.8830 (JRC-6-47, No. 1) 2,4,6-trinitrobenzene By L. C. Holt

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JLR-56-47, No. 1

Serial Number 18830

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E. I DuPont de Nemours & Company

Jackson Laboratory

May 3, 1944

2,4,6-Triethyl-Bromobenzene

Problem Report

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2,4,6-Triethyl-Bromobenzene
(Project 3439)

L. C. Holt

JLR-56-47, No. 1 Serial Number 18830

Object of the Work:

To work out a plant process for the manufacture of 2,4,6-triethyl-bromobenzene which will react with 1,4-diamino-anthraquinone and yield a base which on sulfonation will produce a satisfactory quality of an anthraquinone milling blue.

Period Covered by the Report:

January 12, 1944 to April 29, 1944.

Historical Background:

A patented anthraquinone milling blue (Brilliant Alizarine Milling Blue BL) the starting intermediate for which is symmetrical trimethyl benzene, has been on the market. A product to compete with this dyestuff is desirable. D. X. Klein made a laboratory sample of 2,4,6-triethyl-bromobenzene and converted this to an analagous color. This product has been accepted as a satisfactory competitive material, (Reference 1). A patent application has been filed on this new dyestuff (Reference 2).

The method used by Klein in preparing his intermediates was employed only as a quick means of getting information on the problem and had no commercial prospects. The developing of a practical commercial method of getting the necessary 1, 3,5-triethyl benzene and its bromo derivative was therefore taken up.

Conclusions:

Tentative plant processes were developed which are expected to give the desired intermediate at attractive cost. 1,3,5-triethylbenzene is made by the ethylation of benzene with ethyl chloride in the presence of aluminum chloride, separated from other materials by fractional distillation

and treatment with sulfuric acid, giving a satisfactory intermediate for the preparation of a bromo derivative for condensation with 1,4-diaminoanthraquinone to produce a milling blue.

A commercial sample of triethylbenzene which was probably produced by the action of ethylene on benzene was found to be unsatisfactory for our purpose.

Summary:

Benzene has been reacted with ethyl chloride in the presence of a small amount of aluminum chloride to form a mixture of ethylated benzenes. A mixture of 1,3,5- and 1,2,4-triethyl benzenes can be separated by fractional distillation. Both the lower and the higher ethylated benzenes can be returned to the reaction vessel and further treated. The only products removed are thus the two triethyl products, these being the final form in which all of the benzene appears. The yield from both benzene and ethyl chloride approaches the quantitative point, the only losses being due to the volatility of the materials being handled and to mechanical operations.

A satisfactory quality of 1,3,5-triethyl benzene can be obtained from the above mixture by agitating it with half its weight of 98% sulfuric acid at about 60°C. and separating off the unsulfonated layer. About 65% of the weight of the mixture is obtained as usable material.

The 1,3,5-triethylbenzene as prepared above can be readily brominated to a product which on distillation is satisfactory for the production of the desired milling blue.

Patent Status:

The final dyestuff to be made as a result of this work is covered by a U.S. Patent application owned by the DuPont Co. (Reference 2).

Triethyl benzenes and their monobromo derivatives are old products. The principle phases of the methods by which they have been made in this work have been described in the literature. See AN-2407.

Experimental:

Two alternative methods for the manufacture of ethylated benzenes are known. The commercial method used for the production of ethylbenzene for conversion to styrene is by the condensation of ethylene with benzene. Triethylbenzenes can be obtained by pushing the same procedure further (Reference 3). This method was not adopted because no ethylene is available at the Chambers Works except it be purchased in cylinders. Such ethylene has no cost advantage over ethyl chloride produced locally. In addition the reaction between ethylene and benzene is not as controllable as with ethyl chloride. For the limited amount of triethylbenzene required, the synthesis from ethyl chloride appeared more attractive.

The reaction between ethyl chloride and benzene has been exhaustively studied and reported on by Smith and Guss in reference 4. They passed ethyl chloride vapor into an agitated suspension of aluminum chloride in benzene at 70 to 75°C. until approximately 80% of the theoretical amount necessary to produce triethylbenzene had been added. The reaction mass on standing separated into a clear, yellow upper layer and a dark red lower layer. They worked up the two layers separately and found that the upper layer had more of the desired triethylbenzenes than the lower layer and the latter more of the higher alkylated benzenes. The aluminum chloride catalyst was in the dark lower layer.

It appeared possible to continue ethylating benzene without the use of fresh catalyst by drawing off the upper layer and then adding more benzene and ethyl chloride to the lower layer. This method of operation proved to be practical so it was adopted for all the work done.

During the early stage of the work the upper layers were fractionally distilled, the triethylbenzenes removed and the lower alkylated benzenes returned to the alkylation step. The tetra and higher alkylated benzenes were rejected. Later it was demonstrated that the higher alkylated benzenes are reduced to the lower members of the series when returned to the catalyst layer in the presence of benzene. With this method of operation the yield of triethylbenzenes, which are the only products removed, approaches quantitative except for losses due to the volatility of the materials being handled and to mechanical operations.

The reaction was carried out in an apparatus, a picture of which is attached to this report. Ethyl chloride was dropped from a cooled measuring burette into a heated vaporization flask. The vapors were passed into an agitated flask in which was the reaction mass. The hydrogen chloride evolved passed out through a cold reflux condenser past a sampling tube into an absorber. The hydrogen chloride was completely absorbed and at the end of the run its amount was determined by taking the specific gravity of the aqueous hydrochloric acid resulting. From the amount of hydrogen chloride evolved and also by analysis of samples of the escaping gas it became quickly evident that the ethyl chloride introduced reacts practically quantitatively.

After the desired amount of ethyl chlordie had been introduced into any reaction mass the agitator was stopped and after a few hours the clear upper layer removed by decantation. This was washed with water to remove dissolved hydrogen chloride and a trace of aluminum chloride. The washed product was then distilled through a 33.5 inch fractionating column with a head constructed for complete return flow or a divided return and forward flow. The triethyl benzene fraction could be easily separated in this column and the other fractions returned for further treatment.

When benzene alone is treated with ethyl chloride in the presence of fresh aluminum chloride the reaction does not begin at once. Considerable ethyl chloride will pass through unreacted until the aluminum chloride begins to liquefy. When a previously liquefied catalyst is used the reaction begins at once and no ethyl chloride is lost. If it is necessary at any time to start a fresh catalyst this can best be done by adding aluminum chloride to a mixture of benzenes and alkylated benzenes. If such a mixture is stirred a short time the aluminum chloride liquefies, due apparently to the formation of complexes with the ethylated benzenes. Such a liquefied catalyst is immediately reactive and no ethyl chloride is lost at the beginning of the addition.

The temperature of 70 to 75°C. given by Smith and Guss is unneccessarily high. At this temperature benzene vapors are carried out with the hydrogen chloride and unless the reflux condenser on the equipment is very effective losses will occur. We have found that a temperature of 45 to 50°C. is to be preferred when much benzene is present in the reaction mass. As the amount of benzene decreases

the temperature of reaction can be raised but even then 60°C. is amply high to promote complete reaction.

1. Triethyl benzenes

Experiment 1 - (Book 4268 - 100 to 119)

There was charged in all 3100 g. of benzene in 9 separate runs to 190 g. of aluminum chloride. In addition to the benzene charged the low boilers obtained in each run were added to subsequent runs. Ethylated benzenes higher than the tri products were discarded. There was charged in 7635 g. of ethyl chloride. The theory yield of triethylbenzenes from the benzene charged is 6440 g. and from the ethyl chloride charged 6410 g. There was obtained 3652 g. of good triethylbenzenes and there remained 995 g. of slightly low boiling material which for yield calculations can be assumed to be triethyl benzene without appreciable error. This is a yield of 72.5% of theory either from benzene or from ethyl chloride.

When the run was brought to a close the catalyst was apparently just as active as at the beginning. The lower catalyst layer was decomposed with water and acid. There was obtained 261 g. of oil which on distillation proved to be mostly tetra ethyl and higher ethylated benzenes (Book 4268-122). In addition to this material from the catalyst layer we had rejected 794 g. of high boilers during the run.

Experiment 2 - (Book 4268 - 121 to 131)

320 Grams of fresh aluminum chloride was charged into the reactor together with the low boilers remaining from Experiment 1 together with fresh benzene. The increased amount of catalyst was used to determine if this had an effect upon the amount of triethylbenzenes in relation to other alkylated benzenes or if it influenced the ratio between the 1,3,5 and 1,2,4 tri isomers. Addition of ethyl chloride together with fresh benzene and returned low boilers was continued through 5 charges. The total amount of benzene charged in Experiments 1 and 2 together was now 5206 g. The total amount of ethylchloride charged was 12274 g. If all the benzene and all of the ethyl chloride charged had reacted to give ethylated benzenes we should have 10546 g. of product. The amount of good distilled triethylbenzenes obtained was 6282 g. or 60% of theory. There remained to be worked up 1332 g. of slightly low boilers which for all practical purposes can be assumed to be triethylbenzenes. This makes the total yield 72.6% of theory.

There was no evidence in the results of this experiment that the use of a larger amount of aluminum chloride had any appreciable effect on the value of the final products.

Experiment 3 - (Book 4268 - 134 to 150)

A fresh run was started with 175 g. of aluminum chloride, adding the low boilers from past runs together with fresh benzene. In all 8 charges were run with this catalyst. In each charge about 80% of theory of ethyl chloride necessary to convert the total benzene and ethylated benzenes to the tri derivative was added. During this run 2652 g. of benzene and 7250 g. of ethyl chloride were charged. The catalyst was still fully active at the end of the last charge. During the last charge of this run samples of the gas evolved from the reactor were repeatedly caught. The gas was 96 to 97% soluble in water, indicating that at the most 3 to 4% of the ethyl chloride charged could have been escaping. In all of these runs the products boiling above triethylbenzene were rejected.

The total amount of benzene charged in the three experiments above combined was 7936 g. The ethyl chloride charged was 19626 g. The theoretical yield of triethylbenzene from either benzene or ethyl choride was 16500 g. At the close of this run there was only 242 g. of low boilers left over. This amount was neglected in the weight figure for triethylbenzene. The triethylbenzenes produced in the three experiments was 11551 g. or 74% of theory.

Experiment 4 - (Book 4268 - 175-183 and 155-156)

This experiment was run to determine if the ethylated benzenes with more than 3 ethyl groups could be returned to the reaction and finally brought out as triethylbenzene.

A considerable amount of high boilers had been accumulated in the course of the first three experiments. A charge was therefore started as follows. 570 Grams of high boilers together with 390 g. of benzene were charged to our reaction flask with 175 g. of aluminum chloride. The mass was stirred and heated at 60°C. The mass turned dark rapidly and the aluminum chloride liquefied. There was evidence of a reaction taking place for the temperature within the flask was 3 to 4° higher than the bath for some time. It was thought that the presence of some hydrogen chloride might aid the rearrangement, so 73 g. of ethyl chloride was run in. The mass was kept at 60 to 65°C. during 5 hours. At the end of

that time it was worked up as usual. There was obtained 583 g. of distilled product all of which boiled below the proper point for triethylbenzenes. This demonstrates definitely that tetra and pentaethylbenzenes can be reduced to lower alkylated products under the conditions of our experiments.

The above charge was repeated with 456 g. of high boilers and 312 g. of benzene. Again the total product boiled below the boiling point of triethylbenzenes.

We now continued using the same catalyst by adding the low boilers obtained in the two runs and ethylating them together with benzene by the addition of ethyl chloride. In each charge the high boilers as well as the low boilers produced in previous runs were added. The only product removed from the reaction was thus triethylbenzenes.

1392 Grams of low boilers from the experiments above and 1326 g. of benzene were charged in 7 runs. In the last run only the low boilers and high boilers from the 6th run were charged with no additional benzene or ethyl chloride. More than half of the product from this last run was triethyl benzene, all of which was formed by readjustment between the high and low boilers.

5008 Grams of ethyl chloride was charged during the first 6 runs. The theoretically possible yield is the sum of alkylated benzenes plus benzene added, 2718 g. plus the weight of C_2H_4 from 5008 g. of ethyl chloride, 2170 g. The maximum possible weight of product would be 2718 g. + 2170 g. = 4888 g. The products obtained were:

4131 g.	of Triethylbenzenes
46 g.	of Low Boilers left over
460 g.	of High Boilers left over
4637 g.	

4637 g. is 95.2% of 4888 g. (Book 4268 - 175 to 184).

2. Distillation of Ethylated Benzene Mixtures

Below are given two distillation results as illustrative of the distillation procedure employed.

(Book 4268-135) 2076 g. of a mixture of ethylated benzenes produced by using 80% of the theory of ethyl chloride necessary to form triethylbenzene was distilled with the following results:

Cut 1 40 to 69°C. at 3 mm. pressure	709 g.
Most of this came over at 51 to 55°C. and is diethylbenzene.	
Cut 2 69 to 73°C. at 3 1/2 mm. pressure	1200 g.
Almost all came over at 71 to 72°C and is triethylbenzenes. The refractive index at 20°C. was 1.4971.	
Cut 3 73 to 90°C. at 3 1/2 mm. pressure	10 g.
A sudden abrupt rise then took place and the distillation was stopped. Residue in still	132 g.
Total accounted for 2051 g. out of 2076 g. charged.	

(Book 4268-147) 1357 g. of a mixture of ethylated benzenes made by the use of 90% of the theoretical quantity of ethyl chloride to form triethylbenzenes was distilled as follows:

Cut 1 Up to 59°C. at 10 mm. pressure	Very small
Cut 2 59 to 61°C. at 10 mm. pressure	68 g.
This is diethylbenzene.	
Cut 3 61 to 84°C. at 10 mm. pressure	90 g.
Cut 4 84 to 90°C. at 10 1/2 mm. pressure	947 g.
This practically all boiled at 88 to 89°C. and is triethylbenzenes.	
Cut 5 90 to 115°C. at 10 1/2 mm. pressure	30 g.
Cut 6 115°C. at 10 1/2 mm, pressure	140 g.
This is pure tetraethylbenzene.	
Residue in still 50 g.	

These two distillations are illustrative of the effect on the composition of the ethylated mixture by increasing the ethyl chloride charge from 80 to 90% of the theory necessary to form triethylbenzenes. It is believed that the most advantageous amount of ethyl chloride to be used is about 90% of theory because the ethyl groups in the high boiling portions are not lost but returned to be converted back to the tri compound. It is easier and more rapid to carry out a distillation with a mimimum of low boilers and an excess of high boilers for as soon as the triethylbenzenes are out the entire residue can be returned to the reaction.

3. Separation of 1,3,5-Triethylbenzene from Triethylbenzene Mixtures.

The separation of 1,3,5 and 1,2,4-triethylbenzenes is described in detail by Smith and Guss, Reference 4. We carried out three separations following their directions (Book 4268 - 118-120).

(a) 200 g. of mixed triethylbenzenes was treated with 400 g. of 96% sulfuric acid at 65 to 70°C. during 3 hours. The mass was allowed to stand over night and then the clear upper layer separated, washed with water and alkali. The dry weight was 73 g. .

The lower layers were poured onto ice and then steam distilled. Up to 125°C. in the liquid, 71.5 g. of oil distilled over. Very little came over at 125 to 140°C. and this was rejected. At 140 to 145°C. 46 g. more of oil distilled out.

Total recovery was 144.5 g. of 1,3,5-triethylbenzene or 72.2% and 46 g. of 1,2,4-triethylbenzene or 23% making a total recovery of 95.2%.

(b) The above separation was repeated using 300 g. of the mixed triethylbenzenes with 600 g. of 96% sulfuric acid. There was obtained 218 g. or 72.6% of the 1,3,5-isomer and 76 g. or 25.3% of the 1,2,4-isomer. The total recovery was 97.9%.

(c) Another separation was run starting with 500 g. of the mixed benzenes. There was obtained 378 g. or 75.6% of the 1,3,5-isomer. The 1,2,4-product was not recovered.

The accumulated 1,3,5-triethylbenzene from the above experiments was distilled. All boiled over down to a minimum still residue at 71°C. at 3 mm. pressure. This product had a refractive index of 1.4958 at 20°C.

After carrying out the above experiments it was obvious that some simplification of the procedure must be developed for plant use. The recovery of material by hydrolysis and steam distillation of a dilute sulfuric acid solution is expensive and very corrosive on equipment. The 1,2,4-isomer is of no value for the present, so the obvious thing to do was to treat with sulfuric acid, separate off the upper layer and reject the rest.

The following method proved to be satisfactory for our purpose (Book 4268-142).

1000 Grams of mixed triethylbenzenes with refractive index of 1.4971 at 20°C. was warmed to 60°C. and violently agitated. 475 Grams of 98% sulfuric acid was dropped in slowly over about 1 1/2 hours. Stirring was continued at the same temperature for about 2 hours more. The upper layer was separated off, washed with water and caustic soda. The turbid product cleared up on standing over night and filtering through filter-cel. There was obtained 643 g. or 64.3% of a product with a refractive index of 1.4959 at 20°C. This has a high refractive index for 1,3,5-triethylbenzene, which is 1.4950, but subsequent tests proved that it is a satisfactory product.

If it is ever found necessary to have a product with a lower refractive index this can be readily obtained by a second washing with sulfuric acid. Thus (Book 4268-149) 1000 g. of a partially purified triethylbenzene mixture was washed with 400 g. of 98% sulfuric acid just as above. There was obtained 775 g. or 77.5% yield of a product with a refractive index of 1.4950.

A Tentative Semi-Works process for the manufacture of 1,3,5-Triethylbenzene, Serial Number 18830-A was written.

4. Preparation of 2,4,6-Triethyl-monobromobenzene

The method of bromination used was that of reference 1. This method was simple and effective and so was adopted without modification except to eliminate the alcohol-caustic treatment.

A bromination of the mixed triethylbenzes as obtained from the ethylation step followed by fractionation was first run (Book 4268-113). The bromo derivative was obtained in low yield and with a wide boiling range of about 8°C. This product was tested by the Ponsol Group and found to be completely unsuitable for conversion to the desired dyestuff.

1,3,5-Triethylbenzene with a refractive index of 1.4959 was brominated as follows: (Book 4268-136)

324 Grams was dissolved in 225 g. of carbon tetrachloride in an agitated blackened flask. This solution was cooled to 0°C. in an ice bath and then 320 g. of bromine diluted with 225 g. of carbon tetrachloride was dropped in over about 4 1/2 hours. The reaction mass was allowed to stand over night and gradually come up to room temperature. The mass was warmed the next morning to about 60°C. to drive off absorbed hydrogen bromide and then washed with water and

dilute caustic soda. The carbon tetrachloride distilled off at atmospheric pressure until the vapor temperature reached 85°C. The recovery of carbon tetrachloride was very good and the recovered product was suitable for reuse in the bromination process.

After removal of the carbon tetrachloride the residue was distilled through the same fractionating column used in distilling triethylbenzenes. A small foreshot of a little carbon tetrachloride and unbrominated triethylbenzene came over and then 409 g. of distillate was obtained at the constant temperature of 120.5°C. at 7 mm. pressure. The residue left in the distilling flask was 38 g., which is not much more than the minimum amount necessary to fill the column. The yield was 85% of theory.

This product was tested by the Ponsol Group and pronounced satisfactory for the manufacture of the desired milling blue.

Two more brominations were run (Book 4268 - 145 and 146). In both of these 1,3,5-triethylbenzene with a refractive index of 1.4959 was used. In the first of these, the yield was 86.3% and the boiling point was 147 to 148° C. under 26 mm. of pressure.

In the second bromination the yield was 85.3% with a boiling point of 121° under 7 mm. of pressure.

The combined bromination product had a bromine content of 32.48% as compared to the theory for the mono-bromo derivative of 33.2%. The refractive index was 1.5363 at 20°C.

In both of these brominations recovered carbon tetrachloride was used. We had consumed in all 1850 g. of fresh carbon tetrachloride and at the end had 1350 g. of recovered material on hand.

A tentative Semi-Works process for the manufacture of 2,4,6-triethyl-monobromobenzene has been written, Serial number 18830-B.

5. Test of a Commercial Sample of 1,3,5-Triethylbenzene. (Book 4268 - 152 and 157).

A commercial sample of what was stated to be 1,3,5-triethylbenzene was received from the Monsanto Co. through Dr. Gubelmann.

This sample had a refractive index at 20°C. of 1.4908.

A sample was brominated following the procedure described above in this report. A 56% yield of a bromo-derivative boiling from 132 to 137°C. under 13 mm. of pressure was obtained. This had a bromine content of 32.92% (theory 33.2%) and a refractive index of 1.5383. This material was tested by the Ponsol Group. It proved to be entirely unsatisfactory in that it gave a low yield of oily base on condensation with 1,4-diamino anthraquinone.

Another portion of the commercial sample was now treated by the procedure described above in this report with 98% sulfuric acid. The reaction mass during sulfonation became very dark and sulfur dioxide was evolved. This is in sharp contrast with the behavior of our product which turns only a pale yellow and gives off no sulfur dioxide. There was obtained a 67% yield of an unsulfonated oil which had a refractive index of 1.4903 at 20°C.

This was brominated by the regular procedure. There was obtained a 57% yield of a monobromo derivative boiling at 110 to 115°C. at 3 mm. pressure.

This bromo derivative was tested by the Ponsol Group and while better than the first sample tested above was still far from satisfactory. The submitted commercial sample can thus be judged to be unsatisfactory for our purposes.

6. Preparation of other Alkyl Benzenes

Three additional alkyl benzenes were prepared following the method developed for making ethylated benzenes.

(a) Normal Amyl Benzene (Book 4268- 168, 169).

For this work a sample of technical normal amyl chloride from the Sharpless Co. was used. 190 G. of this amyl chloride was dropped during 1 1/2 hr. into 260 g. of benzene and 15 g. of aluminum chloride at 40 to 50°C. The evolution of hydrogen chloride was strong and steady. 58.6 G. of chlorine was evolved as HCl compared with the theoretically possible of 63 g.

The upper layer was separated off after hydrogen chloride evolution had ceased and the reaction mass had stood during several hours.

A second addition of the same amount of materials, except that no aluminum chloride was added, was made. The evolution of hydrogen chloride was somewhat slower than in the first run. Due to a leak in the apparatus an accurate result for the evolution of hydrogen chloride could not be obtained. 51.6 Grams of chlorine out of 63 g. was accounted for.

A third addition was now made, again using no fresh aluminum chloride. The evolution of hydrogen chloride was very slow so finally 5 g. more of fresh aluminum chloride was added making 20 g. used in all. The rate of evolution of hydrogen chloride jumped up at once and proceeded briskly to the end. 58.4 Grams of chlorine out of a possible 63 g. was collected.

In these three runs 20 g. of aluminum chloride had been used to convert 570 g. of amyl chloride which is 0.35 parts to 10 parts of the chloride.

The combined products were distilled. There was recovered 426 g. of benzene at atmospheric pressure and there was obtained 359 g. of normal amyl benzene boiling at 37-38°C. at 1 mm. pressure and 178 g. of higher boilers which are probably higher amylated benzenes.

(b) "Lorol" Benzene (Book 4268 - 159 and 170).

147 Grams of aluminum chloride with 234 g. of benzene was charged into our reactor. 6 Successive charges of "Lorol" chloride containing 15.5% of chlorine, with the necessary amounts of benzene, were made to this catalyst. In all but the first run the full amount of chlorine charged in the "Lorol" chloride was recovered as hydrogen chloride. In all, there was charged 20 moles of "Lorol" chloride or 4370 g. and 40 moles or 3120 g. of benzene. Evolution of hydrogen chloride was smooth and vigorous throughout until the last addition when it was necessary to raise the temperature to about 75°C. to complete the reaction. There was used 0.337 parts of aluminum chloride to 10 parts of "Lorol" chloride.

A portion of the reaction product was distilled under reduced pressure without a column. From 1235 g. of product there was recovered 320 g. of benzene, 240 g. of low boilers from the benzene fraction to 147°C. under 16 mm. of pressure and 687 g. of material distilling over at 147 to 195°C. under 14 mm. of pressure. This was assumed to be mainly mono-"Lorol" benzene. The high boilers and residue weighed 233 g.

(c) Alkylated Benzene from No. 30 White Oil Chlorinate (Book 4268 - 163 to 167).

Number 30 White Oil was chlorinated until it had increased its specific gravity from 0.779 to 0.907 or 0.908. This is about the degree of chlorination called for in reference 5.

35 Grams of aluminum chloride and 312 g. of benzene were charged into our reactor. We charged into this 437 g. of white oil chlorinate, which is 2 moles assuming that the average molecular weight is 218.5. The white oil chlorinate was added rapidly at 50-52°C. The evolution of hydrogen chloride was vigorous and steady. The total chlorinate charged was 1748 g. in four runs. During the fourth additon the rate of evolution of hydrogen chloride slowed up and almost ceased. 5 Grams more of fresh aluminum chloride was added, making 40 g. in all. The reaction then completed itself rapidly at 60°C. About 70 g. of chlorine as hydrogen chloride was obtained from each run whereas 71 g. should have been obtained from a monochloro compound with the molecular weight of 218.5. 0.337 Parts of aluminum chloride were consumed to 10 parts of "Lorol" chloride.

500 Grams of the washed product out of a total of 2453 g. was distilled under reduced pressure without a column. 163 Grams of benzene was recovered and 245 g. of product distilling over at 75° to 233°C. under 3 mm. of pressure was obtained. The residue was 65 g. The distilled material is a mixture of mono-alkylated benzenes.

Literature References:

1. Anthraquinone Milling Blue JLR-56-47, No. 11; Serial Number 17608, D.X. Klein.

2. U. S. Patent Application; Serial Number 475809.

3. The Ethylation of Benzene; E. M. Marks, J. M. Almand and E. Emmet Reid, J. Org. Chem. 9, 13 (1944).

4. Smith and Guss; J. Am. Chem. Soc. 62, 2625 (1940)

5. U. S. Patent 2,233, 408 of March 4, 1941. L. Flett to National Aniline and Chemical Co.

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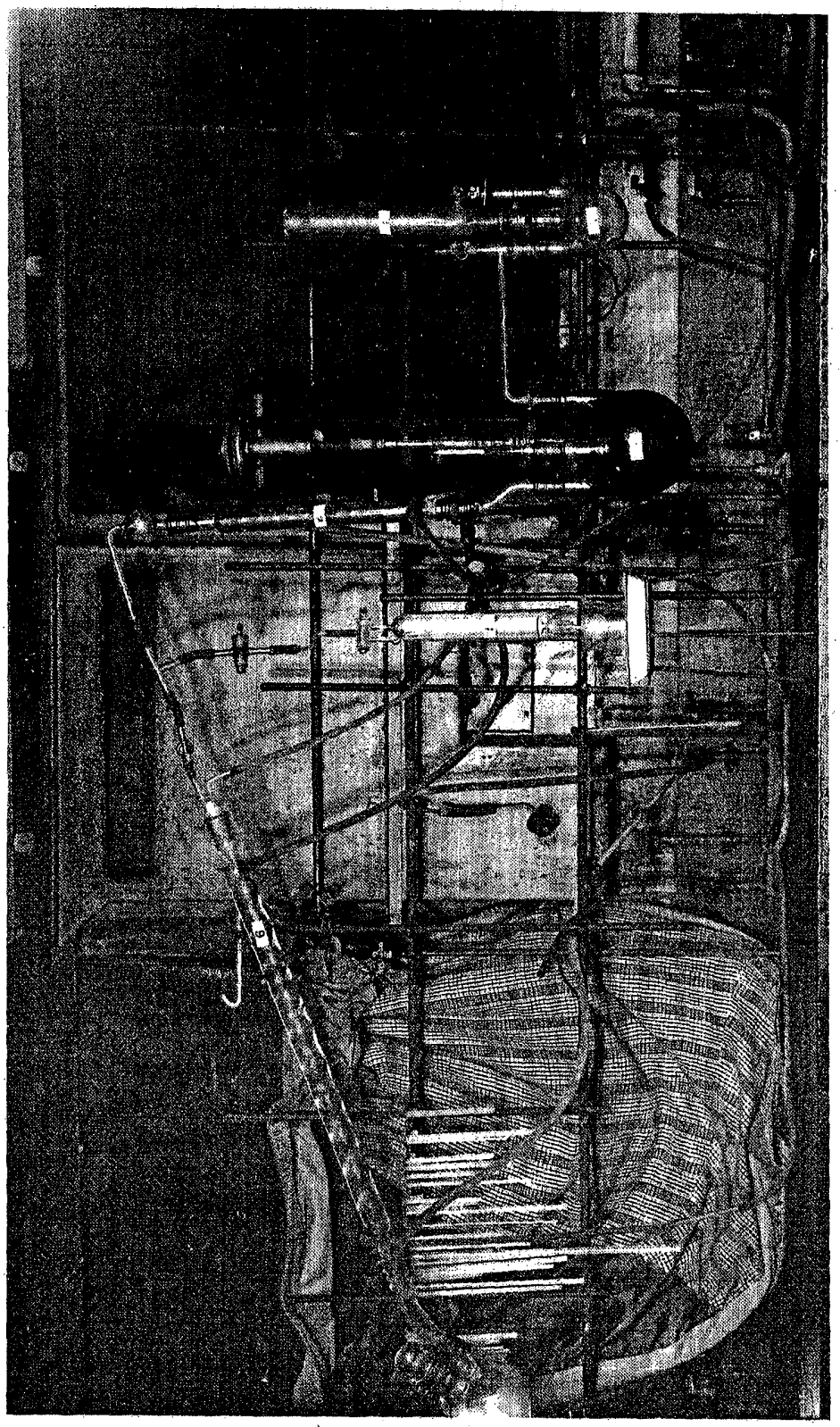

1. Ethyl chloride, jacketed measuring burette.
2. Ethyl chloride vaporizer.
3. Reactor containing aluminum chloride and benzene and alkylated benzenes.
4. Reflux condenser.
5. Sampling device to determine if ethyl chloride is present in the evolved hydrogen chloride.
6. Hydrogen chloride absorber.