[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES OF CONJUGATED SYSTEMS. I. THE CHLORINATION OF PHENYLBUTADIENE[1]

BY IRVING E. MUSKAT AND K. A. HUGGINS

RECEIVED MARCH 15, 1929 PUBLISHED AUGUST 7, 1929

According to Thiele's[2] theory concerning the affinity relations in conjugated systems addition should take place in the 1,4-position. Many exceptions were found to this theory which were explained by Thiele by means of special assumptions. However, the exceptions have increased and there has arisen sharp criticism toward this theory.[3] We cannot here consider the results of the manifold investigations, indicating in each case its bearing on the Thiele theory; nor can we discuss the many explanations offered by various workers in this field regarding the mode of addition in conjugated systems. This much may be said, however, that in general there are two main views: according to the one view, held by Thiele, the addition depends merely on the valence relations in the original compound, while according to the other, the Hinrichsen view, the addition depends not only on the nature of the original unsaturated compound in which the addition is taking place, but also on the electrochemical nature of the entering atoms or groups.[4]

While not any of the many theories suggested explain all of the addition reactions to conjugated systems, nevertheless, it appears that in a series of cases the Hinrichsen view is in better accord with the facts than any of the other theories. Recent work by K. v. Auwers[5] on the addition of hydrogen and bromine to sorbinic acid and related compounds, and still more recent work by Kuhn and Winterstein[6] on the addition of hydrogen and bromine to the diphenyl-poly-enes, clearly indicate the inadequacy of the Thiele theory and offer supporting evidence for the Hinrichsen views.

---

[1] Abstracted from a thesis by Mr. K. A. Huggins, presented to the Ogden Graduate School of Science of the University of Chicago in partial fulfilment of the requirements for the degree of Master of Science.

[2] Thiele, *Ann.*, **306**, 87 (1899).

[3] Michael, *J. prakt. Chem.*, **60**, 467 (1899); Hinrichsen, *Ann.*, **336**, 174 (1904); Vorländer, *Ber.*, **36**, 2339 (1903); Ingold, *J. Chem. Soc.*, **121**, 329, 1306 (1921); Kohler, *Am. Chem. J.*, **31**, 642 (1904); **33**, 153, 333 (1905); **36**, 529 (1907); Straus, *Ber.*, **42**, 2866 (1909); Erlenmeyer, Jr., *Ann.*, **316**, 43 (1901); and many others.

[4] We shall not discuss in this paper the more recent work of Ingold, Claisen, Prevost, Farmer and others, who have shown that addition products in which the addenda are in the 1,4-positions are not necessarily due to 1,4-addition, but rather to a condition of equilibria in three-carbon prototropic systems. We shall be more concerned with the final addition product than the mechanism by which it was formed.

[5] K. v. Auwers, *Ann.*, **434**, 140 (1923).

[6] Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 116, 123 (1928).

Because of the theoretical importance of the addition reactions of conjugated systems it was considered desirable to make a thorough investigation of such addition processes, particularly in simple conjugated systems. The present paper contains the results of an investigation on the chlorination of phenylbutadiene.

Phenylbutadiene was prepared according to the method of Carl von der Heide[7] by the condensation of cinnamic aldehyde with methyl magnesium bromide and the subsequent hydrolysis of the intermediate Grignard addition compound with 30% sulfuric acid. In order to become familiar with the technique and procedure involved in the use of an ozonizer as a tool in the study of such reactions, it was decided to repeat Straus'[8] work on the bromination of phenylbutadiene, in which he found that only 3,4-addition occurred. We confirmed his work in every particular.[9]

The chlorination of phenylbutadiene was then studied. It was found that phenylbutadiene readily absorbs two atoms of chlorine to form a dichloride which boils at 125° under 3 mm. pressure. The chlorination was carried out in various solvents and under different experimental conditions. Chloroform, ligroin, glacial acetic acid and carbon disulfide were used as solvents and the chlorination was carried out at temperatures varying from about −80 to about 150°. The same dichloride was obtained regardless of the experimental conditions. The only effect of the temperature of chlorination was in the amount of decomposition. The dichloride is fairly unstable and loses hydrogen chloride easily, so that at higher temperatures more decomposition takes place. However, in not one of the large number of experiments performed was a different dichloride obtained.

The structure of the dichloride was determined by ozonization. Three dichlorides are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place. On ozonizing the phenylbutadiene dichloride it was possible to obtain an 83% yield of benzaldehyde as calculated from its semicarbazone and the benzoic acid that was recovered. This proves beyond any doubt that chlorine adds to phenylbutadiene in the 3,4-positions. A number of ozonizations were made but in no case was it possible to obtain even the slightest indications for the presence of any of the aldehydes or acids to be expected from the oxidation of compounds resulting from the 1,2- or 1,4-addition of chlorine.

The phenylbutadiene dichloride can be further chlorinated to give a mixture of stereoisomeric tetrachlorophenylbutanes. The tetrachloride

---

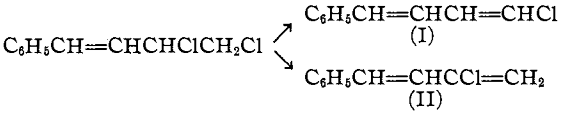
[7] Carl von der Heide, *Ber.*, **37**, 2101 (1904).

[8] Straus, *ibid.*, **42**, 2866 (1909).

[9] We worked up the ozonization product in a different manner. Straus obtained a 50–60% recovery of benzaldehyde, while we were able to recover 73% of the benzaldehyde.

can be completely reduced to phenylbutadiene or partially reduced with zinc to give again the same phenylbutadiene dichloride from which it was made. This shows that the chlorine is more easily removed from the 1,2-positions near the phenyl group, and again indicates the stability of the 3,4-dichloride.

Phenylbutadiene dichloride, when treated with aqueous potassium hydroxide at a temperature of 90° for several hours, loses a molecule of hydrogen chloride and is thus converted into phenylchlorobutadiene, with an almost theoretical yield. The same monochloride may be obtained by merely refluxing the phenylbutadiene dichloride for several hours, but this process entails a large loss due to polymerization. The phenylchlorobutadiene boils at 115.5° under 3.5 mm. pressure. It may be readily seen from the structure of the phenylbutadiene dichloride that hydrogen chloride may be eliminated in either of two ways, thus



$$C_6H_5CH{=}CHCHClCH_2Cl \begin{array}{l} \nearrow \; \underset{\text{(I)}}{C_6H_5CH{=}CHCH{=}CHCl} \\ \searrow \; \underset{\text{(II)}}{C_6H_5CH{=}CHCCl{=}CH_2} \end{array}$$

In order to determine the structure of the monochloride it was treated with a water suspension of silver oxide and warmed. On working up the reaction mixture γ-phenylcrotonic acid ($C_6H_5CH{=}CHCH_2COOH$) was isolated. This proves conclusively that the phenylchlorobutadiene has Structure I, $C_6H_5CH{=}CHCH{=}CHCl$. Since the chlorine atom is removed from the 3-position in preference to the 4-position, it indicates that the 3-chlorine atom is relatively electronegative as compared with the 4-chlorine atom. The significance that this bears on the electronic concept of valence in organic compounds will be discussed in a later paper.

The phenylchlorobutadiene easily absorbs a molecule of chlorine to give a trichloro derivative, boiling at 140° under 5 mm. pressure. Again, there are three trichlorides that may possibly be formed, depending on whether 1,2-, 1,4- or 3,4-addition takes place. The phenylchlorobutene dichloride was ozonized in the same way as the phenylbutadiene dichloride. On hydrolysis of the ozonide formed, it was possible to recover a 50% yield of benzaldehyde as benzoic acid. The isolation of benzaldehyde proves conclusively that 3,4-addition has taken place and, therefore, the structure of the trichloride must be $C_6H_5CH{=}CHCHClCHCl_2$.

The phenylchlorobutene dichloride easily absorbs another molecule of chlorine to give a pentachloride which boils at 162° under 5 mm. pressure. To judge from the constancy of the boiling point of the 1-phenyl-1,2,3,4,4′-pentachlorobutane, it does not consist of a mixture of stereoisomers as did the 1-phenyl-1,2,3,4-tetrachlorobutane previously described.

The experimental results recorded here lend support to the Hinrichsen view of addition to conjugated systems as contrasted to the Thiele view.

That is, the mode of addition to conjugated systems is not only a function of the conjugated compound itself, but also depends on the nature of the addendum. In general, hydrogen is added to the ends of the conjugated system, in the 1,4-positions, particularly so when the conjugation ends in oxygen $>\underset{\vdots}{C}{=}C{-}C{=}\underset{\vdots}{O}$. With other types of addition reagents, the halogens, halogen acids, etc., normal addition to the double bonds of the conjugated system is the rule, just as in the single ethylenic double bonds. More recent work by Ingold, Claisen, Prevost, Farmer and others seems to indicate that even in those cases where 1,4-addition is found, it is not due primarily to direct 1,4-addition but rather to a tautomerization of the 1,2-addition compounds. This will be discussed in a later paper.

Experimental Part

Phenylbutadiene Dibromide.—Phenylbutadiene was prepared according to the method of Carl von der Heide.[7] Phenylbutadiene dibromide was prepared according to the method reported by Straus.[8] The pure dibromide melted at 94°.

Phenylbutadiene dibromide (4.5 g.) was dissolved in chloroform and a current of ozonized oxygen was bubbled through the solution for several hours. An ozonizer similar to the one described by Harries[10] was used. The apparatus was arranged so that any desired ozone concentration, up to 20%, could be obtained. A 3–4% ozone concentration was used in these experiments. After the ozonization was completed the chloroform was removed by suction and the residual viscous ozonide was decomposed with water. To assure the complete decomposition of the ozonide, it was warmed on the water-bath for a short time. The mixture consisted of acids and aldehydes and was separated by extracting the alkaline solution several times with ether. The alkaline solution was then acidified and again extracted with ether. The ethereal solution was dried and the ether removed by vaporization. A solid (1.06 g.) remained which melted at 120°. It was crystallized once from water and melted at 122°, the melting point of benzoic acid. A mixture with pure benzoic acid also melted at 122°.

The ethereal solution containing the aldehydes was again washed with alkali and the ether removed by vaporization. The residue, an oil, was treated with an aqueous solution of semicarbazide hydrochloride containing enough sodium acetate to neutralize the hydrochloric acid in combination with the semicarbazide. A semicarbazone (0.51 g.) was precipitated after a short time. This was removed and dried. It melted at 209°. It was recrystallized several times from alcohol and melted at 214°, the melting point of the semicarbazone of benzaldehyde. When it was mixed with the synthesized product the melting point of the mixture was not lowered. This corresponds to a 73.2% yield of benzaldehyde, while Straus was able to obtain only a 50–60% yield.

Phenylbutadiene Dichloride.—To prepare phenylbutadiene dichloride a stream of dry chlorine was allowed to pass into the pure phenylbutadiene. Absorption took place readily and the reaction mixture became very hot. Hydrogen chloride was liberated as the chlorination proceeded and the reaction mixture assumed a reddish color. When the theoretical quantity of chlorine was absorbed, the reaction mixture was distilled under reduced pressure. A light yellow oil distilled over at 125° under 3 mm. pressure. It was analyzed for chlorine by the Carius method. The analysis of the compound proves that it is a dichloride.

---

[10] Houben-Weyl, "Die Methoden der Organischen Chemie," **1924**, Vol. III, p. 276.

Anal. Subs., 0.2322, 0.2596: AgCl, 0.3308, 0.3698. Calcd. for $C_{10}H_{10}Cl_2$: Cl, 35.28. Found: Cl, 35.25, 35.24.

The conditions under which phenylbutadiene was chlorinated were varied considerably. Various solvents such as chloroform, ligroin, carbon disulfide and glacial acetic acid were used, and the temperature was varied from about −80° (carbon dioxide snow and ether) to about 150°. However, in all cases only one dichloride was obtained. The use of a solvent decreased the amount of tetrachlorophenylbutane obtained, and lowering the temperature decreased considerably the extent of decomposition, but no other effect was observed. The phenylbutadiene dichloride distilled over completely at constant temperature under various pressures, which eliminates the possibility that it consists of a mixture of dichlorides having a constant boiling temperature. It could not be crystallized even in carbon dioxide snow and ether; it merely solidified to a glass.

The phenylbutadiene dichloride was subjected to ozonization and the ozonide thus formed was treated in a manner entirely analogous to that of the dibromide previously described. The acid and aldehyde portions were separated, the acid portion yielding benzoic acid, which was identified by the melting point of a mixture with known benzoic acid, while the benzaldehyde was removed as the semicarbazone, which was identified in a similar manner. From 5.5 g. of phenylbutadiene dichloride it was possible to isolate 2.01 g. of benzoic acid and 1.0 g. of semicarbazone of benzaldehyde. This corresponds to an 83% yield of benzaldehyde. In some cases the ozonide was treated with hydrogen peroxide, which oxidized all of the aldehydes to their corresponding acids. From 6 g. of the dichloride it was possible to isolate 2.5 g. of benzoic acid, which was identified by the melting point of a mixture with known benzoic acid. This corresponds to a 70% yield of benzaldehyde.

This proves conclusively that chlorine had added to phenylbutadiene in the 3,4-positions and not in the 1,2- or 1,4-positions. The structure of the dichloride must be $C_6H_5CH{=}CHCHClCH_2Cl$.

Tetrachlorophenylbutane.—Phenylbutadiene dichloride was dissolved in chloroform and a stream of chlorine gas was allowed to pass in until no more was absorbed. The chloroform was removed by vaporization and the residual reddish colored oil was distilled under reduced pressure. A clear, colorless oil began to distil over at 155° under 7 mm. pressure and the temperature rose gradually, without any abrupt change, to 166°. The distillate was redistilled at 7 mm. pressure and collected in three fractions; each fraction was analyzed for chlorine by the Carius method.

Anal. Fraction I (155–160°), subs., 0.2043: AgCl, 0.4333. Found: Cl, 52.46. Fraction II (160–164°), subs., 0.2637: AgCl, 0.5567. Found: Cl, 52.22. Fraction III (164–166°), subs., 0.2950: AgCl, 0.6203. Found: Cl, 52.02. Calcd. for $C_{10}H_{10}Cl_4$: Cl, 52.18.

It is quite obvious that the tetrachlorophenylbutane consists of a mixture of possibly three stereoisomers. No effort was made to separate them. The tetrachlorophenylbutane did not crystallize even when allowed to remain in a carbon dioxide snow and ether mixture for several hours.

The Reduction of Tetrachlorophenylbutane.—If tetrachlorophenylbutane is treated with powdered zinc at room temperature no reaction takes place. However, if the reaction flask is placed on the water-bath for a short time a vigorous reaction occurs. The product of the reaction depends on the quantity of zinc used.

Tetrachlorophenylbutane was treated with slightly more than two moles of zinc and the reaction mixture was warmed on the water-bath for several hours. The reaction mixture was then extracted with ether and the ethereal solution was dried over calcium chloride. The ether was removed by vaporization and the residual oil distilled under reduced pressure. It distilled at 86° under 11 mm. pressure, the boiling point of phenylbutadiene. That it was phenylbutadiene was further confirmed by the melting point of its tetrabromide, 146°. This shows that the tetrachloride was completely reduced.

The previous experiment was repeated and slightly less than half the amount of powdered zinc was used (one mole of zinc to one mole of tetrachloride). When all of the zinc had reacted the mixture was extracted with ether, the ethereal solution dried and the ether removed by vaporization. The residual oil was distilled under reduced pressure. It distilled sharply at 125° under 5 mm. pressure, the boiling point of 3,4-dichlorophenylbutane. It was ozonized and yielded benzoic acid as one of the oxidation products. This proves conclusively that the structure of the dichloride obtained by the partial reduction of the tetrachlorophenylbutane is identical with that of the dichloride obtained on chlorinating phenylbutadiene.

Phenylchlorobutadiene.—If phenylbutadiene dichloride is treated with an aqueous solution of potassium hydroxide and allowed to stand on the water-bath for several hours, one molecule of hydrogen chloride is eliminated, forming a monochloride. The monochloride was taken up in ether, thoroughly washed free from alkali, dried over calcium chloride, filtered, and the ether removed by vaporization. The residual oil was distilled under reduced pressure. It distilled almost completely at 115.5° under 3.5 mm. pressure. When very pure it crystallized in small, colorless plates, melting sharply at 53°. It was analyzed for chlorine by the Carius method. The analysis of the compound proves that it is a monochloride.

Anal. Subs., 0.0979, 0.1774: AgCl, 0.0849, 0.1536. Calcd. for $C_{10}H_9Cl$: Cl, 21.56. Found: Cl, 21.45, 21.42.

The same phenylchlorobutadiene may be obtained by simply refluxing the phenylbutadiene dichloride for several hours. However, there is a decided difference in the yield obtained by the two methods. The first method, that of warming the dichloride with aqueous alkali, gives an almost quantitative yield of the monochloride, while the second method, refluxing the dichloride, gives about a 60% yield of the monochloride. This is due to the fact that heating promotes the polymerization of the compound.

Phenylchlorobutadiene and water were introduced into a bomb tube, the tube was sealed, placed in a bomb furnace and gradually heated to 150–170°. It was allowed to remain at that temperature for several hours. On cooling the tube was opened and the contents removed. The water solution gave a decided halogen test with silver nitrate, which showed that the chlorine had been removed by hydrolysis. The degree of hydrolysis could be readily followed by the titration of the chloride ion in an aliquot sample of the water solution. The extent of hydrolysis was never more than 3 to 4% in the several experiments that were performed. The water solution gave a positive test for aldehydes with a fuchsin solution and therefore offers supporting evidence for Structure I, $C_6H_5CH{=}CHCH{=}CHCl$. Due to the slight hydrolysis, even at higher temperatures, it was not found possible to isolate the aldehyde.

In order to increase the extent of hydrolysis of the chloride, it was treated with slightly more than two moles of silver oxide suspended in water. No reaction was evident at ordinary temperature, but when the reaction mixture was warmed on the water-bath a reaction did occur and a silver mirror was deposited on the walls of the reaction vessel. This indicates that an aldehyde was formed due to the hydrolysis of the chloride, and that the silver oxide then oxidized the aldehyde to the corresponding acid, $C_6H_5CH{=}CHCH_2COOH$. The reaction mixture was acidified with nitric acid and extracted with ether. The ethereal solution was washed several times with alkali. The alkaline washings were acidified, extracted with ether, the ethereal solution was dried over anhydrous sodium sulfate and the ether was removed by evaporation. An oil remained which was taken up in carbon disulfide. On allowing the carbon disulfide to evaporate slowly, small crystals separated from the solution. These were removed and dried; they melted at 86°, the melting point of γ-phenylcrotonic acid, $C_6H_5CH{=}CHCH_2COOH$. This proves that the monochloride has Structure I, $C_6H_5CH{=}CHCH{=}CHCl$.

1-Phenyl-4-chloro-Δ'-butene-3,4-dichloride.—To prepare phenylchlorobutene dichloride a stream of dry chlorine was allowed to pass into pure phenylchlorobutadiene. Absorption took place readily and the mixture became very hot. The reaction mixture assumed a dark color during the chlorination but became colorless as soon as one mole of chlorine was absorbed. It was distilled under reduced pressure, distilling over at 140° under 5 mm. pressure. It was analyzed for chlorine by the Carius method. The analysis of the compound proves that it is a trichloride.

Anal. Subs., 0.2648, 0.2196: AgCl, 0.4838, 0.4008. Calcd. for $C_{10}H_{10}Cl_3$: Cl, 45.19. Found: Cl, 45.20, 45.19.

The phenylchlorobutene dichloride was subjected to ozonization and the ozonide thus formed was treated in a manner entirely analogous to that of the dichloride previously described. The acid and aldehyde portions were separated, the acid portion yielding benzoic acid, which was identified by the melting point of a mixture with known benzoic acid, while the aldehydes were removed as semicarbazones. The semicarbazones were separated by fractional crystallization into a low-melting semicarbazone (about 130°) and a high-melting semicarbazone (about 206°). However, these could not be purified enough for identification. In another experiment the ozonide was treated with hydrogen peroxide, which oxidized all of the aldehydes to their corresponding acids. From 1.04 g. of the trichloride it was possible to isolate 0.3 g. of benzoic acid, which was identified by the melting point of a mixture with known benzoic acid. This corresponds to a 50% yield of benzaldehyde.

Pentachlorophenylbutane.—Phenylbutadiene trichloride was further treated with an excess of chlorine gas until no more absorption took place. The chlorinated product was distilled under reduced pressure. A clear, colorless oil distilled over at 162° under 5 mm. pressure. It was analyzed for chlorine by the Carius method. The analysis of the compound proves that it is a pentachloride.

Anal. Subs., 0.1941, 0.1032: AgCl, 0.4541, 0.2399. Calcd. for $C_{10}H_9Cl_5$: Cl, 57.88. Found: Cl, 57.87, 57.51.

Summary

1. By chlorination of phenylbutadiene, a dichloride is formed whose structure was proved by ozonization to be a 3,4-derivative, rather than a 1,4-derivative as required by Thiele's theory of addition to conjugated systems.

2. The 3,4-dichlorophenylbutene was further chlorinated to give tetrachlorophenylbutane. It consisted of a mixture of stereoisomers boiling from 155–166° under 7 mm. pressure.

3. Tetrachlorophenylbutane was partially reduced with zinc to give the same 3,4-dichlorophenylbutene obtained by the direct chlorination of phenylbutadiene. It was also completely reduced with zinc to give phenylbutadiene.

4. 3,4-Dichlorophenylbutene loses a molecule of hydrogen chloride to give 1-phenyl-4-chlorobutadiene. Its structure was proved by converting it to γ-phenylcrotonic acid.

5. 1-Phenyl-4-chlorobutadiene absorbed one molecule of chlorine in the 3,4-positions to give 1-phenyl-3,4,4′-trichlorobutene. Its structure was proved by ozonization.

6. 1-Phenyl-3,4,4′-trichlorobutene was further chlorinated to give 1-phenyl-1,2,3,4,4′-pentachlorobutane.

7. Straus' work on the bromination of phenylbutadiene was confirmed in every particular.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE RICE INSTITUTE]

TETRAMETHYLENE GLYCOL AND TETRAMETHYLENE CHLOROHYDRIN

BY W. R. KIRNER AND G. HOLMES RICHTER

RECEIVED MARCH 20, 1929 PUBLISHED AUGUST 7, 1929

Some work published by Bennett[1] suggested a new method for the synthesis of tetramethylene glycol. In the first two papers Bennett gives the preparation of ∂-hydroxybutyl benzyl ether and in the last paper Bennett and Hock described an experiment in which the benzyl group in an entirely different series of benzyl ethers was removed by means of hydrogen bromide, forming benzyl bromide, the residual portion of the ether remaining as an alcohol. By applying this reaction to Bennett's ∂-hydroxybutyl benzyl ether it was found that tetramethylene glycol could be obtained in good yield. The novelty of the reaction is the splitting of the benzyl ether with hydrogen bromide without converting either hydroxyl group of the glycol into a bromide. The glycol was characterized by preparing both the di-phenyl- and di-α-naphthylurethans.

Tetramethylene glycol has been a relatively rare substance and our purpose was to devise a method by which this valuable synthetic reagent might become more easily available. The older methods of synthesis are either very tedious or give poor yields. However, after this work had been completed an article appeared by Müller[2] describing the preparation of tetramethylene glycol by the Bouveault–Blanc reduction of diethyl succinate with a yield of 54%. This is a considerable improvement over the yield reported by Böeseken,[3] who obtained a 31% yield using the same method. Müller ascribes his higher yield to the use of thoroughly dry alcohol and a more efficient method of isolation of the final product. Müller's method thus appears to offer the cheapest and simplest method of preparing tetramethylene glycol which has been published to date.

---

[1] Bennett, *J. Chem. Soc.*, **127**, 1279 (1925); Bennett and Hock, *ibid.*, 475, 481 (1927).

[2] Müller, *Monatsh.*, **49**, 27 (1928).

[3] Böeseken, *Rec. trav. chim.*, **34**, 101 (1915).