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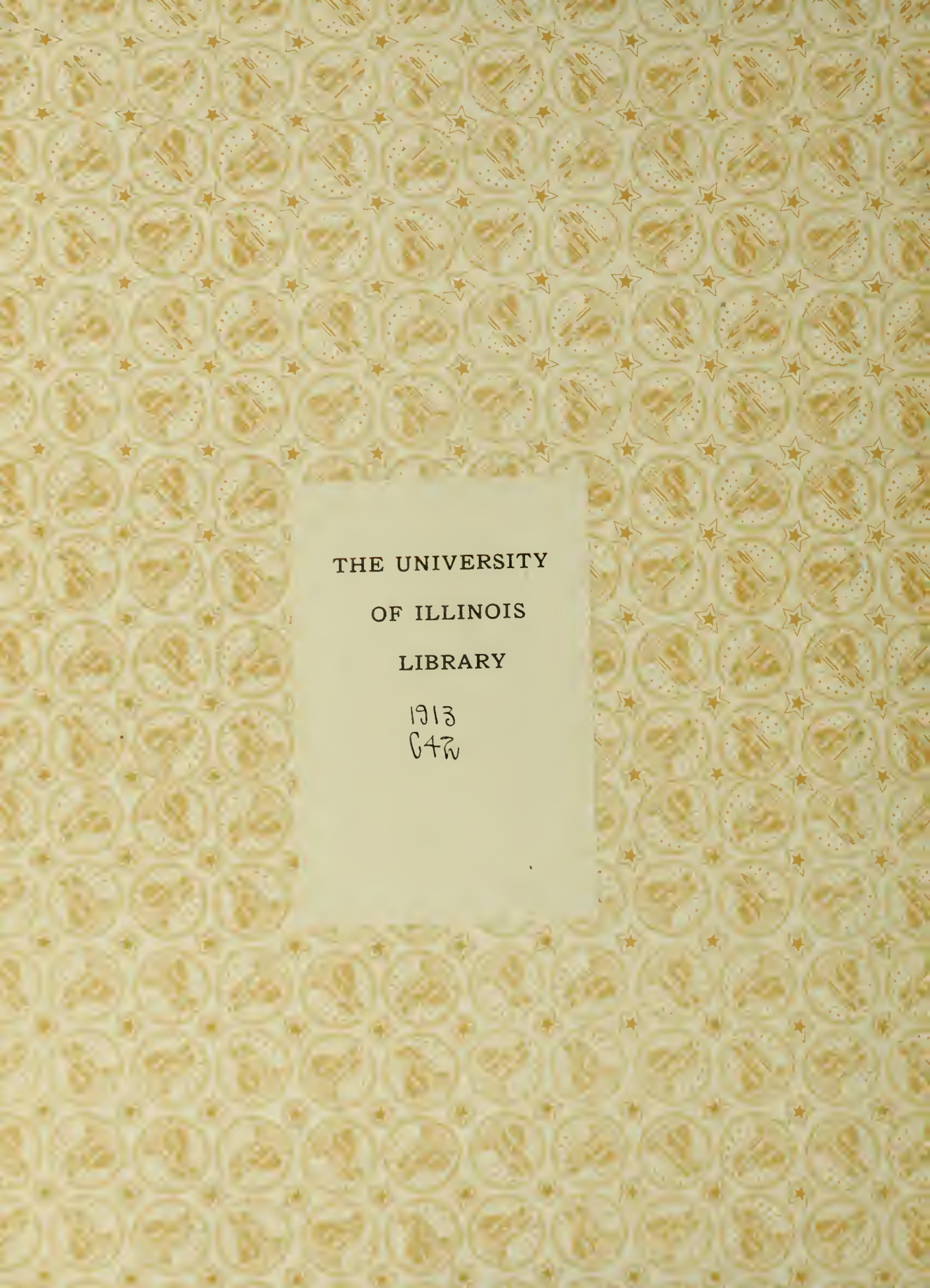
The Synthesis of Meta-Anisidine

Chemical Engineering

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THE SYNTHESIS OF META-ANISIDINE

BY

HUANG CHEN

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF SCIENCE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Huang Chen

ENTITLED THE SYNTHESIS OF META-ANISIDINE

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN CHEMICAL ENGINEERING.

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INTRODUCTION.

In 1883 Frank Pfaff,* in an attempt to prove the constitution of mono-bromo-m-nitroanisole, accidentally obtained m-anisidine from its reduction by means of tin and hydrochloric acid. Thus not only reduction but also debromination took place. He observed that the oily base distilled over at 251°, possessed a pleasing fruit-like smell and formed a beautiful crystalline salt with hydrochloric acid. According to analysis he found it contained nitrogen 11.20%, while the calculated value is 11.38%. Pfaff then proceeded to prepare this aminoanisole by the reduction of m-nitroanisole. He obtained the latter by methylating m-nitrophenol with one equivalent of caustic potash dissolved in methyl alcohol and methyl iodide in excess. This mixture was boiled with reflux condenser for one day and the excess of methyl alcohol and iodide distilled. The methyl ether crystallized in needles and upon recrystallization from alcohol, had a melting-point of 103°-104°.

A few years later Korner and Wender** obtained m-anisidine by the reduction of m-nitroanisole with the same reducing agents as had been employed by Pfaff. They showed that the oily base

* Ber. 16, 614 and 1139 (1883).

** Gaz. 17, 492 (1887).

remained liquid at -12° and distilled at 243.5° at 755.5 mm. and 24° .

The third and latest preparation of m-anisidine was that by F. Mauthner* in 1906. He methylated m-nitrophenol by means of di-methyl sulphate and reduced its methyl ether with tin and hydrochloric acid.

It is clearly seen, then, that Mauthner, Pfaff, Körner, and Wender used the same method for reducing m-nitroanisole, though differing in regard to the methylation of m-nitrophenol. They, however, had not given any record of the yields of m-anisidine.

The results from the experiments as indicated in this article will show that by employing a different method a yield of 85 per cent of the theoretical may be obtained. This is based upon Hoffmann's** reaction by treating an acid amide with bromine and caustic soda or sodium hypobromite. This reaction depends upon the rearrangement of the bromamide $RCONHBr$ when heated, to yield an isocyanic ester $RN=C=O$. Thus $RN=C=O+2NaOH \rightarrow RNH_2+Na_2CO_3$. The best explanation of this reaction seems to be that given by Julius Stielitz,*** based upon the theory of Nef.

* Ber. 39, 3596 (1906).

** Ber. 14, 2725 (1882).

*** Am. Chem. Jour. 18, 751 (1896).

In this research m-methoxybenzamide was used. For its preparation it was necessary to obtain m-hydroxybenzoic acid, m-methoxybenzoic acid and m-methoxybenzoyl chloride.

EXPERIMENTAL PART.

Preparation of M-Hydroxybenzoic Acid.

The m-hydroxybenzoic acid was prepared according to the direction of Heinrich Offermann*. Two hundred grams of benzoic acid were dissolved in 400 gr. of fuming sulphuric acid (20% anhy.) and heated to 210°-220° for about three hours. A test for the completion of the reaction was made by dissolving a few drops of the dark brown liquid in water, whereupon if no benzoic acid separates, the reaction may be considered to have gone to completion. After cooling, the contents of the flask were poured in 1600 c.c. cold water and the whole then added to two liters of a cold saturated solution of common salt. The sodium salt of m-sulphobenzoic acid was filtered off and recrystallized from salt solution. Yield 350 grams, or 94 per cent of the theoretical.

In order to prepare the hydroxy-acid from the above salt, one hundred grams of the latter were treated in a porcelain dish with 40 c.c. of concentrated caustic potash solution. After heating on the water-bath for a few minutes, 25 grams of

* Ann. 280, 5 (1894).

powdered caustic soda were added. When cold, the solidified mass was broken up into small pieces. Into a Nickle crucible, a mixture of 56 grams of powdered caustic potash and 40 grams of powdered caustic soda was heated to fusion. The double salt of the acid was then introduced gradually with stirring and the entire contents kept at 230°-240° for about three hours. During this operation it is advisable to wear a pair of goggles for protecting the eyes from the alkali and also a pair of gloves for the hands. Frequent stirring and constant high temperature favored the reaction. When cold, the mass was dissolved in water and the m-hydroxybenzoic acid precipitated out by adding hydrochloric acid. After recrystallization from hot water an acid having a melting-point of 200° was obtained. Yield 46 grams, or 75 per cent of the theoretical.

Preparation of M-Methoxybenzoic Acid.

The m-hydroxybenzoic acid was methylated according to the method of Grabe["]*. Fifty grams of m-hydroxybenzoic acid were dissolved in a solution of 40 grams of caustic soda in 400 c. c. of water. To this solution 50 c.c. of dimethyl sulphate were added gradually. The reaction caused evolution of heat. After boiling the contents of the flask for some time with reflux condenser, 15.8 grams of caustic soda was introduced in

* Ann. 340, 211 (1905).

order to saponify any ester and the mixture warmed for about one hour. When cold, the m-methoxybenzoic acid was precipitated by adding hydrochloric acid. Upon recrystallization from hot water an acid having a melting-point of 105° was obtained. Yield 50 grams, or 90 per cent of the theoretical.

Preparation of M-Methoxybenzamide.

Meta-methoxybenzoyl chloride was prepared according to the method of Ullman and Goldberg*. Sixty grams of m-methoxybenzoic were mixed with 83 grams of phosphorous pentachloride in a flask. The action began immediately with evolution of fumes of hydrogen chloride. After the contents of the flask changed to liquid, the mixture was heated on the water-bath for a few minutes in order to complete the reaction. The oxychloride was distilled in vacuo. The chloride remaining in the flask was then converted into an amide by pouring it in ammonia water. Ammonia carbonate was also used for this purpose. Upon recrystallization from hot water a product having a melting-point of 134° was obtained:—m-methoxybenzamide. It is very slightly soluble in cold water, legroin, chloroform or benzene; slightly soluble in ether; fairly soluble in acetone, acetic ester, alcohol, or hot water; very soluble in glacial acetic acid.

* Ber. 35, 2813 (1902).

Analysis

| | Calculated for | Found |
|---|----------------|-------|
| | $C_8H_9O_2N$ | |
| N | 9.27 | 9.48 |

Preparation of M-Anisidine.

The sodium hypochlorite was prepared by passing chlorine gas into a solution of 60 grams of caustic soda in 400 c.c. of water. The chlorine gas was generated from a mixture of 22 grams of potassium permanganate and 150 c.c. hydrochloric acid (sp. gr. 1.17). To the sodium hypochlorite solution 52 grams of m-methoxybenzamide were added and the mixture warmed on the water-bath to 80°. The oil which separated on top was extracted with ether. Upon distillation it went over at 240°-242° at 746 mm. and 24°. Yield 19 grams, or 60 per cent of the theoretical.

The use of sodium hypobromite was found to give better results. The hypobromite was prepared by dissolving 42 grams of bromine in a solution of 40 grams of caustic soda in 300 c.c. of water to which had been added 100 grams of ice. The solution was treated with 40 grams of m-methoxybenzamide and the mixture then heated to 80°-90° on the water-bath for about

half an hour. The oily product which separated as an upper layer was extracted with ether. The ethereal solution was dried on caustic potash and, after the removal of the ether on the water-bath, the residual base was distilled. It came over at 242°-243° under a pressure of 742mm. The yield was 28 grams, or 85 per cent of the theoretical.

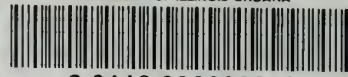
CONCLUSION.

From these experiments it is obvious that the above method is a convenient one for the synthesis of m-anisidine. It has the special advantage of starting with a readily accessible substance, benzoic acid, whereas m-nitrophenol can only be obtained with difficulty. Furthermore, the yields in every step in the process are all that can be desired.





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