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

STUDIES OF CONJUGATED SYSTEMS. IV. THE ADDITION OF HYPOCHLOROUS AND HYPOBROMOUS ACIDS TO PHENYLBUTADIENE

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The addition reactions of conjugated systems have been for some time the subject of an investigation in this Laboratory. The problem has been attacked from several points of view: (1) to accumulate accurate 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; and (5) to show the connection of conjugated systems to aromatic compounds. For our preliminary investigations we have chosen to study the addition reactions of phenylbutadiene ($C_6H_5CH{=}CHCH{=}CH_2$) and vinylacrylic acid ($HOOC-CH{=}CHCH{=}CH_2$), for these conjugated systems afforded us an opportunity to study the problems of immediate interest to us.

Thiele[1] proved that vinylacrylic acid was reduced in the 1,4-position and not in the 1,2-position as claimed by Doebner.[2] Muskat, Becker and Lowenstein[3] have studied the chlorination and bromination of vinylacrylic acid and found that both chlorine and bromine are absorbed in the 3,4-position. They also found that 3-chloro- and 3-bromo-vinylacrylic acids absorb chlorine and bromine, respectively, in the 3,4-position.

Klages[4] studied the reduction of phenylbutadiene and found that hydrogen is absorbed in the 1,4-position. On the other hand, Strauss[5] proved that phenylbutadiene added bromine in the 3,4-position and not in the 1,4-position as claimed by Riiber.[6] Muskat and Huggins[7] confirmed Strauss's work and also studied the chlorination of phenylbutadiene. They showed that both phenylbutadiene and 1-phenyl-4-chloro-butadiene add chlorine in the 3,4-position and not in the 1,4-position, as postulated

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[1] Thiele, *Ber.*, **35**, 2320 (1902).

[2] Doebner, *ibid.*, **35**, 1136 (1902).

[3] Muskat, Becker and Lowenstein, THIS JOURNAL, **52**, 326 (1930); (b) **52**, 812 (1930); see also Farmer, *J. Chem. Soc.*, **130**, 1060 (1927).

[4] Klages, *Ber.*, **37**, 2301 (1904).

[5] Strauss, *ibid.*, **42**, 2866 (1909).

[6] Riiber, *ibid.*, **36**, 1404 (1903).

[7] Muskat and Huggins, THIS JOURNAL, **51**, 2496 (1929).

by Thiele. In continuation of this work Huggins[8] has found that phenylbutadiene adds hydrogen chloride and hydrogen bromide exclusively in the 3,4-position. The present paper contains the results of an investigation on the addition of hypochlorous and hypobromous acids to phenylbutadiene.

A search of the literature revealed but one paper reporting a study of the addition of the hypohalous acids to conjugated systems. Mokiewsky[9] prepared the dichlorohydrin and dibromohydrin of isoprene but did not determine the structure of these compounds. He did not prepare the mono-addition derivatives, and to the best of our knowledge no such derivative of a conjugated compound has been reported. Przybytek studied the addition of hypochlorous acid to a number of diolefins but did not include in his investigation any member of a conjugated system.

The addition of hypochlorous acid to phenylbutadiene was first studied. It was found that phenylbutadiene readily absorbs one molecule of hypochlorous acid to form a monochlorohydrin. The structure of the monochlorohydrin was determined, in part, by ozonization. Six monochlorohydrins are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place and also on the orientation of the hypochlorous acid in the molecule of phenylbutadiene. On ozonizing the phenylbutadiene monochlorohydrin it was possible to obtain a 76% yield of benzaldehyde as calculated from its semicarbazone. No effort was made to identify the second oxidation product, the α-hydroxy-β-chloropropionic aldehyde or the α-chloro-β-hydroxypropionic aldehyde, since the instability of either proscribes its use for the determination of the structure of the chlorohydrin. This proves that hypochlorous acid adds to phenylbutadiene in the 3,4-position, with the formation of a chlorohydrin having the structure I or II.

I $C_6H_5CH{=}CH{-}CH(OH)CH_2(Cl)$ II $C_6H_5CH{=}CH{-}CH(Cl)CH_2(OH)$

In order to distinguish between these two possible structures, I and II, the decomposition products of the chlorohydrin were studied. It was observed that the monochlorohydrin, on distillation under reduced pressure, decomposes with the liberation of water and hydrogen chloride. One of the decomposition products was identified as 1-phenyl-4-chlorobutadiene, which was obviously formed by the elimination of water from the chlorohydrin. This proves that phenylbutadiene chlorohydrin has the structure I, $C_6H_5CH{=}CHCH(OH)CH_2Cl$. The residue from the distillation of the chlorohydrin yielded yellow crystals, m. p. 235°, which analyzed for $C_{10}H_{10}$, which is the empirical formula of phenylbutadiene. It is of interest as one of the few hydrocarbons possessing color.

Phenylbutadiene chlorohydrin readily absorbs two atoms of chlorine to give a trichloride whose structure, based on its method of preparation, is probably $C_6H_5CHClCHClCH(OH)CH_2Cl$.

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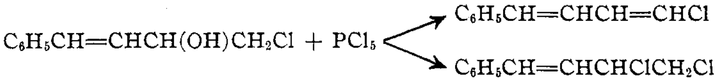
[8] To be published soon.

[9] Mokiewsky, *J. Russ. Phys.-Chem. Soc.*, **30**, 885 (1898).

Phenylbutadiene chlorohydrin was treated with phosphorus pentachloride in dry ether. Two reaction products were isolated: a lower-boiling fraction which proved to be 1-phenyl-4-chlorobutadiene, and a higher-boiling compound which was identified as 3,4-dichlorophenylbutene. In the first reaction phosphorus pentachloride played the role of a dehydrating agent; in the second reaction, that of a chlorinating agent. These two concurrent reactions may be represented as follows

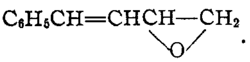


$$C_6H_5CH{=}CHCH(OH)CH_2Cl + PCl_5 \begin{cases} \nearrow C_6H_5CH{=}CHCH{=}CHCl \\ \searrow C_6H_5CH{=}CHCHClCH_2Cl \end{cases}$$

Phenylbutadiene chlorohydrin readily absorbs a molecule of hypochlorous acid to form a dichlorohydrin. Its structure was not determined but it probably consisted of a mixture of stereoisomers of 1-phenyl-1,3-dihydroxy-2,4-dichlorobutane, $C_6H_5CH(OH)CHClCH(OH)CH_2Cl$.

If phenylbutadiene chlorohydrin is treated with an excess of hypochlorous acid, trichlorohydroxyphenylbutane is formed. The first step in the reaction probably is the formation of the dichlorohydrin of phenylbutadiene, which then reacts with the excess of hypochlorous acid to give the trichloro derivative. We did not determine its structure, but from the fact that its boiling point, 164° under 5-mm. pressure, and general behavior were the same as the product obtained by the chlorination of phenylbutadiene chlorohydrin, its probable structure is $C_6H_5CHClCHClCH(OH)CH_2Cl$.

An effort was made to prepare the oxide of phenylbutadiene from its chlorohydrin by the usual methods. It was not possible to prepare a pure oxide since the chlorine was not completely removed.[10] The oxide distilled at about 94° under 6-mm. pressure and must have the structure,



. To the best of our knowledge this is the first time a monoxide of a conjugated system has been reported.[11]

The addition of hypobromous acid to phenylbutadiene was then studied. It was found that phenylbutadiene readily absorbed one molecule of hypobromous acid to form a monobromohydrin. The structure of the monobromohydrin was determined in a manner entirely analogous to that used for the chlorohydrin. The isolation and identification of benzaldehyde as one of the oxidation products of the bromohydrin proved that it also was a 3,4-addition product of phenylbutadiene.

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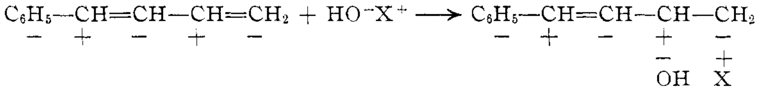
[10] This is in accord with previous reports on the preparation of oxides from the chlorohydrins. See Przybytek, *Ber.*, **17**, 1090 (1884); **20**, 3239 (1887). It is possible that the potassium hydroxide dehydrates the chlorohydrin to give 1-phenyl-4-chlorobutadiene, from which the chlorine can be removed only with great difficulty. A similar interpretation might hold for other chloro- and bromohydrins.

[11] A complete investigation of the oxidation of conjugated systems is now under way in this Laboratory. On oxidizing phenylbutadiene with perbenzoic acid a 1,2-monoxide is formed.

Phenylbutadiene bromohydrin readily absorbs a molecule of hypobromous acid to form a dibromohydrin. Its structure was not determined but it probably consisted of a mixture of stereoisomers of 1-phenyl-1,3-dihydroxy-2,4-dibromobutane, $C_6H_5CH(OH)CHBrCH(OH)CH_2Br$.

It was much easier to prepare the phenylbutadiene oxide from the monobromohydrin than from the chlorohydrin. The oxide prepared from the bromohydrin contained but a trace of bromine.

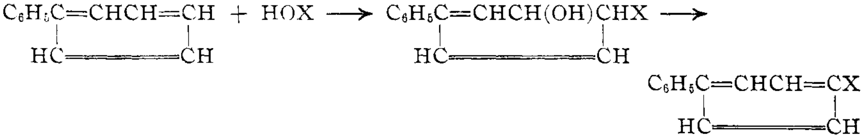
The orientation of the hypochlorous and hypobromous acids in the molecule of phenylbutadiene may be interpreted readily according to the electronic formulations developed by Muskat and Becker[3b]



$$\underset{-}{C_6H_5}-\underset{+}{CH}=\underset{-}{CH}-\underset{+}{CH}=\underset{-}{CH_2} + HO^-X^+ \longrightarrow \underset{-}{C_6H_5}-\underset{+}{CH}=\underset{-}{CH}-\underset{\substack{+\\-\\OH}}{CH}-\underset{\substack{-\\+\\X}}{CH_2}$$

This would also explain the ease of eliminating water from the chloro- and bromohydrins, as compared to the difficulty encountered in removing the halogen, X^+. It would be expected from these considerations that the isomeric chloro- and bromohydrins, $C_6H_5CH{=}CHCH(X)CH_2(OH)$, should lose HX very easily to give a pure oxide. Further work in this direction is now under way.

The elimination of water from the chlorohydrin to give 1-phenyl-4-chlorobutadiene corresponds to the para-chlorination of diphenyl in the aromatic series and suggests that para-halogenation in the aromatic series is preceded by the 3,4-addition of X^-X^+ or HO^-X^+ rather than by 1,4-addition.



Experimental Part

Phenylbutadiene Chlorohydrin.—Phenylbutadiene was prepared according to the method of Muskat and Ludeman[12] by the condensation of cinnamic aldehyde with methylmagnesium bromide and the hydrolysis of the intermediate Grignard addition compound with 30% sulfuric acid. Hypochlorous acid was prepared according to the method of Reformatzky[13] by passing chlorine into a finely divided suspension of mercuric oxide in water at about −5°. A 3–5% solution of hypochlorous acid, free from chlorine, was used in these experiments.

Phenylbutadiene was treated with one mole of a dilute hypochlorous acid solution. The hypochlorous acid must be added slowly and under continuous agitation and cooling, otherwise the reaction becomes too violent. The rate of reaction can be followed readily by the usual iodimetric titrations. After all of the hypochlorous acid had been added, the reaction mixture was allowed to stand overnight. The reaction mixture was taken up in ether, washed free of chlorides, dried over sodium sulfate and the ether

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[12] Muskat and Ludeman, *Ber.*, **62**, 2284 (1929).

[13] Reformatzky, *J. prakt. Chem.*, **40**, 396 (1889).

was removed by suction at ordinary temperature. The chlorohydrin is unstable at higher temperatures and decomposed when distilled even at reduced pressure. It was analyzed for chlorine in the usual manner.

Anal. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.43. Found: Cl, 19.35, 19.26.

The phenylbutadiene chlorohydrin (5 g.), dissolved in chloroform, was subjected to ozonization for several hours. The process of ozonization and the method of working up the oxidized fractions are amply described by Muskat and Huggins.[7] It was possible to recover 3.4 g. of the semicarbazone of benzaldehyde, which corresponds to a 76% yield of benzaldehyde. It was not possible to obtain the slightest indication of the presence of any of the aldehydes or acids to be expected from the oxidation of compounds formed by the 1,2- or 1,4-addition of hypochlorous acid to phenylbutadiene.

When phenylbutadiene chlorohydrin was distilled under reduced pressure, decomposition set in with the liberation of water and hydrogen chloride. A product distilled over at 104–120° under 13-mm. pressure which solidified when placed in a freezing mixture. The crystals were pressed out on a porous plate. They melted sharply at 52°, the melting point of 1-phenyl-4-chlorobutadiene. A mixture with a sample of known origin also melted at 52°. The residue, a black tarry mass, was extracted a number of times with hot benzene. The benzene solution was concentrated and cooled and yellow crystals separated; these were purified by a number of crystallizations from various solvents, but the yellow color remained. It is not very soluble in any solvent; it is more soluble in hot benzene and ether than in the other ordinary organic solvents. It melts at 235° and was analyzed by micro-methods.

Anal. Calcd. for $C_{10}H_{10}$: C, 92.25; H, 7.75. Found: C, 92.22; H, 7.73.

Reactions of Phenylbutadiene Chlorohydrin.—Phenylbutadiene chlorohydrin was chlorinated by allowing a stream of chlorine gas to pass into a solution of the chlorohydrin in chloroform. Absorption took place readily. When the theoretical quantity of chlorine was absorbed, the reaction mixture was distilled under reduced pressure. A light yellow oil distilled over at 164° under 5-mm. pressure. On standing it assumed a greenish color, and finally, after standing for several days, it turned to a dark green color.

Anal. Calcd. for $C_{10}H_{11}OCl_3$: Cl, 41.97. Found: Cl, 41.92, 41.97.

Phenylbutadiene chlorohydrin was treated with phosphorus pentachloride in dry ether. The reaction mixture was allowed to stand overnight. It was then taken up in ether, washed free of chlorides, dried and the ether was removed by vaporization. The residual oil was distilled under reduced pressure. Two fractions were collected: one distilling at 140–150° under 16-mm. pressure, the second distilling at 150–160° under 16-mm. pressure. The first fraction was redistilled, the major portion coming over at 115–117° under 3.5-mm. pressure, the boiling point of 1-phenyl-4-chloro-butadiene. It solidified when placed in a freezing mixture. The crystals melted at 50° and did not lower the melting point of known 1-phenyl-4-chlorobutadiene when mixed with it. The second fraction was also redistilled, the main portion coming over at 140° under 10-mm. pressure, the boiling point of 3,4-dichloro-1-phenylbutadiene. A chlorine analysis verified this conclusion.

Phenylbutadiene chlorohydrin was treated with one mole of hypochlorous acid solution. Absorption took place fairly readily with the formation of a viscous oil. The oil could not be crystallized even when placed in a carbon dioxide snow and ether mixture. It is unstable toward distillation even under reduced pressure. It is obviously a dichlorohydrin of phenylbutadiene.

Anal. Calcd. for $C_{10}H_{12}O_2Cl_2$: Cl, 30.18. Found: Cl, 30.22, 30.18.

Phenylbutadiene chlorohydrin was treated with a large excess of hypochlorous acid and the reaction mixture was allowed to stand overnight. The oily layer was taken up in ether, washed free from chlorides, dried and the ether was removed by vaporization. The residual oil was distilled under reduced pressure. A light yellow oil distilled over at 164–167° under 5-mm. pressure. On standing it assumed a greenish color, which finally, after standing for several days, turned to a dark green.

Anal. Calcd. for $C_{10}H_{11}OCl_3$: Cl, 41.97. Found: Cl, 41.93.

A number of attempts were made to prepare the oxide of phenylbutadiene from its chlorohydrin. Finely divided potassium acetate, silver nitrate, alkali in alcohol and acetone solution and finely powdered potassium hydroxide were used under widely different experimental conditions in an effort to prepare the pure oxide. Of all the methods tried, the one using powdered potassium hydroxide in dry ether was found, on the whole, to be most satisfactory. However, a pure oxide could not be prepared even by this method. It was not possible to remove completely all of the chlorine. The impure oxide obtained by this method distilled at 94° under 6-mm. pressure.

Phenylbutadiene Bromohydrin.—Phenylbutadiene was treated with the theoretical quantity of a dilute hypobromous acid solution. Its method of preparation is identical with that described for the preparation of the chlorohydrin. The bromohydrin is far less stable than the corresponding chlorohydrin. It was stable only when dissolved in an organic solvent. Working very rapidly, it was once possible to obtain a sample for analysis.

Anal. Calcd. for $C_{10}H_{11}OBr$: Br, 35.20. Found: Br, 35.34.

The phenylbutadiene bromohydrin (4.6 g.), dissolved in chloroform, was subjected to ozonization and the ozonide thus formed was worked up in a manner entirely analogous to that described for the chlorohydrin. It was possible to recover 2.6 g. of the semicarbazone of benzaldehyde which was identified by its melting point and a melting point of a mixture with a sample of known origin. This corresponds to a 78% yield of benzaldehyde. It was not possible to obtain even the slightest indication of the presence of any of the aldehydes or acids to be expected from the oxidation of compounds formed by the 1,2- or 1,4-addition of hypobromous acid.

Reactions of Phenylbutadiene Bromohydrin.—Phenylbutadiene bromohydrin was treated with one mole of a dilute hypobromous acid solution. Absorption took place fairly rapidly with the formation of a very viscous oil, which could not be crystallized. It is unstable toward distillation even under reduced pressure. It is obviously a dibromohydrin of phenylbutadiene.

Anal. Calcd. for $C_{10}H_{12}O_2Br_2$: Br, 49.34. Found: Br, 49.30, 48.83.

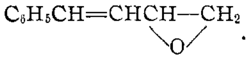
On treating an ethereal solution of phenylbutadiene bromohydrin with powdered potassium hydroxide, the 3,4-monoxide of phenylbutadiene was formed. The oxide prepared from the bromohydrin was purer than that prepared from the chlorohydrin.

Summary

1. Phenylbutadiene absorbs hypochlorous and hypobromous acid in the 3,4-positions to form 3-hydroxy-4-chloro-1-phenylbutadiene and 3-hydroxy-4-bromo-1-phenylbutadiene, respectively.

2. Phenylbutadiene chlorohydrin decomposes, on distillation, to give 1-phenyl-4-chlorobutadiene and a residue from which was extracted a yellow hydrocarbon, which is a polymer of phenylbutadiene.

3. Phenylbutadiene chlorohydrin reacts with phosphorus pentachloride to give, by dehydration, 1-phenyl-4-chlorobutadiene, and, by chlorination, 3,4-dichlorophenylbutene.

4. Phenylbutadiene chlorohydrin readily absorbs a molecule of chlorine to give 1-phenyl-1,2,4-trichloro-3-hydroxybutane.
5. Phenylbutadiene chlorohydrin absorbs a molecule of hypochlorous acid to give a dichlorohydrin. In the same way phenylbutadiene bromohydrin absorbs a molecule of hypobromous acid to give a dibromohydrin
6. On treating with powdered potassium hydroxide, both phenylbutadiene chlorohydrin and bromohydrin lose a molecule of hydrogen chloride and hydrogen bromide, respectively, to give a monoxide of phenylbutadiene,  $\underset{\diagdown O \diagup}{C_6H_5CH{=}CHCH{-}CH_2}$. This is the first time a monoxide of a conjugated compound has been reported.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXIV. THE REARRANGEMENT OF 2-ETHYLMERCAPTO-5-CARBETHOXY-6-THIOCYANPYRIMIDINE INTO ITS ISOTHIOCYANATE MODIFICATION[1]

BY TREAT B. JOHNSON AND YUOH FONG CHI

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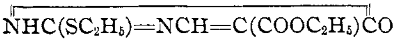
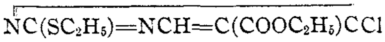
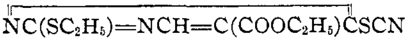
The behavior of several chloropyrimidines toward potassium thiocyanate has been described in previous papers from this Laboratory,[2] but of all the different pyrimidine halides thus far studied in our thiocyanate researches no one has proved to be more interesting than 2-ethylmercapto-5-carbethoxy-6-chloropyrimidine, II, which was first described by Wheeler and Johns.[3] They prepared it by the action of phosphorus oxychloride on 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine, I.


$\overline{NHC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CO}$

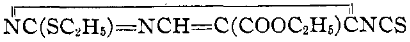
I


$\overline{NC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CCl}$

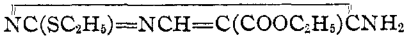
II


$\overline{NC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CSCN}$

III


$\overline{NC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CNCS}$

IV


$\overline{NC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CNH_2}$

V

2-Ethylmercapto-5-carbethoxy-6-chloropyrimidine, II, is another example of a halide in the pyrimidine series which interacts in a characteristic manner with potassium thiocyanate, giving a normal thiocyanate deriva-

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[1] Constructed from part of a dissertation presented by Yuoh Fong Chi to the Faculty of the Graduate School of Yale University in June, 1928, in partial fulfilment of the requirements for the Ph.D. degree.

[2] Wheeler and Bristol, THIS JOURNAL, **23**, 287 (1901); Johnson and McCollum, *Am. Chem. J.*, **36**, 136 (1906); Johnson and Storey, *ibid.*, **40**, 138 (1908).

[3] Wheeler and Johns, *Am. Chem. J.*, **38**, 594 (1907).