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Preparation And Properties Of 2-Chloro-5-Bensaldehyde

James Thomas Bailey
Prairie View State Normal and Industrial College

"PREPARATION AND PROPERTIES OF 2-CHLORO-5-BROMOBENZALDEHYDE"

By

James Thorne Bailey

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A C K N O W L E D G M E N T

The author wishes to express his sincere appreciation to Mr. R. P. Perry for his cooperation and helpful suggestions during this experiment. Furthermore, it is the desire of the author that this work might prove useful to his co-worker as well as to others interested in research.

— J. T. B.

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DEDICATED

-to-

My mother, Mrs. Lois Edwards Bailey,
My uncle and aunt, Mr. and Mrs. R. W.
Bailey, and a friend, Miss M. E.
Sumrow.

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CHAPTER I

INTRODUCTION

Benzaldehyde, the simplest of the aromatic aldehydes occurs in nature as a constituent part of the glucoside, amygdalin, in bitter almonds, in the kernels of peach stones and in some other plants. The glucoside consists of benzaldehyde, glucose, and hydrocyanic acid in combination and hydrolysis of amygdalin yields the three products mentioned in its composition. Benzaldehyde has a strong odor of the natural oil of bitter almonds and is commonly known as the "Oil of Bitter Almonds." It is an important compound in the flavoring of substances, in the preparation of dyes, perfumes and many organic compounds. Because of its easy preparation it has been thoroughly studied and the reactions which it undergoes have been well established. However, as organic research affords so many opportunities for the discovery and recording of new compounds, chemists have retreated to their laboratories and are well at work in an effort to give to

the world useful products derived from benzaldehyde that are in use as well as on record, but because of difficulty in preparation or because of cost of production only a few of the many possible dihalogen derivatives of benzaldehyde have been prepared and are on record.

A study of the literature revealed papers on benzaldehyde derivatives containing bromine, chlorine, iodine and fluorine, some of the dihalogen compounds on record are: 2-Chloro-5bromobenzaldehyde, 2, 3 dibromobenzaldehyde, 3, 5 dichlorobenzaldehyde, and 3, 5 dibromobenzaldehyde.

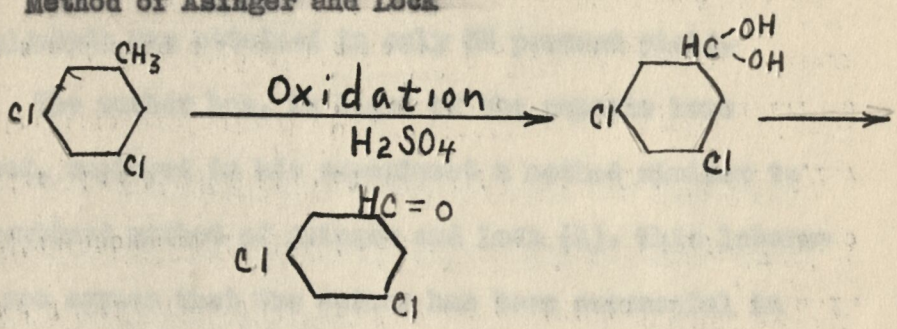
Asinger and Lock (1), by hydrolyzing 4, 6 dichloro-2-methyl-acettoluide with 50 percent sulphuric acid and eliminating the amine, were able to isolate as a product 3, 5 dichlorotoluene. Chlorination of this product at 180-190°C. yielded 3, 5 dichlorobenzalchloride, and then by agitation with fuming sulphuric acid, containing 8 percent SO_3, for 30 hours at room temperature they were able to obtain a 70-80 percent yield of 3, 5 dichlorobenzaldehyde from a 50 gram sample of the aromatic dichloride. This dihalogen benzaldehyde proved to be a solid and the com-

stants determined gave it a melting point of 65°C. and a boiling point of 235-240°C. at 758 mm. Asinger and Lock (1) report also that they were able to prepare from this compound 3, 5 dichlorobenzoic acid, a sodium bisulfite addition compound, aldoxime, m. p. 112°C.; and phenylhydrazone, m. p. 106.5°C.

Lock (2) wrote a paper describing the behavior of the benzaldehyde derivatives containing bromine, iodine or halogen and nitro in the 2, 6 positions. In his study he prepared 2, 6 dibromobenzaldehyde. The method used was similar to that described above in that by side chain bromination of 2, 6 dibromotoluene and subsequent hydrolysis with sulphuric acid he was able to, with much difficulty, produce the benzalbromide of 2, 6 dibromotoluene. The slowness of the bromination of the toluene to the benzalbromide stage is striking; he reports that even with two molecules of bromine the second bromine is introduced only with very great difficulty with the formation of considerable 2, 6 dibromobenzylbromide, m. p. 81°C.

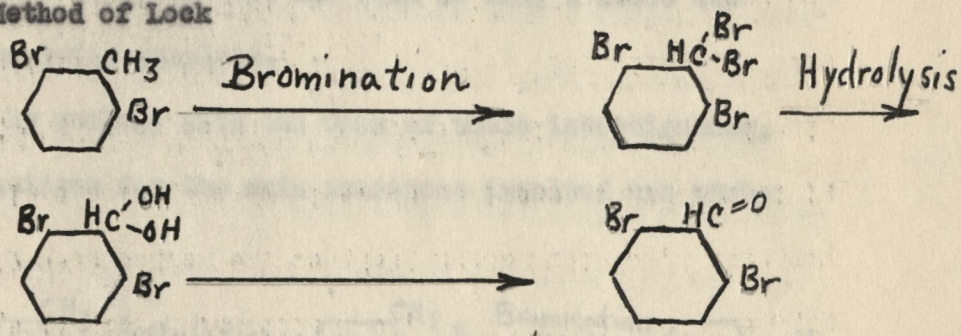
It is reasonable to assume that the probable equations for the reactions described by Asinger and Lock (1) and Lock (2) are as follows:

I Method of Asinger and Lock



3,5-dichlorobenzaldehyde

II Method of Lock



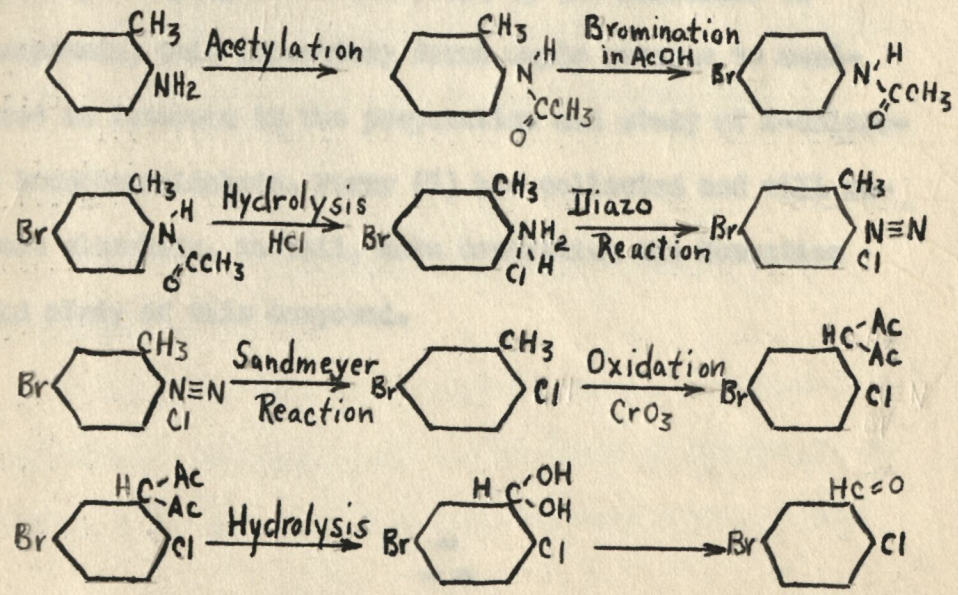
2,6 dibromobenzaldehyde

Lock and Co-workers (5) have prepared 2-chloro-6 fluoro-and 2, 6-difluorobenzaldehyde. The 2-chloro-6-fluorobenzaldehyde was prepared by the horofluoride process from pure 2-chloro-6-aminotoluene. The 2-chloro-6-fluorotoluene obtained from the latter was then converted through the benzalbromide to give the aldehyde in 77 percent yield. When the formation of the aldehyde was at-

tempted by the chromyl chloride oxidation of the toluene, the aldehyde was obtained in only 35 percent yield.

The author has, in light of the reports here covered, employed in his experiment a method similar to the combined method of Asinger and Lock (1). This laboratory now agrees that the author has been successful in synthetically isolating a 2-chloro-5-bromobenzaldehyde. The author realizes that his work is only a start and far from being complete.

By analogy with the work of these investigators, the equations for the main reactions involved are probably:



CHAPTER II

PURPOSE OF THIS WORK

This experiment was attempted with the intention of producing in the laboratory that which had been theoretically produced on paper.

According to Heilbron (4), Beilstein (5), and Mulliken (6) there are few dihalogen benzaldehydes on record. Reports indicate definitely that work as well as information on this class of compounds is limited. Furthermore, inspite of the fact that substituents influence greatly the properties exhibited by the molecules of compounds, this laboratory found ample reasons to manifest an interest in the preparation and study of 2-chloro-5 bromobenzaldehyde. Perry (7) has collected and will report elsewhere, in full, data concerning the formation and study of this compound.

CHAPTER III

EXPERIMENTAL PROCEDURE

The method used in this investigation involved the acetylation of Kahlbaum's o-toluidine in the formation of o-acettoluide. Bromination, by the method of Perry (6), a method similar to that reported by Den Ardel (8) in the preparation of 6-bromo-m-acettoluide, gave the 5-bromo-o-acettoluide in appreciable quantity. The hydrochloric acid hydrolysis of this compound produced the hydrochloride of 5-bromo-o-toluidine. Diazotizing and the subsequent Sandmeyer reaction gave 2-chloro-5-bromotoluene; careful oxidation with chromic acid by the method of Scott and Hamilton (9) gave 2-chloro-5-bromobenzalacetate which on hydrolysis with hydrochloric acid gave 2-chloro-5-bromobenzaldehyde.

Preparation and Properties of 2-Chloro-5-Bromobenzaldehyde

o-Acettoluide

To 100 grams of acetic anhydride there was added 3cc. of concentrated sulphuric acid and 85 grams of Kahlbaum's o-toluidine, a few cc. at a time with constant shaking. Dur-

for one hour under a reflux condenser. Upon cooling the hydrochloride of 5-bromo-o-toluidine separated out in white needles.

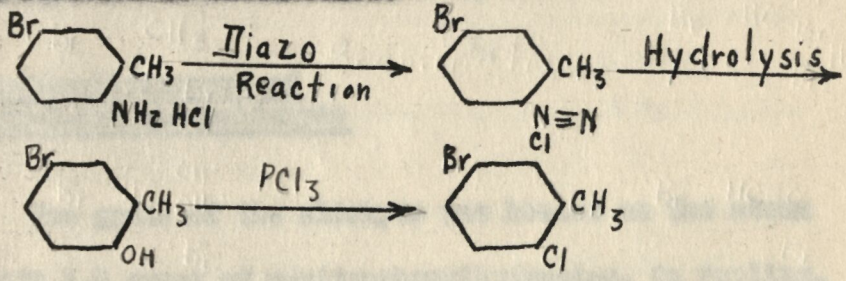
2-Chloro-5-Bromotoluene

Eighty grams of the hydrochloride was made up to a paste with 1:1 hydrochloric acid and the whole kept at 0° to 10°C. The cold mass was then treated with small quantities of solid sodium nitrite. Ten and one-half grams of the nitrite was added over a period of thirty minutes. When all of the nitrite had been added, the mixture was poured with stirring into a cold, freshly prepared solution of 9 grams of cuprous chloride in 75 cc. of concentrated hydrochloric acid. With and without the ice bath this reaction went to completion with the formation of a dark heavy oil, which was separated by means of a seperatory funnel and then distilled through an air condenser.

2-Chloro-5-Bromotoluene From 5-Brom-o-cresol

To a few grams of the freshly prepared hydrochloride of 5-bromo-o-toluidine was added a few cc. of 1:1 HCL and then at 0 to 10 C. diazotization with solid sod-

ium nitrite was carried out. The diazonium salt was then decomposed at the temperature of the steam bath to give 5-bromo-o-cresol. This product was separated carefully and treated with a slight excess of phosphorous trichloride. The oil which was formed was then washed with water and identified as 5-bromo-2-chlorotoluene. This product was thought to be identical with the toluene described above and obtained through the Sandmeyer reaction. The course of the reaction is shown below:



The reaction established the structure of the bromo-chloro-toluene obtained by the Sandmeyer reaction.

2-Chloro-5-Bromobenzaldehyde

A solution of 6 grams of 2-chloro-5-bromotoluene in 32 grams of acetic acid and 12 grams of concentrated sulphuric acid was treated with 32 grams of acetic anhydride and 8 grams of solid chromic oxide added during thirty minutes. The temperature was maintained at 0°- 10°C. Fol-

lowing the addition of all the chromic oxide, the mixture was stirred for thirty minutes at 10°C. and then extracted with two 50 cc. portions of ether. The ethereal extract was taken almost to dryness under diminished pressure and then diluted with distilled water (50 cc.) with the formation of a heavy tan oil thought to be 5-bromobenzalacetate. This oil was separated and then heated on a steam bath with dilute hydrochloric acid to give 2-chloro-5-bromobenzaldehyde, which separated as a heavy colorless oil.

p-Nitrophenylhydrazone of
2-Chloro-5-Bromobenzaldehyde

Two grams of the aldehyde was heated on the steam bath with 1.5 grams of p-nitrophenylhydrazine. On cooling, orange colored crystals of the hydrazone separated. The product was filtered off and air dried. The p-nitrophenylhydrazone melts at 228-230°C./758 mm.

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Table I

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The Properties of 2-Chloro-5-Bromotoluene

Soluble	EtOH and Ether
Insoluble	Hot or cold water
Insoluble	Cold conc. H_2SO_4
Insoluble	NaOH and KOH
Boiling Point	218.75°- 219.50°C.
Specific Gravity	1.5934 @ 25°C.
No reaction with	$FeCl_3$
No reaction with	Phenylhydrazine
Slightly yellow in color	
Aromatic Odor	
Oxidized slowly to corresponding acid by $KMnO_4$	
Oxidized slowly to aldehyde by CrO_3	
Solifies at zero degrees	

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Table II

Properties of 2-Chloro-5 Bromobenzaldehyde

Colorless oil @ room temperature
Volatile with steam
Formed with ease from benzalacetate of 2-chloro-5-bromobenzaldehyde

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CHAPTER IV

SUMMARY AND CONCLUSIONS

1. 2-Chloro-5-Bromobenzaldehyde has been synthesized from 5-bromo-o-toluidine. Each reaction was definitely characterized and the final product identified further by its behavior with an amine to give the p-nitrophenylhydrazone. This paper would tend to establish further that the brominations of Perry and Den Ardel and the aldehyde synthesis of Asinger and Lock all give satisfactory results.

2. A new compound has been isolated. Additional reactions will be studied in order that the compound may be definitely characterized and its behavior reported fully.

3. Further work is in progress.

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BIOGRAPHY

James Thomas Dudley was born February 16, 1917 in Austin, Texas. He received his elementary training in Gregory Elementary School and four years of high school training in the Anderson High School, both of Austin, Texas. It was in high school that he became scientifically inclined and with stimulation in general science, mathematics, and later chemistry he decided to develop this interest in science further.

On graduation from high school he entered Prairie View College in the year 1934-35.

In college his major work was in the field of chemistry under the guidance of Professor H. P. Perry, Head of the Department of Natural Sciences.

He was active in "Y" work and served in the capacity of treasurer of the Y. M. C. A. for 1937-38. He was a member of the Alpha Pi Mu Honorary Society during the whole of his four years of college. He was elected and served as his class president his sophomore year.