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# Preparation of 1-parachlorophenyl- 4-phenylbutadiene and its reaction with nitrogen dioxide

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STUDIES OF CONJUGATED SYSTEMS

THE PREPARATION OF 1-PARACHLOROPHENYL-  
4-PHENYLBUTADIENE AND ITS REACTION  
WITH NITROGEN DIOXIDE

A THESIS

SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR  
THE DEGREE OF MASTER OF SCIENCE

BY

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DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA

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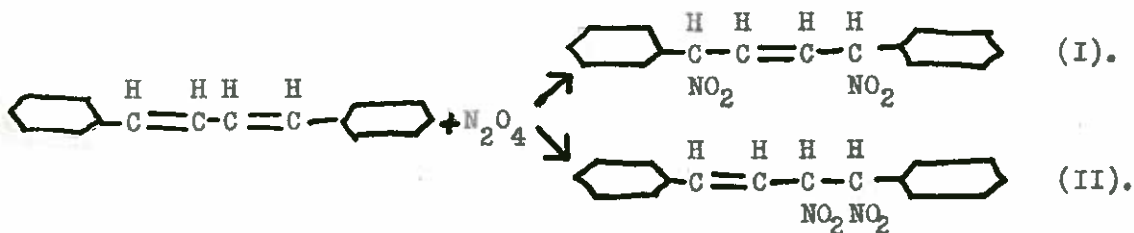
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## Theory

In 1907 Wisland<sup>1</sup> investigated the action of nitrogen dioxide on 1,4-diphenylbutadiene using a mixture of ether and benzene as solvents. A small yield of a crystalline solid was isolated together with a considerable portion of a greenish oil. Analysis of the solid indicated that one mole of nitrogen tetroxide had been added. Reduction of the addition compound with zinc and hydrochloric acid yielded a diamine, thus indicating that a dinitrocompound and not a nitrous ester had been formed.

Two dinitrocompounds of 1,4-diphenylbutadiene are theoretically possible depending on whether 1,4- or 1,2- addition takes place.



Compound I would yield on ozonization and subsequent hydrolysis two moles of  $\alpha$  nitrophenyl acetaldehyde and the corresponding  $\alpha$  nitrophenylacetic acid. A search of the literature indicates that  $\alpha$  nitrophenylacetaldehyde has not been prepared in a pure form. However, it is a well known fact that  $\alpha$  nitrophenylacetic acid decomposes readily giving carbon dioxide and phenylnitromethane when heated with water. Furthermore, phenylnitromethane when heated with water may be converted into benzaldehyde and nitrogen dioxide. Compound II would yield on ozonization and subsequent hydrolysis  $\alpha, \beta$ -dinitro- $\beta$ -phenylpropionaldehyde, benzaldehyde, and the corresponding acids.

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<sup>1</sup>Wisland and Stenzl, Ber., 40, 4825 (1907).

Wieland<sup>1</sup> treated the crystalline dinitrocompound thus isolated with ozone, using chloroform as the solvent. Hydrolysis of the ozonide gave phenylnitromethane, and small amounts of benzaldehyde and benzoic acid. He was unable to isolate any  $\alpha$ , $\beta$ -dinitro- $\beta$ -phenylpropionic acid from the oxidation products. These facts led Wieland to conclude that nitrogen dioxide added to 1,4-diphenylbutadiene in the 1,4-position.

The fact that Wieland did not isolate any  $\alpha$ , $\beta$ -dinitro- $\beta$ -phenylpropionic acid is of no consequence because under the conditions of ozonolysis the compound would have decomposed into  $\omega$  nitrostyrene, nitrous acid, and carbon dioxide. Even if it be granted that the solid crystalline compound was the 1,4-addition product (I), the fact remains that the greater portion of the reaction mixture was an oil which was not identified.

Any study of the action of the oxides of nitrogen on olefinic compounds must take into consideration the influence of solvents. This is apparent from the studies of Michael and Carlson<sup>2</sup> on the addition of the oxides of nitrogen to isobutylene.

These investigators added nitrogen dioxide to isobutylene in ether solution, in petroleum ether, and without a solvent. No appreciable amount of the ester, bis(isobutylene nitrosate),  $\left[ (\text{CH}_3)_2\text{C}(\text{ONO})\text{C}(\text{NO})\text{H}_2 \right]_2$ , could be isolated from the ether solution. In petroleum ether the nitric ester appeared in yields of 0-13.7%. The bis(nitric ester) was isolated from the reaction mixture formed in the absence of solvents in yields of 7-12%. The yields were altered only 4.6% by a change in temperature of 68°.

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<sup>1</sup>Wieland and Stenzl, Ber., 40, 4825-33 (1907).

<sup>2</sup>Michael and Carlson, J. Org. Chem., 5, 1 (1940).

The liquid product in the ether solution consisted of a mixture of a volatile blue oil and a nonvolatile green oil. From the blue oil a small amount of bis(isobutylenepseudonitrosite),  $\left[ (\text{CH}_3)_2\text{C}(\text{NO}_2)\text{C}(\text{NO})\text{H}_2 \right]_2$ , was obtained. Catalytic reduction of the blue oil gave ammonia, isobutylamine, and B-hydroxyisobutylamine. Reduction of the green oil gave ammonia, isobutylamine, and a high boiling liquid, probably  $\text{C}_8\text{H}_{19}\text{N}$ .

Michael and his coworker concluded that the addition of nitrogen dioxide to olefinic hydrocarbons was influenced by the action of solvents.

As a result of our study of the above described work and because the addition of nitrogen dioxide to conjugated systems has received no serious attention by chemists since the classic work of Wieland, it seemed of interest to investigate the reaction of nitrogen dioxide with the cis and trans 1-p-chlorophenyl-4-phenylbutadiene. We realized at the beginning that this problem would present certain difficulties which we might not be able to overcome in the time allotted to us. So far as we have been able to ascertain, this is the only investigation that has been made on this compound. The trans compound had been prepared in this laboratory by Charles Proctor.<sup>1</sup> The cis 1-p-chlorophenyl-4-phenylbutadiene, however, is not known.

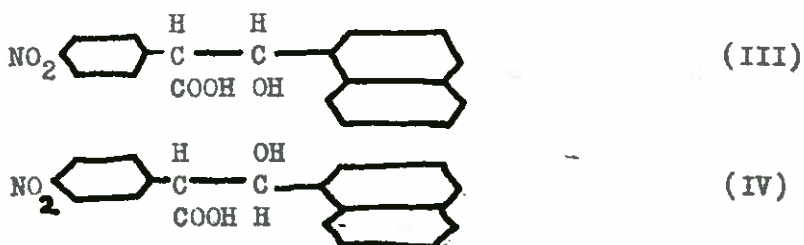
The main objectives of this investigation were (1) to synthesize 1-p-chlorophenyl-4-phenylbutadiene using a low temperature reaction in the hope that the cis-isomer might be isolated, (2) to study the addition of nitrogen dioxide to the two forms of 1-p-chlorophenyl-4-phenylbutadiene and to determine by oxidation the structures of the compounds formed.

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<sup>1</sup>Charles Proctor, "Conjugated Systems, The Preparation and Chlorination of 1-Parachlorophenyl-4-phenylbutadiene." Unpublished Master's thesis, Department of Chemistry, Atlanta University, 1932, p. 22.

The 1-p-chlorophenyl-4-phenylbutadiene was prepared by diazo coupling of parachloroaniline and cinnamylidene acrylic acid in acetone solution by the method used by Bergmann and Weinberg<sup>1</sup> in the preparation of 1-paranitrophenyl-4-phenylbutadiene. The melting point of a mixture of the purified product and 1-p-chlorophenyl-4-phenylbutadiene prepared by the method of Perkin was 161-162°. This fact indicated that the trans isomer of 1-p-chlorophenyl-4-phenylbutadiene (m.p. 163°) had been formed.

That the trans rather than the cis-isomer was formed can best be explained by a review of the work of Ruggli<sup>2</sup> and Taylor<sup>3</sup> who showed that the structure of these acrylic acids corresponds to the cis form of ethylene. Bergmann and Weinberg<sup>4</sup> believed that first the two trans and cis acids are formed, but that the former is more easily decarboxylated than the latter. The authors offer a second acceptable explanation by suggesting that the two stereoisomeric hydroxy acids,



are formed, usually in unequal amounts. The theory furnishes two possibilities for the elimination of the hydroxyl group, (1) by uniting with an adjacent hydrogen atom; (2) by reacting with the carboxyl group. It is highly probable that in compound III the hydroxyl group unites with the neighboring hydrogen because they are trans to each other. For the same reason, in

<sup>1</sup>Bergmann and Weinberg, *J. Org. Chem.*, **6**, 137 (1941).

<sup>2</sup>Ruggli and Staub, *Helv. Chim. Acta.*, **19**, 1288 (1936).

<sup>3</sup>Taylor and Hobson, *J. Chem. Soc.*, 181 (1936).

<sup>4</sup>Bergmann and Weinberg, *J. Org. Chem.*, **6**, 135 (1941).

compound (IV) lactonization with the carboxyl trans to the hydroxyl is the probable mechanism.

According to Bergmann and Weinberg<sup>1</sup> the diazo coupling between cinnamylideneacrylic acid and paranitroaniline gave exclusively ethylene compound,



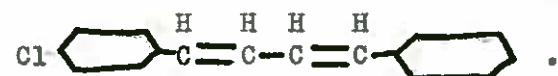
in 25% yields. No trace of the carboxylic acid,



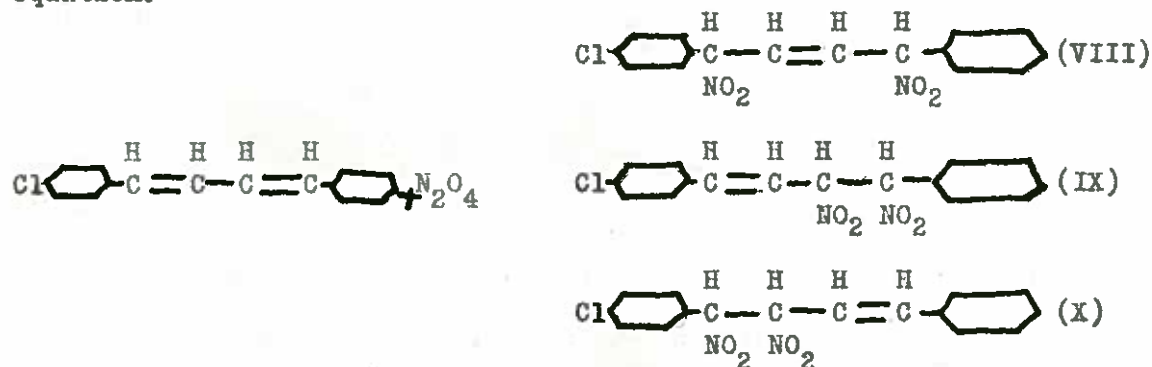
was found. on the basis of the foregoing theory, the diazo reaction between parachloroaniline and cinnamylideneacrylic acid would yield solely the lactone,



This lactone would split off carbon dioxide and form trans 1-parachloro-phenyl-4-phenylbutadiene,



In the addition of nitrogen dioxide to 1-p-chlorophenyl-4-phenylbutadiene three isomers are theoretically possible as shown in the following equation:



<sup>1</sup>Bergmann and Weinberg, *J. Org. Chem.*, **6**, 135 (1941).



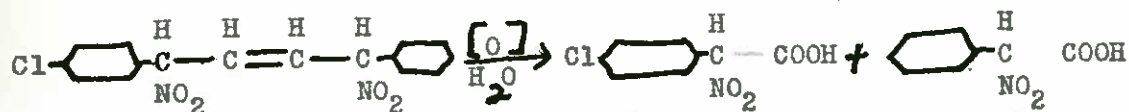
Several attempts were made to add nitrogen dioxide to 1-p-chlorophenyl-4-phenylbutadiene. The solvents used in the experiments were ether, petroleum ether, chloroform, and a mixture of ether and petroleum ether. Various methods were used in adding the nitrogen dioxide to the diene compound. Sometimes the colorless solid was dropped into the solution, at other times the yellow liquid was poured into the solvents, and once the brown gas was bubbled through the reaction mixture. The reactions took place at the temperature produced by an ether carbon dioxide snow bath.

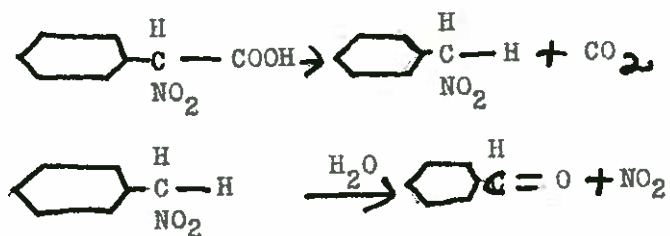
In all but one experiment, the products in each case were a small quantity of a white crystalline solid and a large amount of yellow oil. It was noticeable that in the experiment with chloroform as solvent, the 1-p-chlorophenyl-4-phenylbutadiene was practically insoluble and very little if any reaction took place. Best results were obtained by using a mixture of ether and petroleum ether as the solvent.

Extractions of the oils with ether and petroleum ether yielded very little of the solid addition product. Attempts at low temperature crystallization were unsuccessful. Portions of the oils were set aside for periods ranging from two weeks to six months, but only a few crystals were deposited. These, when purified, melted at 134°.

Analysis of the white crystalline solid indicated that two moles of nitrogen dioxide had been added. Neutral permanganate oxidation of the solid addition compound yielded parachlorobenzaldehyde, parachlorobenzoic acid, and a yellow oil.

These products can be accounted for by assuming that the following reactions took place:





### Experiments

The Preparation of Cinnamylidene Acrylic Acid.<sup>1</sup> --Ninety grams of malonic acid, 66.9 g. of pyridine, and 90 g. of cinnamic aldehyde were heated on a water bath under a reflux condenser for six hours. The reaction mixture was decomposed with ice cold dilute sulphuric acid solution. The filtered acid was recrystallized from dilute alcohol, m.p. 165°, yield 66 g.

The Diazo Coupling of P-Chloroaniline and Cinnamylidene Acrylic Acid.<sup>2</sup>  
 --Fifty grams of p-chloroaniline were suspended in 300 cc. of 12% hydrochloric acid, and diazotised at 0° with 27 g. of sodium nitrite in 60 cc. of water. The diazotised solution was added dropwise to 66 g. of cinnamylidene acrylic acid in 350 cc. of acetone. Cuprous chloride (16.5 g.) and 82.5 g. of sodium acetate in 75 cc. of water were added. The mixture was stirred for one hour at 15°. The reaction mixture was steam distilled, filtered, and extracted with benzene. 1-P-chlorophenyl-4-phenylbutadiene obtained after the removal of the benzene was recrystallized from a mixture of benzene and alcohol. The white crystalline product melted at 162-163°. A mixture of this compound and 1-p-chlorophenyl-4-phenylbutadiene prepared by the method of Perkin melted at 161-162°. The yield was 12.2 g.

The Addition of Nitrogen Dioxide to 1-P-Chlorophenyl-4-phenylbutadiene.

<sup>1</sup>Diels, Ber., 35, 2137 (1902).

<sup>2</sup>Bergmann and Weinberg, J. Org. Chem., 6, 134 (1941).

--Nitrogen dioxide<sup>1</sup> was prepared by heating dry lead nitrate, and passing the evolved gas into a graduated test tube immersed in a carbon dioxide snow bath. Nitrogen dioxide (2.5 g.) was added to a cold suspension of 5.97 g. of 1-p-chlorophenyl-4-phenylbutadiene dissolved in 10 cc. of petroleum ether, and sufficient diethyl ether to effect solution. The reaction mixture was shaken vigorously and set aside over night in an ice bath.

White crystals of the additive compound separated from the yellow oil. The solid compound was purified by recrystallization from a mixture of ether and petroleum ether. It melted at 134°. The yield was 2.14 g. Combustion of two samples gave results as follows:

Anal. Calcd. for  $C_{16}H_{13}N_2O_4Cl$ : N, 8.61. Found: N, 8.55;  
N, 8.46.

Permanganate Oxidation.<sup>2</sup>--Potassium permanganate solution was neutralized with  $MgSO_4$  in acetone. The solid dinitro compound (.3 g.) was dissolved in 10 cc. of acetone and the solution of permanganate was added dropwise with stirring until the color persisted. Manganese dioxide was precipitated. The reaction mixture was filtered and the solvent removed from the filtrate with a stream of air. The precipitate was treated with a solution containing just enough sodium bisulphate and sulphuric acid to bring it into solution, after which it was added to the main part of the filtrate. This filtrate was treated with a dilute solution of sodium carbonate and extracted with ether. The aqueous solution was acidified with dilute sulphuric acid and a crystalline solid which melted at 241° was precipitated. This was identified as p-chlorobenzoic acid by the amide derivative, m.p. 179-180°.

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<sup>1</sup>Michael and Carlson, J. Am. Chem. Soc., 59, 847 (1937).

<sup>2</sup>Farmer and Scott, J. Chem. Soc., 172 (1929).

The ether solution was evaporated and p-chlorobenzaldehyde was isolated. It was identified by the semicarbazone derivative, m.p. 231-232°.

Two oils were separated from the hydrolytic products by fractional distillation with steam; one, evidently phenylnitromethane formed by the decomposition of  $\alpha$  phenyl-  $\alpha$ -nitro acetic acid, boiled at 229-240°, and the other, probably benzaldehyde, boiled at 184° with decomposition at 190-200°. Because of the small yield and limited time no further work was done on these compounds. While not conclusive, the experimental evidence seems to indicate that the solid derivative was formed by the addition of nitrogen dioxide in the 1,4-position to 1-p-chlorophenyl-4-phenylbutadiene.

#### Summary

1. A resume of the work on the action of nitrogen dioxide on olefinic hydrocarbons was given.
2. The trans 1-p-chlorophenyl-4-phenylbutadiene compound was prepared by the method of Bergmann and Weinberg.
3. The addition product of nitrogen dioxide and 1-parachlorophenyl-4-phenylbutadiene was isolated and oxidized.
4. Parachlorobenzoic and parachlorobenzaldehyde were separated from the hydrolyzed oxidation products.
5. The results were analogous to those obtained by Wieland in the addition of nitrogen tetroxide to 1,4-diphenylbutadiene.

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