

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

m-DIETHYLBENZENE AND SOME OF ITS DERIVATIVES¹By J. E. COPENHAVER² AND E. EMMET REID

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Historical

The chemistry of the dimethylbenzenes has been well worked out, while the corresponding ethyl derivatives have been studied to a relatively small extent. The first work upon diethylbenzenes was done by Fittig and König,³ who prepared them from bromobenzene and ethyl chloride by the Fittig synthesis. Aschenbrandt⁴ described the preparation of *p*-diethylbenzene by the Fittig synthesis and from it made several compounds. Anschütz and Immendorff⁵ were the first to prepare the diethylbenzenes by the Friedel and Crafts reaction. They claimed that the *para* isomer was the chief product. Voswinkle⁶ was the first to isolate and critically study the three isomeric diethylbenzenes. He prepared the *meta* and *para* isomers by the Friedel and Crafts reaction. By this procedure he claimed that the *para* compound was the major product and that there was no *ortho* isomer formed. To prepare the latter he used the Fittig synthesis. He separated the *meta* and *para* isomers by the difference in solubility of the barium salts of the sulfonic acids. He prepared a series of compounds from the sulfonated and nitrated derivatives of each isomer. In the nitration of *m*-diethylbenzene, he did not attempt to separate the nitro isomers, which were undoubtedly formed, and any compound made from his nitro would be a mixture of isomers.

Fournier⁷ used the same method of preparation of the *meta* and *para*-diethylbenzenes as Voswinkle, but instead of the barium salt of the *p*-diethylbenzene sulfonic acid, he used the cadmium salt to purify this isomer, since its barium salt is difficult to crystallize.

The Present Investigation

The ethylbenzenes were prepared by the Friedel and Crafts synthesis by passing ethylene into benzene and aluminum chloride heated to 70–80°, the reaction being accelerated by high speed stirring.⁸

By this procedure there are obtained a series of ethylated benzenes,

¹ Presented at the Philadelphia meeting of the American Chemical Society, September, 1926.

² From the Ph.D. dissertation of J. E. Copenhaver.

³ Fittig and König, *Ann.*, 144, 284 (1867).

⁴ Aschenbrandt, *Ber.*, 12, 1303 (1879); *Ann.*, 216, 211 (1883).

⁵ Anschütz and Immendorff, *Ber.*, 18, 661 (1885).

⁶ Voswinkle, *Ber.*, 21, 2829, 3499 (1888); 22, 315 (1889).

⁷ Fournier, *Bull. soc. chim.*, [3] 7, 651 (1892).

⁸ (a) Milligan and Reid, *THIS JOURNAL*, 44, 206 (1922); (b) Milligan and Reid, *Ind. Eng. Chem.*, 15, 1048 (1923); (c) Berry and Reid, *THIS JOURNAL*, 49, 3142 (1927).

from the mono- to the hexa-ethylbenzene, the amounts of these formed depending upon the conditions of the experiment and the amount of ethylene introduced. The present investigation was carried out upon *m*-diethylbenzene, which was obtained, along with the *para* isomer and possibly some *ortho*, by the above reaction. The fraction boiling from 180–185° was used, as the boiling points of the three diethylbenzenes as determined by Voswinkle are: *ortho*, 184–184.5°; *meta*, 181–182° and *para* 182–183°. The *meta* isomer was considered to be the major constituent of the diethylbenzenes from the above method of preparation of ethylated benzenes and our experiments bear out this relation.

The *m*-diethylbenzene was separated from the isomeric mixture by partial sulfonation and fractional crystallization of the barium salt of the diethylbenzene sulfonic acids. Advantage was taken of the property of *m*-diethylbenzene of being more easily sulfonated than the other two isomers and a process was worked out by which 30% of the isomeric diethylbenzenes could be isolated as the pure *meta* compound. The boiling point of *m*-diethylbenzene was found to be 180.55° (corr).

Another method of separation was investigated but with poor results. It consisted of differential oxidation, followed by partial sulfonation and partial hydrolysis, as was applied to the xylenes by Clarke and Taylor.⁹

When this method was tried with the diethylbenzenes, it was found that, by treatment with dilute nitric acid to oxidize the *ortho* and *para* isomers, nitration instead of oxidation took place. We were unable to identify the nitro product formed but the nitration must have taken place in the side chain, as conditions were more favorable for this than for nitration in the ring.

Another method of separation of the *meta* isomer was experimented with, namely, that of complete sulfonation of the diethylbenzenes using equal volumes of the hydrocarbon and concentrated sulfuric acid, followed by fractional crystallization of the barium salt of the sulfonic acid. As there was a possibility of disulfonation and as the recrystallization of the barium salt is more difficult in the presence of the other sulfonated isomers, this method was abandoned for that of partial sulfonation, as outlined above.

When *m*-diethylbenzene is nitrated with a mixture of concentrated and fuming nitric acid at 30°, a mixture of isomeric mononitro derivatives is obtained. Under the influence of the two ethyl groups, the entering nitro group would be oriented to the 2 or 4 position, with a possibility of some going to the 5 position. Voswinkle prepared a mononitro compound but was uncertain as to the position of the nitro group. He did not attempt to separate the isomers and there is little doubt that he had a mixture of isomers from which he prepared several compounds.

⁹ Clarke and Taylor, *THIS JOURNAL*, **45**, 830 (1923).

By passing the nitro product from *m*-diethylbenzene through a high-precision vacuum still¹⁰ we were successful in separating the major isomer from the one or more remaining isomers. This compound constitutes 75% of the total nitro product and is the 4-nitro-*m*-diethylbenzene. Its structure was proved by oxidizing it to the 4-nitro-isophthalic acid by alkaline potassium permanganate. This melted at 245° as given by Huisinga and Holleman.¹¹ 4-Nitro-*m*-diethylbenzene boils at 133° at 4 mm. It is easily reduced to the amine, from which several compounds were made, including a series of azo dyes. The purpose of the preparation of the dyes was to determine the effect upon the color of the ethyl groups as compared with methyl groups in similar dyes.

Experimental

Separation of *m*-Diethylbenzene

To 686 g. (5.12 moles) of the crude diethylbenzenes, boiling from 180–185°, in a two-liter balloon flask, was added 1290 g. (12.5 moles) of concentrated sulfuric acid. The mixture was mechanically stirred at such a rate as to give an emulsion of the hydrocarbon and the acid, the temperature being kept between 15 and 20°. After six hours, when the stirrer was stopped and the mixture allowed to stand for a few minutes, three distinct layers separated. The top layer consisted of the unreacted hydrocarbon; the second, an amber-colored solution, was principally the sulfonated product; and the third, the lowest layer, was almost colorless. It analyzed for approximately 80% of sulfuric acid and contained less than 1% of the sulfonated hydrocarbon. When 300 cc. of water was added, most of it went to the acid layer. After standing for two hours, about half of the lower layer was siphoned off and the remainder, with the two top layers, was transferred to a flask for steam distillation. Steam was passed into the solution and distillation continued until the temperature reached 125° (thermometer in the liquid). This insured complete separation of the unreacted hydrocarbon. There remained in the flask two distinct layers, the top, consisting of the sulfonated hydrocarbon and the lower, the sulfuric acid layer. After cooling, the lower layer was siphoned off, thus freeing the sulfonated hydrocarbon from most of the excess sulfuric acid. The sulfonated hydrocarbon layer was transferred to a three-liter beaker and diluted with 300 cc. of water. A hot, saturated solution of barium hydroxide was added until a slight alkaline reaction to litmus was obtained. It was made again slightly acid with dilute sulfuric acid and then brought to the neutral point with barium carbonate. This procedure avoided the troublesome foaming that results when the carbonate is used exclusively. The solution was diluted to about two and one half liters, boiled and the precipitate filtered off. The barium sulfate cake was washed free of the sulfonated hydrocarbons by boiling with 300–400 cc. of water and filtering. Usually three to four washings were sufficient. The several filtrates were combined and evaporated to about 1500 cc. and then cooled to room temperature. It was found best to stir the solution while it was cooling as this prevented the formation of a hard cake of crystals which, if formed, gave difficulty in filtering. The separation of the pure barium salt of *m*-diethylbenzene sulfonic acid depends upon the fact that this salt is less soluble in water than the barium salts of the other two isomers, as shown by Voswinkle.¹²

¹⁰ Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

¹¹ Huisinga and Holleman, *Rec. trav. chim.*, **27**, 260–286 (1909); *C. A.*, **3**, 420 (1909).

¹² Voswinkle, *Ber.*, **22**, 315 (1889).

The salts of other metals were tried but it was found that the barium salt is the best suited for this separation. The snow-white crystals were placed upon a large Büchner funnel and repeatedly pressed until all of the mother liquor was drawn off. This liquor contained the more soluble barium salts of the *ortho*- and *para*-diethylbenzene sulfonic acids as well as a large quantity of the *meta* isomer. The crystals were dissolved in 300 cc. of water, cooled and filtered as before. Four or five such recrystallizations separated the pure *meta* isomer, as was shown by the melting point of the amide, which was made in the usual way. A second concentration of the combined mother liquors gave a small additional yield of the *meta* isomer. If all of the crystals which came out at room temperature were filtered from the mother liquor, there remained a reddish solution which showed little tendency to crystallize. The barium salt of *m*-diethylbenzene sulfonic acid crystallizes in glistening white plates which are easily soluble in the ordinary solvents. An average run for the separation of the *meta* isomer is as follows: from the 686 g. of the isomeric diethylbenzenes initially used, 292 g. was recovered unreacted, 210 g. (30%) was isolated as the *meta* isomer and the remainder washed into the filtrate. Taking into consideration the large amount of the *meta* isomer isolated and the amount washed into the filtrate to secure the pure fraction, one would be safe in assuming the *meta* isomer to be the major constituent of the isomeric diethylbenzenes.

The amide of *m*-diethylbenzene sulfonic acid crystallizes easily from alcohol and water in long, flat, white needles, forming star-shaped clusters. It melted at 101–101.5°, as given by Voswinkle. The amide of the *ortho* isomer melts at 119° and the *para* at 85°, according to the same author.

The sulfonic acid group was easily removed from the *m*-diethylbenzene sulfonic acid by the method described by Armstrong and Miller.¹³ Equal amounts, by weight, of the barium salt of the sulfonic acid and concentrated sulfuric acid were placed in a balloon flask and steam distilled. The sulfuric acid was diluted with an equal volume of water before it was added to the barium salt. Barium sulfate was precipitated and the benzene sulfonic acid went into solution. Steam was passed into the solution and by external heating of the distillation flask the temperature was increased to 130° (thermometer in the liquid). At about this point the *m*-diethylbenzene sulfonic acid began to hydrolyze, yielding the free hydrocarbon. Then the temperature was gradually increased to 160°, the major portion of the *m*-diethylbenzene coming over between 140 and 150°. Distillation was continued until all of the *m*-diethylbenzene sulfonic acid was hydrolyzed. There was a slight coloration on the remaining acid layer, which showed some decomposition by the acid. From the wide temperature range, it can be readily seen that no narrow temperature limits can be assigned for the hydrolysis of *m*-diethylbenzene sulfonic acid by steam and sulfuric acid. The *m*-diethylbenzene was dried over calcium chloride and distilled. The purity of the compound was indicated by the fact that about 95% of it distilled at one definite temperature, which was 180.55° (corr.). Yield, from the barium salt to the hydrocarbon, 95–97%. The physical properties of *m*-diethylbenzene resemble very closely those of the xylenes, it being a colorless, very mobile liquid with a pleasant, sweetish odor; $d_4^{20} = 0.8798$; $d_{25}^{25} = 0.8597$; $n_D^{25} = 1.4926$; $n_D^{20} = 1.4955$; $n_D^{15} = 1.4778$; $n_D^{10} = 1.4998$.

4-Nitro-*m*-diethylbenzene.—To obtain the formation of only the mononitro derivative of *m*-diethylbenzene, a number of experiments were made to determine the optimum temperature and concentration of nitric acid to give approximately 50% nitration, which would minimize the formation of higher nitro products. Sulfuric acid could not be used to take up the water formed in the reaction as *m*-diethylbenzene sulfonates easily, even at low temperatures. The following method was found to be very satisfactory. A mixture of 60 g. of concd. nitric acid (sp. gr. 1.42) and 40 g. of fuming

¹³ Armstrong and Miller, *J. Chem. Soc.*, 45, 148 (1884).

nitric acid (sp. gr. 1.49–1.50) was used for each 100 g. of *m*-diethylbenzene. The acid was added slowly to the hydrocarbon while the mixture was well stirred and the temperature kept below 30°. The mixture was stirred at 30° for one and one-half hours after all of the acid was in and then diluted with 100 cc. of water. The oil layer was removed and washed with water and with a 10% sodium hydroxide solution to remove any phenols. After washing it free of the alkali, it was diluted with a small amount of ether, dried over calcium chloride and distilled. After removing the unreacted *m*-diethylbenzene, it was found that the nitro product distilled over a range of 105–138° at 5 mm. pressure, which strongly indicated a mixture of isomeric mononitro derivatives. A small residue in the distilling flask showed the formation of some of the higher nitro compounds.

In order to secure a separation of these nitro isomers, a high-precision fractional vacuum still was built as described by Peters and Baker,¹⁰ with slight changes to suit our needs. The inner column was sealed directly to the distilling flask and was one continuous piece throughout the apparatus. This column was 225 cm. long and 25 mm. in diameter. No pre-air heater was used and the distillate receiver was arranged so that the measured distillate could be removed without breaking the vacuum on the whole system. By running the mixture of isomers through this still, reading every minute the temperature of the distillate and the volume distilled, the points at which cuts should be made were clearly indicated when these data were plotted. After determining these points the isomers could be sharply separated by redistillation. The lower-boiling isomers distilled between 107 and 120° at 4 mm. pressure, there being no marked temperature break within that range. From 120° the temperature rose sharply to 133°, pressure constant, and remained at that point throughout the distillation. This isomer composed 75% of the mixture and was the 4-nitro-*m*-diethylbenzene. The structure was definitely proved by oxidizing it to 4-nitro-isophthalic acid, which melted at 245°. From the boiling point data, the low-boiling fraction seemed to consist of two possible isomers, namely, 2-nitro-*m*-diethylbenzene and 5-nitro-*m*-diethylbenzene. As there was only a small quantity of this mixture, no further study of it was made. Voswinkle gave 280–285°, with decomposition, as the boiling point of the mononitro derivative which he prepared. The nitro derivatives are amber-colored (reddening upon standing for several months), pleasant-smelling liquids. 4-Nitro-*m*-diethylbenzene boils at 133° at 4 mm.; $d_4^{20} = 1.0860$; $d_{25}^{25} = 1.0644$; $n_D^{25} = 1.5300$.

4-Amino-*m*-diethylbenzene.—The 4-nitro-*m*-diethylbenzene was easily and completely reduced to the amine by iron filings and acetic acid. The reaction was complete in about six hours when the mixture was heated on a boiling water-bath. The solution was made alkaline, the amine steam distilled, dried over calcium chloride and distilled under reduced pressure. The freshly distilled amine was almost colorless but gradually assumed a reddish color upon standing. It is insoluble in water, soluble in ether, alcohol, etc. The amine hydrochloride formed very easily and crystallized in long, clustered, anhydrous needles which are very soluble in water. Voswinkle prepared the acetyl derivative and gave 194° as its melting point. We prepared the same derivative and found that it crystallizes in long, flat, anhydrous, white needles that melt at 112–113.5° (corr.). The benzoyl derivative crystallizes in white, anhydrous, lustrous plates which melt at 176.5° (corr.). The boiling point of the amine is 116.5° (corr.) at 12 mm. and 141° (corr.) at 30 mm. pressure; $d_4^{20} = 0.9651$; $d_{25}^{25} = 0.9545$; $n_D^{25} = 1.5395$.

Anal. Calcd. for C₁₀H₁₆N: N, 9.40. Found: 9.44.

4-Hydroxy-*m*-diethylbenzene.—This phenol was prepared by heating the diazotized amine and steam distilling the product. It was washed with 50% sulfuric acid, dried over potassium carbonate and distilled in a vacuum; yield, 78%. An attempt was made to prepare the phenol from the sodium salt of *m*-diethylbenzene sulfonic acid

but with little success. It is an amber-colored liquid, completely soluble in sodium hydroxide solution, very slightly soluble in water and soluble in ordinary organic solvents. It has a distinct phenolic odor. It gave no color with aqueous ferric chloride but with an alcohol-water solution it gave a green coloration. 4-Hydroxy-*m*-diethylbenzene boils at 124.5–125.5° (corr.); $d_4^0 = 0.9986$; $d_{25}^{25} = 0.9794$; $n_D^{25} = 1.5218$.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.40. Found: C, 79.79; H, 9.73.

4-Chloro-*m*-diethylbenzene.—This compound was prepared from the amine by the Sandmeyer reaction, using the procedure outlined by Marvel and McElvain for the preparation of the chlorotoluenes.¹⁴

The amine was diazotized and added to the freshly prepared cuprous chloride solution at 0°. After stirring for two hours, the brown addition product was decomposed by gradually heating, and the chlorine compound steam distilled. It was washed with sodium hydroxide and sulfuric acid, dried and distilled in a vacuum; yield, 50%. Istiate¹⁵ prepared the chloro derivatives of the diethylbenzenes from monochlorobenzene, ethylene and aluminum chloride, but did not attempt to separate the different chloro isomers. The 4-chloro-*m*-diethylbenzene is a colorless, pleasant-smelling liquid boiling at 94.5° (corr.) at 12 mm.; $d_4^0 = 1.0335$; $d_{25}^{25} = 1.0119$; $n_D^{25} = 1.5149$.

Anal. Calcd. for $C_{10}H_{13}Cl$: Cl, 21.04. Found: 20.66.

4-Bromo-*m*-diethylbenzene.—The bromine derivative was prepared by the Sandmeyer reaction by adding the diazotized amine to the cuprous bromide-hydrobromic acid mixture at 0–5° and also at 105°. The yield at both of these temperatures was very poor but the low-temperature reaction gave the best yield, it being about 19%. Voswinkle prepared the monobromo derivative by direct bromination but here again he was uncertain as to the position of the bromine atom. The purification of this halide was similar to that for the chlorine compound. It is a colorless liquid boiling at 106.5° (corr.) at 12 mm.; $d_4^0 = 1.2709$; $d_{25}^{25} = 1.2462$; $n_D^{25} = 1.5359$.

Anal. Calcd. for $C_{10}H_{13}Br$: Br, 37.52. Found: 38.55.

4-Iodo-*m*-diethylbenzene.—This compound was prepared by the usual method of adding potassium iodide to the diazotized amine. It was purified by the method given under the chloro derivative. It is a colorless liquid boiling at 131.5° (corr.) at 12 mm.; $d_4^0 = 1.5026$; $d_{25}^{25} = 1.4740$; $n_D^{25} = 1.5729$.

Anal. Calcd. for $C_{10}H_{13}I$: I, 48.81. Found: 47.16.

m-Diethylbenzene Iodoso Chloride.—This compound was prepared by treating 4-iodo-*m*-diethylbenzene, dissolved in carbon tetrachloride, with chlorine at 0°. The iodoso chloride is very soluble in this solvent and separated out in yellow crystals as the latter evaporated. This compound was quite unstable, even at low temperatures, and decomposed, giving off free chlorine. The freshly prepared crystals melted with decomposition at 51–53°. Attempts to prepare the iodoso oxide were unsuccessful.

4-Cyano-*m*-diethylbenzene.—This nitrile was prepared from the amine by the Sandmeyer reaction.¹⁶ The neutralized diazonium chloride was added to the cuprous cyanide solution at 0–5° and the diazonium complex decomposed by heating, the nitrile being purified in the usual way. It is a yellowish liquid boiling at 134° (corr.) at 12 mm.; $d_4^0 = 0.9699$; $d_{25}^{25} = 0.9507$; $n_D^{25} = 1.5195$.

Anal. Calcd. for $C_{11}H_{13}N$: N, 8.80. Found: 8.45.

¹⁴ Marvel and McElvain, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 33; *C. A.*, 20, 173 (1926).

¹⁵ Istiate, *Ann. chim. phys.*, [6] 6, 413 (1885).

¹⁶ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, p. 69; *C. A.*, 20, 181 (1926).

m-Diethylthiocarbaniide.—This derivative was prepared by the method given by Snedker,¹⁷ which consisted of using one molal proportion of the amine to 1.25 moles of carbon bisulfide and cooling to about 10°. While the solution was being stirred a 40% solution of sodium hydroxide was added. After stirring for a few minutes, the carbon bisulfide was allowed to evaporate. The *m*-diethylthiocarbaniide crystallized in very fine, white needles which, when recrystallized from alcohol and water, melted at 144.5° (corr.); yield, 36.5%.

Anal. Calcd. for C₂₁H₂₃N₂S: S, 9.42. Found: 9.39.

Comparison of Azo Dyes Prepared from Aniline, 4-Amino-*m*-Dimethyl-Benzene and 4-Amino-*m*-Diethylbenzene

In order to see what effect the ethyl groups of 4-amino-*m*-diethylbenzene would have upon the color of dyes prepared from it, in comparison with those obtained from 4-amino-*m*-diethylbenzene and aniline, a series of dyes was made from these amines. They were diazotized and each coupled with R-salt, chromotrope, H-acid, etc., as second components. The dyes were made and applied to the wool without isolation from solution. The procedure for the three amines and ten second components is as follows.

One-hundredth of a mole of each amine was diazotized in the usual way and the solution diluted to 100 cc. One-thousandth of a mole of each of the ten second components was placed in a beaker and to each was added 50 cc. of water and 2.5 cc. of a 10% sodium carbonate solution. After obtaining complete solution of the naphthalene salt, the solution was cooled to 5° and 10 cc. of the cold diazotized amine solution was added, with stirring. The coupling was usually very rapid and in most cases the dye was in complete solution. The dye solution was kept cold for about an hour and then allowed to come to room temperature. Each dye solution was diluted to 100 cc. and 50 cc. of this solution was used for each dyeing. The 50 cc. of dye solution taken was diluted to 200 cc. and 10 cc. of 5% sulfuric acid added. The entering of the skeins, etc., was carried out as is usual for wool dyeings. The dye-bath was heated until complete exhaustion of the dye by the wool, which required from thirty to sixty minutes. By the above procedure the amount of dye on the wool varied from one component to the other but the amount formed from the three amines with any one second component was practically the same.

Table I is a classification of the dyes from the three amines. The introduction of the methyl groups in the molecule has a very pronounced effect, giving a change in color as would be expected. In comparing the methyl and ethyl groups, there is little change in the color but the intensity of the color is increased in a majority of the comparative dyeings, namely, nos. 1, 2, 4, 6, 7 and 9, and in 5 and 10 the intensity is the same. In numbers 3 and 8, the reverse is true but this is possibly due to incomplete coupling.

¹⁷ Snedker, *J. Soc. Chem. Ind.*, **44**, 486T (1925).

Taking the series as a whole, we can definitely say that the presence of the ethyl groups in the amine molecule gives a decided effect over the methyl groups in the intensity of the color of the dye.¹⁸

TABLE I

CLASSIFICATION OF AZO DYES MADE FROM ANILINE, *m*-DIMETHYLANILINE AND *m*-DIETHYLANILINE BY COUPLING WITH NAPHTHALENE DERIVATIVES

Second component	Aniline	<i>m</i> -Dimethylaniline	<i>m</i> -Diethylaniline
1. H-acid	Bordeau	Bordeau	Deeper Bordeaux
2. Chromotrope	Red	Crimson	Deeper crimson
3. Armstrong's acid	Yellow	Dull yellow	Yellow
4. Schaeffer's salt	Orange	Scarlet	Deeper scarlet
5. R-salt	Deep orange	Red	Red
6. J-acid	Yellow-brown	Red-brown	Deeper red-brown
7. <i>p</i> -Aminobenzoyl-J-acid	Burnt orange	Red	Deeper red
8. J-acid urea	Orange	Red	Lighter red
9. <i>p</i> -Aminobenzoyl- <i>p</i> -aminobenzoyl-J-acid	Orange	Red	Deeper red
10. Neville and Winther's acid	Deep orange	Red	Red

Summary

1. *m*-Diethylbenzene has been separated from its isomers by partial sulfonation and fractional crystallization of the barium salt of the sulfonic acid.

2. 4-Nitro-*m*-diethylbenzene has been separated from its isomers and reduced to the amine, from which several derivatives were made by standard methods.

3. A series of azo dyes was made from aniline, *m*-diethylbenzene and *m*-diethylbenzene to determine the influence of the ethyl groups over the methyl groups in the color of the dyes. It was found that the colors were the same but the intensity of the color was increased.

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¹⁸ The authors wish to thank the Jackson Laboratory and the Technical Laboratory of E. I. du Pont de Nemours and Co. for advice in the preparation of the dyes, for furnishing the second components and for classifying the dyeings.