

A Study of Procedures for a
Laboratory Course in General Organic Chemistry

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A THESIS

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Introduction

This Thesis is a study of certain organic reactions with a view of adapting them to use in the laboratory instruction in a course in general Organic Chemistry.

.Project No. 1 , pages 1 thru 5, deals with the formation of a wide variety of azo coloring matters by diazotization, including a list of coloring matters which are recommended to the students as best bringing out this wide variety, together with laboratory instruction for their formation.

Project No. 2, pages 6 thru 10, deals with the conditions and time required, for the hydrolysis of an ester, e.g. n-butyl acetate and the identification of the products of the hydrolysis, together with procedures recommended to the students for such a hydrolysis, and speedy, but accurate proof of the products formed.

Project No. 3, pages 11 and 12, deals with the reactivity of the alkyl halogens when under the influence of activating groups, with a summary of the results obtained.

Project No. 4 , pages 13 and 14, deals with the reactivity of aryl halogens when under influence of nitro groups, with a list summarizing the results, and facts shown by the experiment, together with a procedure suggested for the conversion of 2-4 dinitro chloro benzene to 2-4 dinitroaniline by a test tube reaction.

Project No.5, page 15, which deals with the method for testing primary amines and amides by treating with nitrous acid, with evolution of nitrogen, with suggested procedure for the elimination of the difficulties brought about by presence of the oxides of nitrogen.

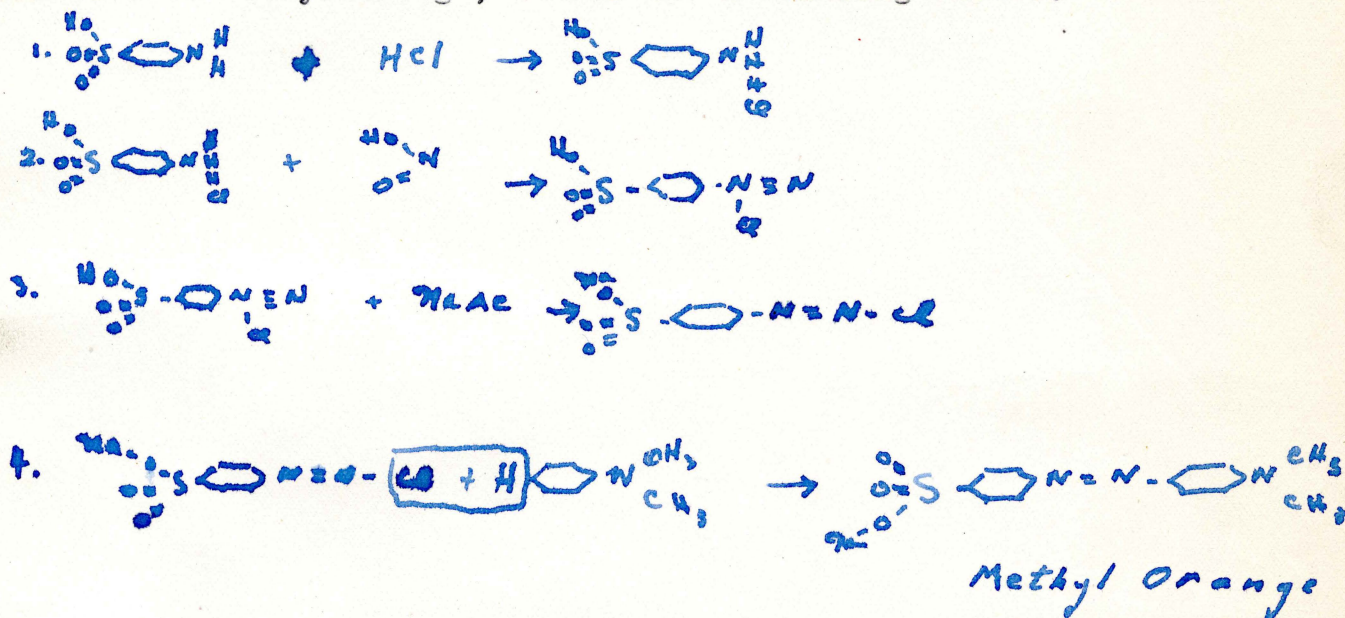
Project No.6, page 16 and 17, which deals with the synthesis of n-butyl ethyl ether by use of ethyl sulphate instead of ethyl bromine, with summary of results obtained, and conditions which give best results, together with a suggested procedure for a test tube experiment illustrating this reaction.

. Project No. 7, pages 18 and 19, which deals with the effects of the substituents R & R' upon the rate of reaction of the ethylene compounds, as illustrated by the addition of bromine. A quantitative procedure by which this was studied is given , and a qualitative procedure by which the students may readily see the effect of various substituents is suggested.

Project No. 1: To Demonstrate the Formation of a Wide Variety of Azo Coloring Matters by Diazotization.

The Azo dyes are formed by mono-diazotization, or by a series of two or more diazotizations. The simplest are the mono-azo dyes. These are formed by addition of a solution of sodium nitrite to a HCl salt of an amine, e.g. m-nitro-aniline, or to an amino group, as found in sulphaniic acid; and then to the diazotized substance is added a second portion of the amine, or another amine. This reaction is usually carried out at low temperatures, about zero degrees, but for laboratory demonstration it can be carried out at room temperature.

An example of this reaction is the diazotization of sulphaniic acid, with subsequent addition of dimethylaniline for the formation of Methyl Orange, a well known coloring matter.



For the demonstration of these coloring matters I made solutions up as follows:

- Sol. 1. 2 grams of the substance to be diazotized
20cc of Conc. HCl
200 cc of water
- Sol. 2. 2 grams of Sodium Nitrite
100 cc of water.
- Sol. 3. 60 grams of Sodium Acetate
200 cc Of water

I mixed equal portions of the solutions, in order given above, and poured about 2cc. into each of a series of test tubes. To these I now added a series of aromatic compounds containing either a primary amino or phenolic (including naphtholic) group, or both.

I then recorded colors produced. The first color produced is in slightly acid solution, and is therefore placed under column marked. Acidic- if this gave no reaction or coloring matter, I added a few drops of sodium hydroxide and if a color was produced placed it under column marked Basic.

1. Coupling of various compounds with diazotized Aniline.

| Second Component. | Colored Ppt. Produced. | |
|-----------------------|------------------------|---------------|
| | <u>Acidic.</u> | <u>Basic.</u> |
| 1. Phenol | ----- | Light Brown |
| 2. Salicylic Acid | ----- | |
| 3. Aniline | Yellow | |
| 4. Resorcinol | ----- | Orange red. |
| 5. b- Naphthol | ----- | Brick Red. |
| 6. o-toluidine | Yellow | |
| 7. Sulphanilic acid | ----- | ----- |
| 8. Nitroso b naphthol | ----- | ----- |
| 9. Peri Acid | Bluish Red | |
| 10. 1-2-4 Acid | ----- | ----- |
| 11. H acid | Purple | |
| 12. Brenner's acid | Orange yellow | |
| 13. Laurents Acid | Orange Red | |
| 14. Gamma Acid | Orange Red | |
| 15. Amino G Salt | ----- | ----- |
| 16. Badisches Acid. | ----- | ----- |

2. Coupling of various compounds with diazotized p-nitro-aniline

| Second Component. | Colored ppt. Produced. | |
|------------------------|------------------------|--------------|
| | <u>Acidic</u> | <u>Basic</u> |
| 1. Phenol | Orange | Deep Red. |
| 2. B-Naphthol | Bright Red | |
| 3. Aniline | ----- | Orange |
| 4. Salicylic Acid. | ----- | Grape Red. |
| 5. Resorcinol | Brownish Red | Purple |
| 6. Sulphanilic Acid | ----- | ----- |
| 7. O-Toluidine | Orange | |
| 8. Nitroso b- naphthol | Yellow | Brown |
| 9. Peri Acid | Purple | Brown |
| 10. 1-2-4 Acid | Yellow | Brown |
| 11. H Acid | Purple | |
| 12. Broenner's Acid | Redish Purple | |
| 13. Laurents Acid | Purple | |
| 14. Amino G Salt | Light Red | |
| 15. Hydroxyl Amine HCl | Yellow | |
| 16. Di methyl Amine | Bright Red. | |

3. Coupling of various compounds with diazotized Sulphanilic Acid.

| Second Component | Colored ppt. Produced. | |
|--------------------|------------------------|--------------|
| | <u>Acidic</u> | <u>Basic</u> |
| 1. Dimethylaniline | Yellow | Red |
| 2. p-nitro aniline | ----- | |
| 3. phenol | ----- | |

Project 1: (Con't)

§. (Con't)

| | | |
|-----------------------|----------------|--------|
| 4. Aniline | Yellow | ----- |
| 5. Sulphanilic | ----- | ----- |
| 6. b-naphthol | Reddish Orange | ----- |
| 7. nitroso-b naphthol | ----- | ----- |
| 8. o-toluidine | ----- | Yellow |
| 9. Peri Acid | ----- | ----- |
| 10. 1-2-4 acid | ----- | Brown |
| 11. H Acid | ----- | ----- |
| 12. Broenner's acid | Orange | ----- |
| 13. Laurents Acid | ----- | ----- |
| 14. Gamma Acid | ----- | ----- |
| 15. Koch Acid | ----- | ----- |
| 16. Amino G Salt | ----- | ----- |
| 17. Badisches Acid | ----- | ----- |

4. Coupling of various compounds with diazotized a-naphthalamine.

| Second Component. | Colored ppt. Produced | |
|------------------------|-----------------------|-----------------|
| | <u>Acidic.</u> | <u>Basic-</u> |
| 1. Nitroso b naphthol | ----- | Brown |
| 2. Sulphanilic Acid | ----- | ----- |
| 3. Phenol | ----- | Brownish Orange |
| 4. O-toluidine | Yellowish Orange | ----- |
| 5. Resorcinol | ----- | ----- |
| 6. Aniline | Light Red | ----- |
| 7. Salicylic Acid | ----- | Reddish Brown |
| 8. B-Naphthol | ----- | Bluish Red |
| 9. B-NaphtholamineHCl | Bright Orange | ----- |
| 10. A-NaphthalamineHCl | Reddish Orange | ----- |
| 11. PhenylhydrazineHCl | Rust Color | ----- |
| 12. Broenner's Acid | Browish Orange | ----- |
| 13. Peri Acid | ----- | Brownish Sol. |
| 14. 1-2-4 Acid | ----- | Brown. |

From the above results I recommend the following, as a clear way to bring before the students the wide variety of azo coloring matters produced by diazotization and coupling.

Two students may prepare the solutions of Sodium Acetate, Sodium Nitrite, Aniline HCl, Sulphanilic Acid, p-nitro-aniline HCl, and a-Naphthalamine HCl. These solutions are prepared in this way.

Sol. 1. 2 grams of substance to be diazotized.
20 cc of Conc HCl
200 cc of water.

Sol. 2 2 grams of sodium nitrite
100 cc of water

Project 1. Con't.

Sol. 3. 60 grams of Sodium Acetate.
200 cc. of water.

When ready to start the experiment take 25cc of sol.

2. and pour into 25 cc of solution 1. (Solution 1. being the one containing the substance to be diazotized.) To this now add 25 cc of solution 3. which is to repress the ionization of H⁺ ion. Now place 5cc of this mixture in each of five test tubes. Add a few drops of the solutions of the following compounds and record color obtained- If no color is obtained at first (In acid sol) then add a drop or two of sodium hydroxide.

Substances to be added (Second Component)

- | | |
|---------------|--------------------|
| 1. Aniline | <i>yellow</i> |
| 2. b-Naphthol | <i>brown red</i> |
| 3. Phenol | <i>brown (alk)</i> |
| 4. Peri Acid | <i>bluish red</i> |
| 5. H Acid | <i>purple</i> |

Repeat the above procedure using diazotized p-nitro-aniline placing five cc in each of five test tubes, and adding the following- recording colors produced.

- | | | |
|-----------------|------------------|-------------------|
| 1. Phenol | <i>orange</i> | <i>(deep red)</i> |
| 2. b-naphthol | <i>brown red</i> | |
| 3. Resorcinol | | <i>purple</i> |
| 4. Amino G salt | <i>light red</i> | |
| 5. H Acid | <i>purple</i> | |

Repeat procedure using diazotized sulphanilic acid and placing five cc. in each of three test tubes, and adding the following- recording colors produced.

- | | |
|-------------------|---------------|
| 1. Aniline | <i>yellow</i> |
| 2. diphenyl amine | |
| 3. b- naphthal | |

Repeat procedure using diazotized a-naphthalamine and placing five cc. in each of three test tubes, and adding the following- recording colors produced.

- | | |
|------------------------|---------------------|
| 1. b-Naphthalamine | <i>light orange</i> |
| 2. a-Naphthalamine | <i>red orange</i> |
| 3. phenylhydrazine HCl | |

Project 1. (Con't)

Arrange the test tubes containing the coloring matters formed, in a series ranging from the lightest formed, yellow, to the darkest formed, purple. This will give a clearer conception of the wide variety produced, even with the mono-azo dyes.

I followed this suggested procedure and obtained the following series.

| | <u>Diazotized Sub.</u> | <u>Second Component</u> | <u>Color</u> | <u>Medium.</u> |
|---|------------------------|-------------------------|---------------|----------------|
| ✓ | 1. Aniline | Aniline | Yellow | Acid |
| × | 2. Sulphanilic Acid | Aniline | Yellow | Acid |
| × | 3. " " | Diphenylamine | Light Orange | " |
| ✓ | 4. a Naphthal Amine | B-naphthalamine | Bright Orange | " |
| ✓ | 5. " " | a-naphthalamine | Red-orange | " |
| × | 6. Sulphanilic Acid | b-naphthalamine | Deep orange | " |
| | 7. P-nitro-aniline | AminoG Salt | Light Red | " |
| ✓ | 8. " " | b-Naphthal | Bright Red | " |
| ✓ | 9. " " | Phenol | Deep Red | Basic |
| | 10. Aniline | b-naphthal | Brick Red | " |
| ✓ | 11. P-nitro-aniline | Resorcinol | Brownish Red | Acid |
| | 12. a-naphthalamine | PhenylhydrazineHCl | Rust Color | " |
| ✓ | 13. Aniline | Phenol | Brown | Basic |
| | 14. " " | Peri Acid | Bluish Red | Acid |
| | 15. " " | H-Acid | Purplish Red | " |
| ✓ | 16. p-nitro-aniline | H-Acid | Purple | Basic. |

Project No. 2: To work out conditions for hydrolysis of n-butyl-acetate and identification of products.

It is a well known fact that an ester can be hydrolyzed by water with formation of the alcohol and acid from which it came. This reaction however is never complete, as the reverse reaction sets in. Also it may take an indefinitely long time. However it is possible to hydrolyze an ester completely by use of dilute acids or bases. It is in this manner that I have worked out the conditions for the hydrolysis of n-butyl acetate.

I STANDARDIZATION AND HYDROLYSIS.

I weighed out approximately 25 grams of NaOH and dissolved it in 500 cc of water. I then measured out three 25cc portions of the hydroxide and titrated with .2263 N HCl. The sodium hydroxide required 140.52, 138.52, and 139.8 cc. of acid. From this I found that the alkali solution was 1.2621 N. and therefore contains 10.0969 grs. of sodium hydroxide per 200cc.

I placed 25grams of n-butyl acetate and 200 cc of the hydroxide solution in a 200cc round bottom flask and refluxed for 1 hour. Then stopped the reaction and removed three 10 cc portions of the lower layer, which contains the unused NaOH, and NaAc. I titrated these portions with the standard acid above and found that it required: 26.85, 26.81, and 26.83 cc to neutralize. From this data I calculated that the NaOH was .607163 N. and therefore contains 4.85728 Grams of sodium hydroxide. $10.0968 - 4.85728 = 5.2395$ grams used up in the reaction. Now according to the relation

$$\frac{25}{116.0} = \frac{x}{40.0}$$

we find that requires 8.6 grams of sodium hydroxide to completely hydrolyze 25 grams of the ester. Now since we have found that 5.2395 grams have been used up. Dividing this by the 8.6 grams that will be used up when completely hydrolyzed, I find that the ester is 60.9 % hydrolyzed at the end of one hour.

I repeated the above procedure and refluxed for 2 hours and again withdrew 10 cc portions and titrated. I found that it now required 8.34 and 8.35 cc of acid. This gives a normality of .18895

Project No. 2 Con't:

Normal, to the NaOH, or that it contains 1.5112 Grams of sodium hydroxide. Subtracting this from the original amount of sodium hydroxide, 10.0968 I find that 8.5856 grams have been used up, and dividing this by 8.6 the amount required for 100% hydrolysis, I get 99.8% hydrolysis. Therefore it may be said that using sodium hydroxide of this concentration, that the ester will be completely hydrolyzed at the end of 2 hrs.

III Identification of Products.

After the hydrolysis I removed contents of flask to a distilling flask, and distilled until drops of water began to get prominent in the distillate. I then added anhydrous potassium carbonate to remove water which came over in distillate. Distillate was an alcohol and was tested for by the following processes.

(a) Oxidation of Butanol to Butyric acid.

I took about 2 drops of the alcohol and dissolved them in 5 cc. of water. Then added 1 cc. of conc. sulphuric acid and 1 gr. of potassium dichromate, and heated. An odor of rancid butter came off from the butyric acid formed, thereby proving presence of butanol.

I also tried oxidation with potassium permanganate in acid and basic solution. The acid solution and permanganate gave same reaction as the dichromate, but the alkaline sol. gave more of an odor of n-butyl-butyrate.

(Note- It is necessary to have the alcohol very dilute before oxidation, else part is oxidized and part is not, with subsequent formation of n-butyl-butyrate.)

(b) I took some of the pure dry alcohol and obtained the B.P. according to the Lowy- Baldwin method- It was 116 degrees.

(c) Formation of a derivative.

Following the procedure outlined in Mullican, using phosphorous pentichloride and 3-5 di-nitro-benzoic acid, I formed 3-5 dinitro-butyl-benzoate. The M.P. I obtained was 62.5- The true m.p. of this compound is 64.

Project No. 2; Con't

II Identification of products continued.

After the Butanol has been distilled off a little of the residue is made exactly neutral and to it is added a little portion of exactly neutral ferric chloride. A deep red coloration formed, proving presence of acetate ion. Therefore if residue is acidified we have acetic acid. (Note: Both solutions must be exactly neutral, else a ppt. of ferric hydroxide will form which will be mistaken for the ferric acetate.)

I also prepared a derivative in the following manner. I took .6 of a gram of sodium acetate, obtained by evaporating the residue, .3 cc of sulphuric acid, and one cc. of aniline, heated them together on a watch glass. The product obtained was Acetanilide as determined by the M.P. I obtained a melting point of 114 and it should melt at 116.

III Hydrolysis of a Phenolic Ester.

I placed 25 grams of phenyl-salicylate and 20 grams of sodium, in a round bottom flask, with 200 cc of water. I refluxed the mixture for two hours. In the flask there were then the sodium salts of phenol and salicylic acid. I acidified, which liberated both acids, which are insoluble in water at room temperature, at least practically so. Phenol being 6.7 parts in a hundred soluble at 16 degrees, and salicylic insoluble. I heated the mixture up, nearly to 100° and filtered. The majority of the phenol passes thru the filter while the salicylic acid remains on the filter.

A more satisfactory way to separate the two, is to pass a stream of carbon dioxide thru the mixture of the salts. The phenol being the weaker acid is ppt. from its salt, while the salicylic acid being stronger than the carbonic acid is left in solution. I tried this

Project No. 2 Cont.

Hydrolysis of a Phenolic Ester con't

out by dissolving 5 grams of each in sodium hydroxide and passing a stream of carbon dioxide thru the mixture for 2 hours. It worked but not very efficiently, as I only recovered 3.5 grams Phenol, which left part of the phenol still mixed with the salicylic acid.

The identification of these products is rather difficult since they both have very nearly identical properties. This eliminates the ferric chloride test. The phenol solution can be concentrated however, bromine added and the tri-brom phenol be identified. I did this and obtained a M.P. of 90.2 (Actual M.P. is 92.) This is not a certain test as bromine removes the carboxyl group from salicylic acid and would therefore give the same. However it might not do this in dilute solutions, while it would form the tri-bromophenol. The Salicylic acid was tested for by addition of methyl alcohol and sulphuric acid with formation of the well known and easily recognizable Oil of Wintergreen.

IV Suggested Laboratory Procedure for Hydrolysis of N Butyl Acetate.

Part 1.

Take 10 grams of n-butyl acetate and 5 grams of sodium hydroxide dissolved in 200 cc of water, and reflux for 2 hours. Stop the heat and after contents of flask have cooled somewhat pour into a distilling flask, connect to a condenser, and distill until drops of water start coming over with the alcohol in large amounts. Some water will come over anyhow as the alcohol boils near the boiling point of water. To the distillate add anhydrous potassium carbonate and let stand for a while. Then pour off

the alcohol. Take about three drops of alcohol and dissolve in 5 cc of water. Add 1 cc of conc. Sulphuric Acid and 1 gram of potassium dichromate, and heat. Note odor- an odor of rancid butter, which is given by butyric acid proves presence of butyl alcohol. Take a small portion of the residue and make it exactly neutral, and add to it a few drops of exactly neutral ferric chloride. A reddish ppt. proves presence of acetate ion.

Part. 2

Dissolve equal portions of phenol and salicylic acid in sodium hydroxide and pass a current of carbon dioxide thru the mixture. A ppt. forms. What is it?

Test this ppt. by adding bromine, which forms a derivative. The M.P. will show that it is tri-bromo phenol. The solution will be salicylic acid. Test this by addition of methyl alcohol and sulphuric acid. It should give a smell of oil of wintergreen, proving presence of salicylic acid. What does this show as to relative strengths of the two acids, (Phenol and salicylic acid.)

Project No. 3: To demonstrate reactivity of alkyl halogen when under influence of activating groups.

The reaction by which this can be tested is based upon the fact that the halides are hydrolyzed in water with liberation of the halogen ion with subsequent reaction with silver nitrate to form silver chloride.

I prepared solutions of the halides, in 80% Ethyl alcohol solution, which were to be tested and used alcoholic silver nitrate to test them with, in order to insure solubility. Below is a list of the halides I tested and the results found.

1. Ethyl Bromide. Slight cloudiness after 5 minutes.
Strong cloudiness after 45 minutes.
White ppt. after $1\frac{1}{2}$ hours.
2. Ethyl Brom Acetate. Cloudiness after $\frac{1}{2}$ minute
Very cloudy after 5 minutes.
Ppt. after 10 minutes.
3. Ethylene Bromide. Immediate yellowish white ppt.
4. Ethylene Chlorohydrin. Slight cloudiness immediately.
Turbidity in 2 minutes.
5. a- bromopropionic acid. Strong cloudiness immediately.
Ppt. in 1 minute
6. Iso-propyl bromide. Ppt. after 2 minutes.
7. Chloroacetic acid. Only slight turbidity after a while.
8. Iodo- acetic acid. Immediate ppt.

From the above experiments I made a list of the halides in the order of their reactivity. The most reactive first, and so on down.

1. Ethylene Bromide
2. a-bromo propionic acid
3. Iso- propyl bromide
4. Iodo-acetic acid
5. Ethyl brom acetate
6. Ethylene chlorohydrin
7. Ethyl Bromide
8. Chloro acetic acid.

Project No. 3 Con't:

Two things are illustrate by the above experiment . One is that the halides of the more complexed order, as ethyl-brom acetate, and a-bromo-propionis acid, are more reactive than the simple halides like ethyl bromide. The second thing it shows the greater activity of the iodide than the chloride, as is shown by the reaction of Iodo- acetic acid and chloro-acetic acid.

Project No 4: To demonstrate increased reactivity of aryl halogen with increase of nitro groups.

The reaction by which I proved this was the reaction of silver nitrate on the halide ion with formation of silver chloride. I followed two procedure one in the cold with alcoholic silver nitrate, the second by heating with KOH, acidifying and then adding the silver nitrate. The first is placed under column marked In Cold, the second in column marked Hot.

Below is a list of the substances so tested and the results obtained.

| | <u>In Cold.</u> | <u>Hot.</u> |
|-----------------------------|-------------------|----------------------|
| 1. Chloro toluene | No reaction | Cloudiness |
| 2. Chloro benzene | No reaction | No reaction |
| 3. 2-4 dinitro chlorbenzene | Cloudiness | Immediate ppt. |
| 4. Benzyl Chloride | Immediate ppt. | |
| 5. Picryl chloride | Cloudiness | Immediate ppt. |
| 6. o-nitro chloro benzene | Slight cloudiness | Stronger cloudiness. |
| 7. | | |

From this I made up a table of increasing reactivity beginning with least reactive to the most.

1. Chloro-benzene
2. Chloro-toluene
3. o-nitro chlor-benzene
4. 2-4 dinitro chloro benzene
5. Picryl chloride (Tri nitro chlorbenzene)
6. Benzyl Chloride.

This table shows the following facts.

1. That halogen on the side chain is more reactive than on neucleous
2. That Neuclear halogen is made more reactive by presence of other groups attached to neucleous.
3. That addition of nitro groups increases the reactivity of halogen, in proportion to number of nitro groups attached.

Part 2.

Can 2-4 dinitrochlorobenzene be converted into 2-4 dinitro-aniline? by use of amonium or amonium salts?

I took 10 grams of 2-4 dinitrochlorobenzene, 80 cc of alcohol, and 80 cc. of conc. Amonium Hydroxide and refluxed for an hour. When it was cooled I filtered, rechrystalized from hot alcohol, and obtained 7 grams or 77.2 % yield of 2-4 dinitro-aniline, which had a melting point of 180.5. The M.P. should be 182.

Project No 4 Con't.

Test tube experiment.

Take 1 gram of 2-4 dinitro-chlorobenzene and 5 grams of ammonium acetate and heat for five minutes in a test tube. Pour into water, filter, recrystallize from hot alcohol and determine M.P. Reporting also any change in appearance of substance. What is it?

I tried the above experiment and obtained practically quantitative yield of the 2-4 dinitro aniline as shown by M.P. I obtained a M.P. of 180.7. The correct M.P. is 182.

This experiment gives a method for the replacement of the Halogen in a compound by the amino group.

Project No. 5 : To show that Nitrogen is evolved when a primary amine or amide is treated with nitrous acid.

This reaction of a primary amine or amide with nitrous acid is a well known reaction. The difficulty is that in adding the acid to sodium nitrite, oxides of nitrogen come off, and these make it impossible to tell whether we are getting off Nitrogen or not. This difficulty is removed in the Van Slyke method of determining nitrogen in amino groups. (Described in Hawk's Physiological Chemistry) However we can easily see that this method requires apparatus that is too costly, and requires too much time for an ordinary laboratory test for primary amines. Yet we can use a very important Idea of Van Slyke's, that of absorbing the oxides of Nitrogen in an alkaline solution of potassium permanganate.

I made up my permanganate solution as follows.

6 grams of Potassium permanganate
4 grams of Potassium Hydroxide
200 cc. of water.

In a test tube with delivery tube attached I 5 cc of 20% solution of sodium nitrite and 3 cc of N/10 sulphuric acid. The end of the delivery tube was placed under a test tube filled with the permanganate solution and inverted over an evaporating dish filled with the permanganate sol. The test tube was filled with a gas from the reaction, which for the most part was air from the apparatus. I then placed the delivery tube under a second tube, but only a very little bit of the solution was forced out by gas, even when heat was applied.

After this blank run, I placed the same amounts of acid and sodium nitrite in the reaction tube and added a gram of Methyl Amine HCl. I again caught the gas over permanganate however this time collecting three tubes of gas. I discarded the first two. Into the third I placed a glowing splinter which was immediately put out. Now according to the equation for this reaction of an amine with nitrous acid this gas should be nitrogen. The fact that in the blank run, only one tube was filled with gas, and that in the second run three tubes were given off show that some gas from the reaction must have come off. The glowing splinter ~~test~~ ^{being extinguished} given a rather substantial pro_of of Nitrogen.

Project No. 6 : Synthesis of Ethyl-Butyl Ether by use of Ethyl Sulphate instead of Ethyl Bromide.

The older method in which Ethyl bromide and n-butyl bromide were used has many drawbacks, chief among them the repeated fractionations required, and the difficulty of having efficient condensation.

A test tube experiment performed by L.J. Desha, 3/18/28 in which a mixture of n-butanol and ethyl sulphate were placed in a test tube and a small piece of sodium hydroxide added, gave a violent reaction. After reaction had ceased a little water was added, the tube shaken, and allowed to settle. Two layers were observed, the upper layer giving indications of being Ethyl-Butyl Ether.

Cade in Chem. and Met. Vol. 29, page 230 gives procedure for making Phenetol by use of ethyl sulphate, and says it can be used for other mixed ethers, for example ethyl-butyl ether. Taking this suggestion and altering somewhat I prepared this ether and obtained good results. Three variations were tried.

In the first method tried I placed a mol of Butanol and a mol of sodium hydroxide in a 500cc round bottom flask, connected with a long water condenser. Heated the mixture up to 100 degrees and added slowly a mol. of ethyl sulphate. A vigorous reaction set in. when this had slowed down some what I refluxed it at about 100 for 4 hours, removed flame allowed to cool, and then set up apparatus for distillation under reduced pressures. I distilled off the ether formed at 40 degrees and a pressure of 100 mm. Then dried with anhydrous potassium carbonate. Then distilled off the ether. It came off between 86 and 98 degrees. Yield was about 89.9 grams or 87.8 % yield. The total time required is about 5 hours, not counting time for the drying of the ether.

In the second method I used $\frac{1}{2}$ mol of sodium hydroxide and n-butanol. Heated the mixture to 100 degrees and then discontinued the external heating. Now added $\frac{1}{2}$ mol of ethyl sulphate. Utilizing only the heat of the reaction, which lasts about 45 mins. I then added about 4 times the volume of the mixture of water, poured into a separatory funnel. Draw off lower layer which is water, and pour the upper layer into a distilling flask. Dry with

Project No. 6 Con't:

anhydrous potassium carbonate and distill. It came off between 85 and 95 degrees. I obtained a yield of 34.2 grams or 66.7 % yield. Total time required is only a little over an hour, not counting time for drying of the ether.

The last method I tried is practically the same as the second. Using one mol each of butanol and ethyl sulphate, but only 1/2 mol of sodium hydroxide. I also refluxed for 1/2 hour, before addition of water. Separated as before, dried and distilled. I obtained 77.3 grams or 75.3% yield.

I recommend the last method as it is much shorter than the first method, eliminated the distillation under reduced pressures and requires less NaOH. It gives a better yield than the second method.

Test tube experiment. Which I tried successfully.

Add a small piece of sodium hydroxide to a mixture of 1 cc each of butanol and ethyl sulphate. Vigorous reaction sets in. when this ceases add about 5 cc of water and shake. Allow to settle and pipette off a little of the upper layer. Dry with small amount of anhydrous potassium carbonate. Test the ether by adding sulphuric acid (Conc) The ether is dissolved with little coloration. When cold water is added it separates out into two layers again, the part of the ether is lost since heat of the sulphuric acid and water is insufficient to evaporate some of it.

Project No. 7: Effects of the substituents R and R' upon the rate of reaction of the ethylene compounds of the type $R-C = R_3$

The way this was made was to measure the rate of addition of Bromine to the double bond in the compounds, Oleic acid, cinnamic acid, and trichloroethylene. I used a quantitative method to make this comparison.

First I made M/10 solutions of the three substances to be tested, in carbon tetrachloride. Also prepared solutions of approximately .25 N. Bromine in carbon tetrachloride, and .10N solution of sodium thiosulphate.

I pipetted out two ten cc. portions of the Bromine solution, added about 2 grams of KI, and some sodium bicarbonate. The Bromine liberates the Iodine from the KI, and the bicarbonate destroys any HI formed. The 10 cc of Bromine required. 24.27 and 24.29 cc of sodium thiosulphate.

I now took two 10 cc portions of bromine and added 10cc of Oleic acid solution. Let them stand $\frac{1}{2}$ hour, then titrated using same procedure as when bromine alone was titrated. It required 16.42 and 16.45cc of thiosulphate. In the same manner I tested portions of Cinnamic acid and trichloroethylene. Results of these experiments were.

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| Oleic Acid | 16.42, 16.45 cc of thiosulphate used. | app. 8cc of Br ₂ |
| Cinnamic acid | 19.25 and 19.27 | " " 5cc of " |
| Trichloroethylene. | 24.05 and 24.05 | " " no Bromine. |

I also tried these same substances at higher temperatures. Mixing them with the bromine and heating to 60 degrees for $\frac{1}{2}$ hour. The results in this case were

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| Oleic Acid. | 12.58 and 12.6 cc of thiosulphate- | app. 12 cc of Br ₂ |
| Cinnamic | 16.54 16.57cc " | " 8 " " |
| Trichlorethylene | 16.24 and 16.25 | " 8 " " |

Project No. 7 Con't:

The above procedures show that in the cold oleic acid adds bromine most rapidly, Cinnamic next and trichloroethylene.least. But that on heating they all require about the same for saturation about 8cc of Bromine. The Oleic seems to take on more, but this is due to some substitution taking place, as is proven by HBr being given off.

For ordinary laboratory experiment I suggest that the student take about 2 cc each of the solutions , of about M/10 strength and add a fewdrops of bromine , in carbon tetrachloride. Note any disappearance of the color. The oleic will be seen to take up bromine rapidly, the cinnamic slower , with formati on of a white ppt. , and the trichloroethylene hardly any. Then place the tubes in water at about 60 degrees and observe that the color leaves all three tubes.