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The Preparation Of Phenylidibromnitromethane

By

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The Preparation of Phenyldibromnitromethane.

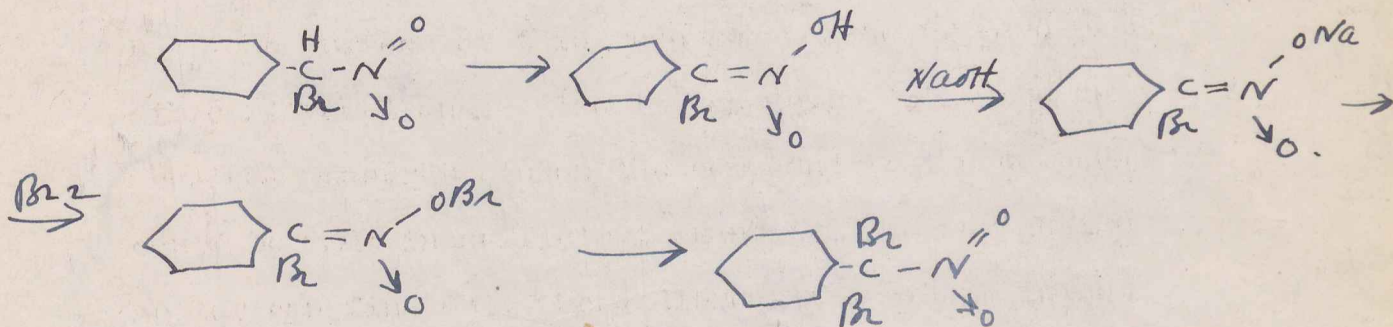
The purpose of this research was to prepare phenyldibromnitromethane. Also it was desired to make some physical measurements on the compound if the compound could be made in sufficient quantity. So far as the author can find out, phenyldibromnitromethane is not described in the literature.

September 12, 1947

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The Preparation of Phenyldibromnitromethane.

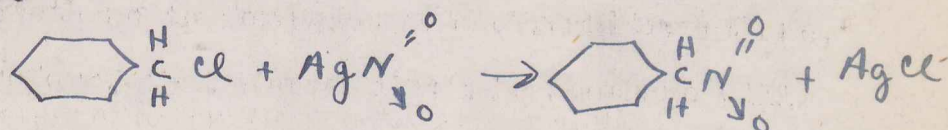
The method used in this synthesis will follow that of Davison.¹ His method consisted of brominating the sodium salt of phenylnitromethane to form phenylmonobromnitromethane. It is assumed, therefore, that phenyldibromnitromethane will be formed by brominating the sodium salt of the monobrom compound.



Phenylnitromethane:

The methods described in the literature dealing with the preparation of phenylnitromethane are as follows: from the nitration of toluene by dilute nitric acid in a sealed tube;² from the reaction between benzenediazonium chloride and nitromethane on alkaline solution;³ and from the reaction between benzyl chloride and silver nitrate.⁴ Wislincez and Endres in 1902 made phenylnitromethane by condensing ethyl nitrate with benzyl cyanide, and then hydrolyzing the addition product in two steps.⁵ Gattermann and Wieland also describe this method.⁶

Because of the danger involved in using the method which requires the use of ethyl nitrate⁵ in part of the synthesis, the author thought it best to omit that procedure insofar as possible. This was thought advisable because of the over-crowded working conditions in the laboratory this year. The chief method used, therefore, was the reaction between silver nitrate⁴ and benzyl chloride⁴.



Preparation:

(1) Silver nitrate:

The silver nitrate⁴ used in this work was prepared in this laboratory by reacting equi-molar amounts of silver nitrate and sodium nitrate⁴ in boiled distilled water at room temperature. The yellow colored silver nitrate⁴ was then filtered on a Buechner suction funnel and washed with distilled water. The washed light sensitive salt was then placed in a dark bottle and dried in a vacuum desiccator over anhydrous calcium sulfate. Because not too high a vacuum was to be had, the drying took about one week.

(2) Benzyl Chloride:

The benzyl chloride used in this work was that that fraction collected between 176-179 degrees centigrade. It was colorless.

(3) Reaction:

The reaction was found to proceed extremely slowly. Therefore, several runs were made and the product accumulated over a period of time.

For each run, 11 grams (.16 mole) silver nitrite were put into 20 ml. (.16 mole) benzyl chloride. The insoluble silver salt and the benzyl chloride were shaken by hand often for two or three hours and then left in a refrigerator for a specified length of time. In runs #3, #4, and #5 about 25ml. of dry diethyl ether was added. This was done in order to increase the volume of the solution and to permit greater dispersion of the silver salt. In each case the ether was later removed by suction, after filtering off the mixed precipitate of silver nitrite and silver chloride.

It was found that the resulting reaction mixture was golden yellow in color but did not darken very much upon standing in sunlight at room temperature. However, a copious quantity of brown fumes which were assumed to be ^{nitrogen dioxide} ~~nitric oxide~~ appeared above the liquid. Also it was noted that when some of the reacted mix^utyre was heated on a steam bath, it decomposed. The liquid turned brown and brown fumes again were given off. The odor of benzaldehyde was also detected. These observations seem to coincide with those made by Davison, except

that he mentions having been able to steam distill phenylnitromethane.

Rather than take a chance on decomposing what phenylnitromethane had formed, the mixture of it and the residual benzyl chloride was used directly.

An approximate calculation of the yield is possible by a method suggested in Findlays' "Practical Physical Chemistry."⁷ If it is assumed that the benzyl chloride and phenylnitromethane form a binary mixture, the following formula may be used:

$$\frac{(n_1-1)}{(d_1)} p = \frac{100(n_2-1)}{(d_3)} - \frac{(n_2-1)}{(d_1)}$$

where n_1 refractive index of benzyl chloride
 n_2 " " " phenylnitromethane
 n_3 " " " solution
 d_1 density of benzyl chloride
 d_2 " " phenylnitromethane
 d_3 " " solution
 p percent of benzyl chloride present

The yields were calculated as follows:

Run	Time Reacted	Refractive index Sol'n (n)	Density sol'n found (d)	% Calc. PNM. in sol'n
1	30 hrs.	1.5378	1.103 grams/cc	4.7
2	8 days	1.5372	1.109 "	15.0
3	14 days	1.5358	1.124 "	41.0
4	21 days	1.5352	1.130 "	50.0
5	33 days	1.5051	1.070 "	68.3

On the basis of the calculations just described, it was estimated that in the remaining 85 ml. of combined residues, there was approximately 35 grams (.25 mole) of phenylnitromethane. This would correspond to about a yield of 21%.

Phenylbromnitromethane:

Preparation:

The residues containing the phenylnitromethane were reacted in two portions with 50% sodium hydroxide solution at room temperature, until the reaction seemed complete. Two layers separated, the upper layer being oily and having the odor of benzyl chloride. The lower water layer was deep red and contained the water soluble sodium salt of phenylnitromethane. The two layers were carefully separated by means of a separatory funnel. The oily layer was then set aside for further separation in case more water layer should come out.

The red water layer was then reacted slowly with bromine and accompanied by vigorous shaking. A white solid formed which, upon further treatment with bromine, gave a heavy red colored oil. Bromine was added in slight excess in order to insure complete reaction of the sodium salt. The red oil was then separated from the water solution and washed with sodium bicarbonate solution in order to neutralize any excess bromine which might be present. The oil was then steam distilled and dried over anhydrous sodium sulfate. The yield was about 14.4 grams or 9.4 ml. The refractive index taken on a small sample was found to be 1.5681, which agrees closely with that found by Davison. The product was dark yellow color and did not change color appreciably when exposed to light.

Phenyldibromnitromethane:

Preparation:

14 grams of phenylbromnitromethane were treated with 50% sodium hydroxide . The reaction was slow, but with vigorous shaking, a yellowish orange solid and some white flaky material separated out. Neither solid seemed to be soluble in the water solution which had turned a pale yellow color. A few extra ml. of sodium hydroxide solution were added in order to make sure that no more solid would form.

The solid materials and the water solution were treated with bromine along with vigorous shaking. It was observed that a heavy amber colored oil formed. More bromine was added until the oil formation reached completion.

The oil and water mixture was then steam distilled. The oil was then collected and washed with bicarbonate solution, and then further washed several times with plain water. It was then dried over anhydrous sodium sulfate over night. When filtered about .7 ml. of amber colored oil was recovered. This was the total yield.

The refractive index was found to be 1.5925 at 23 C . When corrected to 20 C it has a value of 1.5937 . Exposure to light and room temperature apparently has no effect on the compound, since no color change has been observed. The oil solidified when its' temperature was lowered to between *-20 and -30 degrees Centigrade. When the temperature was raised to about 125 Centigrade the oil decomposed and turned a red brown color.

It was observed also that the oil when ignited burned with a smoky flame. A Beilstein test for halogen was positive.

The author regrets that there was not enough product left for a density determination, since without a check between the theoretical and experimental molar refractions, it cannot be proved that this material is phenyldibromnitromethane. However, the reaction did seem to follow the expected plan.

Other Attempts to Make Phenylnitromethane:

- (1) The author made two attempts to make phenylnitromethane by the reaction between benzene diazonium chloride and nitromethane in alkaline solution. The procedure was followed exactly as directed, but no product was obtained.
- (2) The author made one attempt to make phenylnitromethane by the method using ethyl nitrate. The synthesis was abandoned at the ethyl nitrate stage because of an explosion, which was witnessed by Professor Schmidt.

Summary

The author attempted to synthesize phenyldibromnitromethane by brominating the sodium salt of phenylbromnitromethane, although the product formed has not been definitely established as the dibrom compound, because it was made in such a small quantity as to prevent sufficient physical measurements to be made. However, the great increase in refractive index over that of the monobrom compound suggests strongly that another atom of bromine has been added. This added to the fact that the reaction seemed to occur as expected, also favors the suspicion that phenyldibromnitromethane has been formed.

The compound formed has the following characteristics:

amber colored oil	
non-light sensitive	
decomposition point	approximately 120°C
freezing point	-20° to -30°C
refractive index	1.5937 at 20°C

Suggestions for Future Work

It is strongly suggested that at sometime or other someone should make a critical study and experimental evaluation of the various methods used in making the fundamental compound, namely phenylnitromethane. Then having found a safe satisfactory method of making it, it would be interesting to study the reaction rates of each compound in the series, phenylnitromethane, the monobrom derivative, the dibrom derivative, and whatever other derivatives can be made.

The author thinks that the kinetics of the fundamental reaction between benzyl chloride and silver nitrite would be especially worth investigating, because if a method could be found to speed up the reaction, quantities of phenylnitromethane could be made simply and easily for use in synthesizing the halogen derivatives.

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