes.
Benzalacetone

Benzalacetone, CH₃.CO.CH.CH₆H₅, is a solid crystallizing in the form of yellow tabular crystals. It boils at $\Delta_0^°$ C., melts at $\Delta_0^°$ C., and has a characteristic odor. It is insoluble in cold water but soluble in alcohol and in ether. With sodium bisulphite and hydroxylamine benzalacetone forms compounds which crystallize definitely.

Sodium Nitroprusside Test--Shake 0.05 gm. of the powdered substance with 2 cc. of alcoholic sodium hydroxide (see "Procedure A"--IV) and add 2 drops of a 1 % aqueous solution of sodium nitroprusside. The solution is violet. Divide it into two portions, "a" and "b". To "b" add 3 drops of glacial acetic acid. This portion changes to a deep blue. At the end of 20 minutes both portions have faded about one tint.  

Time--25 minutes.

Salicylic Aldehyde Test--To 0.05 gm. of the powdered substance in 10 cc. of water, add 1 gm. of solid potassium hydroxide and 10 drops of salicylic acid. Warm to 70° C. an water bath. A purple-red ring appears or the entire solution may be colored purple-red.  

Time--10 minutes.

Concentrated Hydrochloric Acid Test--To 0.05 gm of the substance add 2 cc. of concentrated hydrochloric acid. The solution is colored yellow, the undissolved crystals red.  

Time--3 minutes.
Concentrated Sulphuric Acid Test--To 0.05 gm. of the substance add 2 cc. of concentrated sulphuric acid. A clear yellow brown liquid results. Time--3 minutes.

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Concentrated Nitric Acid Test--To 0.05 gm. of the substance add 2 cc. of concentrated nitric acid. The resulting liquid is yellow, with an orange-colored oil on top.

Time--3 minutes.

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Concentrated Sulphuric and Nitric Acids--To 0.05 gm. of the substance add 2 cc. of concentrated sulphuric acid and then gradually 2 cc. of concentrated nitric acid. A clear brown liquid results. Time--5 minutes.

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Bromine Water Test--To 0.05 gm. of the substance add 2 cc. of concentrated nitric acid and 1 cc. of bromine water. This is decolorized and an opaque solution results.

Time--5 minutes.
Benzoin

Benzoin, \( \text{C}_6\text{H}_5.\text{CH(OH).CO.C}_6\text{H}_5 \), is a solid ketone; it occurs in the form of pale, sulphur-yellow, fluorescent, hexagonal crystals. It is insoluble in cold water, soluble in hot alcohol. It melts at 133° C., boils at 343° C. On being heated it gives off the odor of benzaldehyde.

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Fehling’s Solution Test—Heat 0.05 gm. of the substance with 5 cc. of Fehling’s solution. (The solution used is Benedict’s Modification of Fehling’s Test: Dissolve 173.0 gm. of sodium citrate and 100 gm. of sodium carbonate in 600 cc. of water. Filter, if necessary, and make up to 850 cc. Dissolve 17.3 gm. of copper sulfate in water and make up to 150 cc. To the solution containing the sodium citrate and sodium carbonate add the copper sulfate solution with constant stirring.) A red precipitate forms, showing that the Fehling’s solution is easily reduced.

Time—5 minutes.

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Sodium Hydroxide Test—If 0.05 gm. of benzoin is boiled with 10 cc. of normal sodium hydroxide in a porcelain dish while air is blown through it it assumes an R V T color.

Time—5 minutes.

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Molisch Test—Heat 0.05 gm. of the substance with 5 cc. of Molisch solution to boiling. (The Molisch solution is a 15%
alcoholic solution of alpha naphthol.) The solution is de-
colorized. Time--5 minutes.

Concentrated Nitric Acid Test--Heat 0.05 gm. of the substance
with 2 cc. of concentrated nitric acid; the solid dissolves.
Benzoin is insoluble in cold nitric acid.

Time--5 minutes.

Concentrated Sulphuric Acid--To 0.05 gm. of the substance
add 2 cc. of concentrated sulphuric acid. An olive green
coloration results. Time--5 minutes.

Test with Concentrated Sulphuric and Nitric Acids--To 0.05
gm. of the substance add 2 cc. of concentrated sulphuric acid
and then gradually 2 cc. of concentrated nitric acid. This
produces a clear wine-colored solution.

Time--5 minutes.
Benzophenone

Benzophenone, C₆H₅.CO.C₆H₅, is a crystalline solid of characteristic, faintly aromatic odor. It melts at 46° C. and boils without decomposition at 307° C. It is insoluble in water, slightly soluble in alcohol, and very soluble in ether.

Hydroxylamine Test—Convert 0.05 gm. of the substance into benzophenoneoxime following the regular method of Procedure 1, except that the period of heating should be extended to ten minutes. After the precipitation of the oxime with acid, collect in the point of a small filter, and wash it thoroughly with 10-15 cc. of cold water applied in small successive portions. Dry for half an hour and determine the melting point. Benzophenoneoxime is obtained in this test as a floculent white precipitate soluble in acids or caustic alkalies and melting at 141°-142° C. Time—40 minutes.

Concentrated Hydrochloric Acid Test—To 0.05 gm. of the powdered substance add 2 cc. of concentrated hydrochloric acid. This gives a yellow orange coloration. Time—3 minutes.
Concentrated Nitric Acid Test--To 0.05 gm. of the powdered substance add 2 cc. of concentrated nitric acid. A clear yellow solution with a yellow oil on top results. Time--3 minutes.

Concentrated Sulphuric Acid Test--To 0.05 gm. of the powdered substance add 2 cc. of concentrated sulphuric acid. A clear yellow solution results. Time--3 minutes.

Concentrated Sulphuric and Nitric Acids Test--To 0.05 gm. of the powdered substance add 2 cc. of concentrated sulphuric acid and then gradually 2 cc. of concentrated nitric acid. A yellow coloration results. Time--5 minutes.
Camphor Dextro-rotary

Camphor, C₁₀H₁₆O, is slightly soluble in water; soluble in alcohol, and very soluble in ether. It melts at 176.4⁰ C., boils at 205.3⁰ C. It occurs in the form of tough, white, slightly unctuous crystals, with a peculiar penetrating, fragrant odor, and a bitter, pungent taste. Small fragments of camphor thrown upon pure water float and assume irregular circulatory movements which immediately cease upon the addition of a drop of oil. Camphor is very volatile, subliming crystalline on the sides of the vessel in which it is contained at ordinary temperatures.

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Hydroxylamine Test—Convert the ketone into the oxime, according to Procedure A, using twice the specified quantities and boiling for one hour instead of for 5 minutes. Collect on a small filter and wash with 10 cc. of cold water applied in small portions, the filter being allowed to drain after each addition. Dry at about 50⁰ C. for 20 minutes and determine the melting point. Camphor oxime melts at 118⁰-119⁰ C.

Time—90 minutes.

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Concentrated Nitric Acid Test—To 0.05 gm. of the powdered substance add 2 cc. of concentrated nitric acid. This gives a pink coloration; a colorless oil remains on the surface of
the liquid. \hspace{1cm} \text{Time} \hspace{0.5cm} \text{3 minutes.}

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\textbf{Concentrated Sulphuric Acid Test} -- To 0.05 gm. of the powdered substance add 2 cc. of concentrated sulphuric acid. An orange coloration results. \hspace{1cm} \text{Time} \hspace{0.5cm} \text{3 minutes.}

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\textbf{Concentrated Sulphuric and Nitric Acid Test} -- To 0.05 gm. of the substance add 2 cc. of concentrated sulphuric acid and then gradually 2 cc. of concentrated nitric acid. A clear orange solution results. \hspace{1cm} \text{Time} \hspace{0.5cm} \text{5 minutes.}

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**Ethyl Propyl Ketone**

Ethyl Propyl Ketone, \( \text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{C}_3\text{H}_5 \), is a yellow liquid with a characteristic alcoholic-ethereal odor. It boils at 102° C., and has a specific gravity of 0.812. It is very slightly soluble in water; but soluble in alcohol and in ether.

Fehling's Solution Test—To 1 cc. of the ketone add 5 cc. of Fehling's solution and heat to boiling. The solution becomes green. Time—5 minutes.

Concentrated Hydrochloric Acid Test—To 5 drops of the ketone add 2 cc. of concentrated hydrochloric acid. An opaque orange-brown liquid results. Time—5 minutes.

Mercuric Chloride Test—A saturated mercuric chloride solution is precipitated by alcoholic sodium hydroxide. To 5 cc. of this add 1 cc. of the liquid to be tested, shake well, and filter. In the presence of ethyl propyl ketone the filtrate contains mercury which may be detected by ammonium sulphide. Time—5 minutes.

Concentrated Nitric Acid Test—To 5 drops of the ketone add 2 cc. of concentrated nitric acid. The liquid separates
into two layers; the lower one is orange, the upper, red.

Time--5 minutes.

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**Bromine Water Test**--If 2 cc. of concentrated nitric acid are added to 5 drops of the ketone and 1 cc. of bromine water then introduced, the bromine water is not discolorized and a dark upper layer separates from the orange solution.

Time--5 minutes.

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**Salicylic Aldehyde Test**--To 10 cc. of dilute ethyl propyl ketone (20 % ethyl propyl ketone) add 1 gm. of solid potassium hydroxide and 10 drops of salicylic aldehyde. Warm to 70° C. on a water bath. A purple-red ring appears or the entire solution may be colored purple-red.

Time--10 minutes.

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**Sodium Nitroprusside Test**--Shake 5 drops of the ketone with 2 cc. of cold water. Filter through a wet filter and to the clear solution add 2 drops of a 1 % aqueous solution of sodium nitroprusside, and then 2 drops of sodium hydroxide, (1 : 10). The solution is red. Divide it into two equal portions, "a" and "b". To portion "b" add 3 drops of glacial acetic acid; "b" remains red. At the end of 20 minutes "a"
changes to orange but the color of "b" still persists.

Time--24 minutes.

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Concentrated Sulphuric Acid Test--To 5 drops of the ketone add 2 cc. of concentrated sulphuric acid. A wine-colored solution results.

Time--3 minutes.

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Concentrated Sulphuric and Nitric Acid Test--To 5 drops of the ketone add 2 cc. of concentrated sulphuric acid and then gradually 2 cc. of nitric acid. A yellow orange coloration results.

Time--5 minutes.
Methyl Ethyl Ketone

Methyl Ethyl Ketone, CH₃.CO.C₂H₅, is a colorless liquid with an odor like that of acetone. It has a specific gravity of 0.805 and boils at 81°C. It is soluble in water, alcohol, and ether.

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Concentrated Hydrochloric Acid Test--To 5 drops of the ketone add 2 cc. of concentrated hydrochloric acid. A clear brown solution results. Time--3 minutes.

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Mercuric Chloride Test--A saturated mercuric chloride solution is precipitated by alcoholic sodium hydroxide. To 5 cc. of this add 1 cc. of the liquid to be tested, shake well, and filter. In the presence of methyl ethyl ketone the filtrate contains mercury which may be tested by ammonium sulphide. Time--5 minutes.

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Concentrated Nitric Acid Test--To 5 drops of the ketone add 2 cc. of concentrated nitric acid. This gives a brownish orange coloration. Time--3 minutes.

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Bromine Water Test--If 2 cc. of concentrated nitric acid are added to 5 drops of the ketone and 1 cc. of bromine water then introduced, the solution is decolorized. Time--5 minutes.
Salicylic Aldehyde Test--To 10 cc. of methyl ethyl ketone (20% methyl ethyl ketone) add 1 gm. of solid potassium hydroxide and 10 drops of salicylic aldehyde. Warm to 70°C on a water bath. A purple-red ring appears or the entire solution may be colored purple-red.

Time--10 minutes.

Sodium Bisulphite Test--To 3 cc. of a saturated solution of sodium bisulphite add 2 cc. of the ketone. Crystals deposit gradually on standing; it may be necessary to let them stand over night.

Sodium Nitroprusside Test--Shake 5 drops of the ketone with 2 cc. of cold water, add 2 drops of a 1/3 aqueous solution of sodium nitroprusside and 2 drops of sodium hydroxide, (1:10). The solution becomes red. Divide it into two equal portions, "a" and "b". To portion "b" add 3 drops of glacial acetic acid; "b" assumes an orange coloration. At the end of 20 minutes "a" has changed to yellow but the color of "b" still persists. Time--25 minutes.

Concentrated Sulphuric Acid Test--To 5 drops of the ketone add 2 cc. of concentrated sulphuric acid. A red color results.

Time--3 minutes.
Concentrated Sulphuric and Nitric Acid Test--To 5 drops of the ketone add 2 cc. of concentrated sulphuric acid and then gradually 2 cc. of concentrated nitric acid. This gives a clear brownish orange solution.

Time--5 minutes.

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VII---Experimental Procedure for Applying General Tests for Detecting Ketones (IV)
VII—Experimental Procedure for Applying General Tests for Detecting Ketones (IV).

Procedure A—To be applied to a solid compound having a melting point above 300°C.

To 0.05 gm. of the powdered substance add 0.5 cc. of hydroxylamine hydrochloride solution and 2 cc. of alcoholic sodium hydroxide solution. Charge a second tube, which is to be used for a blank experiment, in the same manner except that 0.5 cc. of 25% alcohol is to be substituted for the hydroxylamine. Boil for 5 minutes; cool; dilute with 10 cc. of cold water and shake vigorously. Filter through double wetted filters, and to the filtrate add one drop of phenolphthalein and dilute hydrochloric acid until the red color is just discharged. Close the mouth of each tube and shake vigorously. If the solution from the tube to which the hydroxylamine solution was added gives a precipitate or becomes opaque while the blank experiment remains clear or only becomes opalescent or only slightly turbid, the compound under examination is a ketone.

Procedure B—To be employed if the compound under examination is a liquid or a solid melting below 300°C.

If the unknown compound is soluble in water, dissolve one drop in 2 cc. of cold water and add 4 drops of a phenylhydra-
zine solution. If the compound is not soluble in water substitute for the latter 2 cc. of dilute alcohol. Charge a second tube, which is to be used for a blank experiment, in like manner, omitting, however, phenylhydrazine solution. Sway the tube gently for one minute. Then if the solution remains clear heat it for 5 minutes. Allow the solution to stand for 30 seconds and note its degree of transparency and its color.

**Possibilities in Procedure B.**

The unknown compound is a ketone:

(a) If an opaque solution is obtained on treating it with phenylhydrazine in the cold.

(b) If an opaque solution is obtained during 5 minutes' heating or within 30 seconds after its removal from the bath, provided the blank experiment remains clear.

(c) If the two solutions become opaque after heating but the blank remains unchanged in color while the suspended matter in the test becomes yellow.
VIII---General Instructions for Applying Specific and Semi-Specific Tests for Ketones.
VIII---General Instructions for Applying Specific and Semi-Specific Tests for Ketones---(VI).

After the compound under examination has been positively identified as a ketone, the next step is to go through the specific and semi-specific tests for the individual ketones. These tests fall into two groups according as they are applied to solids or to liquids: Group A includes those solid ketones which have melting points above 300°C; Group B refers to liquid ketones and to those solid ketones which have a melting point not higher than 300°C.

If, however, the unknown substance is in the form of a liquid, a drop or two should be evaporated. If a solid residue is obtained upon evaporation, the tests of Group A should be applied; if no solid separates out, the tests of Group B may then be employed.

The specific and semi-specific tests for ketones are of two kinds: group tests and confirmatory tests. If one desires to identify an unknown substance as quickly as possible, one may merely apply the confirmatory tests. If, however, the time allows, it is advisable to perform more than one test on each compound. This insures the elimination of any error due to faulty manipulation.

In the subsequent tests for individual ketones, the procedures must be followed exactly in detail: the time ele-
ment and the quantities of every reagent employed are very important factors in any determination.

The color tests should be made under a pure white light.
IX—Condensed Tabular Form for Specific Tests for Ketones.
### IX—Condensed Tabular Form for Specific Tests for Ketones.

#### Group A

<table>
<thead>
<tr>
<th>Test</th>
<th>Benzal-acetone</th>
<th>Benzoin</th>
<th>Benzo-phenone</th>
<th>Camphor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fehling's Solution</td>
<td>negative</td>
<td>red precipitate</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>negative</td>
<td>negative</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td>Concentrated Hydrochloric Acid</td>
<td>yellow solution, red crystals</td>
<td>negative</td>
<td>yellow orange coloration</td>
<td>negative</td>
</tr>
<tr>
<td>Hydrozylamine</td>
<td>precipitate</td>
<td>opaque solution</td>
<td>precipitate</td>
<td>solution</td>
</tr>
<tr>
<td>Mercuric Chloride</td>
<td>no precipitate</td>
<td>no precipitate</td>
<td>no precipitate</td>
<td>no precipitate</td>
</tr>
<tr>
<td>Concentrated Nitric Acid</td>
<td>yellow solution, orange upper layer</td>
<td>insoluble in cold acid, soluble in hot</td>
<td>yellow solution, yellow oil on top</td>
<td>pink solution, colorless oil on top</td>
</tr>
<tr>
<td>Molisch</td>
<td>negative</td>
<td>decolorized</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td>Test</td>
<td>Benzalacetone</td>
<td>Benzoin</td>
<td>Benzo-phenone</td>
<td>Camphor</td>
</tr>
<tr>
<td>------</td>
<td>---------------</td>
<td>---------</td>
<td>---------------</td>
<td>---------</td>
</tr>
<tr>
<td>Concentrated Nitric Acid and Bromine Water</td>
<td>decolorized, opaque solution</td>
<td>orange colored solution</td>
<td>yellow coloration</td>
<td>orange coloration</td>
</tr>
<tr>
<td>Salicylic Aldehyde</td>
<td>red coloration</td>
<td>yellow coloration</td>
<td>yellow coloration</td>
<td>yellow coloration</td>
</tr>
<tr>
<td>Sodium Bisulphite</td>
<td>crystalline precipitate</td>
<td>no crystals</td>
<td>no crystals</td>
<td>no crystals</td>
</tr>
<tr>
<td>Sodium Nitroprusside</td>
<td>violet coloration</td>
<td>negative</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>negative</td>
<td>red coloration</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td>Concentrated Sulphuric Acid</td>
<td>clear, yellow-brown solution</td>
<td>olive green solution</td>
<td>yellow coloration</td>
<td>orange coloration</td>
</tr>
<tr>
<td>Concentrated Sulphuric and Nitric Acids</td>
<td>brown coloration</td>
<td>wine-colored solution</td>
<td>yellow coloration</td>
<td>orange coloration</td>
</tr>
</tbody>
</table>
### IX—Condensed Tabular Form for Specific Tests for Ketones

#### Group B

<table>
<thead>
<tr>
<th>Test</th>
<th>Acetone</th>
<th>Acetophenone</th>
<th>Methyl Ketone</th>
<th>Ethyl Ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>crystaline</td>
<td>oil</td>
<td>oil</td>
<td>oil</td>
</tr>
<tr>
<td>Fehling's Solution</td>
<td>negative</td>
<td>negative</td>
<td>negative</td>
<td>green coloration</td>
</tr>
<tr>
<td>Concentrated Hydrochloric Acid</td>
<td>negative</td>
<td>negative</td>
<td>clear brown solution</td>
<td>opaque orange solution</td>
</tr>
<tr>
<td>Iodoform</td>
<td>crystalline</td>
<td>negative</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td>Mercuric Chloride</td>
<td>precipitate</td>
<td>negative</td>
<td>precipitate</td>
<td>precipitate</td>
</tr>
<tr>
<td>Concentrated Nitric Acid</td>
<td>no coloration</td>
<td>yellow solution, brown upper layer</td>
<td>brownish orange coloration</td>
<td>orange solution, red upper layer</td>
</tr>
<tr>
<td>Concentrated Nitric Acid and Bromine Water</td>
<td>decolorized</td>
<td>decolorized</td>
<td>decolorized</td>
<td>yellow solution, red upper layer</td>
</tr>
</tbody>
</table>
### IX—Condensed Tabular Form for Specific Tests for Ketones

#### Group B—continued

<table>
<thead>
<tr>
<th>Test</th>
<th>Acetone</th>
<th>Acetophenone</th>
<th>Methyl Ethyl Ketone</th>
<th>Ethyl Propyl Ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl-hydrazine</td>
<td>oil</td>
<td>crystalline precipitate</td>
<td>oil</td>
<td>oil</td>
</tr>
<tr>
<td>Salicylic Aldehyde</td>
<td>red coloration</td>
<td>red coloration</td>
<td>red coloration</td>
<td>red coloration</td>
</tr>
<tr>
<td>Sodium Bisulphite</td>
<td>crystalline precipitate</td>
<td>no crystals</td>
<td>crystalline precipitate</td>
<td>no crystals</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>negative</td>
<td>negative</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td>Sodium Nitroprusside</td>
<td>orange coloration</td>
<td>red coloration</td>
<td>red coloration</td>
<td>red coloration</td>
</tr>
<tr>
<td>Concentrated Sulphuric Acid</td>
<td>orange yellow coloration</td>
<td>brown viscous liquid</td>
<td>brownish orange coloration</td>
<td>wine colored solution</td>
</tr>
<tr>
<td>Concentrated Sulphuric and Nitric Acids</td>
<td>wine colored solution</td>
<td>brown liquid</td>
<td>brownish red coloration</td>
<td>yellow orange coloration</td>
</tr>
</tbody>
</table>
Colorations with Sodium Nitroprusside,

The colorations with sodium nitroprusside are so characteristic of some ketones that I thought it well to arrange the results of these tests in tabular form. The method of procedure is to shake 5 drops of the ketone with 2 cc. of cold water--if the ketone is solid, shake 0.05 gm. with 2 cc. of alcoholic sodium hydroxide. Filter the solution and to the clear filtrate add two drops of a 1 % aqueous solution of sodium nitroprusside, and then 2 drops of sodium hydroxide (1 : 10). Without any unnecessary delay carefully note the color, and then quickly divide the solution into two equal portions, "a" and "b". To portion "b" add 3 drops of glacial acetic acid and immediately note the color. Allow both solutions to stand for 20 minutes and again carefully compare the color of each.

### Colorations with Sodium Nitroprusside

<table>
<thead>
<tr>
<th>Substance Tested</th>
<th>&quot;a&quot; to which sodium hydroxide has been added</th>
<th>Immediate Color</th>
<th>Color after 20 minutes</th>
<th>&quot;b&quot; to which sodium hydroxide and glacial acetic acid have been added</th>
<th>Immediate Color</th>
<th>Color after 20 Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>orange</td>
<td>yellow</td>
<td>purple-red</td>
<td>red</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetophenone</td>
<td>red</td>
<td>yellow</td>
<td>blue</td>
<td>blue</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzalacetone</td>
<td>violet</td>
<td>violet</td>
<td>blue</td>
<td>blue</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl Propyl Ketone</td>
<td>red</td>
<td>orange</td>
<td>red</td>
<td>red</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>red</td>
<td>yellow</td>
<td>orange</td>
<td>orange</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
X---A Scheme for the Separation of Ketones and Identification of Individual Ketones.
X--A Scheme for the Separation of Ketones and Identification of Individual Ketones.

**Group A--Solid Ketones**

If the compound under examination is in the form of a solid, or if it is a liquid which on evaporation yields a solid residue, the melting point of which is above 30°C., the ketone may be benzalacetone, benzoin, benzophenone, or camphor.

Apply the *Mercuric Chloride Test*; if this gives no precipitate the ketone is benzalacetone, benzoin, benzophenone, or camphor.

To the compound apply the *Fehling's Solution Test*.

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>No Precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoin</td>
<td>Benzalacetone</td>
</tr>
<tr>
<td></td>
<td>Benzoin</td>
</tr>
<tr>
<td></td>
<td>Benzophenone</td>
</tr>
<tr>
<td></td>
<td>Camphor</td>
</tr>
</tbody>
</table>

Confirmatory tests:
- Sodium Hydroxide
- Molisch
- Sulphuric Acid

To separate Benzalacetone, Benzoin, and Camphor, apply the *Hydroxylamine Test* to the original compound.

<table>
<thead>
<tr>
<th>No Precipitate</th>
<th>Precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camphor</td>
<td>Benzalacetone</td>
</tr>
<tr>
<td></td>
<td>Benzophenone</td>
</tr>
</tbody>
</table>

Confirmatory test:
- Sulphuric Acid
To distinguish between Benzalacetone and Benzo-phenone apply the **Salicylic Aldehyde Test** to the original compound.

<table>
<thead>
<tr>
<th>violet-red color:</th>
<th>pale yellow color:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzalacetone</strong></td>
<td><strong>Benzophenone</strong></td>
</tr>
<tr>
<td>Confirmatory Tests:</td>
<td>Confirmatory Tests:</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>Nitric Acid</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>Sodium Nitroprusside</td>
<td></td>
</tr>
</tbody>
</table>
**Group B—Liquid Ketones**

If the compound under examination is in the form of a liquid and if a drop or two on evaporation does not yield a solid residue, or if the compound is a solid melting below 300° C., it may be acetone, acetophenone, methyl ethyl ketone, or ethyl propyl ketone.

Apply the Sodium Nitroprusside Test; if the gives any coloration the ketone is acetone, acetophenone, methyl ethyl ketone, or ethyl propyl ketone.

To the compound apply the Iodoform Test

<table>
<thead>
<tr>
<th>Precipitate:</th>
<th>No precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Acetophenone</td>
</tr>
<tr>
<td>Confirmatory tests:</td>
<td>Methyl Ethyl Ketone</td>
</tr>
<tr>
<td>Sodium Nitroprusside</td>
<td>Ethyl Propyl Ketone</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td></td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td></td>
</tr>
</tbody>
</table>

To separate Acetone, Methyl Ethyl Ketone, and Ethyl Propyl Ketone, apply the Mercuric Chloride Test to the original compound.

<table>
<thead>
<tr>
<th>No precipitate</th>
<th>Precipitate:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone</td>
<td>Methyl Ethyl Ketone</td>
</tr>
<tr>
<td>Confirmatory tests:</td>
<td>Ethyl Propyl Ketone</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td></td>
</tr>
<tr>
<td>Sodium Nitroprusside</td>
<td></td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td></td>
</tr>
</tbody>
</table>
To distinguish between Methyl Ethyl Ketone and Ethyl Propyl Ketone, apply the **Nitric Acid Test** to the original compound.

<table>
<thead>
<tr>
<th>orange-brown coloration:</th>
<th>orange solution with red upper layer:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Methyl Ethyl Ketone</strong></td>
<td><strong>Ethyl Propyl Ketone</strong></td>
</tr>
<tr>
<td>Confirmatory tests:</td>
<td>Confirmatory tests:</td>
</tr>
<tr>
<td>Sodium Nitroprusside</td>
<td>Sodium Nitroprusside</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>Sulphuric Acid</td>
</tr>
</tbody>
</table>
### Group B

**Sodium Nitroprusside—coloration**

<table>
<thead>
<tr>
<th>Acetone</th>
<th>Acetophenone</th>
<th>Methyl Ethyl Ketone</th>
<th>Ethyl Propyl Ketone</th>
</tr>
</thead>
</table>

**Iodoform**

- precipitate
- no precipitate

<table>
<thead>
<tr>
<th>Acetone</th>
<th>Acetophenone</th>
<th>Methyl Ethyl Ketone</th>
<th>Ethyl Propyl Ketone</th>
</tr>
</thead>
</table>

**Mercuric Chloride**

- precipitate
- no precipitate

<table>
<thead>
<tr>
<th>Methyl Ethyl Ketone</th>
<th>Ethyl Propyl Ketone</th>
<th>Acetophenone</th>
</tr>
</thead>
</table>

**Nitric Acid**

- orange brown coloration
- orange coloration
- red upper layer:

<table>
<thead>
<tr>
<th>Methyl Ethyl Ketone</th>
<th>Ethyl Propyl Ketone</th>
</tr>
</thead>
</table>
XI---Bibliography.

---------------
XI—Bibliography.

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