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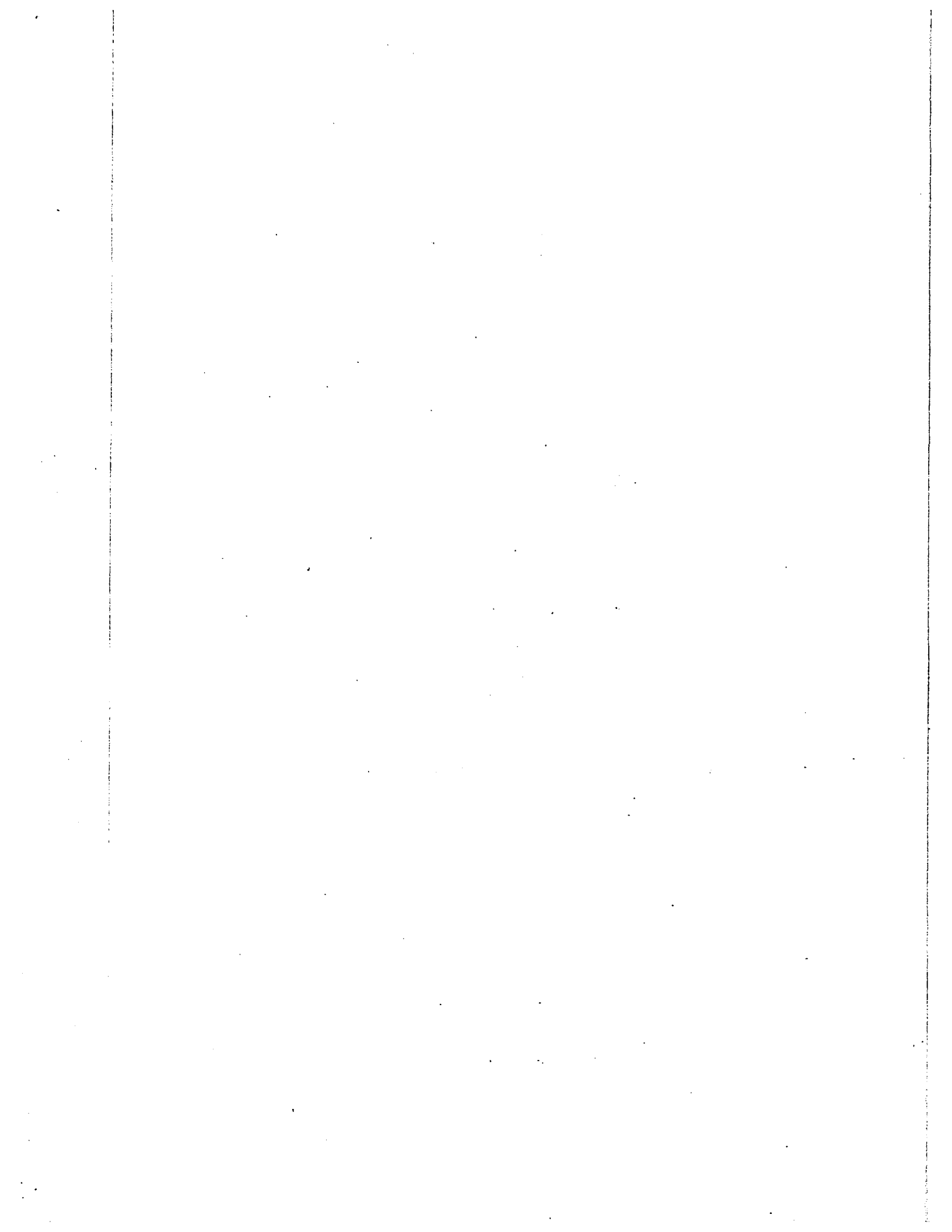
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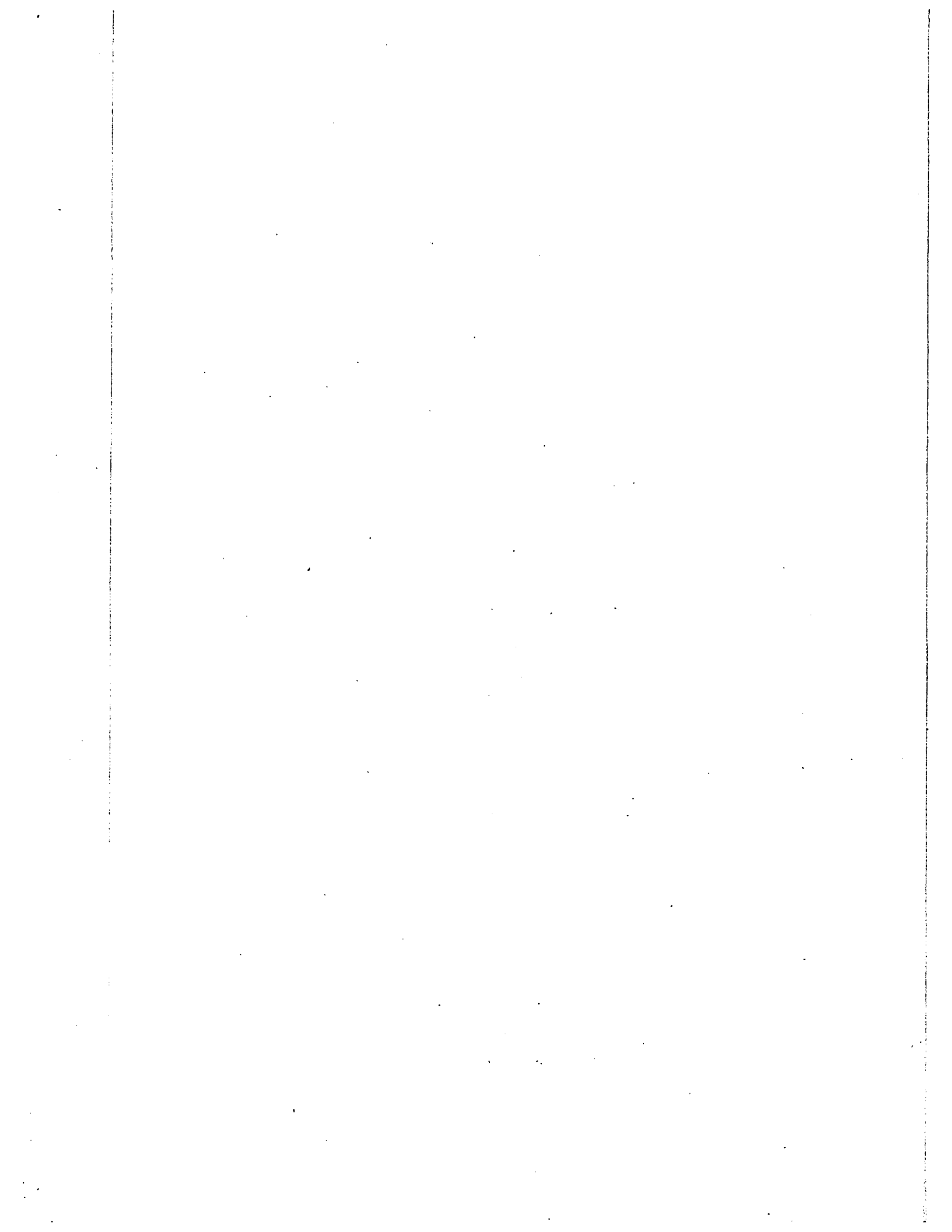
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TABLE OF CONTENTS

CHAPTER		PAGE
	Acknowledgments	i
I	Theoretical	1
II	Experimental	10
	Summary	14
	Bibliography	15

CHAPTER I

THEORETICAL

In 1899 Johannes Thiele¹ published an article in which he set forth a theory to explain the properties of compounds that contained what he called a "conjugated system," $C = C - C = C$. This article has been the basis of so many investigations that it has been considered the beginning of modern interest in valence,² and surely a study of the addition reactions of conjugated systems will throw some light upon several points of theoretical interest alive today.

Thiele³ sought to explain the properties of conjugated double bonds by a theory of partial valence. The addition of two univalent atoms or groups to such a chain often took place at the carbon atoms 1 and 4, with the subsequent formation of a double bond between carbon atoms 2 and 3:

$$3: \begin{array}{cccc} 1 & 2 & 3 & 4 \\ C = C - C = C & \longrightarrow & C - C = C - C. \\ & & \text{X} & \text{X} \end{array}$$

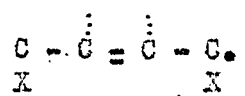
The postulation here is, that in unsaturated compounds the whole of the affinity of the double bond is not employed, but that a part, called the residual affinity, remains free; it is in this free partial valence that the source of the addition capacity is found. He expressed the idea by the symbols, $\overset{\cdot\cdot}{C} = \overset{\cdot\cdot}{C}$, $\overset{\cdot\cdot}{C} = \overset{\cdot\cdot}{C}$, etc., in which the dotted lines denote partial valencies, but in a conjugated system the central carbon atoms (i.e., 2 and 3 above) appear to have lost a considerable part of their additive functions, for hydrogen adds first to

¹Ann., 306, 87 (1899).

²Holson and Falk, Jour. Amer. Chem. Soc., 32, 164 (1910).

³Op. cit., p. 87.

the two end carbons. This is inconsistent with his scheme $\overset{\cdot\cdot}{\text{C}} = \overset{\cdot\cdot}{\text{C}} - \overset{\cdot\cdot}{\text{C}} = \overset{\cdot\cdot}{\text{C}}$, and a new form of double linking is produced, having no partial valencies between carbon atoms 2 and 3 as, $\overset{\cdot\cdot}{\text{C}} = \overset{\cdot\cdot}{\text{C}} - \overset{\cdot\cdot}{\text{C}} = \overset{\cdot\cdot}{\text{C}}$. However, after the extremes of a conjugated system exert their additive power, the central carbon atoms become active, and their partial valencies reappear as indicated:



Although Thiolo's¹ writings leave little room for doubt that he originally intended his hypothesis to imply universal 1,4-addition in conjugated systems of two double linkings,² it has long been known that this position cannot be maintained, so that the Thiolo hypothesis, even with its later extensions, has not the diagnostic value which it was once imagined to possess. In short, there exists no theory of orientation in additions to conjugated systems comparable in range and definition with the orientation theory which has been developed for substitutions in aromatic systems.

We know now that universal 1,4-additions do not occur in the use of conjugated unsaturated systems, and that the Thiolo hypothesis is, though valid for certain types of addenda, does not hold for all types. Since space and time do not permit a detailed discussion of some of the recent workers in the field of conjugated systems, we might mention here a few men who have contributed greatly to our present knowledge of additions to the unsaturated double bonds. Some of the more important

¹Op. cit., p. 87.

²H. Burton and C. K. Ingold, Jour. Chem. Soc., Pt. 1, p. 901 (1928).

workers are: Anwers,¹ Ingold,² Farmer,³ Jones,⁴ and others.

More recently Luskat and Grinsloy⁵ studied the addition reactions of conjugated systems through the addition of hypochlorous and hypobromous acids to phenylbutadiene. The objectives were as follows: (1) to accumulate data as to the type of addition, 1,2; 1,4 or 3,4, taking place in conjugated systems; (2) to study the influence of the directing group R, in $R - CH = CH - CH = CH_2$, on the type of addition; (3) to study the effect of different addenda on the type of addition, i.e., to determine whether or not the type of addition was dependent on the nature of the addition reagent; (4) to attempt to correlate the data on conjugated systems and interpret them according to an electronic formulation of conjugated systems; (5) to show the connection of conjugated systems to aromatic compounds. Their investigation proved that phenylbutadiene adds hypochlorous and hypobromous acids in the 3,4-positions to form 3-Hydroxy-4-chloro-1-phenyl- Δ^2 -butene and 3-Hydroxy-4-bromo-1-phenyl- Δ^2 -butene, respectively. The authors proved the structures of these compounds by ozonization.

In 1904 Klages⁶ studied the modes of additions to conjugated systems, and showed that phenylbutadiene added hydrogen in the 1,4-positions giving phenyl- Δ^2 -butene. This was in accord with the already es-

¹J. Prakt. Chem. 2 37, 64 (1911).

²Op. cit.

³Jour. Chem. Soc., Part II, p. 3233 (1931).

⁴Jour. British Chem. Soc., Pt. 1, p. 829 (1934).

⁵Jour. Amer. Chem. Soc., 52, 1574 (1930).

⁶Ber., 37, 2301 (1904).

tablished theory regarding additions to unsaturated bonds.

Lator, Strauss¹ proved that phenylbutadiene added bromine in the 3,4-positions, which was a contradiction to the theory of Riiber,² that bromine adds in the 1,4-positions. Strauss based his proof on a study of the ozonization products. He isolated benzaldehyde and dibromopropionaldehyde. The work of Strauss was confirmed by Luskat and Muggins³ who also studied the addition of chlorine to phenylbutadiene.

In order to account for 3,4 additions of bromine to conjugated systems, these investigators applied the theory which had been developed by Luskat and Northrup.⁴ This theory is based on the supposition that conjugated systems differ from non-conjugated systems only in so far as the former may exhibit α (alpha) γ (gamma) rearrangement while the latter cannot exhibit this phenomenon. It further makes the assumption that the addition of both components to an ethylenic double bond does not occur simultaneously but rather that the essential feature is the attraction of the positive substituting group to the negative carbon valence irrespective of complete saturation.

A careful search of the early literature reveals only a few men who have studied the addition of hypohalous acids to conjugated unsaturated double bonds. In 1884 Przybytok⁵ studied the addition of hypohalous acids to a number of diolefines but did not include in his investigation the conjugated unsaturated system. Mokiosky⁶ prepared the dichloro-

¹Jour. Amer. Chem. Soc., 42, 2866 (1909).

²Jour. Amer. Chem. Soc., 36, 1404 (1903).

³Jour. Amer. Chem. Soc., 51, 2496 (1929).

⁴Jour. Amer. Chem. Soc., 52, 4043 (1930).

⁵Ber., 17.1 1091 (1884).

⁶J. Russ. Chem. Soc., 30, 985 (1908).

hydrin of isoprene but did not determine the structures of these compounds. He did not prepare the mono-addition derivative. Braun¹ attempted to add hypochlorous acid to vinylacrylic acid and reported that vinylacrylic acid is easily oxidizable with hypochlorous acid. However, he did not isolate any products.

Later, in 1931, Muehlt and Hudson² found that vinylacrylic acid readily absorbed one mole of hypochlorous acid to form a monochlorohydrin, which melted at $71^{\circ} - 74^{\circ}$. The structure of this compound was determined by ozonization. The authors found further that the monochlorohydrin absorbed one mole of hypochlorous acid to form a dichlorohydrin, which melted at 143° . They did not determine the structure of this compound.

The present investigation had for its objective the addition of hypobromous acid to 2:3-dimethylbutadiene. Only a few studies have been made on the addition of hypobromous acid to conjugated unsaturated compounds. A few of the most important workers were mentioned above.

1-Hydroxy-4-bromo-2:3-dimethyl- Δ^2 -butene was prepared in two ways. First it was prepared according to the method of A. W. Francis,³ by treating pure 2:3 dimethylbutadiene with hypobromous acid, which had been freed from excess bromine by shaking it several hours with silver sulphate. The yields were poor and in every case mixtures of the mono-derivative and the di-derivative were obtained. The monobromohydrin,

¹Jour. Amer. Chem. Soc., 52, 3186. (1930).

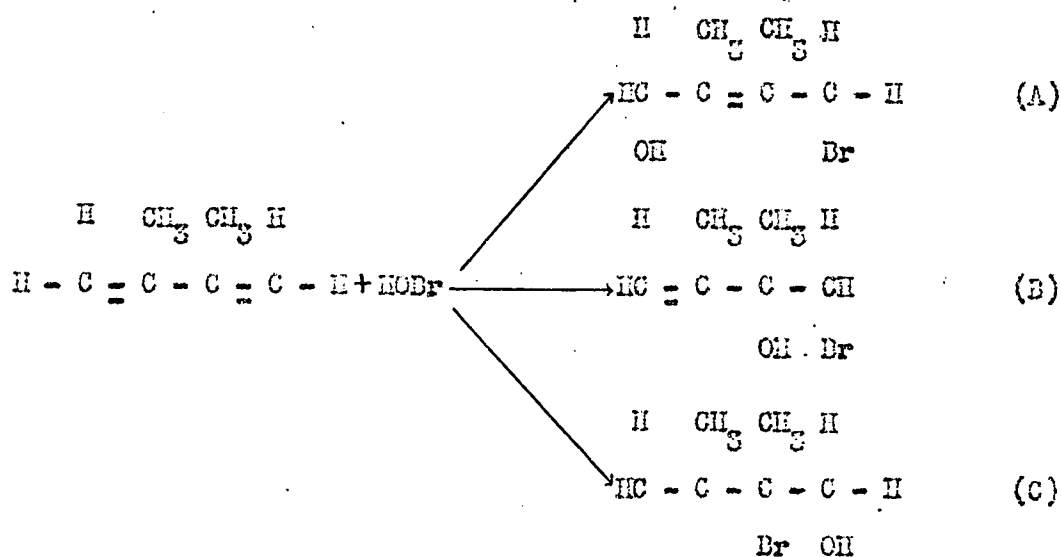
²Jour. Amer. Chem. Soc., 53, 3178 (1931).

³Jour. Amer. Chem. Soc., 47, 2340 (1925).

contaminated with the corresponding di-derivative, decomposed upon attempted distillation.

The best results were obtained when the hypobromous acid was prepared by the hydrolysis of sodium hypobromite in the presence of sodium bicarbonate. This method was employed by Walker,¹ who prepared the hypochlorous acid derivatives of propylene, acetylene and a number of other compounds in good yields.

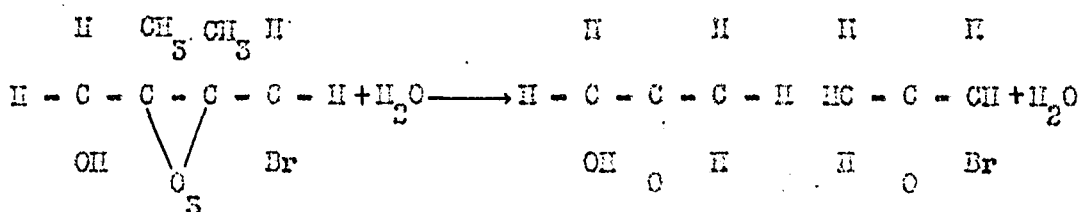
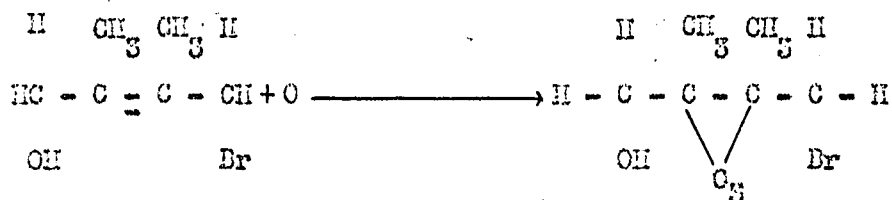
The stable bromohydrin distilled smoothly at 62° - 65° under 4-5 mm. pressure. Its structure was determined by ozonization. It can be seen that three different isomers are possible when 2,3-dimethylbutadiene reacts with one mole of hypobromous acid.



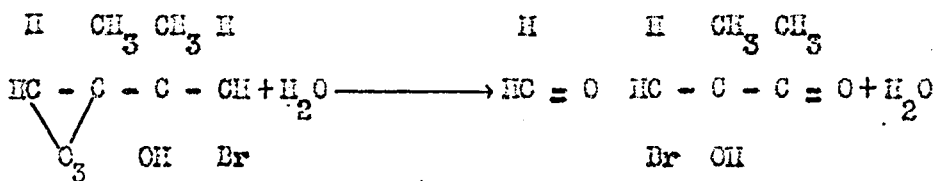
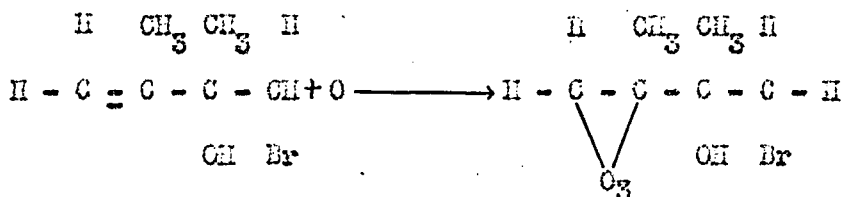
Compound (A) on ozonization and subsequent hydrolysis would yield hydroxy acetone and bromoacetone as the following equation will

¹ U. S. Pat., 972.

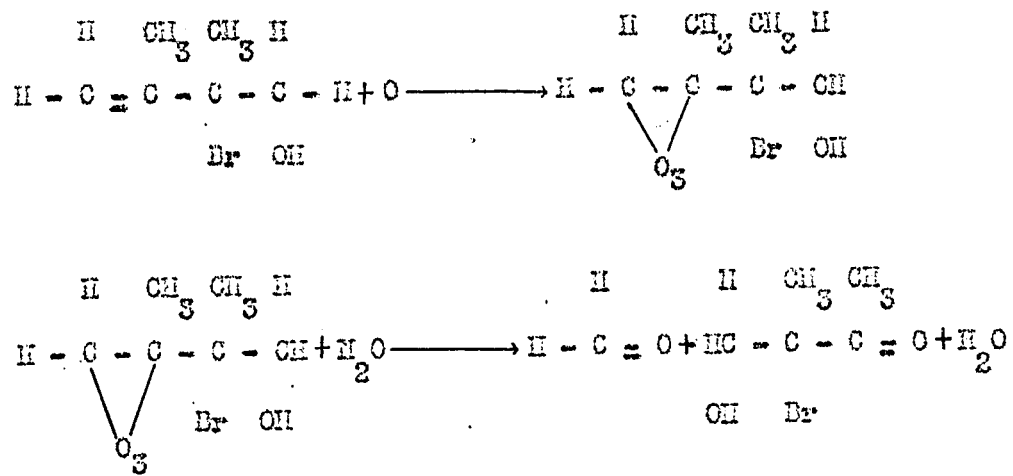
show:



Compound (B) on ozonization and subsequent hydrolysis would give formaldehyde and 1-bromo-2-hydroxy propyl methyl ketone according to the following equation:



If compound (C) be ozonized and hydrolyzed it would yield formaldehyde and 1-hydroxy-2-bromo propyl methyl ketone according to the following equation:



The investigator found that when the bromohydrin was ozonized and worked up according to the method of Whitmore and Church,¹ it was possible to isolate bromoacetone in the form of its semicarbazone, melting at 143°. A mixture of this semicarbazone with authentic semicarbazone of bromoacetone melted at 143°. The presence of hydroxyacetone was indicated by the fact that we were able to isolate the semicarbazone of pyruvic aldehyde, melting at 254°. It is a well known fact that when hydroxy acetone is heated with semicarbazide hydrochloride, and enough sodium acetate to neutralize the hydrochloric acid combined with the semicarbazine, that a derivative of pyruvic aldehyde is formed. This proves that the bromohydrin is a 1:4-compound, having structure (A).

The bromohydrin was treated with a saturated solution of sodium hydroxide according to the method employed² in the formation of an oxido compound from o-chloro-m-hydroxy cyclohexanone. The method proved unsatisfactory because all of the bromine could not be removed.

¹Jour. Amer. Chem. Soc., 56, 178 (1934).
²Organic Synthesis, Vol. V, p. 55 (1925).

Finally the bromohydrin was heated with dry potassium hydroxide, and distilled under a small column. After three or four distillations a small quantity of a halogen-free compound was isolated which gave a carbon and hydrogen analysis that checked with the theoretical for the oxide. It distilled at 50° under atmospheric pressure.

A complete investigation regarding the formation of an oxide from bromohydrin is under way in our laboratory. We hope by this method to isolate the dimethylidihydro furan of this compound and determine its structure.

¹
Luciat and Grimsley attempted to form the oxide of phenylchlorohydrin and met with difficulty. They attributed their failure to the fact that the potassium hydroxide used, dehydrated the phenylchlorohydrin to give a chloro derivative of phenylbutadiene ($C_6H_5-CH=CH-CH=CH-Cl$) from which the chlorine could be removed only with great difficulty. The authors stated however that bromine could be removed much easier than chlorine.

¹Op. Cit., p. 4045.

CHAPTER II

EXPERIMENTAL

Preparation of 2,3-Dimethylbutadione:- 2,3-Dimethylbutadione was prepared from pinacone. Acetone was reduced to pinacone hydrate by the method given by Marvol¹ and the hydrate was converted into pinacone by heating it on a water bath at 70° under reduced pressure until all of the water was removed. Pinacone was converted to 2,3-dimethylbutadione by the method of Kyrialides² by heating it with a few milliliters of 48 per cent hydrobromic acid. Realizing the importance of working with the compound in its purest state, the investigator purified the hydrocarbon according to the method of Farnor and Warren³ by washing it twenty times with water, drying it over calcium chloride and finally over anhydrous calcium sulphate, and twice distilling it over sodium. It boiled at 69° - 70° under atmospheric pressure. The pure product was used in the preparation of 1-hydroxy-4-bromo-2,3-dimethyl- Δ^2 -butone.

Preparation of Hypobromous Acid:- Two methods were employed for the preparation of the hypobromous acid used in this investigation. In the first method⁴ 102 grams of bromine and 300 grams of mercuric oxide were added gradually in portions of 30 grams of mercuric oxide and 10 grams of bromine, with constant shaking, to one liter of water. The vigorous shaking was continued ten minutes after the last portion had been

¹Organic Synthesis, Vol. V, pp. 37-39 (1925).

²Jour. Amer. Chem. Soc., 36, 991 (1914).

³Jour. of Chem. Sec., Part II, p. 3253 (1931).

⁴Houben, Die Methoden der Organischen Chemie, Vol. 3, (1930).

added. A straw colored solution resulted which was quickly filtered from the excess mercuric oxide and kept cool in an ice bath. This solution was added dropwise to 35 grams of 2,3 dimethylbutadiene dissolved in 250 cc. of ether.

The second method employed¹ for the preparation of hypobromous acid involved a reaction whereby the acid was used up as fast as it was formed. In a two liter flask was placed 120 grams of sodium bicarbonate in about 400-500 cc water. A calculated amount of the hydrocarbon dissolved in ether was poured into the flask, which was kept below 0°. A solution of sodium hypobromite, formed by the addition of 19 cc. of bromine to 30 grams of sodium hydroxide in 300 cc. of water was cooled in an ice mixture, and allowed to drop into the large flask on the bicarbonate solution with constant stirring. The stirring was continued two or three hours after the last drop had been added, until the lower aqueous layer gave no test for hypobromous acid.

This method was interesting as well as valuable because as fast as the hypobromous acid was formed in the reaction, it was utilized in adding to the hydrocarbon. The other interesting thing about this method of formation was that the hypobromous acid was prepared free from any bromine. The bromohydrin was produced in a much greater yield than was obtained by the first method and the percentage of the corresponding di-derivative was almost negligible. This method gave excellent results and was employed throughout this investigation.

Preparation of 1-Hydroxy-4-bromo-2,3-dimethyl- Δ^2 -butene:- Into a saturated solution of 120 grams of sodium bicarbonate in 400 cc. of water,

¹Walker, U. S. Pat., 972.

maintained below 0° with a salt-ice mixture, was placed 40 grams of 2,5-dimethylbutadiene dissolved in 500 cc. of ether. To this was added dropwise an ice cold solution of 30 grams of sodium hydroxide and 19 cc. of bromine in 500 cc. of water with constant stirring. The mixture was stirred with a mechanical stirrer until the lower aqueous layer gave no test for hypobromous acid, after which the ether extract was separated from the aqueous layer, dried over calcium chloride and finally over calcium sulphate, and the ether removed on a water pump.

The slightly yellow bromohydrin distilled smoothly at $62^{\circ} - 65^{\circ}$ under reduced pressure of 4-5 mm. A beautiful almost colorless liquid was isolated.

Anal. Subs., 0.1280, 0.1182: AgBr, 0.1345, 0.1247.

Calcd. for $C_{11}H_{11}OBr$: Br, 44.89. Found: Br, 44.72, 44.90.

Anal. Subs., 0.4996, 0.1765: CO_2 , 0.7358, 0.2597: H_2O , 0.2761, 0.0964

Calcd. for $C_{11}H_{11}OBr$: C, 40.22; H, 6.14. Found: C, 40.19, 40.18;
H, 6.17, 6.13

Ozonization of 1-hydroxy-4-bromo-2,3-dimethyl- Δ^2 -butene:-- The bromohydrin was ozonized at the temperature of a freezing mixture of chloroform. After ozonization was complete, the chloroform was removed on a water pump, and the ozonide treated with water and warmed on a water bath to decompose the ozonide. A portion of the aqueous solution was treated with an acetic acid solution of phenylhydrazine and warmed on a water bath for two hours. A yellow solid which melted at 145° was isolated. The phenylhydrazone of pyruvic aldehyde melted at 145° . The isolation of phenylhydrazone

of pyruvic aldehyde was evidence for the presence of hydroxy acetone as one of the fragments of ozonolysis.

To another portion of the hydrolyzed ozonide was added a solution of semi-carbazide hydrochloride, containing enough sodium acetate to neutralize the hydrochloric acid combined with the semicarbazone. The solution was kept cold in an ice bath. After standing several hours, a white solid separated, which, after being crystallized several times from benzene, melted at 143° , the melting point of the semicarbazone of bromoacetone. A mixture of this substance with authentic semicarbazone of bromoacetone melted at 143° . This proved that the bromohydrin, prepared according to the method just described, is a 1,4-compound.

SUMMARY

1. The addition of hypobromous acid on 2,3-dimethylbutadiene has been studied and a satisfactory method of preparing 1-hydroxy-4-bromo-2,3 dimethyl- Δ^2 -butene has been outlined.

2. The stable bromohydrin prepared boiled at 62° - 65° c., under 4-5 mm. pressure.

3. The structure of the bromohydrin was determined by isolating and indentifying hydroxy acetone and bromoacetone as fragments of ozonization.

4. An oxide of the bromohydrin was prepared which gave carbon and hydrogen analysis that checked with the theoretical. Investigation is still under way to determine the structure of this oxide.

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