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UNIVERSITY OF LOUISVILLE

STUDIES IN THE DIPHENYL SERIES:
THE MOTILITY OF THE CHLORINE ATOMS ON THE NUCLEI

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

Adolph Rebernak

1931

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INTRODUCTION

OBJECTIVE

Negative substituents on a benzene ring affect the reactivity or motility of other substituents on the same ring. It has been postulated that phenyl groups are negative, but whether they are more or less negative than a nitro group is not definitely known, though probably less so. Hence a substituted diphenyl, which has two directly connected benzene rings, affords an ideal compound for investigation along this line. The primary purpose of this study was to measure the degree of negativity of the phenyl group by determining, upon hydrolysis by means of sodium hydroxide, the motility of the chlorine attached to a diphenyl compound.

Since this study led to the need of a highly nitrated body (one containing at least three nitro groups), direct nitration of 4,4'-dichlorodiphenyl was effected. The dichlorodiphenyl was used to avoid any controversy as to the directing influence on the entering groups.

HISTORICAL

Diphenyl is being used as an indirect heating medium because of its high boiling point and low vapor pressure at elevated temperatures. The commercial preparation consists of passing benzene vapors at a temperature of approximately 750° C. through a porcelain tube (1). Recently, the Federal Phosphorus Corporation has developed a commercial method by which the price has been reduced from thirty-six dollars to thirty cents per pound in carload lots. This same company has also been successful in the commercial preparation of the chlorinated derivatives, both the mono- and di-chlorodiphenyl, which are starting points for other complicated derivatives, some of which are already showing promise as dye intermediates. Other chlorinated diphenyls, composed of mixtures of isomers of varying degrees of chlorination, have not only the usual possibilities of high boiling organic liquids, gums, and resins, but because of their stability, also have specific application in water-proofing, fire-proofing, and electrical uses. The

other primary derivatives of diphenyl are also showing promise of profitable commercial application. Thus the developing of a compound of seemingly limited possibilities has opened up a wide field of research (2).

THEORETICAL

As would be expected, the availability of diphenyl in large quantity at a rather low price has stimulated research, resulting in the production of many derivatives. The relation between diphenyl and benzene suggests the synthesis of new compounds in which diphenyl is substituted for the single benzene ring. Inasmuch as there are many varieties of benzene compounds, the possibilities would seem unlimited. Similarly the substitution of diphenyl for naphthalene in naphthalene derivatives should also afford interesting possibilities. At present these and analogous studies are being investigated in numerous research laboratories (2).

It has long been known that the chlorine substituent in chlorobenzene can be replaced by the hydroxyl group only by using sodium hydroxide at high temperature and pressure in the presence of a catalyst. This is a modern method for the commercial manufacture of phenol (3). Invariably the question arises as to why the simple halogen substitution

products of benzene show a marked contrast to the alkyl halides in that they do not hydrolyze under ordinary laboratory conditions, nor do they react with ammonia, potassium cyanide, and other compounds as readily as do the alkyl halides (4).

The stability of halogen substitution products of benzene toward hydrolysis and other double decomposition reactions seems to be closely associated with the unsaturation of the group attached to the halogen. In this respect, chlorobenzene resembles vinyl chloride

while dichlorobenzene, which is also non reactive, resembles ethene dichloride.

Although the ordinary double bonds as postulated by the Kekule formula probably do not exist in the phenyl radical, there is some degree of unsaturation. Should the conception of partial valence be applied to vinyl chloride, the structural formula would be written thus.

The residual valence represented by the dotted

lines is not actually utilized in the double bond. Perhaps some of this valence energy, which is not used in the double bond, is not residual but is used up in holding the chlorine atom more tightly than it would otherwise be held. This would furnish an explanation for the similar inactivity of the phenyl halides since the carbon atoms holding the halogens have, according to the partial valence structure (Baeyer formula), residual valence. Even though this explanation may not be true, it emphasizes the fact that whenever an atom or group is attached to the phenyl radical, it is held more tightly than when attached to an alkyl group. Of course this statement does not hold true in the substituted phenyl groups (5).

On the removal of a hydrogen halide from an alkyl halide, the hydrogen comes from the atom adjacent to the atom losing the halogen, thus constituting a typical olefinic loading. This property is common to the following compounds; vinyl chloride,

1,2- dichloroethene,

chlorobenzene,

and dichlorobenzene,

(assuming the olefinic structure for benzene) and that all are comparatively alike in resisting hydrolytic double decomposition. Hence, the stability in these cases is a function of the structure and not unique to chlorobenzene (6).

If in addition to halogen there are other groups substituted on the phenyl radical, as a nitro and a chlorine, a nitro and two chlorine, or several negative groups, one or more of which is nitro, they affect one another, and often other substituents not of the "negative" family. This reactivity is shown in the form of a considerable increase in the ease of double decomposition with these negative groups, hydrolytic and analogous reactions, whereas the nucleus itself, holding these substituents, remains stable to hydrolytic and oxidative agents. The position of the groups in relation to one another must be considered, but there is no general rule by which the outcome of such a reaction may be predicted. There is likewise a definite and pronounced contrast

between the lack of reactivity of a single "negative" substituent on a phenyl radical and the reactivity when several are present, particularly the nitrochloro- combinations. The combinations showing the greatest reactivity are those having the nitro group situated ortho- or para- to a chlorine or two nitro groups ortho- and para-. For example: If 2,4-dinitrochlorobenzene is heated at atmospheric pressure with a dilute alkali solution, 2,4-dinitrophenol is formed (7).

This is an essential step in the modern commercial preparation of picric acid (8). Thus the halogen becomes as mobile as in an ordinary aliphatic halogen compound for it is under the influence of both an ortho- and a para- nitro group.

In attempting to prove this generalization of the motility of halogen under the influence of ortho- and para- nitro groups,

These results indicate that when several "negative" groups are attached to the radical, motility is particularly noticeable in those groups that are not in position to one another that they would have if the normal orientation had taken place. As a rule the normal orientation may be considered to be that which would take place if the strongest negative (generally nitro) group were the cause of the directive effect.

In the previously discussed examples, it should be observed that the groups ortho- and para- to the nitro are those easily displaced, while those in the meta- position are not. When there are two or more "substituents" out

of position on the nucleus, either nitro or halogens, there is difficulty in predicting which group will become mobile. This behavior may be explained on the basis of the "negative" substituents absorbing more than their share of valence, thus depriving the chlorine of some of the force holding it to an unsubstituted benzene ring.

Nitration

Considerable difficulty was met with in introducing more than two nitro groups into 4,4'-dichlorodiphenyl by direct nitration, although in the preparation of 4,4'-dichloro-3,3'-dinitrodiphenyl, H.H. Hodgson and F.C. Gorowara (10) state that nitration must be conducted rapidly to prevent tetranitration. Analysis of an accidentally over nitrated body showed 13.3% nitrogen, but these investigators made no further attempt to verify their results, nor to purify the compound. W. Borsche and B.G.B. Sholten (11), using various conditions, found the nitration of 4,4'-dichlorodiphenyl to yield only the 4,4'-dichloro-3,3'-dinitro-

diphenyl. They were successful however, in producing 5,5'-dichloro-2,4,2'4'-tetranitrodiphenyl by directly nitrating 5,5'-dichlorodiphenyl. This peculiarity would suggest that steric hinderance might govern the ease or difficulty of entering groups. Perhaps this is true, for Kaufler has suggested and partially proven that the accepted formula for diphenyl

(where both benzene rings are in the same plane) does not hold true in all cases, especially benzidine (12). He has proposed the following formula,

with the corresponding positions of the two nuclei close together, thus suggesting a solution for the difficulty of nitration in the 4,4'-dichlorodiphenyl.

Another phase may be considered if the

only when no strain exists between them. The position and nature of the substituent groups should influence the motion of the two rings. Some groups such as the amino cause the rings to approach one another closely, as shown by the Kaufler structure I and III, while many other groups are not at all operative in influencing the rings to approach each other, consequently resulting in none of the reactions which would take place if the substituted groups were adjacent (13).

Since 4,4'-dichlorodiphenyl is commercially prepared by the direct chlorination of benzene, there is reason to believe that the ordinary rules of orientation would not hold if the phenyl radical were as negative as a nitro group, for if it were, the chlorine should be directed to the meta, or 3, or 5 positions. Moreover the counter-action, if any, of the chlorine substituents should also be taken into consideration. On the other if normal orientation took place, and if the phenyl radical were negative, four nitro groups should be easier to introduce into 4,4'-di-

chlorodiphenyl than its isomer, 5,5'-dichloro-diphenyl, where two meta positions are occupied.

EXPERIMENTAL

PRELIMINARY HYDROLYSIS

EXPERIMENTS

SODIUM HYDROXIDE AND 2-CHLORODIPHENYL.

A mixture of 4.71 grams (0.025 mol) of 2-Chlorodiphenyl, and 2 grams (0.05 mol) of sodium hydroxide was allowed to reflux in a 250 cc. r.b. flask at a temperature of 255-265°, for 12 hours. After 10 hours, the mass began to turn yellow, and finally became dark brown. On cooling, water was added to dissolve out the excess alkali. This solution was shaken with ether, and the two layers separated. The ether layer contained all the unchanged chlorodiphenyl, together with some resin, while the aqueous layer, on acidifying with hydrochloric acid, yielded a white precipitate. When dried, it was found to be an inorganic powder, as shown by the ignition test. No attempt was made to identify it, for it was probably an inorganic complex silica salt formed by the action of the caustic upon the glass, since the flask was well etched.

The filtrate was steam distilled without results.

SODIUM HYDROXIDE AND 4-CHLORODIPHENYL.

With but a few modifications, the preceding reaction was repeated, using the 4-chlorodiphenyl. The temperature was maintained between 260-285° for six hours. The substance retained by the filter was only slightly soluble in ligroin and still less soluble in ether. On crystallization from ligroin, a yellow to dark brown residue formed, which after purifying with benzene melted at 90-95°.

SODIUM HYDROXIDE AND A MIXTURE OF 4-CHLORO-4'-NITRODIPHENYL AND 4-CHLORO-2'-NITRODIPHENYL.

These two compounds can be separated by fractional distillation, but this is difficult. Attempts were made to separate them by fractional crystallization, but the results were not encouraging. The literature gives a method for the preparation of 4-chloro-4'-nitrodiphenyl (14), but no mention of the 4-chloro-

2-nitrodiphenyl could be found.

Using a mixture of the two isomers, 2.25 grams (0.01 mol), together with 1 gram (0.025 mol) of sodium hydroxide in a 50% solution, and allowing them to reflux on a water bath for 16 hours, the usual resinification resulted. The reaction products were washed out with hot water, and filtered, but no separation into a definite compound could be effected. On crystallization from benzene, there remained an amorphous dark brown substance, probably a mixture of the nitro compound, and some which had been decomposed.

SODIUM HYDROXIDE AND 4,4'-DICHLORO-X,X'-DINITRODIPHENYL.

While there is conflicting evidence as to the exact positions of the nitro groups in the dinitrated 4,4'-dichlorodiphenyl and also their melting points, the 4,4'-dichloro-X,X'-dinitrodiphenyl used (15), had the same melting point as the 4,4'-dichloro-2,2'-dinitrodiphenyl (16). Some investigators

contend that the 4,4'-dichloro-2,2'-dinitrodiphenyl melts at 136° , while others have found it to melt at 140° (17). The compounds made in the laboratory (table II, p.39) containing from 11.03-11.19% nitrogen, had melting points ranging from $143-147^{\circ}$.

A mixture of 3.129 grams (0.01 mol) of 4,4'-dichloro-X,X'-dinitrodiphenyl, and 1 gram (0.025 mol) of sodium hydroxide, was refluxed on a water bath for 15 hours. The whole mass soon became dark brown, due probably, to the decomposition of the nitro compound into complex resins. Some had become water soluble, but most of the nitro compound remained unchanged.

In a second run, 3.13 grams (0.01 mol) of 4,4'-dichloro-X,X'-dinitrodiphenyl, and 2 grams (0.05 mol) of sodium hydroxide in a 50% solution, were allowed to reflux on an oil bath for 20 hours. During the first 8 hours, the temperature was kept between $140-150^{\circ}$, and thereafter between $180-200^{\circ}$. Hot water was used to extract the reaction product by decantation, leaving the un-

changed material behind. The filtrate was shaken with ether, and the two layers separated. The ether layer was found to contain nothing. The dark brown water solution, upon acidification with hydrochloric acid, precipitated a dark brown substance, which was removed by filtration, leaving a golden yellow filtrate. The precipitate would neither burn nor melt. The filtrate was steam distilled without success, but on the sides of the flask there remained a white substance, probably an inorganic silica compound, and a plastic dark brown one on the bottom.

FINAL HYDROLYSIS

EXPERIMENTS

The preceeding methods furnished a foundation upon which to build the actual experimental work. It served to prove that too high a temperature does not aid in the hydrolysis, but on the other hand merely produces a greater quantity of resinous material, which is always to be avoided, because of the great difficulty experienced in purification (3). Hydrolysis was continued, but the method was somewhat varied in that no attempt was made to separately identify the remaining substances, since the preliminary experiments showed the futility of this. Instead, the solution from the reaction was titrated by the Volhard method (18), for any chlorine which might have been freed and united with the sodium of the sodium hydroxide (3). Blank runs were made on the materials used in order to calculate the amount of free chlorine contained in them.

SODIUM HYDROXIDE AND 4-CHLORODIPHENYL.

The reaction was carried out by refluxing, with continuous stirring, 2.3 grams (0.0122 mol) of 4-chlorodiphenyl, 3.91 grams (0.098 mol) of sodium hydroxide in a 30% solution, and 1 gram of copper shavings (19), at a temperature of 110-120°, for 10 hours. No change seemed to take place. The solution was filtered, acidified with chlorine free nitric acid, made up to 500 cc. with distilled water and titrated for chlorine.

Calcd: Cl, 18.83%; Found: Cl, .00% (Volhard)

SODIUM HYDROXIDE AND 4,4'-DICHLORO-X,X'-DINITRODIPHENYL.

Using 3.13 grams (0.01 mol) of 4,4'-dichloro-X,X'-Dinitrodiphenyl, 3.98 grams (0.1 mol) of sodium hydroxide in a 30% solution, and 1 gram of copper shavings, the reaction was carried out in the same manner as the one above. The nitro compound soon began to decompose, as shown by the dark brown color of the solution, and after $3\frac{1}{2}$ hours, the entire mass became viscous. On cooling, 100 cc. of water was added, and the mixture refluxed in order to

dissolve out all of the sodium chloride which might be mechanically enclosed. The solution was filtered, removing the copper and all unchanged dichlorodinitrodiphenyl, and then acidified with nitric acid, whereupon a dark brown precipitate was formed. This precipitate failed to ignite or melt. The filtrate, which was a golden yellow was made up to 500 cc., and titrated for chlorine.

Calcd: Cl, 22.68%; Found: Cl, .00% (Volhard).

Inasmuch as no positive results had been obtained on the foregoing hydrolyses, it was now decided to determine the motility of the chlorine in a higher nitrated body.

SODIUM HYDROXIDE AND AN ISOMERIC MIXTURE OF 4,4'-DICHLOROTRINITRODIPHENYL.

The compound used in this reaction had been prepared in the laboratory (table II, p. 39, reaction I). It was probably a mixture of isomers of 4,4'-dichlorotrinitrodiphenyl, for it had no definite structure, being of a resinous nature, and was found to contain 11.35% nitrogen.

A mixture of 1.016 grams (0.003 mol) of the nitrated product, 3.46 grams (0.087 mol) of sodium hydroxide in a 30% solution, and 1 gram of copper shavings was allowed to reflux at a temperature of 50-60°. The solution soon turned black and on filtering, the nitrated product was found to be unaffected. The filtrate was acidified with nitric acid, filtered, to remove the dark brown precipitate formed, and the solution made up to 500 cc., to be titrated for chlorine.

Calcd: Cl, 19.83%; Found: Cl, .00% (Volhard).

Evidently the time of the reaction had been insufficient to bring about double decomposition, so the experiment was repeated, using 1.0147 grams (0.0028 mol) of the nitrated product, 7.11 grams (0.178 mol) of sodium hydroxide in a 30% solution, and 1 gram of copper shavings. A temperature of 90-100° was maintained for 10 hours. Then 100 cc. of water was added, heat applied, and the whole well agitated. The solution was then filtered, acidified with nitric acid, precipitating a dark brown substance which was removed by filtering. This resinous material burned when

held in an open flame. The filtrate was made up to 500 cc. and titrated for chlorine.

Calcd: Cl, 19.83%; Found: Cl, 10.66% (Volhard).

In still another run, 1.003 grams (0.0028 mol) of the same nitro compound, 3.2 grams (0.08 mol) of sodium hydroxide in a 50% solution, and 1 gram of copper shavings were refluxed, for 10 hours, at a temperature of 110-120°. The remainder of the procedure was identical with that of the above experiment, the usual precipitation of the dark resin, in an acid solution, taking place.

Calcd: Cl, 19.83%; Found: Cl, 13.03% (Volhard).

Sodium Hydroxide and 4,4'-DICHLOROTRINITRO-DIPHENYL.

The material used in the following experiment had been prepared in the laboratory. It melted at 145-147° (table II, p. 39, reaction II), and contained 11.05% nitrogen.

A mixture composed of 1 gram (0.0028 mol) of 4,4'-dichlorotrinitrodiphenyl, 3.83 grams (0.096 mol) of sodium hydroxide in a 30% solution, and 1 gram of copper shavings,

was allowed to reflux at a temperature of 110-120°, for 10 hours. The solution soon began to decompose. On cooling, 100 cc. of water was added, and thoroughly agitated to dissolve out all sodium chloride present. The filtered material was acidified with nitric acid, precipitating the usual black tarry substance. After its removal, the filtrate was made up to 500 cc., and titrated for chlorine.

Calcd: Cl, 19.83%; Found: Cl, 10.58% (Volhard).

In a second run, 1 gram (0.0028 mol) of 4,4'-dichlorotrinitrodiphenyl (table II, p. 39, M.P. 144-147°, reaction III), 3.86 grams (0.0965 mol) of sodium hydroxide in a 5% solution, were refluxed at a temperature of 110-120°, for 10 hours. After the first two hours of heating, the solution gradually darkened, until it finally became dark brown. The solution was then filtered and acidified with nitric acid, resulting in the usual precipitation. On drying, this tarry matter became hard, and on ignition, burned with a sputtering flame, similar to that of the untreated nitro compound. There is reason to

believe that it was the hydroxy or dihydroxy-trinitrodiphenyl, since sodium phenolate is converted into phenol by means of an acid (8). The golden yellow filtrate was titrated for chlorine.

Calcd: Cl, 19.83%; Found: Cl, 2.89% (Volhard).

From the results of the preceeding experiment, the absence of the copper catalyst would appear to be responsible for the low percentage of hydrolysis, more so than the weaker alkali used. Copper acts as a catalyst in the removal of halogens from benzene halides. It is now being used in this capacity in a commercial process for the manufacture of phenol (3).

In a third run, 1 gram (0.0028 mol) of 4,4'-dichlorotrinitrodiphenyl (table II, p. 39, M.P. 144-147°, reaction III), 2.12 grams (0.053 mol) of sodium hydroxide in a 5% solution, and 1 gram of electrolytic copper were treated in the same manner as in the above experiment.

Calcd: Cl, 19.83%; Found: Cl, 7.90% (Volhard).

I

HYDROLYSIS TABLE

Diphenyl Derivative	Conc. NaOH	Cata- lyst	Calcd. % Cl	Found % Cl
1. 4-chloro-	30%	Cu	18.83	.00
2. 4,4'-chloro- X,X'-nitro-	30%	Cu	22.68	.00
3. Iso.mix. of 4,4'- dichlorotrinitro-	30%	Cu	19.83	.00
4. " " " "	30%	Cu	19.83	10.66
5. " " " "	50%	Cu	19.83	13.03
6. 4,4'-dichloro- trinitro-	30%	Cu	19.83	10.58
7. " " "	5%	None	19.83	2.89
8. " " "	5%	Cu	19.83	7.90

NITRATION EXPERIMENTS

A. Preliminary.

A mixture of 10 grams (0.0449 mol) of 4,4'-dichlorodiphenyl and 20 cc. of concentrated sulphuric acid was refluxed on a sand bath for two hours at a temperature of 150-175°. On cooling, 40 cc. of concentrated sulphuric acid were added and the mass agitated. Then a mixture of 25 cc. of red fuming nitric acid (sp.gr. 1.6) and 25 cc. of concentrated sulphuric acid was introduced while the flask was immersed in an ice bath. The acid mixture was added drop by drop in order to avoid too violent a reaction. After allowing to stand one-hour at room temperature, it was heated on a water bath for $2\frac{1}{2}$ hours. The materials were constantly stirred during the entire time of the reaction. The flask was then immersed in an ice bath while cold water was added with continuous stirring. The solution began to decompose, turning dark green, whereupon a large lump of nitrated

material settled to the bottom. On purification, first by crystallization from butyl alcohol and finally from ethyl alcohol, a very small quantity of a canary yellow powder was obtained, melting at 160-161.5°. The remaining reddish-brown resinous substance could not be separated into its constituents by fractional crystallization.

In a second run, nitration was directly carried out, instead of first sulphonating as in the preceeding experiment. To the acid mixture consisting, of 50 cc. of red fuming nitric acid and 200 cc. of concentrated sulphuric acid, which was placed in a 500 cc. flask immersed in an ice bath, were slowly added 10 grams (0.0449 mol) of powdered 4,4'-dichlorodiphenyl. Then the flask was heated on a water bath for three hours with occasional shaking. The dark yellow layer which formed on top of the mixture became semisolid when the flask was cooled. It was removed by filtering the solution through glass wool. The spent acid was then slowly added to ice water, keeping the temperature below 10°, for too

high a temperature caused the nitrated compound to decompose. The white plastic material which precipitated out in the ice water, was filtered, thoroughly washed to remove all traces of acid and dried. It was then purified by crystallization from hot ethyl alcohol, the impurities composed of resinous materials being very soluble, while the principal product was only slightly soluble in this solvent. The pure product melted at 160-161.5°.

The impure substance became hard and lighter in color when washed with hot water. It was steam distilled without result, but a violent explosion occurred when the flask ran dry.

B. Final.

Further nitration was continued since the preliminary experiments yielded a compound not listed in the literature. See table II, p. 39.

A mixture of 410 grams of red fuming nitric acid was placed in a 2 liter flask provided with a thermometer and a mechanical mixing device, and cooled to -5°. While

stirring, 50 grams (0.224 mol) of finely powdered 4,4'-dichlorodiphenyl was slowly added, keeping the temperature below 10° . As soon as the addition was finished, 1425 grams of 30% fuming sulphuric acid were added with constant stirring. Then the flask was heated on a water bath for $2\frac{1}{2}$ hours. On cooling the mixture was filtered through glass wool, as before, removing the yellow plastic insoluble material, most of which had finally separated out as a resinous mass. The spent acid was slowly poured over cracked ice (20), precipitating the white plastic substance previously noted. This material, when filtered out, repeatedly washed, and dried, melted at $52-58^{\circ}$. When crystallized several times from hot glacial acetic acid, it melted at $144-145^{\circ}$.

Yield: 12 grams (15.00%); nitrogen: 11.03%.

The acid mixture insoluble plastic material was washed with cold water and then with cold glacial acetic acid, the acid extracting the resinous material, leaving a light canary yellow powder which was slightly soluble in the cold solvent. On crystallization from

the hot acid, the melting point was increased to 158-159°.

Yield: 5 grams (?%); nitrogen: 12.83%.

The material soluble in cold acetic acid, on continuous washing with hot water became hard, but still remained amorphous. It was ground up and dried on a porous plate, but on standing it united into a solid mass, melting at 52-58°.

Yield: 5 grams (6.24%); nitrogen: 11.35%.

In a second run, 600 grams of 30% fuming sulphuric acid (solid) and 453 grams of red fuming nitric acid were introduced into a 2 liter flask and cooled to 0°. Then while stirring, 100 grams (0.449 mol) of powdered 4,4'-dichlorodiphenyl were added, the temperature being kept below 5°. When the addition was completed, the flask was heated on a water bath for three hours. On cooling an insoluble material remained on top of the spent acids. It was removed by pouring the reaction mass into a separatory funnel, separating the two layers, and removing the last traces by filtering the acid solution through glass wool. The liquid was then slowly poured over cracked ice, whereupon a white plastic

precipitate came out, which was filtered and washed. It was purified by repeated crystallization from hot glacial acetic acid. When all the impurities had been removed, it was washed with water, to remove the excess acid. After it was dried, and preserved on a porous plate over soda-lime in a vacuum desicator (21), it melted at 164-165°.

Yield: 1 gram (0.62%); nitrogen: 11.69%.

The material insoluble in the spent acids was poured into cold water, causing it to solidify. The water was then heated to boiling, decanted, more water added, and the process repeated till no more free acid remained in the compound. The product was slightly soluble in hot water. It was then recrystallized several times from hot glacial acetic acid, thus removing the resin, which was very soluble in cold acid, while the pure product was only slightly so. The pure material, a light yellow powder, was washed with water, dried, and preserved on a porous plate over soda-lime in a vacuum desicator. It melted at 145-147°, and a mixed melting point with 4,4'-dichloro-X,X'-dinitrodiphenyl was 114-120°.

Yield: 38 grams (23.62%); nitrogen: 11.05%.

The resinous material extracted from the above compound with acetic acid was concentrated, washed with water, redissolved in 100 cc. of acetone, and filtered. The acetone solution was diluted with water, precipitating the resin, which became hard. After it was ground and dried on a porous plate as before, it melted at 70-80°.

Yield: 58 grams (?%); nitrogen: 10.21%.

In a third run, 453 grams of red fuming nitric acid were poured into a 2 liter flask and 100 grams (0.449 mol) of powdered 4,4'-dichlorodiphenyl were slowly added, while the temperature was kept below 5°. When 600 grams of 30% fuming sulphuric acid had been added, the temperature was allowed to rise. The flask was heated on a water bath for three hours. The spent acid was then separated from the undissolved materials as before. The material precipitating from the acid solution, on purification by recrystallizing from hot glacial acetic acid, melted at 164-165°.

Yield: 3 grams (1.87%); nitrogen: 11.64%.

The insoluble material was purified in

the manner indicated in the preceeding experiment.

Yield: 58 grams (36.14%); nitrogen 11.19%.

The resinous acetic acid soluble material melted at 55-65°.

Yield: 14 grams (?%); nitrogen: 10.46%.

In a fourth run, 450 grams of red fuming nitric acid and 600 grams of 30% fuming sulphuric acid (solid) were placed in to a 2 liter flask and cooled. While 100 grams (0.449 mol) of 4,4'-dichlorodiphenyl was slowly added, the temperature was held at 15-20°. The flask was then heated on a water bath for three hours. The two layers were then separated in the usual manner, and the substance precipitating from the acid solution was purified as before. It had a melting point of 164-165°.

Yield: 3 grams (1.87%); nitrogen: 11.66%.

The insoluble material was poured into cold water. The temperature was slowly raised to boiling, causing the compound to soften, then the water decanted. This process was repeated until all free acids had been removed. The product was then purified as in the preceeding experiments,

separating into the usual light yellow powder, melting at 145-147°, and an amorphous resin. Yield: 47 grams (29.28%); nitrogen: 11.09%.

The acetic acid containing the resin extracted from above, was evaporated down, separating out much light yellow powder. Water was then poured into the solution, precipitating the nitrated compound. The acid was then removed by boiling in water and decanting. After it was ground and dried in the usual way, it melted at 55-60°.

Yield: 18 grams (?%); nitrogen: 10.59%.

In a fifth run, 1104 grams of 20-30% fuming sulphuric acid and 1200 grams of red fuming nitric acid were poured into a 2 liter flask. Keeping the temperature at 50-60°, 100 grams (0.449 mol) of powdered 4,4'-dichlorodiphenyl was slowly added. Then the reaction was carried out as in the above experiments. The precipitate from the spent acids melted at 164-165°.

Yield: 8 grams (4.98%); nitrogen: 11.71%.

The light yellow powder from the insoluble layer melted at 143-147°.

Yield: 35 grams (21.81%); nitrogen: 11.07%.

The resinous acetic acid material, after

washing with hot water and drying was taken up with ether. The ether dissolved out a soft plastic substance which hardened after several days. It melted at $90-106^{\circ}$.

Yield: 8 grams (?%); nitrogen: 10.82%.

Nitrogen determinations on the above compounds were made by the modified Kjeldahl-Gunning method (22).

Approximately .5 to 1 gram of nitro compound was placed in a Kjeldahl flask. To this were added 30 cc. of concentrated sulphuric acid and 1 gram of salicylic acid. Then 5 grams of sodium thiosulphate were added with shaking, after which 1 gram of copper sulphate and 10 grams of potassium sulphate were added. The flask was heated until the solution became clear.

II

NITRATION TABLE

Re- action	Product	Wt. Gm.	M.P.	Percent Yield	Percent Nitrogen
I	Powder	5	158-159	-----	12.83
	"	12	144-145	15.00	11.03
	Resin	5	52-58	6.24	11.35
II	Powder	1	164-165	.62	11.69
	"	38	145-147	23.62	11.05
	Resin	58	70-80	-----	10.21
III	Powder	3	164-165	1.87	11.64
	"	58	144-147	36.14	11.19
	Resin	14	55-65	-----	10.46
IV	Powder	3	164-165	1.87	11.66
	"	47	145-147	29.28	11.09
	Resin	18	55-60	-----	10.59
V	Powder	8	164-165	4.98	11.71
	"	35	143-147	21.81	11.07
	Resin	8	90-106	-----	10.82

RESULTS AND CONCLUSIONS

RESULTS AND CONCLUSIONS

In summing up, it may be said that hydrolysis of the chlorine atoms cannot be accomplished when there are only two evenly distributed negative groups (one in each ring) in a substituted diphenyl. From the results obtained (see table I, p. 28), the conclusion was reached that the phenyl radical is not as negative as a nitro group.

The degree of hydrolysis taking place in substituted chlorinated diphenyl compounds seems to depend on the time and temperature of the reaction and the use of a catalyst, as in the case of the benzene halides. Too high a temperature decomposes some of the compound into resins. When hydrolysis took place, the percentage of hydrolyzed chlorine was always less than the theoretical, due probably to insufficient time for the reaction to go to completion, and also to the partial decomposition of the compound into resins.

Since analysis of the compounds prepared in the laboratory showed a nitrogen content of 11.03-11.71%, as compared with the theoretical

11.73%, there is reason to believe that there were three nitro groups present.

The partial hydrolysis of these compounds would also furnish further evidence of the presence of more than two nitro groups, for no hydrolysis took place with the dichlorodinitrodiphenyl.

The light yellow compounds melting at 143-147° and 164-165° (table II, p. 39) were probably isomers of 4,4'-dichlorotrinitrodiphenyl. A mixture of the compound melting at 143-147° and the 4,4'-dichloro-X,X'-dinitrodiphenyl lowered the melting point to 114-120°, thus indicating that the two compounds were different.

The amorphous compound, without a definite melting point and having a nitrogen content of 10.21-10.82%, was perhaps a mixture of a dinitro- and a trinitro- derivative of the substituted diphenyl

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The author, Adolph Rebernak, was born in Louisville, Kentucky, August 16, 1907. His high school education was received at St. Xavier's High School, Louisville, Kentucky. He received his under graduate education at the University of Louisville, from which he was graduated in June 1930. He did his graduate work at the University of Louisville from September 1930 to June 1931.