PREPARATION OF ISOMETRIC METHYL DERIVITIVES OF DIAZOBENZENE-ACETOACETANILIDE

A THESIS

by

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Presented to the faculty of the Virginia Polytechnic Institute as a partial requirement toward the degree of Master of Science in chemistry.

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PREFACE

This is a thesis written as a partial requirement toward the degree of Master of Science in Chemistry. The investigations outlined herein were carried out entirely in the chemical laboratories of the Virginia Polytechnic Institute.

Before entering into the discussion, the author wishes to take this opportunity to thank Professor J.B. Lucas, Dr. J.E. Hussey, Dr. J.W. Watson, and Miss Ella Russell, of the chemistry department of V.P.I., and Mr. E.F. Hitch, of the E.I. DuPont de Nemours Company, for very helpful suggestions

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I-INTRODUCTION-A BRIEF HISTORY OF THE DIAZO DYES

"The coal tar industry holds a unique position in the industrial world, as it is entirely the outcome of scientific research. The first seed was planted in 1825 when Faraday discovered benzene, which he obtained from the liquid products condensed on compressing the gas obtained from coal oil. A year later, 1826, Unverdorben obtained aniline by the mere distillation of indigo and called it 'crystalline'. Runnge afterwards obtained it from coal tar oil and, having observed that it produced a violet blue coloration with chloride of lime, called it 'kyanol'. It was subsequently obtained from Indigo by Fritsche by distilling this coloring matter with caustic alkali. Mitscherlich later obtained benzene from benzoic acid and from this produced nitrobenzene, this discovery paving the way for Zinin, who showed that benzidam (aniline) could be produced by the action of sulphuretted hydrogen in the presence of ammonia on an alcoholic solution of nitrobenzene."

"Hoffman, in his first published paper, showed that Unverdorben's crystalline, Runge's kyanol, Fritsche's aniline and Zinin's benzidam were all the same compound, and for which he selected Fritsche's name aniline. His work on the separation of aniline from coal tar started in 1843, and continued after his arrival in England in 1845 -------."

"At this time, 1843, organic chemistry was still in its infancy as coal tar naptha had not yet been investigated. Runge had isolated phenol, aniline, and quinoline. Napthalene was known to exist in the tar, having been separated by Garden as early as 1820 and finally Dumas had discovered anthracene."

"In 1845 Hoffman showed that benzene must exist in coal tar naptha, as he found that aniline could be produced from it. Upon his suggestion Charles Mansfield undertook to investigate the liquid hydrocarbons of coal tar and after much patient and persevering experimentation finally produced benzene and toluene in a pure state. From the latter Hoffman produced toluidine."

"To Perkin (one of Hoffman's students), however, belongs the credit for the introduction and development of the industry, for he quickly realised the commercial importance of the numerous discoveries in coal tar chemistry which now followed in tumultous succession." *

It was Perkin who synthesised the first aniline dye in 1856. "Despite the dissuading advice of Hoffman, Perkin, at eighteen, left college to continue his investigations and to proceed with the production of this dyestuff. A general patent was taken out to include the oxidation products of salts of

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*Abstract - Perkin and Armstrong. Hoffman Memorial Lecture. Trans. of Chem Soc., 1896 - This abstract obtained by the author from 'Aniline and its Derivitives' by Groggins.

aniline, toluidine, xylidine and cumidine. In June, 1857, with the assistance of his father and friends, construction of a plant at Greenford Green near Harrow to manufacture dyes was commenced.*

Now the synthetic dye industry has practically replaced the natural dye industry.

II-SCOPE OF THE WORK DONE BY THE AUTHOR

The more important synthetic dyestuffs can be classified as follows:-[1]

A. Nitroso- and nitro-dyestuffs.

B. Azo-dyes

C. Stilbene, pyrazole, and thiazole dyestuffs.

D. Di- and Tri-phenylmethane dyes.

E. Xanthene dyestuffs.

F. Acridine and Quinoline dyestuffs.

G. Indamine and Indophenol dyestuffs.

H. Azines, Oxazines, and Thiazines.

I. Hydroxy-Ketone dyestuffs.

J. Sulphide dyes.

K. Vat dyestuffs: Indigo and Indanthrenes.

The author has dealt, in his investigations, only with that class known as the Azo dyes. Using ortho-, meta-, and para-toluidine, acetoacetic ester, and aniline, he has attempted to produce three normal dyes, and their isomeric forms.

*Abstract-Perkin and Armstrong, Hoffman Memorial Lecture. Trans. of Chem. Soc., 1896.

[1] Textbook of Organic Chemistry-Bernthsen-Sudborough.

III-PREVIOUS WORK DONE ON THIS SUBJECT

As far as the author and his associates have been able to determine from available literature ,no records have been previously made of attempts to prepare the isomeric methyl derivitives of diazobenzene acetoacetanilide.

IV-EXPERIMENTAL WORK

Aniline,the simplest of the aromatic bases,may be regarded as benzene in which one hydrogen atom has been replaced by the amino-group. As is well known to every organic chemist,there may exist,not only a monoamine of benzene,but also a diamine(containing $2NH_2$) and a triamine(containing $3NH_2$) of benzene. The base,toluidine ($C_6H_4.CH_3.NH_2$),which the author used in his experiments,may be considered from the standpoint of a diamine of benzene,in which one of the amino-groups has been replaced by a methyl group. Thus,the similarity between the structure of aniline and the structure of toluidine may be readily seen.

Aniline is very easily diazotised according to the following reactions:

$C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_2.HCl$
aniline — aniline hydrochloride

$C_6H_5NH_2.HCl + HONO \longrightarrow C_6H_5N{=}N{-}Cl + 2H_2O$
diazobenzene chloride

This diazobenzene chloride,which is the ultimate product of the diazotization of aniline,is easily coupled with other compounds to form certain dyestuffs.

From the similarity of the structures of aniline and the toluidines(ortho-,meta-,and para-)and the ease with which aniline is diazotized and coupled,it seemed that the three touluidines might be diazotized and coupled to form dyestuffs.

To determine whether or not this was the case,the following experiments were performed:

I.Preparation of acetoacetanilide(to be used as a dyestuff intermediate).

A quantity of acetoacetic ester was purified under a vacuum by distillation. A similar quantity of aniline was purified by distillation at ordinary pressure until water white. Into a three neck flask,set up according to figure 1 ,32.5 grams of the purified acetoacetic ester were placed and heated on an oil bath until the temperature reached 130° C. When this temperature had been reached ,25.5 grams of the water white aniline

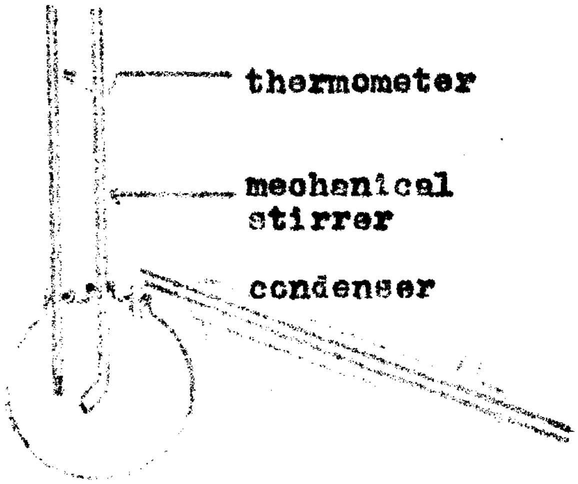


Figure 1.

were slowly added and the whole mixture kept at a temperature of 130°C. until the reaction was complete.

This required about five hours of heating, during which time, the liquid changed to a dark brown color. On cooling, the crystallisation was very slow.

The acetoacetanilide produced was purified by recrystallisation from water and toluene. A better yield was obtained by using the toluene.

Yield(recryst. from water) 12.6 grams(60%)

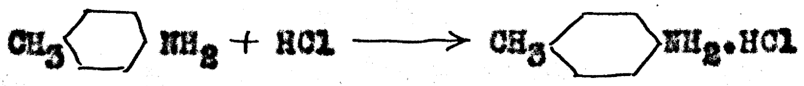
II, Purification of ortho-, meta-, and para-toluidine

These compounds were purified as needed by the use of water, ether, or toluene.

III, Preparation of Paramethyl-diazobenzene-acetoacetanilide, the first dye.

The principle involved in this preparation is that of diazotising para-toluidine, and coupling the diazotised compound with acetoacetanilide.

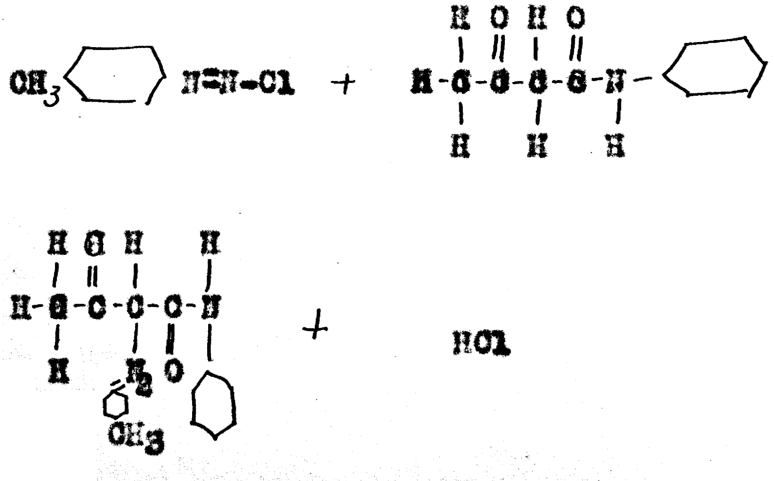
6 grams of para-toluidine were added to 50 cc. of water contained in a beaker, 22.5 grams of concentrated hydrochloric acid were added to this and the whole stirred thoroughly. The following reaction took place:



To the above 50 grams of ice were added and the beaker placed in a salt and ice bath and allowed to stand there until the temperature approached 0°C.

A 10% solution of sodium nitrite was made by dissolving 3.5 grams of the salt in distilled water. When the temperature of the first solution had reached 0° C., the sodium nitrite solution was slowly added, with continual stirring, through a tube leading under the surface of the liquid. The completion of the diazotization was determined by placing a drop of the liquid on a starch iodide paper. A distinct blue color, forming at once, indicated the completion of the reaction.

9.6 grams of acetoacetanilide were dissolved in 200 cc. of water containing a small amount of sodium hydroxide. To this solution the diazo solution was slowly added. The whole solution was allowed to stand for fifteen or twenty minutes and then, if not already alkaline, was made just alkaline with a 10% sodium carbonate solution. The presipitate was filtered off on a Buchner funnel, washed thoroughly with lukewarm water and dried.



The product obtained from this preparation was paramethyl-diazobenzene-acetoacetanilide, a beautiful yellow pigment.

Yield: 8.5 grams (76%); Melting Point (Purified with water): 120° C.

The above procedure was repeated in order to see if the preparation could be duplicated. This was successful, also.

Yield: 7.9 grams; Melting Point (Purified with water): 118° C.

IV-Preparation of the second dye, orthomethyl-diazobenzene-acetoacetanilide.

The procedure for the preparation of the second dye, orthomethyl-diazobenzene-acetoacetanilide, was exactly the same as given above for the preparation of the first dye, except that 6 grams of ortho-toluidine were used instead of the para-toluidine.

Yield: 8.3 grams (73%); Melting Point (Purified with water): 155° C.

This preparation was also repeated to see if the dye could be duplicated. Results were successful.

Yield: 7.9 grams (70%); Melting Point (Purified with water): 155° C.

The compound prepared thus was also a beautiful shade of yellow, a bit lighter than the color of the paramethyl-diazobenzene-acetoacetanilide.

V, Preparation of the third dye, metamethyl-diazobenzene-acetoacetanilide.

The use of the meta-toluidine in the preparation of a dye presented a more difficult problem. In this case it was necessary to perform the operations with as much speed as possible and with as low a temperature as possible in order to prevent the decomposition of the diazotised meta-toluidine.

6 grams of meta-toluidine were added to 50cc. of distilled water and 22.5 grams of concentrated hydrochloric acid contained in a beaker. 50 grams of ice were added to this and the beaker was placed in a salt and ice bath until the temperature had fallen as low as possible. When the solution had reached the lowest temperature possible(-4°C.) a 10% solution of sodium nitrite, made by dissolving 3.5 grams of the salt in water, was added slowly through a tube leading under the surface of the solution. A reddish brown precipitate formed at this stage, due to the partial decomposition of the diazotised meta-toluidine(This precipitate may or may not form, depending on the conditions under which the operations are carried out). This precipitate was filtered off. 9.6 grams of acetoacetanilide, dissolved in 200 cc. of water containing a small amount of NaOH, were added as quickly as possible to the filtrate, and the whole allowed to stand for fifteen or twenty minutes. At the end of that time, if not already alkaline, the solution was made just alkaline with 10% sodium carbonate solution, the yellow pigment was filtered off on a Buchner funnel, washed with distilled water, and dried.

Yield:8.4 grams(74%);Melting Point(Purified with toluene): 112°C.

This preparation was duplicated, also, and the results were found to be satisfactory.

Yield:7 grams(61.5%);Melting Point(Purified with toluene) 111° C.

Attention was next turned toward the preparation of the isomeric forms of the compounds prepared above. Intermediates were made by coupling ortho-,meta-,or para-toluidine,respectively with acetoacetic ester by the following process.

VI,VII,VII,Preparation of intermediates to be used in the preparation of the isomeric forms of of the dyes made above.

In a condensing flask,set up as shown in figure 1, 65.5 grams of ortho-(meta-,or para-,as the case may be) toluidine and 50 grams of acetoacetic ester were placed. The flask with these ingredients was heated on an oil bath for five hours at a temperature of 125°-150°C. At the end of this time the product was removed from the flask,purified with toluene,and dried.

The preparation of these three intermediates was performed without any difficulty,whatsoever.

It now became necessary to couple the intermediate with aniline which had been previously diazotized by the usual method. To do this, it was, of course, necessary to dissolve the intermediate in some medium which would not affect the coupling. Each of these intermediates resisted solution to any appreciable extent in any of the ordinary solvents, with the exception of 95% acetic acid and ethyl alcohol, niether of which could be used on account of their reactions with diazotized aniline. Such solvents as water (both hot and cold) carbon tetrachloride, ether, benzene, chloroform, and sodium hydroxide solutions of various strengths, were used, but without any solution taking place, whatsoever. Metallic sodium failed to show any action, whatsoever, on the intermediated, due, probably, to steric hindrance. Therefore, it was quite evident that the proposed method of coupling ortho-(meta-, or para-) methyl acetoacetanilide with diazotised aniline would not be successful, unless some suitable solvent for the former compounds could be found.

Attention was next turned to the possibility of forming an intermediate by coupling the sodium salt of acetoacetic ester with diazotized aniline, and then coupling this intermediate with ortho-, meta-, or para-toluidine. This possibility was tried repeatedly with no success, whatsoever, due to the impossibility of obtaining a suitable condensate from the diazotized aniline and sodio acetoacetic ester.

V-CONCLUSION

Paramethyl-(orthomethyl-, or metamethyl-)diazobenzene acetoacetanilide may be prepared respectively by the coupling of acetoacetanilide with diazotized para-(ortho-, or meta-) toluidine.

Intermediates for the preparation of the isomeric forms of the compounds given above(paramethyl-, orthomethyl-, or metamethyl-diazobenzene acetoacetanilide may be prepared by condensing together acetoacetic ester and para-, ortho-, or meta-toluidine, as the case may be.

Further progress toward the preparation of the isomeric forms was hindered due to the insolubility of the three intermediates.

The suggested method of forming the isomeric forms by coupling the sodium salt of acetoacetic ester with diazotized aniline and then coupling the intermediate formed thus with ortho-, meta-, or para-toluidine proved to be a failure due to the impossibility of obtaining a suitable intermediate .

Investigations into the preparation of the isometric methyl derivitives of diazobenzene acetoacetanilide appear to be rather unlimited, but the short length of time allotted to this subject allowed the author to perform only the experiments outlined above.

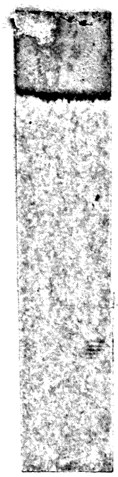
It is gratifying to know, however, that more work on the subject will be done in the near future at the Virginia Polytechnic Institute.

TABLES

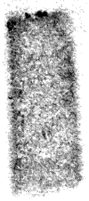
	Yield	Melting Point
Paramethyl-Diazobenzene-Acetoacetanilide	8.5 grams (76%)	120° C. (Purified with water)
	7.9 grams (70%)	118°C. (Purified with water)
Orthomethyl-Diazobenzene-Acetoacetanilide	8.3 grams (73%)	155°C. (Purified with water)
	7.9 grams (70%)	155° C. (Purified with water)
Metamethyl-Diazobenzene-Acetoacetanilide	8.4 grams (74%)	112° C. (Purified with toluene)
	7.0 grams (61.5%)	111° C. (Purified with toluene)

PIGMENT TESTS

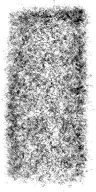
Paramethyl-
Diazobenzene-
Acetoacetanilide



Orthomethyl-
Diazobenzene-
Acetoacetanilide



Metamethyl-
Diazobenzene-
Acetoacetanilide



Comparison tests
of all three of
the above pigments