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NAVY DEPARTMENT
BUREAU OF ENGINEERING

Report
on
The Qualitative Identification of the
Various Functional Groups Present
in Aviation Gasoline.

FR-1394

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INTRODUCTION

(a) Authorization

1. This problem was authorized by Bureau of Aeronautics letter Aer-E-46-MN JJ7G1 of 30 September 1936.

(b) Statement of Problem

2. Part of the problem as stated in the letter of authorization is to study the stability of aviation blends. This report will discuss the methods of identification of functional groups that may be present either in the original gasoline or the gasoline after storage.

(c) Known Facts Bearing on the Problem

3. The information given in this report has been collected from various sources and has been correlated for the study of hydrocarbon samples. It is especially useful for those samples which have become oxidized either in an oxygen bomb or in long storage. Details of the various tests, too voluminous for the main body of the report, will be found in Appendices A and B.

(d) Theoretical Considerations

4. A special emphasis is placed in this study on the identification of unsaturated hydrocarbons and peroxides, because these may be the primary cause of long-time storage difficulties. Each group will be discussed separately and then a general survey will be made for identification of one group in the presence of others.

(e) Narrative of Original Work Done at this Laboratory

5. Work at this Laboratory completed to date on this subject has been described in Naval Research Laboratory Report No. P-1360 on the "Acid Heat of Aviation Gasolines" and its extension in Naval Research Laboratory Report No. P-1391 on the "Use of Infra-Red Absorption Data for Showing Presence of Unsaturation and Aromatic Components in Aviation Gasoline." These reports are primarily concerned with unsaturated and aromatic hydrocarbons.

METHODS

(a) Hydrocarbons

6. Since gasolines may contain both saturated and unsaturated aliphatic hydrocarbons as well as hydrocarbons of the aromatic series, the first problem was to devise methods for differentiating hydrocarbons of these various types. Two general methods were used to differentiate unsaturated hydrocarbons of the aliphatic type, namely, (1) alkaline permanganate and (2) bromine in carbon tetrachloride. Both tests were

used since the first will give a positive test if certain reactive groups, such as the alcoholic group, are present, whereas bromine in carbon tetrachloride reacts negatively with hydroxyl groups such as are present in alcohols, but positively with unsaturated hydrocarbons of the aliphatic series. Since several double bonds may be present such as found in the dienes, it is necessary to distinguish between hydrocarbons containing two double bonds of the conjugated type and the simple mono-olefins. The reagent used for this differentiation was maleic anhydride. This reagent reacts positively with dienes containing conjugated double bonds and is a specific reagent for this test. The test which was used to identify hydrocarbons containing triple bonds was an ammoniacal solution of cuprous chloride. This is a specific reagent for hydrocarbons containing the $-C \equiv CH$. The tests used for differentiating aliphatic from aromatic hydrocarbons were 20% fuming sulfuric acid or di-methyl sulfate. These tests are based upon the fact that aromatic hydrocarbons are soluble in the two reagents. With the former, the hydrocarbon goes into solution as sulfonation takes place, while in the latter the aromatic hydrocarbon dissolves readily without any apparent reactivity between solvent and solute. Since paraffinic hydrocarbons react slightly with fuming sulfuric acid at elevated temperatures, it is very important that the reaction be carried out at approximately 20°C. For this reason the di-methyl sulfate test gives better results for this differentiation. To differentiate between various aromatic hydrocarbons containing one or more benzene rings, the anhydrous aluminum chloride test was found to be very useful. In this test a typical color is produced with hydrocarbons containing one or more benzene nuclei. For example, benzene and its homologues produce a typical orange to red color; naphthalene and its homologues a blue color; bi-phenyl gives a purple color, while anthracene produces a green. The nature of these colored compounds is believed to be due to halochromic salts of tri-aryl methane. Under no conditions will hydrocarbons of the aliphatic or hydro-aromatic series give positive tests with the above reagents.

(b) Oxygen Compounds

7. Since gasolines may contain saturated or unsaturated hydrocarbons which on standing or on storage in contact with air may form oxygenated compounds, and also since alcohol and other oxygen compounds are sometimes blended with gasoline, it seems desirable to formulate a test for the presence of such compounds. The test which is described in the appendix is based upon the test of Piccard¹. The test depends upon the solubility of

1. Helv. Chim. Acta 5, 243 (1922).

iodine in the compound to be tested. If oxygen is present in the molecule the solution assumes a brown color; on the other hand, if no oxygen be present, the solution will exhibit a violet color. It is therefore obvious that the test is limited to those liquids and to those compounds which will dissolve iodine.

(c) Peroxides

8. It has been shown by Yule and Wilson² and others that peroxides

2. Ind. Eng. Chem., 23, 1254 (1931).

are formed when gasolines containing unsaturated hydrocarbons are stored for a certain period of time. It is believed that peroxides are the precursors of undesirable gums in gasolines which have caused considerable trouble in internal combustion engines. The test which was used in this work for detecting the presence of peroxides was the potassium iodide method. It is based upon the fact that in the presence of peroxides, free iodine will be liberated from the potassium iodide and the solution will assume a yellow to brown color depending upon the concentration of iodine present. Therefore, the depth of the color is an index as to the amount of peroxide present in the sample of gasoline.

(d) Alcohols

9. As mentioned in the test for oxygen compounds, alcohols are sometimes blended with gasolines and may also be formed by the splitting of peroxides. To detect the presence of alcohols in gasoline several reagents may be used, such as metallic sodium, acetyl chloride, or benzoyl chloride. By using sodium as the reagent a positive test is indicated by the evolution of hydrogen when a clean, bright piece of the metal is placed in the sample under observation. This test is based upon the fact that metallic sodium displaces hydrogen in an OH group with the liberation of the gas. Unfortunately, water and enolic substances will also give this test. However, the presence of water may be shown by testing the sample with anhydrous copper sulfate or with aluminum ethylate. With the former a blue color is imparted to the copper sulfate, while with the latter reagent a precipitate of aluminum hydroxide is produced. Enolic substance may be detected by the formation of a purple color when a sample is tested with a 1% solution of ferric chloride. With acid chlorides, such as acetyl and benzoyl chlorides, alcohols react almost instantaneously to form the pleasant-smelling esters which may be readily detected by their fruity odor. Since there are three types of alcoholic groupings, namely, primary $\text{-CH}_2\text{OH}$, secondary >CHOH , and tertiary >C-OH , after showing the presence of an alcoholic group it is also desirable to show the type of alcoholic group present. For this purpose the method of Lucas³ was used. When a tertiary

3. J. Am. Chem. Soc. 52, 803 (1930).

alcoholic group is present, two layers are immediately formed. In the presence of a secondary alcoholic group, two layers are formed within five minutes, while the primary alcoholic group does not react with the above reagent under the conditions of the experiment. This test is based upon the fact that hydrochloric acid in the presence of anhydrous zinc chloride reacts with the OH group as shown above, its speed of reaction depending upon the strength of the bond between the carbon and hydroxyl groups.

(e) Aldehydes and Ketones

10. As mentioned above, gasolines may contain alcohols as blends, or if peroxides be present, the latter may ~~split~~, forming alcohols. Since alcohols are susceptible to oxidation and since the products formed when an alcohol is oxidized depend upon the type of alcoholic group present, it was necessary to formulate tests which would serve to identify the oxidation products of alcohols. The alcohols containing a primary alcoholic group, $-\text{CH}_2\text{OH}$, give aldehydes in the first stage of oxidation. The latter finally yield acids upon further oxidation. Alcohols containing a secondary alcoholic group, $>\text{CHOH}$, yield ketones upon oxidation. These substances are not further oxidized unless the carbon to carbon bond is broken. This usually does not take place except when drastic oxidizing agents are used. Since it is obvious that aldehydes and ketones may be produced in the partial oxidation of alcohols, and since both types of compounds contain a common group, the carbonyl group, $>\text{C}=\text{O}$, several reagents were used to detect the presence of this group, namely, 2,4-dinitrophenyl hydrazine, phenylhydrazine, and sodium bisulfite. Of these reagents, 2,4-dinitrophenyl hydrazine is by far the best since it reacts readily with all types of carbonyl compounds to produce an insoluble yellow to orange precipitate even with very dilute concentrations of aldehydes or ketones. Phenylhydrazine does not always produce a solid derivative, particularly with the lower molecular weight carbonyl compounds. Sodium bisulfite is useful as a reagent only where there are appreciable quantities of carbonyl compounds present. Since a positive test with 2,4-dinitrophenyl hydrazine indicates the presence of an aldehyde or ketone, it is therefore necessary to further differentiate between these two types of compounds. For this differentiation two tests may be used - Schiff's test and the silver mirror test. Schiff's reagent is a decolorized solution of p-rosaniline hydrochloride. When a drop or two of an aldehyde is added to a small amount of this reagent the red color of the dye is restored to this solution. This test is extremely sensitive and will detect even minute traces of aldehydes. High molecular weight water-insoluble aldehydes sometimes require a few minutes before an appreciable color is produced with the reagent. This may be facilitated by adding a solvent such as aldehyde-free alcohol to the test solution. Ketones will not respond to the above test. The silver mirror test depends upon the ability of the aldehyde group to undergo oxidation with this reagent. As oxidation of the aldehyde group proceeds, the silver is reduced and deposited on the sides of the test tube which gives the appearance of a mirror. Ketones will not show this behavior since they contain no easily oxidizable group. In order for any oxidation to take place with ketones, it would be necessary for a carbon to carbon bond to be broken. The solution of ammoniacal silver oxide, which is the active reagent in this case, is not strong enough to break this bond.

(f) Acids

11. The acids which may be present in the oxidation products of gasoline may be derived in several ways. In the first place, peroxides may split to produce the simple fatty acids. On the other hand, the presence

of aldehydes may also produce acids by further oxidation. Also, when ketones and tertiary alcohols, >C-OH , are drastically oxidized, fatty acids may be produced containing a fewer number of carbon atoms which results from the splitting of a carbon to carbon linkage. Perhaps the simplest method to detect the presence of acids is by the use of an indicator, and for this purpose the litmus test is very satisfactory. Another test which works equally well is the reaction with sodium bicarbonate. Evolution of carbon dioxide with this reagent constitutes a positive reaction. There are, however, several classes of compounds other than acids which may cause evolution of carbon dioxide. Any substance that is hydrolyzed under the conditions of the test to give an acid stronger than carbonic acid will react positively. Examples of such substances are low molecular weight acid anhydrides and acid chlorides. Phenols, on the other hand, are usually too weakly acidic to displace carbonic acid from its salts and hence will not give a positive reaction with the above reagent.

(g) Esters

12. Esters may be derived from two sources. In the first place they may be produced by dismutation of aldehydes which do not contain a hydrogen atom attached to the alpha-carbon atom. Examples of such dismutations would be the intermediate step in the Cannizzaro Reaction. If this reaction is carried out in the presence of sodium or potassium hydroxide, the ester is saponified and methyl alcohol and sodium formate are the resulting products. It is also possible for aldehydes in the presence of certain metal catalysts to undergo dismutation with the resulting formation of an ester. An example of this type of reaction is the formation of ethyl acetate from acetaldehyde. In the second place, esters may be formed by the interaction of alcohols and acids which may be present in oxidized gasolines. The concentration of esters depends upon several factors, such as the concentration of the alcohol and acid as well as the temperature. The presence of esters may be detected by their fruity or pleasant odor and by their ability to undergo saponification and ammonolysis. It has recently been shown by Buehler that benzylamine produces solid derivatives with even the low molecular weight esters. This serves as an excellent method for their detection and determination.

(h) Ethers

13. Ethers may be present in gasoline as a blend or may be formed in the decomposition of peroxides. At present there is no satisfactory qualitative test for aliphatic ethers since they contain a very inert group. In view of the fact that this group of compounds contains such an inert functional group, they are usually identified by the process of elimination. That is, if oxygen compounds as shown by the test above are found to be present and tests for all the subsequent oxygenated compounds are negative, the source of oxygen compounds is then believed to be due to the presence of ethers. This is proved by distilling the mixture and identifying the ether by its physical constants and also by its conversion into the 3,5-dinitrobenzoate. The latter is about the only satisfactory solid derivative that can be made from an aliphatic ether.

(i) Derivatives

14. In the identification tests which are mentioned above, positive tests for the functional groups are indicated either by color reactions or by the formation of a precipitate. After showing the presence of the type of compound present, such as hydrocarbons, alcohols, aldehydes, ketones, etc., it is sometimes desirable to show what specific member in the homologous series is present. That is, the reagent may show that an alcohol is present. To show what particular alcohol is present, it is therefore necessary to prepare a suitable derivative which may be used to characterize the individual alcohol. Therefore, for the purpose of specific identification of each member of a given homologous series, a table of the physical constants of various solid derivatives of the members of each homologous series is given in the appendix. Also the specific directions for the preparation of these derivatives are given. Only those derivatives which have been shown to be entirely satisfactory are listed in the appendix. Some of the requirements for satisfactory derivatives may be mentioned here:

- (1) The compounds selected for a derivative should possess chemical and physical properties which will enable absolute differentiation to be made between the individual possibilities.
- (2) Solid derivatives are preferable because of the ease of manipulation of small quantities in preparation and purification as well as in the determination of constants.
- (3) The derivative should be prepared by a reaction which gives a good yield of a fairly pure product since this will save time in the purification of the derivative.
- (4) The derivative should be prepared, if possible, by a general reaction which under similar conditions would yield a definite derivative of other possibilities. This eliminates the necessity for a series of specific reactions.

15. The derivatives which are listed in the appendix meet the aforementioned requirements. There are instances where certain compounds form a solid derivative, easily prepared in a good yield, but higher or lower homologues will not form the derivative. These are listed in the appendix as special tests. Examples of such tests are Penzoldt's Test and Claisen Condensation for acetone, Resorcinol test for formaldehyde, and the Iodoform test for methyl ketones and those substances containing a CH_3CO group joined either to a carbon or hydrogen atom, or which may be converted to such a structure under the conditions of the experiment.

APPLICATION OF METHODS DESCRIBED

16. To illustrate the application of the above tests to detect the presence of functional groups in aviation gasoline, two hydrocarbons

were used as an example. Analyses were run on samples of pure iso-octane and on pure di-iso-butylene before and after oxidation in the bomb. The results of the analyses before oxidation are given in Tables 1 and 2. The hydrocarbons were each subjected to oxygen in the bomb at an initial pressure of 100 pounds and at a temperature of 100°C. for a period of five hours and again analyzed for functional groups as shown in Tables 3 and 4. The pressure drop when di-iso-butylene was subjected to oxygen under the above conditions was 72 pounds as shown in Table 4. There was no drop in pressure when iso-octane was subjected to oxygen under similar conditions. It will be noted that no oxygen compounds are present in the untreated iso-octane and di-iso-butylene samples, although the latter does give positive tests for unsaturated hydrocarbons as shown by the alkaline potassium permanganate and also the bromine in carbon tetrachloride. Also, negative results were obtained for oxygenated compounds when iso-octane was subjected to oxygen in the bomb tests. This is to be expected since no drop in pressure was obtained when this substance was heated under pressure with oxygen in the bomb. In the case of di-iso-butylene, heavy tests were obtained for peroxides, carbonyl compounds, aldehydes, methyl ketones, acetone, and acidic substances. It is reasonable to expect appreciable amounts of oxygenated compounds of the aforementioned types to be present in this material. As mentioned above, there was a drop in pressure of 72 pounds which indicates that a considerable amount of oxygen has been absorbed and subsequent decomposition has resulted. Further application of the above tests on aviation gasoline will be given in a subsequent report.

DATA OBTAINED

17. The data obtained is given in tabular form, as follows:

Table 1

Sample - Iso-octane (freshly distilled).
Bomb treatment - None.
Pressure drop in bomb - None.

I. Physical Properties -

Color - Colorless.
Odor - Aliphatic hydrocarbons.
Water - None.
Solids - None.

II. Chemical Properties -

Litmus	- Neutral.
Oxygen compounds	- Negative.
Peroxides	- Negative.
Carbonyl compounds	- Negative.
Aldehydes	- Negative.
Iodoform test	- Negative.
KMNO ₄	- Negative.
Br in CCl ₄	- Negative.

Table 2

Sample - Di-isobutylene (freshly distilled).
Bomb treatment - None.
Pressure drop - None.

I. Physical Properties -

Color - Colorless.
Odor - Aliphatic hydrocarbon.
Water - None.
Solids - None.

II. Chemical Properties -

Litmus - Neutral.
Oxygen compounds - Negative.
Peroxides - Negative.
Carbonyl compounds - Negative.
Aldehydes - Negative.
Iodoform test - Negative.
KMNO₄ test - Positive.
Br₂ in CCl₄ - Positive.

Table 3

Sample - Iso-octane.
*Bomb treatment - Subjected to oxygen for five hours
at 100 pounds pressure and a
temperature of 100°C.
Maximum pressure - 126 pounds per square inch.
Minimum pressure - 126 pounds per square inch.
Pressure drop - None.

I. Physical Properties -

Color - Colorless.
Odor - Aliphatic hydrocarbons.
Water - None.
Solids - None.

II. Chemical Properties -

Litmus - Neutral.
Oxygen compounds - Negative.
Peroxides - Negative.
Carbonyl compounds - Negative.
Aldehydes - Negative.
Iodoform test - Negative.
Acetone - Negative.
KMNO₄ - Negative.
Br₂ in CCl₄ - Negative.

* (See next page).

Table 4

Sample - Di-isobutylene.

*Bomb treatment - Subjected to oxygen for five hours at 100 pounds pressure and a temperature of 100°C.

Maximum pressure - 140 pounds per square inch.

Minimum pressure - 68 pounds per square inch.

Pressure drop - 72 pounds per square inch.

I. Physical Properties -

Color - Pale yellow.
Odor - Slightly pungent.
Water - Present.
Solids - None.

II. Chemical Properties -

Litmus - Acidic.
Oxygen compounds - Positive.
Peroxides - Positive.
Carbonyl compounds - Positive.
Aldehydes - Positive.
Iodoform test - Positive.
Acetone - Positive.
KMNO₄ - Positive.
Br₂ in CCl₄ - Positive.

* NOTE: These bombs are the same as described by Aldrich and Robie, Vol. 30, No. 5, p. 198 (1932) and Hunn, Fischer and Blackwood, Vol. 26, No. 1, p. 31 (1930). The sample to be studied is placed in a glass bottle in the bomb. The bomb is cooled to 10°C and put under 100 pounds oxygen pressure. The bomb is then placed in an oil bath at 100°C and the pressure rises to the value known as maximum pressure. This may vary from 125 to 145 pounds dependent upon the vapor pressure of the gasoline at 100°C. At the end of five hours the pressure is read again and reported as minimum pressure. These bomb experiments will be reported in detail in a future report.

CONCLUSIONS AND RECOMMENDATIONS

18. A more extended investigation of the mechanism of gum formation should be made through a study of the behavior of pure hydrocarbons and certain selected gasolines or gasoline blends now used or proposed for use by the Navy.

19. A further study of accelerated oxidation in a bomb should be made in an effort to correlate the effects so obtained with the results experienced under actual conditions of storage.

SUMMARY AND DISCUSSION

20. In this report are given the methods that will be used in the future studies of the oxidation products of aviation gasoline.

21. The examination of the behavior of the two hydrocarbons studied above shows that iso-octane, a saturated hydrocarbon, is entirely resistant to rather severe treatment with molecular oxygen. Di-iso-butylene, on the other hand, is sensitive to oxygen, suffering under the conditions

of the test extensive oxygenation. Therefore, it is reasonable to conclude that the former will be stable in contact with atmospheric oxygen, while the latter will in all likelihood absorb oxygen from the air during periods of storage. Such oxidation gives rise to aldehydes, peroxides, and other substances which are thought to be precursors of gum. The resinification and the polymerization of these substances during oxidation and on storage thereafter leads to gum formation with a resulting deterioration of the quality of gasolines containing oxygen-sensitive hydrocarbons.

APPENDIX A

METHODS FOR THE IDENTIFICATION OF THE OXIDATION PRODUCTS OF AVIATION GASOLINE.

1. Test for Presence of Oxygen Compounds.

To 1 cc of the liquid to be tested, add a small crystal of iodine (10 mg) and shake until solution takes place. At this point an oxygen compound changes the color to brown. Hydrocarbons and non-oxygen compounds generally exhibit a violet color. The test is limited to those liquids in which iodine will dissolve.

2. Test for Peroxides.

To 1 cc of the substance, add 4 drops of diluted hydrochloric acid and 1 cc of an aqueous solution of potassium iodide. Shake vigorously and allow to stand for several minutes. If peroxides are present, iodine will be liberated, thus producing the typical brown to purple color. The intensity of the color will be proportional to the concentration of the iodine and hence to the peroxide present.

Hydrocarbons

3. Tests for Unsaturation.

(a) Bromine in carbon tetrachloride solution.

In this test 0.1 g (0.2 cc of a liquid) of the compound to be tested is added to 2 cc of carbon tetrachloride and a 5 per cent solution of bromine in carbon tetrachloride is added drop by drop (with shaking) until the bromine color persists.

(b) Alkaline potassium permanganate solution.

To 2 cc of a 5 per cent solution of sodium carbonate, add 0.1 g (or 2 cc) of the compound to be examined. Then add a 2 per cent potassium permanganate solution drop by drop with shaking until the purple color of the permanganate persists. The presence of impurities may give a slight reaction and should not be confused with a positive test. In testing compounds which are insoluble in water it is usual to dissolve them in acetone free from methyl alcohol before trying the test.

(c) Test for conjugated diene hydrocarbons.

An equivalent of the diene is gradually added to a cooled suspension of an equivalent of maleic anhydride in five times its weight of benzene. In many cases reaction commences immediately with the evolution of heat. The anhydride dissolves and the product commences to separate

even before all the diene has been added. The product is filtered and crystallized from petroleum ether. The corresponding acid may be obtained by boiling with water.

An alternative method is to mix 4 g of maleic anhydride with 2 to 2.5 g of the diene in 10 cc of pure benzene and place in a sealed tube for 12 hours. It is then heated at 100° for five hours. On cooling, a white paste of crystals is obtained. It is collected by filtration and crystallized from petroleum ether. When boiled with water the corresponding acid is produced.

(d) Test for acetylenic hydrocarbons.

Cuprous chloride and acetylene. Cuprous chloride is prepared by boiling a mixture of 5 g each of copper oxide and metallic copper in a 1:1 solution of hydrochloric acid. This is done in a flask with a funnel in its neck to prevent access of air. After the solution has become a straw-yellow in color, it is cooled under the tap, decanted, and made ammoniacal. Five cubic centimeters of this solution are added to a sample of the hydrocarbon. Note the color of the voluminous precipitate formed. This reaction is a test for the group $-C \equiv CH$. Acetylenes of this type also react with ammoniacal silver nitrate, with the production of a white precipitate. These acetylides are dangerously explosive when dry, and the precipitate should be acidified and discarded into the sink.

4. Tests for Differentiating Aliphatic from Aromatic Hydrocarbons.

(a) Twenty per cent fuming sulfuric acid.

To $1\frac{1}{2}$ cc of hydrocarbon, add $1-1\frac{1}{2}$ cc of 20% fuming H_2SO_4 . Mix by shaking at first gently and then more vigorously. Allow the mixture to stand for several minutes to determine whether solution has taken place. Aromatic hydrocarbons are soluble in this reagent.

(b) Dimethyl sulfate.

To $1\frac{1}{2}$ cc of the hydrocarbon, add 1 cc of dimethyl sulfate. (Precaution!) If solution takes place the hydrocarbon is aromatic.

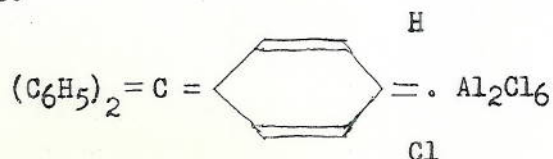
The reagent must not contain free sulfuric acid. Because of the reported toxicity of dimethyl sulfate, great care must be taken in handling it. The products from the above experiments are poured into 1:1 ammonia water to decompose the sulfate. If a drop of the ester touches the skin, the latter should be washed with water and then with ammonia solution.

(c) Anhydrous aluminum chloride test.

To 2 cc of dry chloroform in a test tube, add 0.1 cc (or 0.1 g) of hydrocarbon. Mix thoroughly, and incline the test tube so as to moisten

the wall. Then add about 0.5 to 1.0 g of anhydrous aluminum chloride so that some of the powder strikes the side of the test tube. Note the color of the powder on the side, also the color of the solution.

The colors, produced by the reaction of aromatic compounds with chloroform and aluminum chloride, are quite characteristic. Aliphatic compounds do not give any color, or only a very light yellow. The colored compounds are thought to be halochromic salts of triphenylmethane of the following structure:



Typical colors produced are the following:

<u>Compound</u>	<u>Color</u>
Benzene and its homologues	Orange to red
Aryl halides	Orange to red
Naphthalene	Blue
Biphenyl	Purple
Phenanthrene	Purple
Anthracene	Green

After standing for some time the colors change to various shades of brown.

5. Preparation of Derivatives of Hydrocarbons.

(a) Aliphatic hydrocarbons.

(1) Alkanes.

Use physical constants.

Paraffins and Cycloparaffins.

<u>Name</u>	<u>B.P.</u>	<u>Sp. Gr.</u>	<u>n_D</u>
Isopentane	31°	0.613 14/4	1.355
Pentane	36	0.631	1.3570
Cyclopentane	50	0.750	1.4093
n-Hexane	68	0.660	1.3754
Cyclohexane	80	0.790	1.4312
n-Heptane	98	0.700	1.385
Methylcyclohexane	100	0.769	1.4235
n-Octane	125	0.703	1.3890
n-Nonane	149	0.733	1.405
Diisoamyl	158	0.735 10/4	1.408
p-Menthane	169	0.796 15/4	1.437

(Continued)

Paraffins and Cycloparaffins (Continued).

<u>Name</u>	<u>B.P.</u>	<u>Sp. Gr.</u>	<u>n_D</u>
n-Decane	173	0.745	1.415
Decalin (trans.)	185	0.872	1.4701
Decalin (cis.)	192	0.894	1.4828
n-Undecane	194	0.745 15/4	1.4184
n-Dodecane	215	0.755 15/4	1.4209

(2) Alkenes.

Unsaturated Hydrocarbons.

<u>Name</u>	<u>B.P.</u>	<u>M.P.</u>	<u>Sp.Gr.</u>	<u>n_D</u>	<u>Derivative M.P.</u>
3 Methyl-1-butene	21°	--	0.660 15/15	--	
2-Pentene	36	--	0.651	1.3789	
Trimethylethylene	38	--	0.668 13/4	1.3855	
Cyclopentadiene	42	--	0.805 19/4	1.4470	
Diallyl	59	--	0.690	1.4010	
Cyclohexene	84	--	0.809	1.4492	Adipic acid 152°
3-Tetrahydrotoluene	103	--	0.799	1.4430	β-Methyladipic acid 93
2-Tetrahydrotoluene	105	--	0.805	1.4454	α-Methyladipic acid 64
1-Tetrahydrotoluene	111	--	0.809	1.4496	Nitrosochloride 97
Phenylacetylene	140	--	0.930	1.5524	Mercuride 124
Styrene	146	--	0.925	1.5485	Dibromide 73
d- or l Pinene	156	--	0.858	1.4653	Dibromide 164
1-Camphene	160	42°	0.822	1.4621	Dibromide 89
Limonene	176	--	0.846 18/4	1.4727	Tetrabromide 104
Sylvestrene	176	--	0.851 16/4	1.4774	Tetrabromide 135
Allylbenzene	177	--	0.914 15/15	1.5143	
Indene	180	--	1.040 15/4	1.5710	Picrate 98
Dipentene	181	--	0.854 16/4	1.4730	Tetrabromide 124
Dihydronaphthalene	212	15	0.998	1.5740	
Stilbene	306	125	0.970 125/15	--	Dibromide 237

(b) Aromatic hydrocarbons.

(1) Nitration.

The nitration of aromatic compounds, especially when one is dealing with an unknown substance, should be carried out with special precautions since many compounds react violently.

A. About 1.0 g of the compound is added to 4 cc of concentrated sulfuric acid. Four cubic centimeters of concentrated nitric acid

are added drop by drop, with shaking after each addition. The flask is connected to a reflux condenser and placed in a beaker of water at 45° for five minutes. The reaction mixture is poured on 25 g of cracked ice and the precipitate is collected on a filter. It may be recrystallized from dilute alcohol.

B. The same procedure outlined above is followed except that 4 cc of fuming nitric acid is used instead of concentrated nitric acid, and the mixture warmed on the steam cone for ten minutes. Occasionally, with compounds which are difficult to nitrate, fuming sulfuric acid may be substituted for the concentrated sulfuric acid.

Discussion. The first procedure above will yield m-dinitrobenzene from benzene or nitrobenzene and the p-nitro derivative of chlorobenzene, bromobenzene, benzyl chloride, and toluene. Phenol and acetanilide yield dinitro derivatives. The second procedure above yields the dinitro derivatives of alkylbenzenes, and halogenated benzenes. Mesitylene, the xylenes, and pseudo-cumene yield trinitro derivatives. Naphthalene and biphenyl yield mononitro derivatives by the first procedure.

(2) Oxidation of side chain.

A. Dichromate oxidation. In a small flask are placed 15 cc of water, 7 g of sodium dichromate, and 2 to 3 g of the compound to be oxidized. Ten cubic centimeters of concentrated sulfuric acid are added, the flask is attached to a reflux condenser, and the mixture is thoroughly shaken. The flask is then heated carefully until the reaction starts; then the flame should be removed and the flask is cooled if necessary. After the mixture has ceased to boil from the heat of the reaction it is heated under reflux for two hours. The contents of the flask are then poured into 25 cc of water and the precipitate collected on a filter. The precipitate is warmed on a steam cone with 20 cc of 5 per cent sulfuric acid and stirred vigorously. The mixture is cooled, and the precipitate is separated and washed with 20 cc of water. The residue is dissolved in 20 cc of 5 per cent sodium hydroxide solution and filtered. The filtrate is poured, with vigorous stirring, into 25 cc of 10 per cent sulfuric acid. The precipitate is collected on a filter washed with water, and purified by recrystallization from alcohol or benzene.

B. Permanganate oxidation. One gram of the compound is added to 80 cc of water containing 4 g of potassium permanganate. One cubic centimeter of 10 per cent sodium hydroxide solution is added and the mixture is heated under reflux until the purple color of the permanganate has disappeared (one-half to three hours). At the end of this time the mixture is allowed to cool and is carefully acidified with sulfuric acid. The mixture is again heated for one-half hour and then cooled. Any excess manganese dioxide is removed by the addition of a little sodium bisulfite solution. The precipitated acid is collected on a filter and recrystallized from benzene or alcohol. Occasionally it may be necessary to extract the acid from the solution by means of benzene or ether.

(3) Aroylbenzoic acids.

To a solution of 1 g of the dry aromatic hydrocarbon and 1.2 g of phthalic anhydride in 10 cc of dry carbon disulfide is added 2.4 g of anhydrous aluminum chloride. The mixture is heated under a reflux condenser in a boiling water bath for thirty minutes, and is then cooled. The carbon disulfide layer is decanted, and 10 cc of concentrated hydrochloric acid and 10 cc of water are added. The acid should be added slowly at first, with cooling by ice if necessary, and the final mixture should be thoroughly shaken. If the aroylbenzoic acid separates as a solid, it is immediately collected on a filter and washed with cold water. If an oil separates, the mixture is cooled in an ice bath for some time in order to induce crystallization. If the product remains oily, the supernatant liquid is decanted, and the oil is washed with cold water. The crude product, whether a solid or an oil, is boiled for one minute with 30 cc of 10 per cent ammonium hydroxide solution to which has been added about 0.1 g of norite. The hot solution is filtered and cooled; 25 g of crushed ice is then added, and the solution is acidified with concentrated hydrochloric acid. The aroylbenzoic acid is removed by filtration and is recrystallized from dilute alcohol (30 to 80 per cent). In some cases, it is necessary to allow the product to stand overnight in order to obtain crystals.

(4) Picrate formation.

A. A sample of the compound (about 0.3 to 0.5 g) is added to 10 cc of 95 per cent alcohol. If solution is not complete the mixture is shaken until a saturated solution results and is then filtered. The filtrate is added to 10 cc of a saturated solution of picric acid and in 95 per cent alcohol and the solution is heated to boiling. The solution is allowed to cool slowly and the yellow crystals of the picrate are removed by filtration and recrystallized from alcohol. Certain picrates cannot be recrystallized since they dissociate on heating. In such cases the original precipitate should be washed with a very small amount of ether and dried on a clay plate in preparation for the melting-point determination. Caution! Some picrates explode when heated.

B. Equal amounts of the compound and picric acid are mixed in a test tube which is then heated on the steam cone for ten minutes, or over a very low flame until the mixture melts. The mixture is allowed to cool and is recrystallized from alcohol.

(c) Physical constants of aromatic hydrocarbons and certain derivatives.

Aromatic Hydrocarbons (Liquids)

Name	B.P.	Sp.Gr.	Nitration Product		M.P.	Aroyl- benzoic Acid	Picrate
			Position				
Benzene	80°	0.874	1,3		89°	127°	84°
Toluene	111	0.881 4/4	2,4		70	137	88
Ethylbenzene	135	0.876 19/4	2,4,6		37	122	96
p-Xylene	137	0.866 14/4	2,3,6		137	132	90
m-Xylene	139	0.871 12/4	2,4		83	126	91
o-Xylene	142	0.890 4/4	4,5		71	178	88
Isopropylbenzene (Cumene)	153	0.875 4/4	2,4,6		109	133	-
n-Propylbenzene	158	0.861	-		-	125	103
Mesitylene	164	0.869 10/4	2,4		86	211	97
Pseudocumene	168	0.895	3,5,6		185	-	97
p-Cymene	175	0.857	2,6		54	123	-
m-Diethylbenzene	182	0.860	2,4,6		62	114	-
n-Butylbenzene	182	0.862	-		-	97	-
Isodurene	195	-	-		-	213	-
Tetralin	206	0.971	5,7		95	153	-
1,3,5-Triethyl- benzene	218	0.863	2,4,6		108	129	-
Cyclohexylbenzene	237	0.955	4		58	-	-
α-Methylnaphthalene	240	1.001 19/4	4		71	-	141

Aromatic Hydrocarbons (Solids)

Name	M.P.	Nitration Product		M.P.	Aroyl- benzoic Acid	Picrate
		Position				
Diphenylmethane	26°	2,4,2',4'		172	-	-
β-Methylnaphthalene	32	1		81	-	116
Pentamethylbenzene	51	6		154	-	131
Dibenzyl	52	4',4'		180	-	-
Biphenyl	70	4',4'		233	224	-
Durene	79	3,6		205	263	-
Naphthalene	80	1		59	172	149
Triphenylmethane	92	4,4',4''		206	-	-
Acenaphthene	95	5		101	198	161
Retene	98	-		-	-	124
Phenanthrene	100	-		-	-	133
Fluorene	115	2,7		199	227	84
Hexamethylbenzene	162	-		-	-	170
Anthracene	216	-		-	-	138

Alcohols.

6. Tests for Alcohols.

(a) Metallic sodium.

Add a small thin slice of bright metallic sodium to 1 cc of the alcohol and note whether the sodium dissolves with the evolution of hydrogen. Enolic substances and water will interfere with this test. Hence the absence of the latter must be shown.

(b) Acetyl chloride.

To 0.3 g of the substance in a dry test tube is added 0.3 cc of acetyl chloride.

(Caution! Hood! Some substances react with acetyl chloride with almost explosive violence. Protect the eyes!)

If two layers form, the mixture is shaken well. A very definite rise in the temperature of the contents of the tube within a minute or two indicates the presence of a compound containing hydroxyl or amine groups. It should be borne in mind that any substance containing an appreciable amount of water will appear to react positively in this test.

Compounds containing phenolic or alcoholic hydroxyl groups or amine groups react exothermically with acetyl chloride. With a large number of such substances the reaction is rapid enough so that a rise of temperature can be readily observed. It is necessary to be cautious in performing this test because the reaction in some cases is vigorous enough to cause violent, sometimes almost explosive, ebullition.

(c) Benzoyl chloride (Schotten-Baumann Method).

Into a 30 cc glass-stoppered bottle, place 2 cc of the alcohol dissolved in 10 cc of water. Add 1 cc of benzoyl chloride and 10 cc of 20% NaOH solution. Shake the mixture vigorously for five minutes. A positive test is the evolution of heat and the separation of the insoluble benzoate.

(d) Differentiation of primary, secondary, and tertiary alcohols with hydrochloric acid - zinc chloride reagent.

To 1 cc of the alcohol in a test tube add 6 cc of the hydrochloric acid-zinc chloride reagent at 26-27°C. Stopper the tube and shake the mixture and then allow to stand. Note the time required for the formation of the alkyl chloride which appears as an insoluble layer or emulsion.

Tertiary alcohols react at once to give two phases, the formation of which is indicated by a cloudy appearance of the mixture. Secondary alcohols react within five minutes to give a cloudy solution. Saturated

primary alcohols do not react under the above conditions. The above test is limited to alcohols of six carbon atoms or lower.

The above reagent is made by dissolving 136 g (1 mol) of anhydrous zinc chloride in 105 g (1 mol) of concentrated hydrochloric acid, with cooling.

7. Preparation of Derivatives for Alcohols.

(a) Phenyl- and α -naphthylurethans. One gram of the anhydrous alcohol or phenol is placed in a test tube and 0.5 cc of phenyl isocyanate or α -naphthyl isocyanate added. If a spontaneous reaction does not take place the solution should be warmed on the steam bath for five minutes. It is then cooled in a beaker of ice and the sides of the tube are scratched with a glass rod in order to induce crystallization. The urethan is purified by dissolving it in 5 cc of petroleum ether or carbon tetrachloride, filtering the hot solution, and cooling the filtrate in an ice bath. The crystals are collected on a filter and dried on a clay plate; the melting point is then determined.

(b) 3,5-Dinitrobenzoates. One-half gram of 3,5-dinitrobenzoic acid is mixed with 1 g of phosphorous pentachloride in a test tube and the mixture is warmed gently to start the reaction. After the initial rapid reaction has subsided the mixture is heated for about four minutes in such a manner as to cause vigorous bubbling. While still liquid the mixture is poured on a watch glass, and the mass is allowed to solidify. The material is transferred to a clean clay plate and rubbed with a spatula in order to remove phosphorous oxychloride. The 3,5-dinitrobenzoyl chloride which remains is mixed with 1 cc of the alcohol in a test tube and the mixture boiled gently for five minutes. Then 10 cc of distilled water is added and the solution is cooled in an ice bath until the precipitate solidifies. The precipitate is filtered, washed with 10 cc of 2 per cent sodium carbonate solution, and recrystallized from 5 to 10 cc of a mixture of ethyl alcohol and water of such composition that the ester will dissolve in the hot solution but will separate when the solution is cooled. The crystals are filtered and dried on a porous plate, and the melting point is determined.

(c) Physical constants for alcohols and certain derivatives.

Alcohols (Liquids)

Name of Compound	B.P.	Derivatives		
		<u>α-Naphthyl- urethan</u>	<u>Phenyl- urethan</u>	<u>3,5-Dinitro- benzoate</u>
Methyl alcohol	66°	124°	47°	107°
Ethyl alcohol	78	79	52	92
Isopropyl alcohol	83	78	90	122
tert-Butyl alcohol	83	101	136	142
Allyl alcohol	97	109	70	48
n-Propyl alcohol	97	80	58	73
sec-Butyl alcohol	99	97	30	75
tert-Amyl alcohol	102	71	42	117
Isobutyl alcohol	108	104	80	64
Methylisopropylcarbinol	113	-	-	-
n-Butyl alcohol	116	71	57	64
Diethylcarbinol	116	71	48	97
sec-Amyl alcohol	119	76	-	61
Ethylene glycol monomethyl ether	124	-	-	-
sec-Butylcarbinol	128	97	-	62
Ethylene chlorohydrin	129	101	51	-
Isoamyl alcohol	130	67	55	62
Ethylene glycol monoethyl ether	134	-	-	-
n-Amyl alcohol	138	76	46	46
Cyclopentanol	140	118	132	-
Triethylcarbinol	142	-	-	-
Ethylene bromohydrin	149	86	-	-
Di-n-propylcarbinol	156	-	-	-
n-Hexyl alcohol	160	59	42	58
Cyclohexanol	160	128	82	112
Trimethylene chlorohydrin	161d.	76	-	-
2-Methylcyclohexanol	165	155	103	-
Furfuryl alcohol	170	129	45	80
Pinacol	172	-	-	-
4-Methylcyclohexanol	174	160	125	-
3-Methylcyclohexanol	175	122	96	-
n-Heptyl alcohol	176	62	68	47
1,3-Dichloro-2-propanol	176	115	73	-
Trimethylene bromohydrin	176d.	73	-	-
2-Octanol	179	63	114	32
2,3-Dichloro-1-propanol	182	93	73	-
Propylene glycol	188	-	153	-
n-Octyl alcohol	192	66	74	61
Ethylene glycol	197	176	157	(Dibenzoate 73)
Linalool	197	53	65	-

Alcohols (Liquids) (Continued)

Name of Compound	B.P.	Derivatives		
		<u>α-Naphthyl-</u> <u>urethan</u>	<u>Phenyl-</u> <u>urethan</u>	<u>3,5-Dinitro-</u> <u>benzoate</u>
Methylphenylcarbinol	203°	106°	94°	-
Benzyl alcohol	205	134	78	112°
3-Chloro-1,2-propanediol	215d	-	-	-
n-Nonyl alcohol	215	-	62	52
Trimethylene glycol	216	164	137	(Dibenzoate 53)
β -Phenylethyl alcohol	219	119	79	-
2,3-Dibromo-1-propanol	219	-	77	(α,β -Dibromopropionic acid 64)
Ethylphenylcarbinol	219	102	-	-
1,3-Dibromo-2-propanol	219d	-	84	-
Citronellol	222	-	-	(3-Methyl adipic acid 89)
Geraniol	229	47	-	62
n-Decyl alcohol	231	71	60	57
α -Phenylpropyl alcohol	235	-	47	-
Cinnamyl alcohol	250	114	90	-
Diethylene glycol	250	-	-	-
Glycerol	290d.	191	180	(Tribenzoate 76)

Alcohols (Solids)

<u>Name of Compound</u>	<u>M.P.</u>	<u>α-Naphthyl- urethan</u>	<u>Phenyl- urethan</u>	<u>Miscellaneous</u>
Cyclohexanol	16°	128°	82°	3,5-Dinitrobenzoate 112°
Lauryl alcohol	24	80	-	-
Cinnamyl alcohol	33	114	90	-
Pinacol	35	-	-	Tetramethylethylene dichloride 160
α -Terpineol	35	147	112	3,5-Dinitrobenzoate 78
Myristyl alcohol	39	-	-	4'-Iodobiphenyl- urethan 146
l-Menthol	42	128	111	Benzoate 55
Anisyl alcohol	45	-	-	Anisic acid 184
Pinacol hydrate	46	-	-	-
Cetyl alcohol	50	82	73	-
Terpinol	102	-	-	Hydrochloride 50
Terpinol hydrate	117	-	-	Hydrochloride 50
Sitosterol	137	-	-	Acetate 127
l-Cholesterol	148	160	168	Benzoate 150
Triphenylcarbinol	162	-	-	Triphenylmethane 92
Ergosterol	165	-	-	Acetate 180
d-Mannitol	166	-	303	Hexaacetate 120
d-Borneol	208	132	138	p-Nitrobenzoate 137
Inositol	225	-	-	Hexaacetate 216
Pentaerythritol	253	-	-	Tetraacetate 84

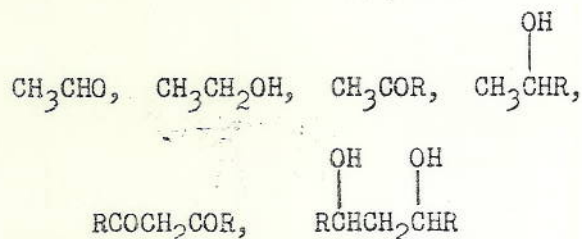
8. Specific Tests for Individual Alcohols.

(a) Iodoform test.

Place four drops of the liquid (0.1 g of the solid) to be tested in a test tube (15 mm wide). Add 5 cc of dioxane and shake until all the sample has gone into solution. Add 1 cc of 10 per cent sodium hydroxide solution and then add iodine-potassium iodide solution¹, with shaking, until a slight excess yields a definite dark color of iodine². If less than 2 cc of the iodine solution is decolorized, place the test tube in a water bath maintained at a temperature of 60°. If the slight excess of iodine already present is decolorized, continue the addition of iodine solution (keeping the dioxane solution at 60°), with shaking, until a slight excess of iodine solution again yields a definite dark color. The addition of iodine is continued until the dark color is not discharged by two minutes' heating at 60°. This excess of iodine is removed by the addition of a few drops of 10 per cent sodium hydroxide solution, with shaking. Now fill the test tube with water and allow to stand for fifteen minutes. If the compound is a solid it is advisable to collect the iodoform on a filter and determine its melting point; this should be 119-121°. If the iodoform is reddish in color, dissolve in 3 to 4 cc of dioxane, add 1 cc of 10 per cent sodium hydroxide solution, and shake until only a light lemon color remains. Dilute with water and filter.

This test is positive for compounds which contain the grouping $\text{CH}_3\text{CO}-$, $\text{CH}_2\text{ICO}-$, or $\text{CHI}_2\text{CO}-$ when joined to a hydrogen atom or to a carbon atom which does not carry active hydrogen atoms or groups which provide an excessive amount of steric hindrance. The test will, of course, be positive also for any compound which reacts with the reagent to give a derivative containing one of the requisite groupings. Conversely, compounds which contain one of the requisite groupings will not give iodoform if that grouping is destroyed by the hydrolytic action of the reagent before iodination is complete.

Following are the principal types of compounds which give the test:



1. The iodine-potassium iodide solution is made by adding 200 g of the iodide and 100 g of iodine to 800 cc of distilled water and stirring until solution is complete.
2. The iodine-potassium iodide solution must be added until a slight excess yields a dark color because a few compounds give a yellow color on treatment with hypoiodite. If dilution with water takes place here, no iodoform is obtained.

(R = Any alkyl or aryl radical except a di-ortho-substituted aryl radical.)

The test is negative for compounds of the types $\text{CH}_3\text{COCH}_2\text{CO}_2\text{R}$, $\text{CH}_3\text{COCH}_2\text{CN}$, $\text{CH}_3\text{COCH}_2\text{NO}_2$, etc., because in such compounds the acetyl group is cleaved by the reagent to acetic acid which resists iodination.

Aldehydes and Ketones.

9. Tests for the Carbonyl Group.

(a) 2,4-Dinitrophenylhydrazine.

To 3 cc of the 2,4-dinitrophenylhydrazine reagent, add one or two drops of the compound to be tested and shake vigorously. Allow the solution to stand fifteen minutes if no precipitate forms immediately. The dinitrophenylhydrazones of all aldehydes and ketones are very insoluble and usually precipitate immediately. The precipitate may be oily at first but on standing becomes crystalline.

Reagent. The reagent is prepared by dissolving 2 g of 2,4-dinitrophenylhydrazine in 15 cc of concentrated sulfuric acid. This solution is then added, with stirring, to 150 cc of 95 per cent alcohol, and the solution is diluted to 500 cc with distilled water. The solution is mixed thoroughly and filtered. Since it is very dilute it serves as a qualitative reagent only.

(b) Phenylhydrazine.

A. Water-soluble aldehydes and ketones. Prepare some phenylhydrazine solution by dissolving 1 cc of liquid phenylhydrazine in 3 cc of 30 per cent acetic acid. Add $1/2$ cc of this solution to a $1/4$ cc portion of the aldehyde or ketone dissolved in 3 cc of water. The separation of an oily precipitate which may crystallize on standing shows the presence of aldehydes or ketones.

B. Water-insoluble aldehydes and ketones are best tested in the following manner: Dissolve $1/2$ g (or less) of the material in a few cubic centimeters (usually 2 cc) of ordinary alcohol. Now add water, drop by drop, until the precipitate barely redissolves. If by mistake a slight excess of water has been added, a few additional drops of alcohol must be used. To the clear solution, add a quantity of phenylhydrazine equal in weight to that of the unknown being tested. Observe. If the solution remains clear for several minutes, add 1 drop of acetic acid. If a cloudiness fails to appear in the solution, or no precipitate forms, the test is negative.

(c) Sodium bisulfite.

Prepare an alcoholic solution of sodium bisulfite by adding 3 cc of ethyl alcohol to 12 cc of a 40 per cent aqueous solution of the salt. A small amount of salt will be precipitated by the alcohol and must

be separated by decantation or filtration before the reagent is ready for use.

Place 1 cc of the reagent in a test tube and add 0.3 cc of a water-insoluble aldehyde or ketone. Stopper the test tube and shake vigorously.

The formation of bisulfite addition compounds is a general reaction of aldehydes. Most methyl ketones, low molecular-weight cyclic ketones (up to cyclooctanone), and certain other compounds having very reactive carbonyl groups behave similarly. Some methyl ketones, however, form the addition compounds only slowly or not at all. Aryl methyl ketones, pinacolone, and mesityl oxide give no addition compounds; on the other hand, cinnamaldehyde forms an addition compound containing two molecules of bisulfite.

10. Differentiation of Aldehydes and Ketones.

(a) Schiff's Test (Fuchsin Aldehyde Test).

Place 2 cc of the fuchsin-aldehyde reagent in a test tube and add one drop of an aldehyde. If an aldehyde is present a red color will be produced.

In this test the reagent should not be heated, and the solution tested should not be alkaline. Whenever the test is being used on an unknown, run a simultaneous test on a known aldehyde for comparison.

Reagent. Dissolve 0.5 g of pure fuchsin (p-rosaniline hydrochloride) in 500 cc of distilled water, and filter the solution. Saturate 500 cc of distilled water with sulfur dioxide, mix thoroughly with the filtered fuchsin solution, and allow to stand overnight. This produces a practically colorless and very sensitive reagent.

(b) Silver mirror test (Tollen's reagent).

Prepare Tollen's reagent according to the directions below. To this solution 1 g of substance is added. The mixture is shaken and set aside. The formation of a mirror on the sides of the tube is a positive test. The tubes containing the silver mirror should be treated with dilute nitric acid and poured in the sink, since upon becoming dry their contents are highly explosive.

Reagent. In a thoroughly clean test tube place 2 cc of a 5 per cent solution of silver nitrate, and add a drop of dilute sodium hydroxide solution (10 per cent). Add a very dilute solution of ammonia (about 2 per cent) drop by drop, with constant shaking, until the precipitate of silver oxide just dissolves. In order to obtain a sensitive reagent it is necessary to avoid a large excess of ammonia.

This reagent should be freshly prepared just before use and should not be stored, since the solution decomposes on standing and deposits a highly explosive precipitate. If no reaction takes place in the cold the solution should be warmed slightly.

11. Preparation of Derivatives of Aldehydes and Ketones.

(a) 2,4-Dinitrophenylhydrazones.

A mixture of 1.5 g of dinitrophenylhydrazine, 2 cc of the aldehyde or ketone, and 100 cc of 95 per cent alcohol is brought to boiling. The flame is removed and 2 cc of concentrated hydrochloric acid is added. The color usually changes and the solution becomes clear. The mixture is then boiled under a reflux condenser for two to five minutes and is allowed to cool to room temperature. The hydrazone is removed by filtration, washed with a little cold alcohol, and recrystallized from hot alcohol, ethyl acetate, or chloroform.

(b) Oximes.

About 0.5 g of hydroxylamine hydrochloride is dissolved in 3 cc of water; 2 cc of 10 per cent sodium hydroxide solution and 0.2 g of the aldehyde or ketone are then added. If the latter is water-insoluble just sufficient alcohol is added to the mixture in order to give a clear solution. The mixture is warmed on the steam bath for ten minutes and then cooled in an ice bath. In order to hasten crystallization the sides of the flask are scratched with a glass rod. Occasionally the addition of a few cubic centimeters of distilled water will assist in causing the oxime to separate. The product may be recrystallized from water or dilute alcohol.

(c) Semicarbazones.

A. For water-soluble compounds. One cubic centimeter of the aldehyde or ketone, 1 g of semicarbazide hydrochloride, and 1.5 g of sodium acetate are dissolved in 10 cc of water in a test tube. The mixture is vigorously shaken and the test tube is placed in a beaker of boiling water and allowed to cool. It is then placed in a beaker of ice; the sides of the tube are then scratched with a glass rod. The crystals of the semicarbazone are removed by filtration and recrystallized from water or 25 to 50 per cent alcohol.

B. For water-insoluble compounds. One cubic centimeter of the aldehyde or ketone is dissolved in 10 cc of alcohol. Water is added until the solution is faintly turbid, and the turbidity is removed with a few drops of alcohol. Then 1 g of semicarbazide hydrochloride and 1.5 g of sodium acetate are added and from this point procedure A is followed.

12. Physical Constants of Aldehydes and Ketones and Certain Derivatives.

Aldehydes and Ketones (Liquids)

<u>Name of Compound</u>	<u>B.P.</u>	<u>Derivatives</u>			
		<u>Oxime</u>	<u>Semi-carba- zone</u>	<u>Phenyl-hydra- zone</u>	<u>2,4-Dinitro- phenyl- hydrazone</u>
Formaldehyde	21°	-	169°	-	167°
Acetaldehyde	21	47°	162	63° 99	164
Propionaldehyde	50	-	89 154	270	155
Glyoxal	50	178	270	180	328
Acrolein	52	-	-	-	165
Acetone	56	59	187	42	128
Isobutyraldehyde	64	-	125.	-	182
n-Butyraldehyde	74	-	106	-	122
Ethyl methyl ketone	80	-	135	-	115
Diacetyl	88	74 (mono) 245 (di)	278	245	315
Isovaleraldehyde	92	-	107	-	123
Isopropyl methyl ketone	94	-	113	-	117
Chloral	98	56	-	-	-
Methyl n-propyl ketone	102	58	110	-	141
Diethyl ketone	102	69	139	-	156
n-Valeraldehyde	103	52	-	-	98
Crotonaldehyde	103	119	144	56	190
Pinacolone	106	74	157	-	125
Isobutyl methyl ketone	119	-	135	-	95
Chloracetone	119	-	164d.	-	-
α, β-Dichloracetone	120	-	163	-	-
Paraldehyde	124	-	-	-	-
n-Caproaldehyde	128	51	115	-	104
n-Butyl methyl ketone	129	49	122	-	106
Mesityl oxide	130	49	164	-	200
Cyclopentanone	131	56	205	50	142
Acetylacetone	139	149	-	-	-
Di-n-propyl ketone	145	-	133	-	75
Hydroxyacetone	146	71	196	103	129
n-Amyl methyl ketone	151	-	127	-	89
Cyclohexanone	155	90	166	77	160
n-Heptaldehyde	156	57	106	-	106
Furfural	161	89 74	202	97	202
2-Methylcyclohexanone	163	43	195	-	137
Diacetone alcohol	164	57	-	-	202-203

Aldehydes and Ketones (Liquids) (Continued)

Name of Compound	B.P.	Derivatives			
		Oxime	Semi-carbazone	Phenylhydrazone	2,4-Dinitrophenylhydrazone
3-Methylcyclohexanone	169°	-	180°	-	-
4-Methylcyclohexanone	169	37°	199	-	-
n-Hexyl methyl ketone	172	-	122	-	58°
Bromal	174	115	-	-	-
Benzaldehyde	179	35	222	158°	235
Cycloheptanone	181	23	163	-	148
Di-n-butyl-ketone	187	-	90	-	-
Phenylacetaldehyde	194	103	156	58	110
Salicylaldehyde	196	57	231	142	248
Phorone	198	48	186	-	-
m-Tolualdehyde	199	60	224	84	-
o-Tolualdehyde	200	49	218	101	-
Acetophenone	200	59	198	105	237
α-Thujone	202	55	174	-	114
p-Tolualdehyde	204	79 } 110 }	234	121	234
Citronellal	206	-	82	-	78
l-Menthone	207	59	187	53	145
o-Chlorobenzaldehyde	208	75	225	86	-
m-Chlorobenzaldehyde	208	70	228	134	-
Phenyl n-propyl ketone	220	50	184	200	-
Cinnamaldehyde	220d.	138	215	168	248
Methyl p-tolyl ketone	222	85	205	94	-
Hydrocinnamaldehyde	224	94	127	-	-
Carvone	225	72	142	106	189
Di-n-amyl ketone	226	-	-	-	-
Citral	228d.	-	164	-	110 } 96 }
p-Chloroacetophenone	232	95	-	114	-
Propiophenone	240	53	174	-	-
o-Methoxybenzaldehyde	243	92	203	120	250

Aldehydes and Ketones (Solids).

Name of Compound	M.P.	B.P.	Oxime	Derivatives		
				Semi-carba- zone	Phenyl- hydra- zone	2,4-Dinitro- phenyl hydrazone
Phorone	28°	198°	48°	186°	-	-
Dibenzyl ketone	34	330	125	146	120°	-
o-Methoxybenzaldehyde	35	243	92	203	120	250°
Piperonal	37	263	110	230	100	265
p-Methoxyacetophenone	38	258	87	198	-	-
Benzalacetone	41	262	115	187	157	223
o-Nitrobenzaldehyde	44	-	102	256	156	192
α,α'-Dichloracetone	45	173	-	-	-	-
Thymoquinone	45	232	162	202	93*	180*
p-Chlorobenzaldehyde	47	214	106	230	127	-
Benzophenone	48	305	141	164	137	229
ω-Bromoacetophenone	50	-	88 97 }	146	-	-
p-Bromoacetophenone	51	255	128	-	126	-
Phenyl p-tolyl ketone	54	326	154 116 }	-	109	-
Phthalaldehyde	56	-	-	-	191	-
m'-Nitrobenzaldehyde	58	-	120	246	120	268d.
ω-Chloroacetophenone	59	244	89	156	-	-
α-Naphthaldehyde	60	-	-	245	206d.	-
Benzalacetophenone	62	-	-	168 180 }	-	208
p-Methoxybenzophenone	62	-	116 138 }	-	132 90 }	-
p-Toluquinone	68	-	134	179	130*	128*
2,4-Dichlorobenzaldehyde	71	-	136	-	-	-
d-3-Bromocamphor	76	274	-	-	-	-
Vanillin	80	285d.	117	229	105	-
Fluorenone	83	241	195	-	151	-
Di-p-tolyl ketone	92	-	163	-	-	-
Benzil	95	347	137 (mono) 237 (di)	182 (mono) 244 (di)	225 (di)	185
p-Nitrobenzaldehyde	106	-	129	221	159	320
p-Bromophenacyl bromide	109	-	115	-	-	-
Dibenzalacetone	112	-	144	190	-	-
Metaldehyde	115	-	-	-	-	-
p-Hydroxybenzaldehyde	115	-	72	224	177	157
Benzoquinone	115	-	240d.	243	152*	231*
Terephthalaldehyde	116	245	200	-	154 278 }	-

Aldehydes and Ketones (Solids) (Continued)

Name of Compound	M.P.	B.P.	Oxime	Derivatives		
				Semi-carba- zone	Phenyl-hydra- zone	2,4-Dinitro- phenyl- hydrazone
β -Naphthoquinone	120°	-	169°	184°	138°*	-
α -Naphthoquinone	125	-	207	247	206*	-
p-Phenylphenacyl bro- mide	125	-	-	-	-	-
Vanillidineacetone	130	-	-	-	-	-
Benzoin	133	343°	151	206d.	106	234°
Quinhydrone	171	-	-	-	-	-
Xanthone	173	350	161	-	152	-
dl-Camphor	178	205	118	-	-	-
d-Camphor	179	205	118	237	233	175
Camphorquinone	198	-	170	236 } 147 }	170*	36 }* 190 }
			(mono)			
			140 (di)			
Phenanthraquinone	207	360	158	220d.	165*	~~312-313~~
			(mono)			
			202 (di)			
Anthraquinone	273	-	224	-	183*	-
Alizarin	289	-	-	-	-	-

* These melting points are those of the addition compounds of the quinones and substituted hydrazines. The products are not true hydrazones.

13. Special Tests.

(a) Acetone (Claisen Condensation).

Three drops of the ketone are dissolved in 2 cc of alcohol and 0.5 cc benzaldehyde and 1 cc dilute alkali added. The mixture is heated to boiling for a minute, cooled, and then agitated in order to cause the supercooled oil to solidify. Crystallization from alcohol yields a pure material (M.P. 111-112°).

(b) Iodoform test for methyl ketones and acetaldehyde.

See Test 8a above for procedure.

(c) Penzoldt's Test for acetone.

To .5 cc of the liquid suspected to contain acetone is added 2 cc of 10% sodium hydroxide solution. To this solution is added an equal volume of a saturated aqueous solution of o-nitrobenzaldehyde. The solution is vigorously shaken and set aside. If acetone is present the color of the solution at first is yellow. It then becomes green and a blue precipitate of indigotine is formed in 10 to 15 minutes. When indigotine is present in traces only, the solution should be shaken with a few drops of chloroform. The chloroform dissolves the coloring matter and becomes blue.

(d) Resorcinol Test for formaldehyde.

To 5 cc of a 5% aqueous solution of resorcinol is added an equal volume of a 40% solution of sodium hydroxide. Mix the contents of the tube and add an equal volume of aqueous solution suspected to contain formaldehyde. Heat to boiling and maintain at that temperature for about 30 seconds. Traces of formaldehyde produce a distinct red color. The limit of delicacy of this test is said to be one part in 10,000,000.

Acids

14. General Tests for Acids.

(a) Reaction with sodium bicarbonate.

Two-tenths of a gram of substance is dissolved in water and several drops of a saturated solution of sodium bicarbonate are added. If the substance is insoluble in water, it is dissolved in 2 cc of alcohol and diluted with an equal volume of water before the addition of the bicarbonate. Evolution of carbon dioxide is the criterion of a positive reaction. Observations should be carefully made. In case alcohol is used as the solvent in this test, no attention is to be paid to the formation of a precipitate on the addition of the sodium bicarbonate. This precipitate is crystalline sodium bicarbonate which is relatively insoluble in alcohol.

Several classes of compounds other than acids will cause evolution of carbon dioxide in this test. Any substance that is hydrolyzed under the conditions of the test to give an acid stronger than carbonic acid will react positively, for example, many acid anhydrides, acid chlorides, etc. Most phenols are too weakly acidic to displace carbonic acid from its salts.

(b) Ester formation.

To 1 cc of the test material add 1 cc of n-butyl alcohol and 1 drop of concentrated sulfuric acid. Boil the mixture carefully for several minutes. Cool, neutralize with sodium carbonate and pour on a watch glass. The fruity odor of an ester indicates the presence of organic acids.

15. Derivatives of Acids.

(a) Amide formation.

One gram of the acid is heated under reflux with 5 cc of thionyl chloride for fifteen to thirty minutes. The reaction mixture is poured into 15 cc of concentrated ammonia. The precipitated amide is separated on a filter and purified by recrystallization from water or dilute alcohol.

(b) Anilides and p-toluides.

One gram of aniline or p-toluidine, 0.5 g of the powdered sodium salt of the acid, and 0.5 cc of concentrated hydrochloric acid are mixed in a dry test tube and heated under a reflux condenser for forty-five to sixty minutes. The reaction mixture is diluted with 15 cc of water and cooled in a beaker of ice. The precipitate is removed by filtration and purified by recrystallization from water or dilute alcohol.

(c) p-Nitrobenzyl and p-phenylphenacyl esters of acids.

One gram of the acid is added to 5 cc of water in a small flask and is carefully neutralized with 10 per cent sodium hydroxide solution. A few drops of the acid is added, the addition being continued until the solution is just acid to litmus. If the original acid is obtained as the sodium salt, 1 g of the salt is dissolved in 5 to 10 cc of water. If this solution is alkaline a drop or two of dilute hydrochloric acid is added. Ten cubic centimeters of alcohol and 1 g of the phenacyl bromide are added; the mixture is then heated under reflux for one hour if the acid is monobasic, two hours if dibasic, and three hours if tribasic. Occasionally the addition of a few more cubic centimeters of alcohol may be necessary if a solid separates during the refluxing. The solution is allowed to cool, and the precipitated ester is purified by recrystallization from alcohol.

16. Constants of Acids and Certain Derivatives.

Acids (Liquids).

<u>Name of Acid</u>	<u>B.P.</u>	<u>Derivatives</u>			
		<u>Anilide</u>	<u>p-Toluide</u>	<u>p-Nitro- benzyl Ester</u>	<u>p-Bromo- phenacyl Ester</u>
Thioacetic	93°	-	-	-	-
Formic	101	47°	53°	31°	135°(140°)
Acetic	118	114	147	78	85
Acrylic	140	104	141	-	-
Propionic	140	103	124	31	63
Propiolic	144d.	-	-	-	-
Isobutyric	155	105	104	-	77
n-Butyric	163	90	72	35	63
Pyruvic	165d.	104	109	-	-
Crotonic (cis)	165d.	102	132	-	-
Ethylmethylacetic	176	110	-	-	-
Isovaleric	176	109	98	-	68
α-Chloropropionic	186	92	124	-	-
n-Valeric	186	63	70	-	75
Dichloracetic	189	118	153	-	-
Diethylacetic	193	124	-	-	-
Isocaproic	195	111	-	-	-
Methoxyacetic	203	58	-	-	-
n-Caproic	205	95	75	-	72
α-Bromopropionic	205	99	125	-	-
Ethoxyacetic	206	-	32	-	-
α-Bromo-n-butyric	217d.	98	92	-	-
Heptoic	224	71	80	-	72
Hexahydrobenzoic	232	139	-	-	-
n-Caprylic	236	57	70	-	67
α-Bromo-n-caproic	240	-	-	-	-
Levulinic	250d.	-	-	61	84
Pelargonic	253	57	84	-	68
Capric	270	62	78	-	67
Undecanoic	275d.	71	80	-	68
Undecylenic	295	-	-	-	-

Acids (Solids).

Name of Acid	M.P.	Derivatives			
		Anilide	Amide	p-Nitro- benzyl Ester	p-Bromo- phenacyl Ester
dl-Lactic	18°	59°	74°	-	112°
Thiobenzoic	24	-	-	-	-
α-Bromopropionic	24	99	123	-	-
Undecylenic	24	-	85	-	-
Undecanoic	29	71	103	-	-
Hexahydrobenzoic	30	139	186	-	-
Capric	30	62	108	-	67
Levulinic	33	-	108	61	84
β-Chloropropionic	42	-	-	-	-
Lauric	43	76	98	-	76
Hydrocinnamic	48	92	82	36	104
Bromoacetic	50	131	91	88	-
Elaidic	51	-	93	-	-
Myristic	54	84	102	-	81
Trichloroacetic	57	94	141	80	-
Margaric	60	-	106	-	83
β-Bromopropionic	62	-	-	-	-
Palmitic	62	90	106	42	86
Chloroacetic	63	134	120	-	-
α,β-Dibromopropionic	64	-	130	-	-
Cyanoacetic	66	198	123	-	-
Chaulmoogric	68	-	106	-	-
Stearic	69	93	108	285	90
Crotonic (trans)	72	118	160	-	-
Phenylacetic	76	117	154	65	89
Glycolic	79	96	120	-	138
α-Hydroxyisobutyric	79	136	98	80	-
β-Iodopropionic	82	-	101	-	-
Iodoacetic	84	143	95	-	-
Citraconic	91	175	187d.	-	-
Phenoxyacetic	96	99	101	-	-
Glutaric	97	126	174	69	137
l-Malic	100	-	102	124	179
			(mono)		
			156 (di)		
Citric (hydrated)	100	-	210	102	148
o-Methoxybenzoic	100	62	128	-	-
Oxalic (hydrated)	101	245	419d.	204	-
o-Toluic	102	125	142	91	57
Pimelic	105	155	-	-	137
Azelaic	106	185	175	44	131
m-Toluic	110	-	97	86	108
Ethylmalonic	111	150	214	75	-

Acids (Solids) (Continued)

<u>Name of Acid</u>	<u>M.P.</u>	<u>Derivatives</u>			
		<u>Anilide</u>	<u>Amide</u>	<u>p-Nitro- benzyl Ester</u>	<u>p-Bromo- phenacyl Ester</u>
dl-Tropic	117°	-	169°	-	-
dl-Mandelic	118	151°	133	-	-
Benzylmalonic	117d.	217	225	119°	-
Benzoic	121	160	128	89	119°
Trichlorolactic	124	164	145	-	-
3-Nitrosalicylic (hydrated)	125	-	145	-	-
o-Benzoylbenzoic	126	195	165	100	-
Maleic	130	187	153	89	168
o-(p-Toluy)l-benzoic	130	-	-	-	-
Furoic (Pyromucic)	133	123	141	133	138
Sebacic	133	198	210	72	147
d- or l-Mandelic	133	-	122	-	-
Cinnamic	133	153	141	116	145
Malonic	133d.	224	170	85	-
Acetylsalicylic	135	136	138	90	-
Methylmalonic	135d.	182	217	-	-
Phenylpropionic	136	125	102	83	-
o-Chlorobenzoic	140	114	139	106	-
m-Nitrobenzoic	140	153	142	141	-
meso-Tartaric	140	-	-	-	-
Suberic	140	187	216	85	144
Furylacrylic	141	-	168	-	-
3 Nitrosalicylic	144	-	145	-	-
Diphenylacetic	145	180	167	-	-
o-Nitrobenzoic	146	155	174	112	-
p-Hydroxyphenylacetic	148	-	167	-	-
o-Bromobenzoic	150	141	155	110	-
Benzilic	150	175	154	99	-
Adipic	152	235	220	106	154
p-Nitrophenylacetic	152	-	198	-	-
Citric	153	-	210d.	102	148
m-Bromobenzoic	155	137	155	105	-
Salicylic	157	134	139	96	140
m-Chlorobenzoic	158	122	134	107	-
o-Iodobenzoic	162	142	184	111	-
α-Naphthoic	162	161	205	-	-
d- or l-Tartaric	169	180	195	163	216
3,5-Dinitrosalicylic	173	-	-	-	-
p-Toluic	177	140	158	104	153
Acetylenedicarboxylic	179	-	294d.	-	-
2,4-Dinitrobenzoic	179	-	203	142	-
Anisic	184	168	162	132	152
β-Naphthoic	185	173	195	-	-

Acids (Solids) (Continued)

<u>Name of Acid</u>	<u>M.P.</u>	<u>Derivatives</u>			
		<u>Anilide</u>	<u>Amide</u>	<u>p-Nitro- benzyl Ester</u>	<u>p-Bromo- phenacyl Ester</u>
Acetylanthranilic	185°	167°	171°		
d-Camphoric	187	203	192	66°	
Hippuric	187	208	183	136	151°
Succinic	188	226	242	88	211
Aconitic	191		250d.	76	186
Protocatechuic	194d.	166	212	188	
m-Nitrocinnamic	199		196	174	
Fumaric	200	314	270	151	
Phthalic	200d.	169	149	155	153
m-Hydroxybenzoic	201	155	170	106	
3,5-Dinitrobenzoic	202	234	183	157	
dl-Tartaric	204			147	
p-Coumaric	206		194		
o-Coumaric	207		209d.	152	
Vanillic	207			140	
p-Hydroxybenzoic	213	202	162	198	
Mucic	213d.			310	225
p-Cyanobenzoic	214	179		189	
Piperic	216.			145	
3-Nitrophthalic	218	234	201	189	
2,4,6-Trinitrobenzoic	220d.		264d.		
5-Nitrosalicylic	227	224	225		
Diphenic	228		212	183	
o-Nitrocinnamic	240		185	132	
Gallic	240d.	207	245		
p-Nitrobenzoic	241	204	201	168	
p-Chlorobenzoic	242	194	179	129	
Tetrachlorophthalic	250d.			180	
p-Bromobenzoic	251	197	189	139	
p-Iodobenzoic	265	210	217	141	
Naphthalic	274				
p-Nitrocinnamic	285		160	186	
Isophthalic	300		280	202	179
Terephthalic	300(subl.)			263	225
Trimesic	350				

17. Special Tests for Individual Acids.

(a) Neutral equivalent.

Procedure. A sample of the acid (about 0.2 g) is weighed out accurately and is dissolved in 50 to 100 cc of water or alcohol. The mixture may be heated if necessary to dissolve all the compound. This solution is titrated with a previously standardized sodium hydroxide solution having a normality factor (N.F.) of about 0.1, phenolphthalein being used as the indicator. The neutral equivalent of the acid is calculated according to the formula -

$$\text{Neutral equivalent} = \frac{\text{Weight of sample} \times 1000}{\text{Volume of alkali (cc)} \times \text{N.F.}}$$

Discussion. The molecular weight of an acid may be determined from the neutral equivalent by multiplying that value by the number of acidic groups in the molecule. Acids may also be titrated in a solvent composed of alcohol and benzene or toluene.

A blank must always be run on the solvent; the same amount of phenolphthalein which was used in the titration must be employed in the blank.

In order to give an accurate neutral equivalent the substance titrated must be pure and anhydrous. If the value obtained for the neutral equivalent does not check the theoretical the compound should be recrystallized from a suitable solvent and carefully dried.

(b) Duclaux constants for volatile fatty acids.

Procedure. Three grams of the acid are dissolved in 150 cc of distilled water and the solution is mixed thoroughly. Ten cubic centimeters of the solution are removed by means of a pipet and are titrated against 0.1 N sodium hydroxide solution, phenolphthalein being used as the indicator. Then 100 cc of the solution are placed in a 250 to 300 cc distilling flask and a few pieces of porous plate are added. A thermometer should not be used, but the top of the distilling flask should be stoppered with a clean rubber stopper. The flask is connected to a short water-cooled condenser by means of a rubber stopper in such a way that the side arm of the distilling flask extends well into the narrow portion of the condenser tube. The apparatus should be set up so that the condenser makes about a 45° angle with the desk top. The distilling flask is heated so that drops come from the end of the condenser at a constant rate. The distillation should not be so rapid that a steady stream flows from the condenser or so slow that there is an appreciable time between drops. Three 10-cc fractions (A,B,C) are collected by means of a 10-cc graduate. Each fraction is titrated separately with more of the 0.1 N sodium hydroxide solution used originally. The results are expressed as per cent acidity of the 100 cc used.

$$\text{Duclaux number} = \frac{\text{Volume of alkali (cc) for 10-cc fraction} \times 100}{\text{Volume of alkali (cc) for original 10 cc} \times 10}$$

The Duclaux numbers for the common aliphatic acids are as follows:

<u>Acid</u>	<u>Duclaux Numbers</u>		
	<u>Fraction A</u>	<u>Fraction B</u>	<u>Fraction C</u>
Formic	3.95	4.40	4.55
Acetic	6.8	7.1	7.4
Propionic	11.9	11.7	11.3
n-Butyric	17.9	15.9	14.6
Isobutyric	25.0	20.9	16.0
n-Valeric	24.5	20.6	17.0
Isovaleric	28.7	23.1	16.8
n-Caproic	33.0	24.0	19.0

Discussion. An exactly standardized sodium hydroxide solution is unnecessary but it should be about 0.1 N. This procedure is an empirical one, and the values are only relative. They are an index of the relative volatility of the acid and water at the concentration stated. The volume of the graduate used should be checked against the 10-cc pipet used.

18. Tests for Esters.

(a) Saponification of esters.

Boil 3 cc of the substance in a small round-bottomed flask fitted with an efficient reflux condenser, with 30 cc of 25 per cent NaOH. An ebullator tube will assist in preventing bumping. Saponification will be complete after about thirty minutes, as will be indicated by the disappearance of the ester layer.

A. Examination of the neutral saponification product. From the alkaline solution, distill about 4 cc. This fraction may be used for the identification of the alcohol in the case of an unknown. Water-soluble alcohols can be salted out with K_2CO_3 .

B. Examination of the acidic saponification product. Cool the residue in the distilling bulb and acidify with dilute H_2SO_4 . A solid acid will separate. Do not mistake a precipitate of sodium sulfate for an organic acid. If in doubt, test the solubility of the product in ether. If the acid is a liquid, it may be distilled or extracted with ether at this point.

(b) Ammonolysis of ester.

One gram of the ester and 2 cc of concentrated NH_4OH are placed in a small glass-stoppered bottle and shaken at frequent intervals.

The mixture is allowed to stand at room temperature until it becomes homogeneous. The reaction product is removed, placed in a small flask and distilled. The ammonia, water, and alcohol distill over first and finally the amide. The latter is purified by crystallization from ether or chloroform.

19. Preparation of Derivatives for Esters.

(a) N-Benzylamides.

Non-halogenated esters. The ester, 2 cc, mixed with 4 cc each of benzylamine and water and, when necessary, sufficient ethyl alcohol or dioxane to effect solution are refluxed one hour (for formates), two hours (for acetates) or from four to five hours (for higher esters like caproates). The excess of reagents is removed by distilling up to 200°, after which the derivative in the distillation flask is crystallized from hot ligroin by cooling to room temperature or lower.

N-Benzylamides from Esters of Non-Halogenated Acids.

Ester	Formula	Melting Point, °C.		Nitrogen, per cent	
		Observed	Corrected	Calculated	Found
Ethyl formate	$\text{HCONHCH}_2\text{C}_6\text{H}_5$	59.6-60.2	59.8-60.4	10.37	10.46
Methyl acetate*	$\text{CH}_3\text{CONHCH}_2\text{C}_6\text{H}_5$	60.4-61.0	60.7-61.3		
Ethyl propionate	$\text{C}_2\text{H}_5\text{CONHCH}_2\text{C}_6\text{H}_5$	42.6-43.7	42.6-43.7	8.58	8.46
Ethyl n-butyrate	$\text{C}_3\text{H}_7\text{CONHCH}_2\text{C}_6\text{H}_5$	36.9-38.0	36.9-38.0	7.91	7.89
Ethyl i-butyrate	$\text{C}_3\text{H}_7\text{CONHCH}_2\text{C}_6\text{H}_5$	86.3-87.3	87.0-88.0	7.91	8.07
Ethyl n-valerate	$\text{C}_4\text{H}_9\text{CONHCH}_2\text{C}_6\text{H}_5$	41.1-41.8	41.1-41.8	7.33	7.38
Ethyl n-caproate	$\text{C}_5\text{H}_{11}\text{CONHCH}_2\text{C}_6\text{H}_5$	50.1-51.2	50.3-51.4	6.83	6.88
Ethyl crotonate	$\text{C}_3\text{H}_5\text{CONHCH}_2\text{C}_6\text{H}_5$	111.1-112.2	112.5-113.6	8.00	7.96

* Identical results were obtained with ethyl, propyl, butyl, isobutyl, s-butyl, amyl and isoamyl acetates.

Compounds from Esters of Halogenated Acids.

Ester	Formula	Melting Point, °C.		Literature	Nitrogen, %	
		Observed	Corrected		Calcd.	Found
Ethyl chloracetate	$\text{ClCH}_2\text{CONHCH}_2\text{C}_6\text{H}_5$	92.2-92.8	93.0-93.6	93.5-94.5 (correlated)		
Ethyl chloracetate	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2\text{HCl}$	257.0-259.0	263.6-265.7	255.5-258.0	9.75	9.79
Ethyl bromoacetate	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2\text{HBr}$	218.0-219.0	223.0-224.1	215-216	7.45	7.52
Ethyl dichloroacetate	$\text{Cl}_2\text{CHCONHCH}_2\text{C}_6\text{H}_5$	94.2-95.0	94.8-95.6	95-96		
Ethyl trichloroacetate	$\text{Cl}_3\text{CCONHCH}_2\text{C}_6\text{H}_5$	92.8-93.6	93.6-94.4	90-91	5.55	5.59

20. Special Tests.

(a) Saponification equivalent.

Procedure. I. The preparation of an alcoholic sodium hydroxide solution. Eight grams of sodium are dissolved in 250 cc of absolute alcohol, and after solution is complete, 25 cc of water are added. This solution is standardized by titration with a previously standardized 0.25 N hydrochloric acid solution or by direct titration against a weighed sample of pure potassium acid phthalate.

II. The saponification of the ester. The ester is placed in a weighing bottle containing a small pipet. The weight of the bottle and pipet is determined and a sample of 0.2 to 0.4 g of the ester is transferred to a 150 cc Erlenmeyer flask by means of the pipet, which is then returned to the weighing bottle and the two again weighed. The loss in weight is the weight of the sample. Fifteen cubic centimeters of the above alcoholic sodium hydroxide solution, measured from a buret, is then added to the flask containing the ester. The flask is attached to an efficient reflux condenser by means of a carefully cleaned rubber stopper and the mixture refluxed gently for one and one-quarter to one and one-half hours. At the end of this time the mixture is allowed to cool slightly. The flask is loosened from the condenser and the rubber stopper and condenser tube washed down with a stream of water from a wash bottle, the washings being allowed to run into the saponification mixture. Two drops of phenolphthalein solution are added, and the excess alkali is titrated by means of 0.25 N hydrochloric acid. The end point should be a faint pink. It is best to titrate the solution until the phenolphthalein is colorless, and then back-titrate with the original alkali.

Saponification equivalent =

$$\frac{\text{Weight of sample} \times 1000}{(\text{Volume of alkali (cc)} \times \text{N.F.}) - (\text{Volume of acid (cc)} \times \text{N.F.})}$$

Discussion. The ester must be pure and anhydrous in order to give an accurate saponification equivalent. The following precautions must be observed in order to obtain accurate results.

1. The alcoholic sodium hydroxide solution should be standardized immediately before use and its normality factor (N.F.) recorded.

2. The standard solutions should be measured accurately from a buret, since a slight error in the amount of alkali will cause a large error in the saponification equivalent. This is especially noticeable in the case of high molecular weight esters.

3. Refluxing for one and one-half hours will saponify most esters. For some, a longer time (two to twenty-four hours) may be necessary.

4. Corks must not be used to attach the flask to the condenser since the alcohol vapors extract substances which lower the strength of the alkali. Rubber stoppers, cleaned by warming with dilute alkali and then thoroughly washing with distilled water, should be used.

5. The end point should be a faint pink. This is the color assumed by phenolphthalein at pH 9.0, which represents the hydrogen-ion concentration of solutions of the sodium salts of most organic acids.

6. The molecular weight of the ester is equal to N times the saponification equivalent where N is the number of ester groups in the molecule.

Ethers.

21. Tests for Ethers.

From the standpoint of qualitative organic analysis, the dialkyl ethers are relatively inert. The aryl alkyl ethers are somewhat more reactive since the aryl nucleus will undergo substitution reactions. Since the functional group in ethers is so inert towards chemical reagents, this class of substances is identified by the process of elimination. Hence, they are usually identified by means of their physical constants and their 3,5-dinitrobenzoates as derivatives.

22. Preparation of 3,5-Dinitrobenzoates as Derivatives of Ethers.

A mixture of 1 cc of the ether, 0.15 g of anhydrous zinc chloride, and 0.5 g of 3,5-dinitrobenzoyl chloride is placed in a test tube and attached to a reflux condenser. The mixture is refluxed for one hour and cooled. To it is then added 10 cc of sodium carbonate solution. The mixture is warmed to 90° in a water bath, cooled, and filtered. The precipitate is washed with 5 cc of 5 per cent sodium carbonate solution and 10 cc of distilled water. The residue is dissolved in 10 cc of hot carbon tetrachloride and filtered while hot; the filtrate is then cooled in an ice bath. If the ester does not separate, the carbon tetrachloride is evaporated. The residue is dried on a porous plate and the melting point is determined.

23. Physical Constants for 3,5-Dinitrobenzoates of Ethers.

See 7(c) under alcohols.

APPENDIX B

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(Pages 391-395).

THE USE OF 2:4-DINITROPHENYLHYDRAZINE AS A REAGENT FOR CARBONYL COMPOUNDS.

By N. R. Campbell, A.I.C.

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While employing 2:4-dinitrophenylhydrazine for the characterisation and identification of aldehydes and ketones, it was observed that there were a considerable number of discrepancies in the recorded melting-points. Analysts referring to older tables will also find discrepancies between these and more recent papers. It was considered that a revision of many of these melting-points and a tabulated comparison of the recorded figures might clear the way to a more extended use of this valuable reagent. This has been done and certain hitherto unrecorded derivatives have been prepared and examined.

The 2:4-dinitrophenylhydrazine was prepared by the method of Brady⁵, isopropyl alcohol being used in place of the more costly pure ethyl alcohol. The product was pure and did not require recrystallisation.

The dinitrophenylhydrazones were prepared as suggested by Brady⁵, and certain experimental details may be of interest. It was found that the addition of dilute sulphuric acid was unnecessary, but that even when separation did not occur on cooling, boiling gently under reflux for from five to thirty minutes sufficed for condensation. Purified industrial methylated spirit was used as a substitute for ethyl alcohol, and in no instance did this cause complication. Recrystallisation was effected, whenever possible, from alcohol, but acetic acid was frequently found necessary, and when this solvent failed, xylene usually gave good results.

Two compounds not prepared by Brady's method were the dinitrophenylhydrazones of phenanthraquinone and chrysoquinone. These were obtained by boiling one mol. of the quinone with two mols. of dinitrophenylhydrazine in glacial acetic acid solution for thirty minutes. The crude substances did not require re-crystallisation.

Attention is drawn to the variations in the m.p. of the dinitrophenylhydrazone of acetaldehyde as recorded by various authors. These have been attributed by Bryant⁸ and others to the existence of a meta-stable form melting at 147°C. and a stable form melting at 168°C. It is true that the crude product obtained by Brady's method has m.p. 147°C., but I have been unable to confirm Bryant's statement that a meta-stable modification melting at this temperature is produced when the liquid phase is allowed

to solidify. Indeed, no signs of such a meta-stable modification could be detected when the liquid was undercooled far below its m.p., in a narrow tube, and then inoculated with a crystal of the crude substance having m.p. 147°C . The so-called meta-stable form is undoubtedly merely impure substance, the impurity being probably crotonic aldehyde dinitrophenylhydrazone, derived from some crotonic aldehyde produced from the acetaldehyde by the sulphuric acid used in Brady's method. Confirmation of this was obtained by the addition of excess of freshly distilled acetaldehyde to a cold pyridine solution of dinitrophenylhydrazine. Under these conditions the formation of crotonic aldehyde is very improbable, and the crude product obtained by pouring the solution into water and then adding dilute hydrochloric acid had m.p. 164°C .

There is no difficulty in purifying the acetaldehyde dinitrophenylhydrazone prepared by Brady's method, provided that alcohol is used as a solvent, a single recrystallisation from this usually being sufficient. Benzene, xylene and similar solvents are less suitable, and, if used, often necessitate several re-crystallisations. The possibility of impurities being produced by the aldol condensation is, however, one which should be carefully borne in mind by analysts.

TABLE I

2:4-DINITROPHENYLHYDRAZINE DERIVATIVES OF ALDEHYDES

Aldehyde	Solvent	Color	Melting-point °C.	Recorded melting-points
Formaldehyde	Alcohol	Yellow	166°	(1) 155°, (4) 155°, (6) 167°
Acetaldehyde	Alcohol	Orange-yellow	168°	(1) 147°, (4) 147°, (6) 167°
Propionaldehyde	Alcohol	Orange	154°	(3) 155°, (4) 155°, (6) 156°
n-Heptylaldehyde (Oenanthol)	Alcohol	Yellow	108°	(3) 106°, (4) 106°
Phenylacetaldehyde	Alcohol	Yellow	121°	(5) 110°
Cinnamic aldehyde	Acetic acid	Red	255° (decomp.)	(5) 248°
Furfuraldehyde	Xylene	Red	229°	(1) 202°
Benzaldehyde	Acetic acid	Orange	237°	(1) 203°, (2) 235°
Salicylaldehyde	Acetic acid	Light red	252° (decomp.)	(1) 237°, (2) 248°
m-Hydroxybenzaldehyde	Alcohol	Red	260° (decomp.)	(5) 259°
p-Hydroxybenzaldehyde	Acetic acid	Purple-red	280° (decomp.)	(1) 157°
o-Nitrobenzaldehyde	Xylene	Yellow	250° (decomp.)	(1) 192°
m-Nitrobenzaldehyde	Acetic acid	Yellow	292-293° (decomp.)	(1) 268°
o-Chlorobenzaldehyde	Acetic acid	Orange	206-207°	
Anisaldehyde	Acetic acid	Orange-red	253-254° (decomp.)	(5) 250°
Vanillin	Acetic acid	Red	271° (decomp.)	
Piperonal	Acetic acid	Red	266° (decomp.)	(5) 265°

TABLE I (Continued)

Aldehyde	Solvent	Color	Melting-point °C.	Recorded melting-points
Cumic aldehyde	Acetic acid	Red	243°	(5) 241°
Citral	Alcohol	Orange	116°	(4) 108-110° α , 96° β
Citronellal	Alcohol	Yellow	77°	(4) 78°
n-Butylaldehyde*		Yellow		(3) 122°, (4) 122°, (6) 123°
isoButylaldehyde		Yellow		(3) 182°, (4) 182°, (6) 187°
n-Valeraldehyde		Yellow		(4) 98°
isoValeraldehyde		Yellow		(3) 123°, (4) 123°
Trimethylacetalddehyde		Yellow		(4) 210°
n-Caproic aldehyde		Yellow		(3) 104°, (4) 104°
n-Octyl aldehyde		Yellow		(4) 106°
n-Nonyl aldehyde		Yellow		(3) 96°, (4) 96°
n-Decyl aldehyde		Yellow		(4) 104°
n-Undecyl aldehyde		Yellow		(4) 104°
n-Dodecyl aldehyde		Yellow		(4) 106°
Acrolein		Orange-red		(4) 165°
α -Methyl- β -ethyl acrolein		Crimson		(4) 159°
p-Nitrobenzaldehyde		Orange		(5) 320°
2:4-Dinitrobenzaldehyde		Yellow		(7) 258°
2:4:6-Trinitrobenzaldehyde		Orange		(7) 208°

* The solvents, colors and melting-points of this and the following derivatives tabulated are recorded from the literature for convenience of reference.

TABLE II

2:4-DINITROPHENYLHYDRAZINE DERIVATIVES OF KETONES

Ketone	Solvent	Color	Melting-point °C.	Recorded melting-points °C.
Methyl ethyl ketone	Alcohol	Orange	110-111°	(3) 115°
Acetone	Alcohol	Yellow	126°	(1) 118°, (2) 128°
Methyl propyl ketone	Alcohol	Orange-yellow	143-144°	(4) 141°
cyclopentanone	Alcohol	Yellow	146-147°	(4) 142°
cyclohexanone	Alcohol	Yellow	162°	(4) 160°
Diacetone alcohol	Alcohol	Light red	202-203°	
Benzylidene acetone	Acetic acid	Red	227°	(4) 223°
Dibenzylidene acetone	Acetic acid	Red	180°	
Cinnamylidene acetone	Acetic acid	Purple-red	222-223°	
Dicinnamylidene acetone	Acetic acid	Red	208°	
Pyruvic acid	Alcohol	Yellow	218°	(4) 213°
Acetoacetic ester	Alcohol	Yellow	93-94°	(1) 95°, (2) 96°
Benzoylacetoacetic ester	Acetic acid	Orange	222-223°	
Mesityl oxide	Acetic acid	Red	203°	(4) 200°
Acetylacetone	Alcohol	Yellow	209°	
Diacetyl	Anisole	Orange	Charred above 300°	
Acetophenone	Acetic acid	Orange-red	249-250°	(4) 237°
Benzylidene acetophenone	Acetic acid	Orange-red	244°	(4) 208°
Cinnamylidene acetophenone	Acetic acid	Red	(decomp.) 218-219°	
β-Acetylnaphthalene	Acetic acid	Red	(decomp.) 262°	
1-Carvone	Acetic acid	Red	(decomp.) 193°	(4) 189°
d-Carvone	Acetic acid	Red	190°	
Menthone	Alcohol	Orange	146°	(4) 145°
Pulegone	Alcohol	Red	147°	(5) 142°

TABLE II (Continued)

Ketone	Solvent	Color	Melting-point °C.	Recorded melting-points °C.
Piperitone	Alcohol	Red	119°	(5) coml. 125-128°
α -Ionone	Alcohol	Orange	150°	(5) 175°
d-Camphor	Alcohol	Deep yellow	177°	(1) 229°
Benzophenone	Acetic acid	Orange	238-239°	
β -Benzoylnaphthalene	Acetic acid and alcohol	Orange-yellow	257-258°	
p-Benzoyldiphenyl	Acetic acid	Orange	214°	
Benzoin	Alcohol	Yellow	245°	(4) 234°
Furoin	Alcohol	Orange-red	216-217°	
Benzil	Alcohol	Yellow	189°	(1) 183-184°, (4) 185°
Phenanthraquinone		Dark red	312-313°	
			(decomp.)	
Chrysoquinone		Red-brown	308-309°	
			(decomp.)	
Methyl n-butyl ketone*		Orange-red		(4) 106°
Methyl n-aryl ketone		Orange-yellow		(4) 89°
Methyl n-hexyl ketone		Orange		(4) 58°
Methyl n-nonyl ketone		Yellow-orange		(4) 63°
Methyl n-undecyl ketone		Yellow-orange		(4) 69°
Methyl isopropyl ketone		Yellow-orange		(4) 117°
Methyl isobutyl ketone		Orange-red		(4) 95°
Methyl isoamyl ketone		Orange		(4) 95°
Methyl isohexyl ketone		Orange-yellow		(4) 77°
Methyl cyclohexyl ketone		Orange		(4) 140°
Di-ethyl ketone		Pale orange		(4) 156°
Ethyl n-propyl ketone		Orange-yellow		(4) 130°
Ethyl isobutyl ketone		Orange-yellow		(4) 75°
Di-n-propyl ketone		Orange-yellow		(4) 75°

TABLE II (Continued)

Ketone	Solvent	Color	Melting-point °C.	Recorded melting-points °C.
cycloHeptanone	Alcohol	Orange-yellow		(5) 148°
cycloOctanone	Alcohol	Orange-yellow		(5) 163°
cycloPentadecanone	Alcohol	Yellow		(5) 105°
Benzoyl acetone	Alcohol	Pale yellow		(5) 151°
Allyl acetone		Orange		(4) 104°
Ethyl oxomalonate		Lemon		(4) 128°
Levulinic acid		Yellow		(4) 92°
Methyl benzoyl formate		Orange-yellow		(4) 171°
Fenchone		Orange-yellow		(5) 140°
Pinacolone	Alcohol	Orange-yellow		(4) 125°
Methyl heptenone		Orange-red		(4) 81°
α -Indanone		Orange-red		(4) 258°
n-Butyrolin		Yellow		(4) 99°
pseudolonone		Deep red		(4) 143°

* The solvents, colors and melting-points of this and the following derivatives tabulated are recorded from the literature for convenience of reference.

SUMMARY.--(1) isoPropyl alcohol can be conveniently used in place of the more costly duty-paid ethyl alcohol in the preparation of 2:4-dinitrophenylhydrazine.

(2) The melting-points of many dinitrophenylhydrazones recorded in the literature are erroneous. Tables of corrected melting-points are given, and these tables include all melting-points given in the literature and also the melting-points of several hitherto undescribed dinitrophenylhydrazones.

(3) The so-called meta-stable modification of acetaldehyde dinitrophenylhydrazone is shown to be merely impure material.

(4) Attention is drawn to the possibility of an impure derivative being obtained, owing to the aldol condensation taking place when Brady's method of preparation is used.

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