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UNIVERSITY OF LOUISVILLE

STUDIES IN THE DIPHENYL SERIES III.

4,4'-DICHLOROTRINITRODIPHENYL

A Dissertation

Submitted to the faculty of the Graduate

School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

of Master of Science

Department of Chemistry

By

H. Harris Ruwe

1932.

16 June 33 M.P.S.

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INTRODUCTION

OBJECTIVE

Nitrated dichlorodiphenyls having reported nitrogen contents corresponding to trinitrodichlorodiphenyl have been prepared by direct nitration of 4,4'-dichlorodiphenyl (1). The two products secured by this nitration, one melting at 164-165° and having a nitrogen content of 11.64-11.71 per cent, the other melting at 143-147° and having a nitrogen content of 11.03-11.19 percent, were thought to be isomers. Since the one melting at 143-147° has a range of several degrees in melting point along with a nitrogen content approximately .62 per cent below that of the theoretical for dichlorotrinitrodiphenyl, it was possible that the lower melting compound was identical with the higher one but less pure.

The prime purpose of the work to be described in this thesis was to determine the positions of the nitro-groups in 4,4'-dichlorotrinitrodiphenyl, melting point 164-165 , and to study further the lower melting compound with a view of determining whether or not it was truly isomeric with the first. In addition, a study of the physical and chemical properties of both nitro-derivatives was projected in order to increase the relatively low yield of the higher melting compound through the application of such knowledge.

It was proposed also to check the method of nitration previously referred to, as well as the analytical method, which was more or less new, in application to this type of nitrogen compounds.

HISTORICAL

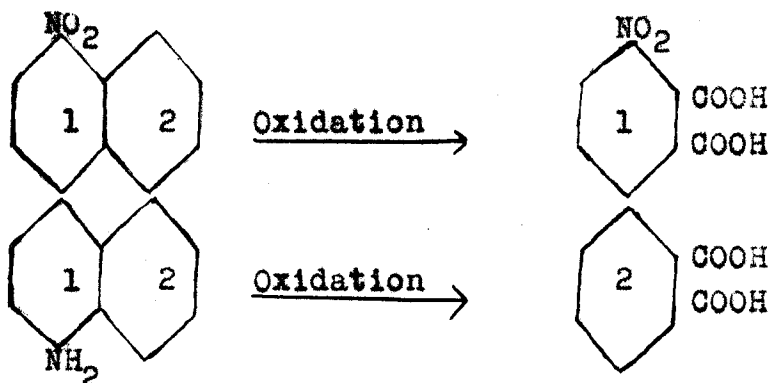
The first diphenyl derivatives of the type to be studied were prepared by a reaction in which substituted aryl halides were treated with copper, thus coupling the benzene nuclei at the point occupied by the halogens. The yields obtained by this method were very low, and in proportion, the cost was so great that only a limited amount of research was carried on. No commercial applications were possible under such conditions.

Recently diphenyl has been made by passing benzene and steam over a cracking surface such as pumice at a high temperature and pressure (2). A large yield was obtained by this method at a relatively low cost, and derivatives of diphenyl are now made from diphenyl itself, by using the well known substitution reactions. A commercial outlet for the chloro- and nitro-derivatives was soon found in the production of stable gums, resins, and dye intermediates. Thus was opened a field of research with seemingly unlimited possibilities.

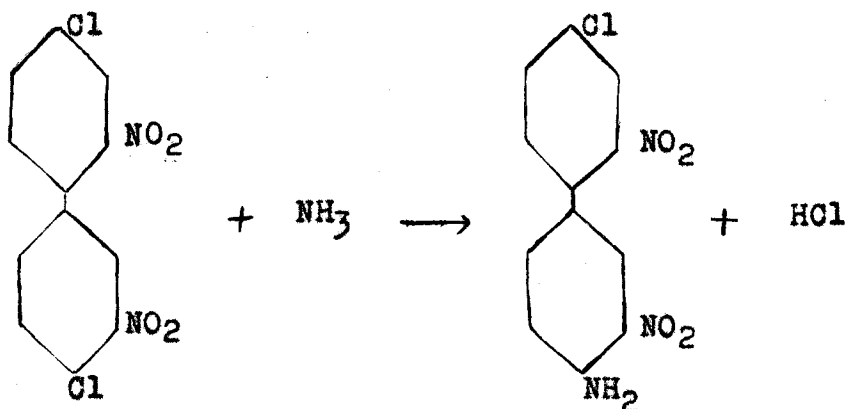
THEORETICAL

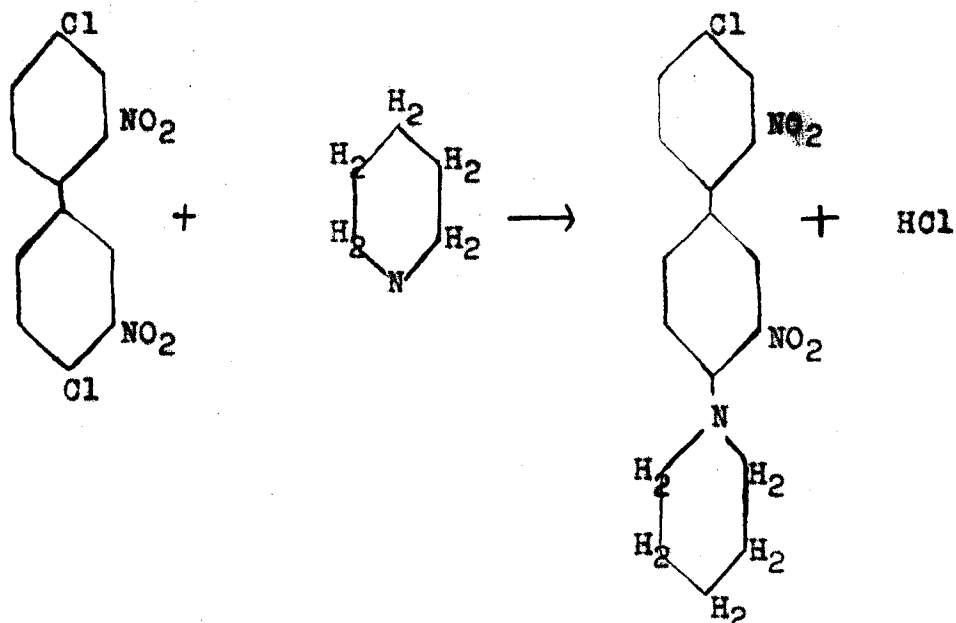
On oxidation of diphenyl, benzoic acid is produced; therefore, on oxidation of a trinitro-derivative of 4,4'-dichlorodiphenyl in which two nitro-groups are on one ring and one nitro-group on the other a 4-chlorodinitrobenzoic acid should be produced. The reason for believing the nitro-groups are distributed in such manner will be readily understood after reading the discussion in regard to the orientation of the first two nitro-groups mentioned later in this section. comparison of the 4-chloro-XY-dinitrobenzoic acid, so produced, with known 4-chlorodinitrobenzoic acids should be sufficient in determining the positions of two of the nitro-groups on one ring.

It has been shown by Erlenmeyer and Graebe that a nitro-group on a benzene ring renders that ring stable toward oxidation, while an amino-group makes the ring more susceptible to oxidation (3). On oxidation of nitronaphthalene, nitrophthalic acid was produced, but when aminonaphthalene was oxidized phthalic acid was produced.



Therefore di- and trinitro-derivatives of diphenyl in which there is at least one nitro-group on each ring, would not be expected to readily undergo oxidation. On the other hand it has been shown that 4,4'-dichlorodinitrodiphenyl, which was also prepared by direct nitration, reacts with alcoholic ammonia and piperidine, under normal conditions, to form 4-chloro-4'-aminodinitrodiphenyl and 4-chloro-4'-piperidinodinitrodiphenyl respectively. These reactions being typical of aliphatic groups, (4), it was thought that one





of the rings may act as an aliphatic grouping, especially when certain groups are present on the ring. Thus it was thought that 4,4'-dichlorotri-nitrodiphenyl, prepared by direct nitration, would have the same properties and possibly undergo direct oxidation. If the 4,4'-dichlorotrinitro-diphenyl would not undergo direct oxidation, then one or more of the nitro-groups could be reduced to the corresponding amino-groups, forming, as mentioned before, a compound which should be quite susceptible to oxidation. However, the location of the position of the third nitro-group necessitates an entirely different and more complicated procedure.

Further nitration of a 4,4'-dichlorodinitro-diphenyl, prepared by direct nitration of 4,4'-dichlorodiphenyl, might reasonably be expected to give a trinitro-body corresponding to one of those under consideration. This, if successful, would

fix the positions of two of the nitro-groups, provided these positions were known prior to the introduction of the third. Such a dinitrodichlorobody was available in 4,4'-dichloro-2,3'-dinitrodiphenyl, so this means of attack was used simultaneously with the one first mentioned.

In connection with the positions of the nitro-groups in the above mentioned compound, a controversy has arisen which it is necessary to discuss briefly. Direct nitration of 4,4'-dibromodiphenyl by Lellman's Method produces a mononitro-compound, melting at 124°, which is identical with 4,4'-dibromo-2-nitrodiphenyl prepared with 2-nitro-benzidine (5). On further nitration of Lellman's mononitro-compound a dinitro-compound was formed, which corresponded with the dinitro-derivative of 4,4'-dibromodiphenyl prepared by Schultz and on reduction a diamine, melting at 89°, was formed which was identical with the diamine prepared by Schultz (6).

The latter diamine would not undergo condensation of the type to be expected of a symmetrical diamine. This peculiarity led Dennet and Turner to believe that the dinitro-derivative was unsymmetrical, (7), and on further study it was found that the dinitro-compound depressed the melting point of the 4,4'-dibromo-2,2'-dinitrodiphenyl prepared from 2,5-dibromonitrobenzene (8). The unsymmetrical dinitro-compound reacted vigorously with pip-

eridine to give a bromopiperidino-nitrodiphenyl. "4,4'-dibromo-2-nitrodiphenyl and 4,4'-dibromo-2,2'-dinitrodiphenyl were not affected by piperidine, and it is therefore clear that the above piperidino-derivative is 4,4'-dibromo-2,3'-dinitrodiphenyl, and that the original dinitro-compound is the 2,3'-derivative."

The dinitro-derivative of 4,4'-dichlorodiphenyl, melting at 140°, described by Schmidt and Schulz was similarly found to be 4,4'-dichloro-2,3'-dinitrodiphenyl (9).

Hodgson also prepared a dinitro-derivative of 4,4'-dichlorodiphenyl from 3,3'(2,3'?)-dinitrobenzidine which was identical with the directly nitrated 4,4'-dichloro-dinitrodiphenyl (10). On treating the dinitro-compound with an excess of alcoholic ammonia he found that only one of the chlorine atoms was readily displaced by ammonia. Therefore, if the dinitro-derivative of benzidine was either of the two possible isomers mentioned, it must have been the unsymmetrical one, (11), as only one chlorine atom reacted with ammonia to form 4-chloro-4'-aminodinitrodiphenyl.

EXPERIMENTAL

EXPERIMENTS

OXIDATION OF 4,4'-DICHLOROTRINITRODIPHENYL

A mixture composed of 3.5 grams (.01 mol) of 4,4'-dichlorotrinitrodiphenyl, melting at 164-165°, 4.7 grams (.03 mol) of potassium permanganate, and 54 grams (3.0 mol) of water was placed in a 200 c.c. flask fitted with a stirrer and a reflux condenser. The mixture was heated on a water-bath with continuous stirring until the permanganate color disappeared, which took 3.5 hours (12).

The mixture was filtered, and the manganese dioxide that remained as a residue was discarded. The filtrate was clarified by treating with animal charcoal, acidified with hydrochloric acid and extracted with ether. After the ether had evaporated a few colorless crystals remained, but the quantity was insufficient for analysis.

This method of oxidation was repeated four times, each time the conditions being varied, as shown in Table 1, but none of the extractions contained organic matter.

Since these results were negative, it seemed necessary that one or more of the nitro-groups would have to be reduced before the compound would undergo oxidation, as was previously mentioned in the theoretical discussion.

I

OXIDATION OF 4,4'-DICHLOROTRINITRODIPHENYL

Run	Substances used	Grams	Mols	Time	Temp.	Yield
1	4,4'-dichloro- trinitrodiphenyl	3.5	0.01			
	KMnO ₄	4.74	0.03			
	H ₂ O	54.	3.	3.5 hr.	100°	.00 gr.
2	4,4'-dichloro- trinitrodiphenyl	7.1	0.02			
	KMnO ₄	9.48	0.06			
	H ₂ O	54.	3.	4.0 hr.	100°	.00 gr.
3	4,4'-dichloro- trinitrodiphenyl	7.1	0.02			
	KMnO ₄	9.48	0.06			
	H ₂ O	54.	3.	5.0 hr.	100°	.00 gr.
4	4,4'-dichloro- trinitrodiphenyl	10.	0.028			
	KMnO ₄	4.74	0.03			
	H ₂ SO ₄	4.2	0.045			
	H ₂ O	11.5	0.6	2.0 hr.	100°	.00 gr.
5	4,4'-dichloro- trinitrodiphenyl	10.	0.028			
	KMnO ₄	9.5	0.06			
	H ₂ SO ₄	8.4	0.09			
	H ₂ O	4.6	0.25	2.0 hr.	100°	.00 gr.

ATTEMPTED REDUCTION OF ONE NITRO-GROUP
OF 4,4'-DICHLOROTRINITRODIPHENYL.

The following method was used in an attempt to reduce only one nitro-group:— a mixture made up of 3.5 grams (.01 mol) of 4,4'-dichlorotrinitrodiphenyl, 41.5 grams (.9 mol) of alcohol, and 7 grams (.2 mol) of ammonium hydroxide was placed in a flask and heated. Hydrogen sulfide was then added until the weight had increased 3 grams (.085 mol). Then 100 grams (5.55 mols) of water was added and the solution neutralized with sodium hydroxide to precipitate the amine (13).

The precipitate, a mixture composed of a reddish brown powder and a small quantity of yellow crystals, was dried and washed with acetone. After the acetone had evaporated, a mixture of brown and yellow crystals remained. The product melted at 122-135°.

There is no doubt that a reaction had taken place in this reduction, as the solutions obtained on dissolving the monoamine in various solvents were highly colored while the solutions made of the same solvents and trinitro compound were clear or slightly yellow. Due to the similarity of 4,4'-dichlorodinitroaminodiphenyl and 4,4'-dichlorotrinitrodiphenyl, it was impossible to obtain the amine in a pure state. A reduction by the use of tin and hydrochloric acid was then attempted, as such a reaction should produce a triamine hav-

ing properties sufficiently different from the mother substance to make a complete separation possible.

ATTEMPTED PREPARATION OF 4,4'-DICHLOROTRIAMIN-
PHENYL

A mixture of 3.5 grams (.03 mol) of tin, 2.16 grams (.12 mol) of water, and 10 grams (.028 mol) of 4,4'-dichlorotrinitrodiphenyl was placed in a 200 c.c. flask fitted with a reflux condenser and stirrer. Then 2.16 grams (.06 mol) of hydrochloric acid were added, and the contents were heated to 70° with constant stirring for 1.5 hours.

The solution was then filtered, and the fluorescent filtrate was neutralized with sodium hydroxide and saturated with sodium chloride. On standing, 2.5 grams of a dark brown resinous product precipitated out.

This method of reduction was repeated several times, being modified each time as shown in table II, in an attempt to increase the yield of 4,4'-dichlorotriaminodiphenyl.

In run number two the reduction was carried out the same as in the first, but was refluxed for 1 hour instead of 1.5 hours. On purification a larger quantity of unchanged tin and 4,4'-dichlorotrinitrodiphenyl remained in the residue.

In run number three the entire residue was dried, washed with acetone, and diluted with hydrochloric acid to precipitate out the trinitro-compound. The solution was then filtered, and the filtrate was evaporated to dryness on a steam-bath.

In run number four the solution was filtered,

and the filtrate was evaporated to dryness on a steam-bath and vacuum distilled. The distillate solidified, forming a yellow powder which melted at 125-133.5°. This product was not easily condensed, much of it being carried over into the vacuum pump.

Runs numbers five and six were purified the same as run number three.

Runs numbers seven and eight were purified as follows:- the entire solution was diluted to 500 c.c. and hydrogen sulfide was added until the tin had completely precipitated. The solution was then filtered and the filtrate dried on a steam-bath. There was a small quantity of impurities in the amine, most of which was thought to be free sulphur.

Although the method used in the purification of runs three, five, and six did not produce yields which were as high as those produced by the method used in the last two runs, the products contained less impurities. It was not possible to purify the compound sufficiently for analysis and complete identification, but the general appearance and properties of the product were such that it was believed that the trinitro-compound had been at least partly reduced. Even partial reduction would have been sufficient for the purpose of rendering one ring more susceptible to oxidation so the next group of experiments were attempts to

oxidize the reduced product to chloronitroben-
zoic acids.

ATTEMPTED PREPARATION OF 4,4'-DICHLOROTRIAMIN-

DIPHENYL

Run	Substances used	Grams	Mols	Time	Temp	Yield
1	4,4'-dichloro- trinitrodiphenyl	10.	0.028			
	Sn	3.5	0.03			
	HCl	2.16	0.06			
	H ₂ O	2.16	0.12	1.5 hr.	75°	2.5 gr.
2	4,4'-dichloro- trinitrodiphenyl	10.	0.028			
	Sn	3.5	0.03			
	HCl	2.16	0.06			
	H ₂ O	2.16	0.12	1.0 hr.	75°	2.3 gr.
3	4,4'-dichloro- trinitrodiphenyl	5.	0.014			
	Sn	3.5	0.03			
	HCl	2.16	0.06			
	CH ₃ COOH	1.8	0.03			
	H ₂ O	20.	1.9	2.0 hr.	100°	2.6 gr.
4	4,4'-dichloro- trinitrodiphenyl	5.	0.014			
	Sn	7.	0.06			
	HCl	2.16	0.016			
	CH ₃ COOH	3.6	0.06			
	H ₂ O	20.	1.9	2.0 hr.	100°	.7 gr.
5	4,4'-dichloro- trinitrodiphenyl	2.5	0.0069			
	Sn	3.5	0.03			
	HCl	1.08	0.03			
	CH ₃ COOH	1.8	0.03			
	H ₂ O	20.	1.9	5.0 hr.	30°	1.6 gr.
6	4,4'-dichloro- trinitrodiphenyl	2.5	0.089			
	Sn	10.5	0.09			
	HCl	25.92	0.72			
	CH ₃ COOH	20.	0.35	5.0 hr.	25°	1.8 gr.
7	4,4'-dichloro- trinitrodiphenyl	2.5	0.089			
	Sn	10.5	0.09			
	HCl	25.92	0.72			
	CH ₃ COOH	20.	0.33	9.0 hr.	25°	1.82 gr.
8	4,4'-dichloro- trinitrodiphenyl	2.5	0.089			
	Sn	10.5	0.09			
	HCl	25.92	0.72			
	CH ₃ COOH	20.	0.33	9.0 hr.	25°	1.82 gr.

OXIDATION OF REDUCED

4,4'-DICHLOROTRINITRODIPHENYL

A mixture of 3.29 grams (.01 mol) of a product believed to be chlorotriaminodiphenyl, 1.58 grams (.01 mol) of potassium permanganate, 3.5 grams (.035 mol) of sulphuric acid, and 10 grams (.55 mol) of water was placed in a 200 c.c. flask fitted with a stirrer and a reflux condenser, and heated on a water-bath with constant stirring until the permanganate color disappeared.

The mixture was filtered, and the manganese dioxide that remained as a residue was discarded. The filtrate was clarified by treating with animal charcoal, acidified with hydrochloric acid, and extracted with ether. After the ether had evaporated a small quantity of brown powder remained, which was then analyzed, and proved to be mostly inorganic matter.

This method was used in the following oxidation, and, as the reagents and quantities are given in table III, only the results of the purifications will be mentioned here.

In run number two, ligroin, benzene, and chloroform were used as extraction solvents. The ligroin and benzene extractions were completely negative, but on evaporation of the chloroform a very small quantity of brown resins remained. The resins were soluble in concentrated hydrochloric acid, but insoluble in both neutral and alkaline solut-

ions. It was therefore thought to be the original triamine-compound.

In run number three, since chromic acid was used as the oxidizing agent instead of potassium permanganate, an entirely new method of purification was necessitated. The solution was made alkaline with ammonium hydroxide, and the chromium hydroxide was filtered off. The red filtrate was divided into two parts: the first was acidified with hydrochloric acid and extracted with ether. The ether extraction was negative. The second portion was saturated with sodium chloride, and a brown precipitate was thrown out of solution. On investigation the brown precipitate was believed to be the original triamine.

In run number four the solution was again neutralized with ammonium hydroxide, but, instead of a green precipitate of chromium hydroxide being formed, a small quantity of brown substance precipitated. The brown substance was soluble in concentrated hydrochloric acid, forming a red solution, and slightly soluble in a neutral solution. It was therefore thought to be the original amine. The filtrate was again acidified, shaken with benzene, and the two layers separated. After the Benzene had evaporated nothing remained. The aqueous layer was then neutralized with sodium hydroxide, and steam distilled, but without success.

In this group of experiments it was shown that the reduction was not sufficient to render one ring susceptible to oxidation. It was possible that the oxidations attempted merely changed any amino-group back to the original nitro-group.

III

ATTEMPTED OXIDATION OF PRODUCT IDENTIFIED AS

4,4'-DICHLOROTRIAMINODIPHENYL

Run	Substances used	Grams	Mols	Time	Temp.	Yield
1	4,4'-dichlorotri-aminodiphenyl	3.29	0.01	2 hr.	85°	.00
	KMnO ₄	1.58	0.01			
	H ₂ SO ₄	3.5	0.035			
	H ₂ O	10.	0.55			
2	4,4'-dichlorotri-aminodiphenyl	3.29	0.01	2.5 hr.	85°	.00
	KMnO ₄	3.16	0.02			
	H ₂ SO ₄	7.	0.07			
	H ₂ O	10.	0.55			
3	4,4'-dichlorotri-aminodiphenyl	1.65	0.005	2.5 hr.	90°	.00
	CrO ₃	1.8	0.018			
	CH ₃ COOH	60.	1.			
4	4,4'-dichlorotri-aminodiphenyl	2.45	0.0075	1.5 hr.	90°	.00
	CrO ₃	3.6	0.036			
	CH ₃ COOH	120.	2.			

NITRATIONS

PREPARATION OF 4,4'-DICHLORO-2,3'-DINITRODIPHENYL

A mixture of 1.96 grams (.02 mol) of concentrated sulphuric acid, specific gravity 1.84, and 7.56 grams (.12 mol) of red fuming nitric acid, specific gravity 1.45, placed in a 200c.c. flask and cooled 0°. Then 14.05 grams (.0606 mol) of 4,4'-dichlorodiphenyl were slowly added. When the addition was completed the contents were heated on a water-bath at 85-90° with constant stirring for 2 hours (14).

The product was washed with water, dried, and divided into two portions. The first was recrystallized from ether. The first fraction to crystallize melted at 127-130°, while the second fraction melted at 76-80°. The second portion was recrystallized from benzene. The first fraction to crystallize, a white powder, melted at 90-115°, while the second fraction, a pale yellow powder, melted at 85-87°. The fraction melting at 90-115° was further purified by the use of benzene, and a new product melting at 131-133° was obtained.

A 50% mixture of 4,4'-dichloro-2,3'-dinitrodiphenyl, melting at 136°, and the product melting at 131-133° increased the melting point of the latter to 132.5-134°.

The 4,4'-dichloro-2,3'-dinitrodiphenyl, melting at 136°, was a commercial product, which had been purified by vacuum distillation; but on further

purification by recrystallization from glacial acetic acid, its melting point has been brought up to 140° . The nitrogen content of the dinitro-compound melting at 136° was checked by the Kjeldahl method and was found to be 8.7%, while the theoretical is 8.9%.

This method of nitration was also used for the following preparations, the modifications in quantities and conditions being given in table IV:

In run number two, the product was also divided into two portions. The first was recrystallized from glacialacetic acid. The first fraction to crystallize melted at $86-92^{\circ}$, while the second fraction melted at $85-96^{\circ}$. The second portion was recrystallized from alcohol. The first fraction to crystallize melted at $97-101^{\circ}$, while the second fraction melted at $94-97^{\circ}$.

In run number three, the vibration of the stirrer cracked the condenser two hours after the run was started, and water ran down into the flask. There was an extreme heat produced by the reaction of the water and the fuming acids, but the heat did not seem to have had any effect on the reaction products as will be seen later.

The product was recrystallized from alcohol. The first fraction to crystallize melted at $126-135^{\circ}$ while the second fraction melted at $95-108^{\circ}$.

A 50% mixture of 4,4'-dichloro-2,3'-dinitrodiphenyl and the product melting at $126-135^{\circ}$ increased

the melting point of the latter to 128-134°.

The latter nitrations proved sufficient insofar as only one dinitro-compound was produced, and the melting point of the slightly impure dinitro-compound was not depressed but raised when mixed with a more pure sample of 4,4'-dichloro-2,3'-dinitrodiphenyl. This compound was prepared for further nitration in an attempt to secure products identical to those formed by uninterrupted nitration of 4,4'-dichlorodiphenyl, the next group of experiments being along that line.

IV

PREPARATION OF 4,4'-DICHLORO-2,3'-DINITRODIPHENYL

Run	Substances used	Grams	Mols	Time	Temp.	Yield*
1	4,4'-dichloro- diphenyl	14.05	0.0608	2 hr.	85-90°	9.6 gr
	H ₂ SO ₄	1.96	0.02			
	HNO ₃	7.56	0.12			
2	4,4'-dichloro- diphenyl	13.4	0.0567	2.5 hr.	75-85°	9.3 gr
	H ₂ SO ₄	1.96	0.02			
	HNO ₃	7.56	0.12			
3	4,4'-dichloro- diphenyl	66.9	0.299	3 hr.	50-60°	54.0 gr
	H ₂ SO ₄	9.8	0.1			
	HNO ₃	37.8	0.6			

* The yield in this table is the total yield of all fractions melting above 125°.

NITRATION OF 4,4'-DICHLORO-2,3'-DINITRODIPHENYL

A mixture composed of 36.8 grams (.375 mol) of 20-30% fuming sulphuric acid and 40 grams (.635 mol) of red fuming nitric acid, specific gravity 1.45, were poured into a 500 c.c. flask and cooled to 0°. Then 14.08 grams (.045 mol) of 4,4'-dichloro-2,3'-dinitrodiphenyl were slowly added. When the addition was completed the contents were heated on a water-bath at 50-60° with constant stirring for three hours.

The entire mixture was separated into two distinct portions by filtering the acid solution through glass wool. The filtrate was then poured over cracked ice, and a white precipitate deposited, which was washed until free from acid. The white precipitate was then recrystallized from glacial acetic acid and dried on a suction filter. The product melted at 156-158°.

The pale yellow crystalline residue retained by the glass wool was washed until free from acid and recrystallized from glacial acetic acid. The first fraction to crystallize melted at 145-152°, while the second fraction melted at 113-120°.

A 50% mixture of the product melting at 156-158° and the 4,4'-dichlorotrinitrodiphenyl, melting at 164-165°, prepared by a Rebernak, melted at 123-129°.

This method of nitration was also used for the following nitrations, modifications in conditions being given in table V: in run number two only the acid

soluble portion was further purified, as the residue was highly contaminated with rubber from the stopper on the flask. It was first recrystallized from glacial acetic acid and dried on a suction filter. The white crystalline product melted at 158-162.5°, and, on further purification by recrystallization from alcohol, the melting point was raised to 162-164°.

A 50% mixture of the product melting at 158-163.5°, and the 4,4'-dichlorotrinitrodiphenyl melting at 164-165°, previously mentioned, melted at 139-145°.

In run number three the acid soluble portion was recrystallized from glacial acetic acid. The first fraction to crystallize melted at 161-168°, while the second fraction melted at 153-162°. The fraction melting at 153-162° was vacuum distilled and a product melting at 158-163° was obtained. The fraction melting at 161-163° was again crystallized from glacial acetic acid, and the melting point was raised to 163.5-164.25°.

A 50% mixture of the product, melting at 163.5-165.25°, and the 4,4'-dichlorotrinitrodiphenyl melting at 164-165°, melted at 163-164.5°. Thus it was believed that the nitro-compounds were identical. The depression in the mixed melting points of the products obtained in the two preceding runs and 4,4'-dichlorotrinitrodiphenyl, melting point 164-165°, may have been due to insufficient purifica-

tion. The reason for believing the products of the two preceding runs were impure is shown by comparing the melting points of those products with the melting point of the product obtained from this run.

In run number four the acid soluble product was recrystallized from glacial acetic acid. The more insoluble fraction melted at 117-135°.

The residue was also purified by the use of glacial acetic acid and two fractions were obtained, one melting at 124-136° and the other melting at 126-140°.

In run number five the filtrate was again recrystallized from glacial acetic acid. The first fraction to crystallize melted at 156-160.5°, while the second fraction melted at 158-162°.

The residue, melted at 125-136°, after being recrystallized from glacial acetic acid.

A 50% mixture of the product, melting at 159-163.5°, and the nitrated 4,4'-dichlorodiphenyl, melting at 164-165°, melted at 160-162°.

In run number six the products were again recrystallized from glacial acetic acid, and the fraction having the highest melting point melted at 152-158°.

A 50% mixture of the latter product and the nitrated 4,4'-dichlorodiphenyl, melting point 164-165°, melted at 159-161.5°.

The results of the mixed melting points, mentioned in connection with the nitrations of 4,4'-dichloro-2,3'-dinitrodiphenyl, were sufficient indication

that the two compounds were identical. The fact that further nitration of 4,4'-dichloro-2,3'-dinitrodiphenyl yielded a compound identical with a 4,4'-dichloro-trinitrodiphenyl, melting at 164-165°, showed that two of the three nitro-groups believed present were in the 2,3'-positions.

V

NITRATION OF 4,4'-DICHLORO-2,3'-DINITRODIPHENYL

Run	Substances used	Grams	Mole	Time	Temp.	Yield *
1	4,4'-dichloro- 2,3'-dinitro- diphenyl	14.08	0.045	3	hr.50-60°	7 gr
	H ₂ SO ₄	36.8	0.375			
	HNO ₃	40.	0.635			
2	4,4'-dichloro- 2,3'-dinitro- diphenyl	14.08	0.045	5	hr.50-60°	9.7 gr
	H ₂ SO ₄	36.8	0.375			
	HNO ₃	40.	0.635			
3	4,4'-dichloro- 2,3'-dinitro- diphenyl	14.08	0.045	3.5	hr.50-60°	8.8 gr
	H ₂ SO ₄	36.8	0.375			
	HNO ₃	40.	0.635			
4	4,4'-dichloro- 2,3'-dinitro- diphenyl	14.08	0.045	4	hr.50-60°	7.5 gr
	H ₂ SO ₄	36.8	0.375			
	HNO ₃	40.	0.635			
5	4,4'-dichloro- 2,3'-dinitro- diphenyl	14.08	0.045	3	hr.50-60°	8.9 gr
	H ₂ SO ₄	46.8	0.375			
	HNO ₃	40.	0.635			
6	4,4'-dichloro- 2,3'-dinitro- diphenyl	14.08	0.045	3	hr.50-60°	9.1 gr
	H ₂ SO ₄	36.8	0.045			
	HNO ₃	40.	0.635			

* The yield is in terms of total yield of fractions melting above 140°.

PURIFICATION OF 4,4'-DICHLOROTRINITRODIPHENYL,
MELTING POINT 143-147°

Further purification of 4,4'-dichlorotrinitrodiphenyl, melting point 143-147°, was attempted by recrystallizing the product from various organic solvents and by vacuum distillation. None of the products obtained by these methods of purification showed any appreciable change in melting point, so the following method was attempted:- to a mixture of 10.8 grams (.11 mol) of concentrated sulphuric acid, specific gravity 1.84, and 17.2 grams (.27 mol) of red fuming nitric acid, specific gravity 1.45, 3 grams (.0084 mol) of 4,4'-dichlorotrinitrodiphenyl, melting point 144-145°, were slowly added. The contents were heated on a water-bath for 2 hours.

The mixture was then filtered through a mat of glass wool. The filtrate was poured over cracked ice, and a white crystalline product deposited. The precipitate was washed until free from acid and dried in a vacuum desiccator. The product melted at 146-149°. The residue that remained on the glass wool was also washed and dried. It melted at 145-147°.

In the second purification a mixture of 7.36 grams (.075 mol) of concentrated sulphuric acid, specific gravity 1.84, 7.2 grams (.074 mol) of 20-30% fuming sulphuric acid, 11.6 grams (.184 mol)

of fuming nitric acid, specific gravity 1.39, and 11 grams (.18 mol) of red fuming nitric acid, specific gravity 1.45, were poured into a 200 c.c. flask and cooled to 0°. Then 5 grams (.0139 mol) of 4,4'-dichlorotrinitrodiphenyl, melting point 145-147°, were slowly added. When the addition was completed the contents were heated on a water-bath for 2.5 hours.

The mixture was then filtered through glass wool. The filtrate was poured over cracked ice and a white crystalline substance deposited. The precipitate was washed until free from acid and dried in a vacuum desiccator. It melted at 146-151°.

The residue that remained on the glass wool was also washed and dried. It was further purified by recrystallization from glacial acetic acid and dried on a suction filter. It melted at 145-148°.

The acid solution used in this purification was made on such basis that it would not exceed the normality of the spent acid solution obtained from the nitration of 4,4'-dichlorodiphenyl by A. Rebernak's method, which was 21-26 normal. As the acidity of the latter solution was approximately 25 normal it was believed that the purification was due to the difference in solubility of the nitrated bodies and further nitration had not taken place.

PURIFICATION AND FURTHER NITRATION OF DICHLOROTRINITRODIPHENYL, MELTING POINT 145-147°.

To a mixture of 110.4 grams (1.125 mols) of 20-30% fuming sulphuric acid and 120 grams (1.905 mols) of red fuming nitric acid, specific gravity 1.45, 10 grams (.028 mol) of 4,4'-dichlorotrinitrodiphenyl, melting point 145-147°, were slowly added. The contents were heated on a water-bath for two hours.

The mixture was then filtered through glass wool. The filtrate was poured over cracked ice and a white crystalline substance deposited. The precipitate was washed until free from acid, dried and recrystallized from glacial acetic acid. It was again washed and dried in a vacuum desiccator. The product melted at 160.5-164°. The residue that remained on the glass wool was washed until free from acid, dried, and recrystallized from glacial acetic acid. The crystals were very pale yellow and melted at 145.5-148°.

A 50% mixture of the fraction, melting at 160.5-164°, and 4,4'-dichlorotrinitrodiphenyl, melting point 164-165°, melted at 161-164°. This melting point indicated that the 4,4'-dichlorotrinitrodiphenyl, melting point 145-147°, was not an isomer of the trinitro-compound, melting at 164-165°, but an impure fraction of the latter.

PURIFICATION & NITRATION OF NITRATED 4,4'-DI-
CHLORO-2,3'-DINITRODIPHENYL, MELTING POINT

110-126°

A mixture of 110.4 grams (1.125 mols) of 20-30% fuming sulphuric acid and 120 grams (1.905 mols) of red fuming nitric acid, specific gravity 1.45, was cooled to 0°. Then 10 grams (.028 mols) of nitrated 4,4'-dichloro-2,3'-dinitrodiphenyl were slowly added. After the addition was completed the contents were heated on a water-bath at 60-70° for three hours.

The mixture was then filtered through glass wool. The filtrate was poured over cracked ice and a white crystalline substance deposited, which was washed until free from acid and dried in a vacuum desiccator. The product melted at 164.5-168°. The residue, remaining on the glass wool, was washed until free from acid, and dried on a suction filter. The dry residue was recrystallized from glacial acetic acid and two fractions were obtained. The first to crystallize melted at 150.5-154°, while the second melted at 144-147°.

This run was made to confirm the belief that only one trinitro-compound is produced on direct nitration.

NITROGEN ANALYSIS

As the nitrogen analysis of 4,4'-dichlorotri-nitrodiphenyl was made by the use of the modified Kjeldahl-Gunning method, which was more or less new in its application to this type of compound, it was checked by the analysis of known compounds (15).

A .5 to 1. gram sample of nitro-compound was placed in a Kjeldahl flask. To the sample were added 30 c.c. of concentrated sulphuric acid, 1 gram of salicylic acid, and 5 grams of sodium thio-sulphate. The contents were then heated until sulphur trioxide fumes ceased to evolve. Then 2 grams of copper sulphate and 5 grams of potassium sulphate were added. The flask was heated until the solution became clear.

Both picric acid and 4,4'-dichloro-2,3'-dinitrodiphenyl were analyzed by this method and accurate results were secured, as shown by the following table.

Compounds	Nitrogen calculated	Nitrogen found
Picric acid	17.5%	17.02%
Picric acid	17.5%	17.23%
4,4'-dichloro-2,3'-dinitrodiphenyl	8.9%	8.7%
4,4'-dichloro-2,3'-dinitrodiphenyl	8.9%	8.68%

The method can therefore be considered as being dependable.

CONCLUSION

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The data collected in this study indicated that two of the nitro-groups in 4,4'-dichlorotrinitrodiphenyl are in the 2,3'-positions, as it has been shown that on further nitration of 4,4'-dichloro-2,3'-dinitrodiphenyl a nitro-compound was formed which was identical with 4,4'-dichlorotrinitrodiphenyl, melting at 164-165°, is produced.

The 4,4'-dichlorotrinitrodiphenyl, melting at 143-147°, believed to have been an isomer of 4,4'-dichlorotrinitrodiphenyl, melting at 164-165°, was shown to be a mixture of di- and trinitro-compounds. By both recrystallization and further nitration of the product melting at 143-147° a product, which was identical with 4,4'-dichlorotrinitrodiphenyl, and which melted at 164-165°, was obtained.

In conclusion the evidence indicated that only one trinitro-compound was produced by direct nitration of 4,4'-dichlorodiphenyl. whether the reaction took place in steps or in one operation.

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AUTOBIOGRAPHY

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