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# Work in Organic Laboratory by
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## Distillation of Benzol.

I used for this an iron mercury bottle to which was attached a column of five compartments and a Liebig condenser. Placed 2500 $cm^3$ commercial benzol in the retort and distilled off about 1/6 below 79°–79°.5, about 1/3 below 82°, 1/3 between 82° & 83° and had 1/6 residue in the still. Afterwards all the last portions were heated in still to 90° distilling off about 1/4 which was to have been redistilled below 83° but was not. The second and third portions were frozen in bottles by immersing in ice and salt and the unfrozen portion drained off.

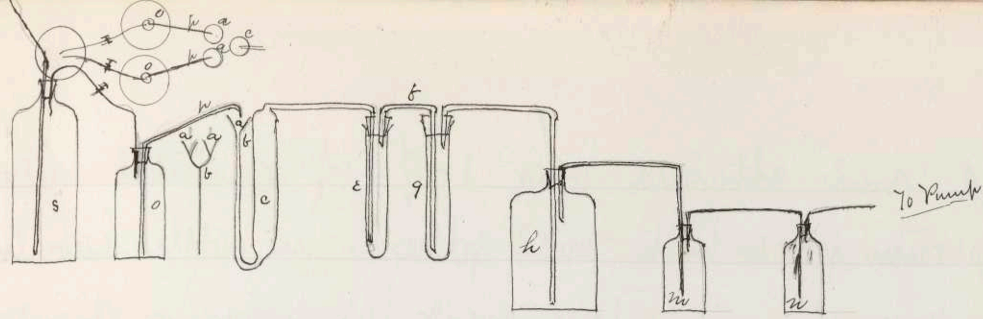
## Nitrobenzol.

I attempted at first to make this by dropping a mixture of $HNO_3$ & $\frac{1}{2}H_2SO_4$ into 500 $cm^3$ benzol shaking as much as possible in a cold water bath. After all acid 600 $cm^3$ was added heated for a short time in a waterbath, separated the two layers with a separator, washed with water & dilute solution of $Na_2CO_3$

until free from acid and obtained 500 $\text{cm}^3$ washed product. Placed this in a 500 $\text{cm}^3$ retort, distilled off $H_2O$ and unconverted benzol below 160° and had 150 $\text{cm}^3$ crude Nitrobenzol remaining. Nov. 8th I repeated this with like result 150 $\text{cm}^3$ nitrobenzol The next process was by dropping 500 $\text{cm}^3$ benzol into 450 $\text{cm}^3$ fuming nitric acid heated in a waterbath shaking constantly and washing product as before. But this product of 500 $\text{cm}^3$ became cloudy and deposited crystals of Dinitrobenzol? on cooling so I concluded to change the whole into dinitro. without purifying as nitrobenzole.

In my next attempt I tried to follow on a small scale the commercial process i.e. mixing thoroughly and in small quantities the benzol and acid with gradual increas of heat as acid became diluted. I first tried a spiral of glass tube but could not get a sufficient mixing and at same time prevent a spattering of the reagents out of upper end of the tube Then the apparatus here represented was tried with very good results.-

a a are two funnels attached to T at b which T opens into larger tube c which is filled with glass beads This tube c, leads to bottom of test tube e. & tube f from



this to bottom of g. thinner tubes lead to bottom of liter bottle h and to smaller bottles m & n. The acid fuming nitric & benzol equal parts are placed in two .5 liter bottles o furnished with delivery tubes p leading to funnels a a. Behind these bottles is large bottle s containing compressed air which is admitted to o o by rubber tubes provided with screw cocks for regulating flow of air & consequently the flow of liquids into a, a, c is placed in cold water bath e in water heated to 60° and g in water at 100°. h & m in cold water, n in a freezing mixture of salt & ice to condense any benzol which might be carried through h & m. The air pump was attached to x with a cock to regulate suction so that a quiet flow of air could be maintained through the apparatus while acid & benzols were dropping into a a at rate of 150-175 drops each per minute the product collecting in h.

The first trial was without test tubes e & g consequently 230 $cm^3$ unconverted benzol from 500 $cm^3$ worked on. This 230 $cm^3$ was again treated with acid in apparatus as represented and obtained over 100% of distilled nitrobenzol a portion of which was placed in bottle labelled Nitrobenzol Two          The next lot was for dinitro. so I used warm water around c and one test tube heated to 100°, Product from 500 cm³ benzol = 500 cm³ Sp Gr about 1,2 after washing. During the reaction hardly any nitrous fumes appeared and amount of benzol in b only 1-2 cm³. It was found that if a freezing mixture was used in m the tube was apt to be clogged by frozen benzol.

In distilling nitrobenzol a 500 cm³ retort was used the washed nitro placed therein with a few grams $CaO_2H_2$ & platinum scraps. The retort was placed in an iron bean pot with tin cover and distillation continued until thermometer stood at 200°. Separated water & nitrobenzol collected, returned the nitro. to the retort and repeated the distillation. The second distillate below 200° was very small. Continued the distillation at 205°-210° until distillate had a reddish tinge

Dinitrobenzol.

Heated 500 cm$^3$ nitrobenzol with equal bulk of fuming nitric acid to boiling for three days & then added contents of retort to a mixture of equal parts fuming nitric & sulphuric acids as long as dissolved. Diluted with 8. liters water filtered & washed the ppt. free from acid. Dissolved in hot alcohol and cooled slowly but quite a quantity of what proved to be on testing unconverted nitrobenzol separated out at bottom below 86°. Decanted supernatant liquid and cooled slowly. Filtered and washed crystals with alcohol, redissolved & recrystallized in long (4 in) crystals almost colorless. Dried in warm place & placed in bottle labelled Dinitrobenzol. The next time I dropped nitrobenzol undistilled into equal parts fuming nitric and sulphuric acids as long as dissolved & then boiled for 15 minutes before diluting. This time no unconverted nitro. was found

## Paranitraniline

Saturated 500 $\text{cm}^3$ Alcohol at about 60° with dinitrobenzol, added 150 $\text{cm}^3$ $NH_4OH$ and passed $H_2S$ through the solution heated to about 65° for 2 days. added 150 $\text{cm}^3$ more $NH_4OH$ and continued passing $H_2S$ until solution was saturated. Then distilled off excess of alcohol and dissolved residue in hot water and crystallized nitraniline by cooling. Redissolved and recrystallized. The crystals were of an orange yellow color while according to Gmelin they should be bright yellow. The delivery for $H_2S$ should be as large as possible to avoid choking up with nitraniline crystals.

## Paradiamidobenzol.

Reduced 50 grms dinitrobenzol with 300 grs Tin and 1 liter $HCl$, 34%, in a two liter flask, cooled in cold water until violence of reaction was over. Then warmed and finally boiled until all tin was dissolved. This precaution was not taken the first time consequently materials were lost by boiling over. The resulting when cooled deposited a large amount of needle shaped crystals which disappeared on heating. Evaporated the solution almost to dryness to expell excess of HCl dissolved in hot water and passed $H_2S$ through solution until all tin was ppt as sulphide. ——— Then I intended to filter evaporate to small bulk and crystallize out $C_6H_4(NH_2)_2$ HCl by cooling and decompose this with Na-O-H.

I tried to decompose the chloride by adding Na-O H before removing the tin but it took so much Na O H to redissolve the Sn compound precipitated and the residue was such a vile looking mess that I did not try to separate the $C_6H_4(NH_2)_2$ by that method

## Aniline

Reduced 200 grms nitrobenzole with 600 grms tin and excess of HCl as in Paradiamido-benzol. Evaporated almost to dryness, diluted with water and precipitated tin with $H_2S$. Filtered and passed steam through filtrate heated to boiling but could smell no nitrobenzol. Added Na O.H to alkaline reaction, washed and distilled collecting about 135 $cm^3$ Aniline

To purify commercial aniline I saturated with HCl heated to boiling and passed steam through the solution until the odor of nitrobenzol which was very strong at first had entirely disappeared. Then added NaOH solution until alkaline, washed with water and distilled. The results by this process were variable. From 500 cm³ commercial aniline I obtained first 300 cm³ next time 150 cm³ before distilling. A third time 415 cm³ before and 375 cm³ after distilling and again from 1 liter obtained 400 cm³ distilled

## Acetanilide

Heated 100 gms aniline with about 100 gms. glacial acetic acid in a flask with inverted condenser until boiling point fell to 110° then distilled off dilute acetic acid until boiling point rose to 120°. inverted again until boiling point rose to 145 and then distilled off excess of acid and water. Dissolved the residue in flask, which became solid on cooling, in hot water, using the same water over and over again, and crystallized the acetanilide by cooling. Redissolved and recrystallized obtaining a pure white product. At the same time I tried to make acetanilide by dropping acetyl chloride into aniline. Poured resulting product into cold water filtered and washed almost free from chloride. Dissolved the product thus obtained in hot alcohol evaporated somewhat and cooled. The crystals were of a very dark brown color. Dissolved them in hot water obtaining a muddy solution which was some what improved by filtering crystallized by cooling obtaining crystals of brownish color which subsequent recrystallizing did not remove. Repeated with glacial acetic acid twice obtaining each time a clean white product, but one lot while lying moist on funnel was exposed to chlorine vapors and assumed a purple color which color it retained after two crystallizations

## Nitracetanilide

Dissolved acetanilide in fuming nitric acid in a cold water bath. diluted with water and filtered obtaining a brick red mass not very soluble in hot water from which it separated on cooling in a flocculent yellowish mass which when filtered appeared brick red. with yellow specks scattered through.

In the above work I have obtained what help I could from — Girard et Delaire - Dérivés de la

Huille — Fehling, Handwörterbuch der Chemie-
Wöhler, Organic Chemistry —
Gmelin. Handbook of Chemistry —