

SWANSEA TECHNICAL COLLEGE.

ORGANIC CHEMISTRY - PRACTICAL.

1. PREPARATION OF ACETALDEHYDE.

Fit distilling flask with a well-fitting cork which carries a dropping funnel. Connect to a water-condenser with adapter attached. Place 1.75 ml. of sulphuric acid (5 ml. water to 1.7 ml. acid) in the flask and add a few pieces of unglazed porcelain. Dissolve 1.25 gm. of sodium dichromate in 1.25 ml. of water, add 1 ml. of alcohol and then place the well stirred mixture in the dropping funnel. Ensure that a rapid stream of cold water is passing through the condenser and that the adapter dips into a 25 ml. conical flask which is surrounded by ice. Heat the acid in the flask until it starts to boil gently, and then remove the flame and run in the dichromate solution slowly. Directly the alcoholic dichromate solution enters the hot acid, a vigorous reaction occurs, and a mixture of acetaldehyde and water, containing a little acetic acid, begins to distil over: the reaction mixture becomes green owing to reduction of the dichromate. Towards the end of the addition of the dichromate it will be necessary to replace the flame under the flask to maintain GENTLE boiling. When the addition of the dichromate solution is complete, a moderately strong aqueous solution of acetaldehyde will have collected in the receiver.

Carry out the general tests for aldehydes ⁿincluding the preparation of the 2:4 dinitrophenylhydrazone. (See Exercise 2.)

2. HYDROLYSIS OF AN ESTER AND ISOLATION AND IDENTIFICATION OF THE PRODUCTS.

HYDROLYSIS.

Place 0.5 ml. of ethyl benzoate into a round-bottomed flask together with 5 ml. of 10% sodium hydroxide solution. Add a few pieces of unglazed porcelain, attach a water-condenser and boil gently for about 50 minutes (until the oily layer disappears). The resulting mixture will contain the alcohol and the sodium salt of the acid.

Distill off 2 ml. of the liquid which will contain most of the liberated alcohol.

ISOLATION OF THE ACID.

By means of a teat pipette transfer about 1 ml. of the solution left in the distillation flask into a crystallising tube. Acidify with dilute hydrochloric acid and filter off the precipitated organic acid on a Willstatter "nail". Wash with a few drops of cold water, recrystallise from hot water, and determine the melting point of the crystals.

PREPARATION OF THE 2:4 DINITROPHENYLHYDRAZONE OF THE OXIDATION PRODUCT OF THE ALCOHOL.METHOD.

In the absorption tube of the aspiration apparatus place 4 ml. of saturated 2:4 dinitrophenylhydrazine in 2N hydrochloric acid.

Place 0.5 ml. of the aqueous distillate obtained above into the evolution tube, together with 2 ml. of 5% potassium dichromate solution and 2 ml. of dilute sulphuric acid.

Assemble the apparatus and draw through it a slow current of air (about 1 to 2 bubbles per second). Slowly heat the evolution tube until gentle boiling occurs and continue heating until precipitation in the absorption tube appears to be complete.

Dismantle the apparatus and filter off the yellow phenylhydrazone on a Willstatter "nail" rinsing with a little 2N hydrochloric acid. Wash the precipitate with water and transfer it to a 5 x 2 cm. crystallising tube, rinsing funnel and filter paper (held in forceps) with a few drops of boiling methylated spirit (heat tube on a water-bath) and allow to cool, first closing the mouth of the tube with a slotted cork, finally cool in ice for 5 to 10 minutes. Filter off the crystals on a Schwinger filter, wash with a few drops of cold methylated spirit, and suck dry (close the mouth of the filter with a cork carrying a calcium chloride tube and cotton wool dust filter and allow the pump to run for about 5 minutes). Record the yield and determine the melting point of the crystals.

3. PREPARATION OF ACETANILIDE.

Add 2 ml. of a mixture of equal volumes of acetic anhydride and glacial acetic acid to 0.5 ml. of aniline contained in a round-bottomed flask. Fit a reflux water-condenser to the flask and boil the mixture gently for 30 minutes. Then pour the hot liquid into 10 ml. of cold water, stirring the latter well during the addition.

The acetanilide crystallises rapidly. Filter on the Willstatter "nail" and wash the crude acetanilide with water. Recrystallise from about 3 ml. of a mixture of equal volumes of acetic acid and water; filter off the colourless crystals on the "nail", again wash well with water, drain, and dry. M. Pt. 113 C.

4. PREPARATION OF METHYL BENZOATE FROM BENZOYL CHLORIDE.



1 ml. of benzoyl chloride are boiled for 10 minutes with 1.25 ml. of methyl alcohol (excess) in a small distilling flask fitted with a reflux condenser. The product is fractionally distilled. When the excess of methyl alcohol has been removed, the water condenser is replaced by an air condenser, and the fraction boiling above 190°C is collected. Yield is almost theoretical.

5. PREPARATION OF PICRIC ACID FROM PHENOL.

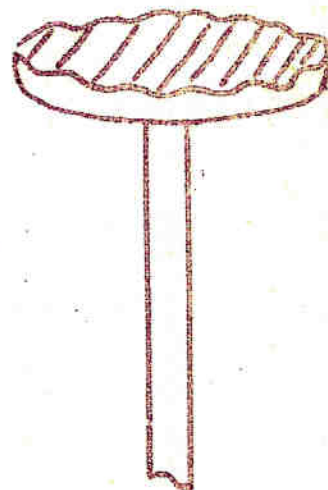
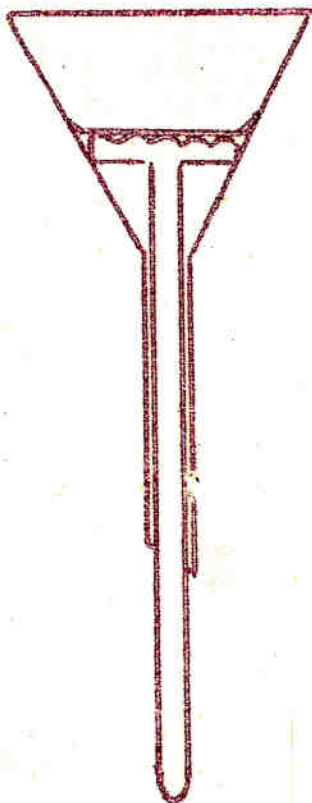
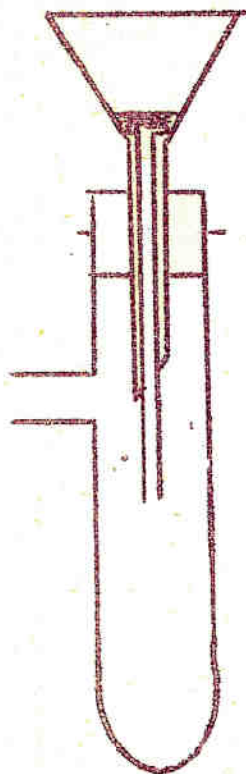
6. PREPARATION OF ANILINE BY THE REDUCTION OF NITROBENZENE.



0.5 gm. of nitrobenzene and 1 gm. of tin are placed in a round-bottomed flask fitted with an air condenser, and 2.5 ml. of concentrated hydrochloric acid are added gradually through the condenser tube in quantities of about 0.25 ml. at a time.

The mixture is shaken well after each addition; it soon becomes warm, but active ebullition must be prevented by cooling the flask when necessary with water to prevent loss of nitrobenzene and aniline. Towards the end of the reaction moderates, and the remainder of the acid may be added more quickly. To ensure complete reduction, the flask is heated on a water-bath until no odour of nitrobenzene can be detected, more tin being added if necessary. To obtain the amine

from the stannichloride, (C H .NH 7HCl) SnCl , the contents of the flask are diluted with water (2 ml.), and then made strongly alkaline by the gradual addition of sodium hydroxide solution (3 grms. in 4 ml. of water). The addition is carried out slowly so as to avoid active ebullition and thus loss of amine. The alkali is added until the stannic hydroxide at first precipitated is completely redissolved, and the mixture shows a strongly alkaline reaction. The aniline separates out as a dark oil, and is removed by steam distillation, the process being continued until the distillate is clear. The distillate is saturated with common salt (about 3 grms. for every 10 ml. of distillate) and extractef with ether. The ethereal solution is separated and dehydrated by allowing to stand for some time over solid potassium hydroxide. The clear liquid is decanted into a distilling flask, the potash and the vessel being washed with a little ether, the ether removed, and the aniline distilled, an air condenser being used.

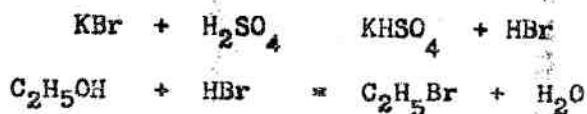


Willstatter "Nail"

7. PREPARATION OF ETHYL BROMIDE - C₂H₅Br. (FROM ETHYL ALCOHOL).

2.5 mls. of concentrated sulphuric acid are placed in a round-bottomed flask and an equal volume of ethyl alcohol added gradually with constant shaking and cooling. 1.2 grams of powdered potassium bromide are then added, the flask connected with a condenser, the open end of which is fitted with an adaptor which dips under ice-cold water in a flask. The mixture is heated quickly on a sand bath, (frothing occurs during the reaction), and the ethyl bromide passes over and collects as a heavy layer at the bottom of the water in the receiver. The distillation is continued until no more oily drops pass over.

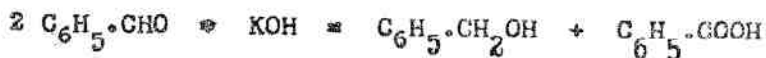
The oil is freed from the aqueous layer by means of a separating funnel; it is washed with water, again separated, and then shaken with dilute sodium carbonate solution (N.B. - During the latter operation the funnel should be inverted and the stop-cock remain open). After another wash with water the ethyl bromide is dried by allowing to stand over granular calcium chloride until the liquid becomes clear. Decant into a distilling flask and collect in a cooled receiver.



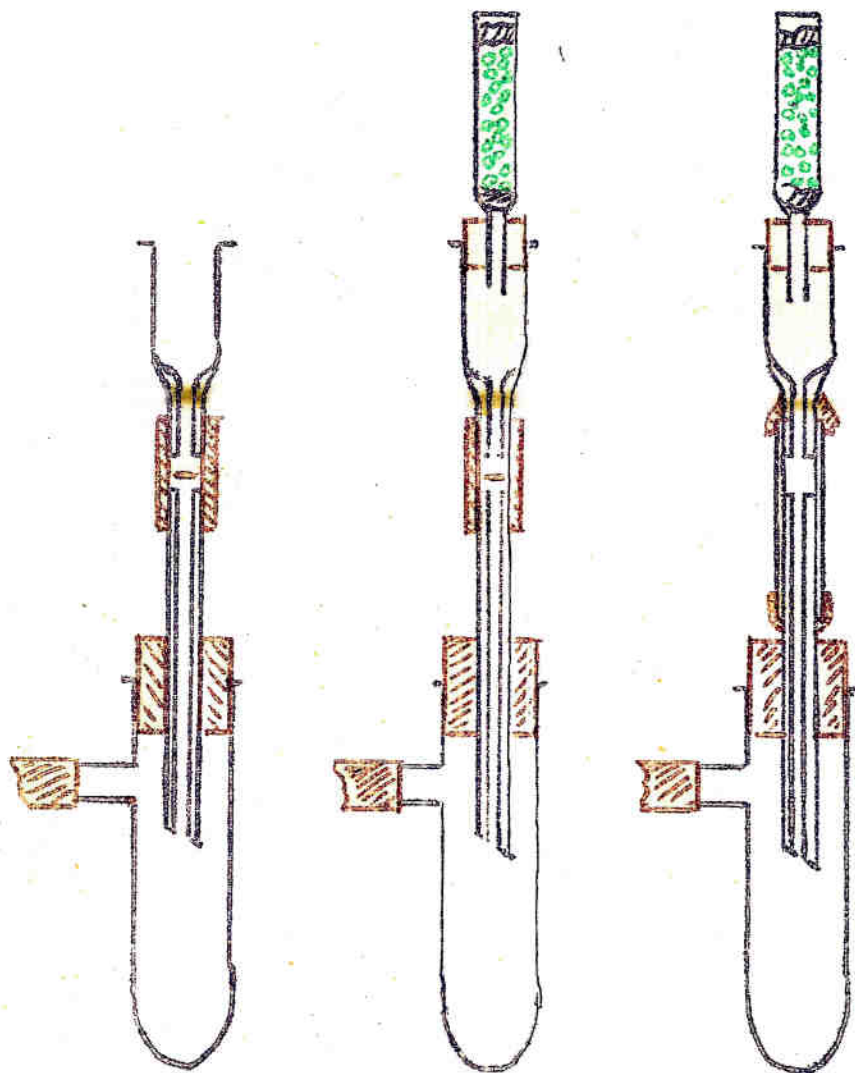
8. PREPARATION OF BENZYL ALCOHOL, C₆H₅.CH₂OH, AND BENZOIC ACID, C₆H₅.COOH, FROM BENZALDEHYDE, C₆H₅.CHO.

2 mls. of benzaldehyde are added to a solution of 1.8 grams of potassium hydroxide in 1.2 mls. of water in a thick walled test-tube closed with a CORK, and the mixture shaken vigorously until a permanent emulsion is formed. It is then allowed to stand overnight, when a thick precipitate of potassium benzoate separates out. The mixture is then treated with water and shaken until a clear solution is obtained. Extract with ether THREE times. Dry the ethereal solution over anhydrous potassium carbonate, pour into a distillation flask and fractionated. After the ether has been removed replace the water condenser with an air condenser, and collect the fraction which distils at 200 - 210 C is collected.

The alkaline solution left after the ether extraction is acidified with moderately strong hydrochloric acid and cooled. Filter off the benzoic acid, wash with water, and recrystallised from hot water. Determine its melting point.



Schwinger Filter



Simple Vacuum Desiccator

