[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES OF CONJUGATED SYSTEMS. V. THE PREPARATION AND CHLORINATION OF BUTADIENE

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The addition reactions of conjugated systems have been for some time the subject of an investigation in this Laboratory.[1] In our earlier work we were mainly concerned with the addition reactions of α-substituted conjugated compounds, $RCH{=}CHCH{=}CH_2$, but in order to ascertain the effect of conjugation, free from the influence of substituent groups, we undertook an investigation of the addition reactions of butadiene, $CH_2{=}CHCH{=}CH_2$. The present paper contains the results of a study of the preparation and chlorination of butadiene.

The preparation of butadiene was first reported by Caventou,[2] who obtained it by passing the vapors of fusel oil through a hot tube. Since then it has been found in varying amounts (usually very small) in the pyrogenic decompositions of a large number of organic compounds. The possibility of using butadiene as a raw material for the production of rubber stimulated a great deal of work on the preparation of this hydrocarbon. Harries,[3] one of the pioneers of rubber chemistry, has shown that while excellent rubber is obtained by the polymerization of isoprene, rubber of still better quality is produced by the polymerization of butadiene. Most of the methods that have been patented for the preparation of butadiene are based on the pyrogenic decomposition and cracking of different petroleum products.[4] However, the yields of butadiene obtained by these methods invariably have been low.

A different method for the preparation of butadiene was suggested by Perkin[5] based on the method he developed for the preparation of isoprene. This method may be formulated as follows

$$\underset{\text{Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{\text{Dry HCl}} \underset{\text{Butyl chloride}}{CH_3CH_2CH_2CH_2Cl}$$

$$\text{Butyl chloride} \xrightarrow{Cl_2} \text{Mixture of } \alpha,\beta\text{-},\ \alpha,\gamma\text{- and } \alpha,\delta\text{-butane dichlorides}$$

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[1] Muskat and Huggins, THIS JOURNAL, **51**, 2496 (1929); Muskat, Becker and Lowenstein, *ibid.*, **52**, 326 (1930); Muskat and Becker, *ibid.*, **52**, 812 (1930); Muskat and Grimsley, *ibid.*, **52**, 1574 (1930).

[2] Caventou, *Ann.*, **127**, 348 (1863).

[3] Harries, *ibid.*, **383**, 213 (1911).

[4] Brooks, "Chemistry of Non-Benzenoid Hydrocarbons," The Chemical Catalog Co., Inc., New York, 1922, gives a rather complete review of the various methods that have been used for the preparation of butadiene.

[5] Perkin, *J. Soc. Chem. Ind.*, 31, 616 (1912).

$$\text{Butane dichlorides} \xrightarrow[\text{at } 470^\circ]{\text{Soda lime}} \underset{\text{Butadiene}}{CH_2{=}CHCH{=}CH_2}$$

He states that he tried this method once and that the yield appeared to be good, but he gave no actual figures.

Since this 1912 paper Perkin has not published further concerning the preparation of butadiene or the development of the process he suggested. It is also of interest that of the many research investigations published since 1912 in which butadiene was used, not any of the investigators prepared the butadiene according to the method suggested by Perkin. We must, therefore, conclude that the method of preparing butadiene devised by Perkin was not considered successful.

Since we intended to make an extended study of butadiene and its addition reactions we made a preliminary investigation of the various methods suggested for its preparation. The method devised by Perkin appeared the most promising and we have developed this method so that it gives a much better yield of butadiene than that obtained by any of the other methods.

n-Butyl alcohol was converted into *n*-butyl chloride according to the method of Norris[6] by heating the alcohol with concentrated hydrochloric acid and anhydrous zinc chloride. The pure chloride was then further chlorinated to the dichloride. In order to insure the complete conversion, as far as possible, of the monochloride to the dichloride without the formation of any higher chlorinated products, a specially designed apparatus was used. This was modeled after a similar apparatus used by Perkin in his work on the chlorination of isoamyl chloride. A detailed description of the apparatus will follow in the Experimental Part. It was possible to chlorinate in this apparatus two liters of butyl chloride to the dichloride in about six hours.

The chlorinated reaction mixture was then distilled through a fractionating column. From the distillation temperatures of the fractions collected it appeared that the chlorinated product consisted of a mixture of some unreacted butyl chloride and the α,β-, α,γ- and α,δ-dichlorobutanes (possibly also some α,α-dichlorobutane). Detailed data concerning the yields of these fractions will be found in the Experimental Part.

Each of the fractions of the dichlorobutanes was distilled over coarse soda lime contained in an iron tube heated at a temperature of about 700–730°. The volatile products coming from the hot tube were passed through several condensers and wash bottles and finally absorbed in chloroform or ligroin to be treated as desired. A diagram of this cracking apparatus is included in the Experimental Part with the yields of butadiene obtained from each fraction of the dichlorobutane mixture. The best yield was obtained from the α,γ-dichlorobutane, which was about 30 mole per cent. of the theoreti-

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[6] Norris, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 27.

cal. This is considerably higher than the yield of butadiene reported from other methods.

The addition of bromine to butadiene was first studied by Griner,[7] then by Thiele[8] and more recently by Farmer and his students.[9] The latter have definitely shown that butadiene unites with bromine to form a mixture of two dibromides. One of these, a liquid, is the 1,2-dibromide, $CH_2BrCHBrCH{=}CH_2$, its structure being proved by ozonization. The other is a solid compound, m. p. 53–54°, proved by Thiele to possess the 1,4-structure, $CH_2BrCH{=}CHCH_2Br$. Farmer further showed that when either the 1,2- or 1,4-dibromide is heated for a few minutes at 100°, the product is a mixture in which the two isomerides appear to be in equilibrium, the equilibrium mixture consisting of 20% of the 1,2- to 80% of the 1,4-isomer. At room temperature the change is very slow. The equilibrium depended in a large measure on the solvent used. Previous to the publication of Farmer's work one of us (M) had determined the same equilibrium between the two dibromide isomers of butadiene and found the equilibrium mixture of the pure compounds to consist of 18% of the 1,2-dibromide to 82% of the 1,4-isomer.

The addition of hydrogen bromide to butadiene was studied by Ipatiew,[10] who obtained an unsaturated bromide, C_4H_7Br, but he was not able to determine its structure.

Lebedev[11] studied the catalytic reduction of butadiene and found that both double bonds are attacked but not at the same rate.

Diels and Alder[12] have found that butadiene will add maleic anhydride, and similar compounds containing the group $C{=}C{-}C{=}O$, in the 1,4-position. The exact mechanism of this reaction is not yet fully understood.

These are the only investigations of the addition reactions of butadiene which have been reported in the literature. As a continuation of our studies on the addition reactions of conjugated systems we have investigated the chlorination of butadiene.

On chlorinating butadiene in carbon disulfide, ligroin or chloroform solution, a mixture of two dichlorides and two tetrachlorides was obtained. The pure dichlorides are colorless oils and distil, under 40 mm. pressure, at 45–45.5° and at 75–76°, respectively. One of the tetrachlorides is an oil, b. p. 110–111° under 40 mm. pressure, while the second tetrachloride, which distilled at 130–134° under 40 mm. pressure, crystallized to a solid, m. p. 72°, which is the same melting point recorded by Henninger[13] for the

[7] Griner, *Compt. rend.*, 116, 723 (1893); 117, 553 (1893).

[8] Thiele, *Ann.*, **308**, 333 (1899).

[9] Farmer, Lawrence and Thorpe, *J. Chem. Soc.*, 729 (1928).

[10] Ipatiew, *J. prakt. Chem.*, [2] **67**, 420 (1903).

[11] Lebedev, *J. Chem. Soc.*, 2190 (1928).

[12] Diels and Alder, *Ann.*, **460**, 98 (1928).

[13] Henninger, *Ann. chim.*, [6] **7**, 229 (1886).

tetrachlorobutane he obtained on treating erythritol with phosphorus pentachloride.

The structures of the two dichlorides were proved by oxidation. Three dichlorides are theoretically possible, one 1,2-addition compound and two 1,4-addition compounds, the *cis* and *trans* isomers. On ozonizing the lower-boiling dichloride it was possible to isolate α,β-dichloropropionic aldehyde. This proves that the lower-boiling dichloride has the structure $CH_2ClCHClCH{=}CH_2$, and was formed by the 1,2-addition of chlorine to butadiene. The 1,2-structure of the dichloride was further confirmed by oxidizing it with potassium permanganate in dilute alcoholic solution. α,β-Dichloropropionic acid was isolated from the reaction product.

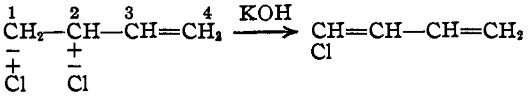
On oxidizing the higher-boiling dichloride with ozone or potassium permanganate in dilute alcoholic solution, it was possible to isolate in each case chloro-acetic acid. This proves that the higher-boiling dichloride has the 1,4-structure, $CH_2ClCH{=}CHCH_2Cl$.

When the lower-boiling dichloride is further chlorinated to the tetrachloride, the liquid tetrachloride is formed to the exclusion of the solid isomer. On the other hand, the higher-boiling dichloride absorbs a molecule of chlorine to give a preponderance of the solid tetrachloride with some of the liquid isomer.

Samples of the two dichlorides and of the two tetrachlorides were reduced with powdered zinc in alcohol. In each case butadiene was formed; this was identified as the tetrabromide, m. p. 114°.

It was possible to control the chlorination of butadiene so that the dichlorides were formed almost exclusively. The detailed procedure will be found in the Experimental Part. From the results of a large number of such chlorinations it appeared that about twice as much of the 1,2-dichloride was formed as of the 1,4-dichloride.

If either of the dichlorides, the 1,2- or 1,4-isomer, is heated to about 90° with twice its weight of dry powdered potassium hydroxide, a vigorous reaction occurs, and a lower-boiling dichloride distils over. After several fractionations a colorless liquid was obtained, b. p. 85° under ordinary pressure, which proved to be monochlorobutadiene, $CHCl{=}CHCH{=}CH_2$. It polymerized on standing to a dark resinous mass. Since the 1,2-dichloride gives the same monochloride as does the 1,4-dichloride, we must conclude that the chlorine atom on carbon atom 2 must be relatively electronegative with respect to the chlorine atom on carbon atom 1, and therefore the terminal carbon atom, 1, must be electronegative relative to carbon atom 2.



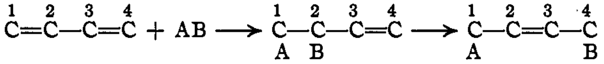
$$\overset{1}{\underset{\substack{-\\+\\Cl}}{CH_2}}-\overset{2}{\underset{\substack{+\\-\\Cl}}{CH}}-\overset{3}{CH}=\overset{4}{CH_2}\xrightarrow{KOH}\underset{Cl}{CH}=CH-CH=CH_2$$

Since many of the more recent interpretations of the addition reactions of conjugated systems are based on the assumption that the formation of 1,4-addition compounds is not due to a direct addition in the 1,4-position but rather to a rearrangement from the 1,2- or 3,4-compound, it was of considerable importance to determine whether the 1,2-dichloride was spontaneously converted into the 1,4-dichloride. In the first part of this paper reference was made to the fact that the 1,2- and 1,4-dibromides of butadiene were actually in equilibrium with each other, the change of one isomer to the other occurring slowly at room temperature but very rapidly at 100°. The change of the dichlorides into each other, if it occurred, could be followed readily by means of their refractive indices: the refractive index of the 1,2-dichloride is 1.4550 at 30.5°, and of the 1,4-dichloride, 1.4745 at 30.5°.

There was no change in the refractive indices of either of the dichlorides even after they were heated to 90° in a sealed tube for four hours, and we must therefore conclude that even under these conditions the dichlorides are stable and do not rearrange into one another.

In attempting to explain addition reactions to conjugated systems in which 1,2- 1,4- and 3,4-addition takes place, some chemists have suggested an extension of Thiele's theory from the point of view of electronic theories of polarization. According to this theory a conjugated system may polarize in two ways, $\overset{+}{C}—\overset{-}{C}—C—C$ and $\overset{+}{C}—C—C—\overset{-}{C}$, leading to reaction at adjacent (1,2 or 3,4) or terminal (1,4) carbon atoms of the chain. This theory is little more than a translation of Thiele's partial valencies into more modern terminology.

Gillet[14] has applied the principles of α,γ-rearrangements to conjugated systems and has suggested that the formation of 1,4-addition compounds is preceded by the formation of 1,2-addition compounds, as follows



$$\overset{1}{C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C} + AB \longrightarrow \underset{A}{\overset{1}{C}}-\underset{B}{\overset{2}{C}}-\overset{3}{C}=\overset{4}{C} \longrightarrow \underset{A}{\overset{1}{C}}-\overset{2}{C}=\overset{3}{C}-\underset{B}{\overset{4}{C}}$$

That this theory is not applicable to all 1,4-addition reactions of conjugated systems has been clearly shown above in the chlorination of butadiene, since the formation of 1,4-butadiene dichloride certainly could not have resulted from the rearrangement of the 1,2-isomer.

Prevost,[15] as a result of his work on conjugated systems, has included both of these possibilities in his interpretation of the addition reactions of conjugated systems, and his views are therefore open to the same criticism.

Farmer,[16] who has made an extended investigation of the addition reactions of conjugated systems, suggests the following mechanism for the bromination of butadiene

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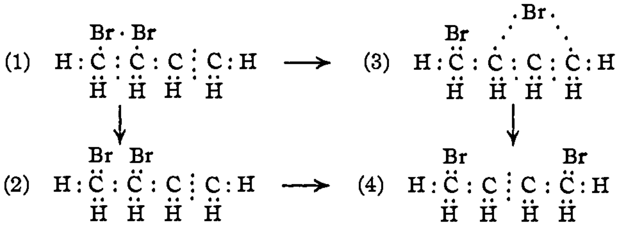
[14] Gillet, *Bull. soc. chim. Belg.*, **31**, 366 (1922).

[15] Prevost, *Ann. chim.*, [10] **10**, 113 (1928).

[16] Farmer, *J. Chem. Soc.*, 729 (1928).



in which he assumes that the first step in the reaction is the molecular addition of bromine to one of the double bonds in butadiene with the formation of the intermediate compound (1). "This has only transient existence, and breaking of the single linkage between the bromine atoms allows activity in two ways: (a) taking the course normal in the bromination of ethylenes, yielding (2), (b) bringing into action the tautomeric capacity of the propene system and passing through (3) to (4)."

Ingold[17] has classified the addenda in conjugated systems "into three categories according to whether (Case I) both parts are stable as anions (*e. g.*, Br_2), (Case II) one part is stable as an anion and the other as a kation (*e. g.*, HBr, HCN), or (Case III) both parts are stable as kations (*e. g.*, H_2)." In discussing Case I he states that in the addition of halogens to a conjugated system in a non-ionizing medium, the *initial* product formed could only be a 1,2-addition compound; the formation of any 1,4-compound would, therefore, result from the rearrangement of the 1,2-compound.

In our studies on the chlorination of butadiene, the chlorination was carried out in non-ionizing solvents (carbon disulfide, chloroform and ligroin) and in each case considerable 1,4-dichloride was formed. Since we have shown that the two dichlorides do not rearrange into one another, it is clear that the interpretation advanced by Ingold cannot explain the formation of 1,4-butadiene dichloride in a non-ionizing solvent.

One of the principal objects in this investigation of the addition reactions of conjugated systems has been to show that these addition reactions could be interpreted without recourse to any special hypothesis of conjugation. Conjugated systems differ from non-conjugated systems only in so far as the former may exhibit α,γ-rearrangements, while the latter cannot exhibit this phenomenon.

It has been quite definitely established that the addition of both components of the addendum to an ethylenic double bond does not occur simultaneously. It is more likely, as has been suggested by Stieglitz,[18] that the essential feature is the attraction of the positive substituting group to the negative carbon valencies irrespective of complete saturation. Confirmatory evidence for this hypothesis has been brought by Terry and Eichel-

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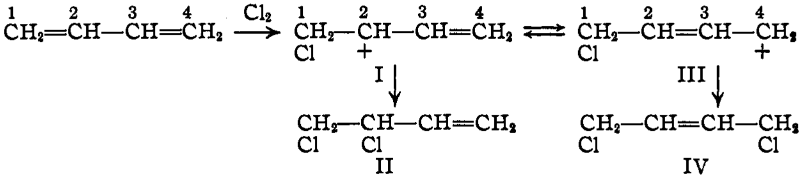
[17] Ingold, *J. Chem. Soc.*, 910 (1928); 2022 (1929).

[18] Stieglitz, This Journal, **44**, 1304 (1922).

berger[19] and by Francis,[20] who have shown that in the addition of halogens to unsaturated compounds the halogen molecule initially supplies only one halogen atom, the positively charged halogen atom, to the unsaturated substance.

Applying these same principles to the chlorination of butadiene we would have as the first step of the reaction the addition of the positive chlorine atom to the terminal carbon atom (see equation on page 4046 to give I).



$$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2 \xrightarrow{Cl_2} \underset{Cl}{\overset{1}{C}H_2}{-}\underset{+}{\overset{2}{C}H}{-}\overset{3}{C}H{=}\overset{4}{C}H_2 \rightleftharpoons \underset{Cl}{\overset{1}{C}H_2}{-}\overset{2}{C}H{=}\overset{3}{C}H{-}\underset{+}{\overset{4}{C}H_2}$$

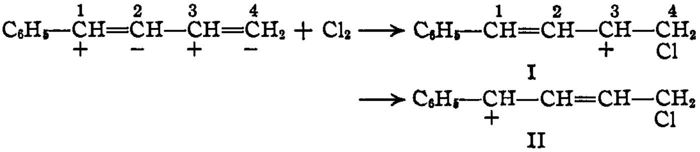
$$\text{I}\downarrow \qquad\qquad \text{III}\downarrow$$

$$\underset{\text{II}}{\underset{Cl}{CH_2}{-}\underset{Cl}{CH}{-}CH{=}CH_2} \qquad \underset{\text{IV}}{\underset{Cl}{CH_2}{-}CH{=}CH{-}\underset{Cl}{CH_2}}$$

In the second phase of this reaction the negative chlorine atom either may satisfy the positive charge on carbon atom 2 to give II, 1,2-butadiene dichloride, in a manner normal to ordinary ethylenic compounds; or this intermediate I may undergo a typical α,γ-rearrangement to III, and the negative chlorine atom would now add to the 4 carbon atom to give IV, 1,4-butadiene dichloride.

The formation of either the 1,2- or 1,4-isomer would then depend on the equilibrium of the two intermediates, I and III. This equilibrium would in turn depend on the effect of the group CH_2Cl, in this case, and upon the experimental environment, such as solvent, etc., in promoting or hindering this α,γ-rearrangement. Ingold and his students have, for some years, studied very extensively the effect of various groups in causing such rearrangements to take place, and they have found that the groups CH_2Cl- and CH_2Br- favor such rearrangements. This theory would suggest that ionization should occur preliminary to an α,γ-rearrangement. This would explain why the 1,2- and 1,4-dibromides rearrange into each other while the corresponding dichlorides do not, since it is well known that the C–Br bond is much easier to break than the C–Cl bond.

The chlorination of phenylbutadiene could be formulated as follows, employing the electronic formula for phenylbutadiene developed by Muskat and Becker[1]



$$C_6H_5{-}\underset{+}{\overset{1}{C}H}{=}\underset{-}{\overset{2}{C}H}{-}\underset{+}{\overset{3}{C}H}{=}\underset{-}{\overset{4}{C}H_2} + Cl_2 \longrightarrow \underset{\text{I}}{C_6H_5{-}\overset{1}{C}H{=}\overset{2}{C}H{-}\underset{+}{\overset{3}{C}H}{-}\underset{Cl}{\overset{4}{C}H_2}}$$

$$\longrightarrow \underset{\text{II}}{C_6H_5{-}\underset{+}{CH}{-}CH{=}CH{-}\underset{Cl}{CH_2}}$$

We would not expect to find addition taking place, in the first phase, to the 2 carbon atom, since it is well known that phenyl groups attached to a

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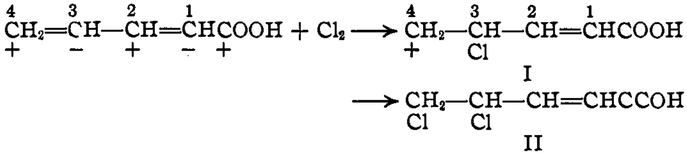
[19] Terry and Eichelberger, This Journal, **47**, 1067 (1925).

[20] Francis, *ibid.*, **47**, 2344 (1925).

double bond hinder addition to that double bond. Now, however, the effect of the phenyl group in retarding such a rearrangement I ⟶ II is far greater than the effect of the CH_2Cl group in promoting this rearrangement, and, consequently, we should expect chlorination to occur mostly in the 3,4-position. This is in agreement with the results of Muskat and Huggins,[1] who found that phenylbutadiene absorbs chlorine in the 3,4-position.

The chlorination of vinylacrylic acid presents a somewhat different condition. Again, employing the electronic formula for vinylacrylic acid developed by Muskat and Becker,[1] we see that the carbon atoms 1 and 3 are the only ones that could react in the first phase with the positive chlorine atom. Since α,β-unsaturated acids are known to add halogen with considerably more difficulty than do the corresponding β,γ- or γ,δ-unsaturated acids



$$\underset{+}{\overset{4}{CH_2}}=\underset{-}{\overset{3}{CH}}-\underset{+}{\overset{2}{CH}}=\underset{-\ \ +}{\overset{1}{CHCOOH}} + Cl_2 \longrightarrow \underset{+}{\overset{4}{CH_2}}-\underset{Cl}{\overset{3}{CH}}-\overset{2}{CH}=\overset{1}{CHCOOH}\quad \text{I}$$

$$\longrightarrow \underset{Cl}{CH_2}-\underset{Cl}{CH}-CH=CHCCOH\quad \text{II}$$

we should expect carbon atom 3 to be attacked by chlorine in preference to carbon atom 1. This is borne out by the fact that we were not able to prepare a tetrachloride of vinylacrylic acid from the 3,4-dichloride. The first step of the chlorination of vinylacrylic acid would be represented as above. Now, however, the intermediate I cannot undergo an α,γ-rearrangement and the negative chlorine atom must add to the terminal carbon atom to give a 3,4-dichloride exclusively. This is in perfect agreement with the results of Muskat, Becker and Lowenstein[1] on the chlorination and bromination of vinylacrylic acid in which they obtained only 3,4-addition products.

This same theory would apply equally well to the addition of HX and HOX to conjugated systems. An extension of this theory to reduction and oxidation of conjugated systems will be presented in a later paper.

Experimental Part

The Preparation of Butadiene.—The preparation of butadiene as finally developed consisted of three major operations: (1) converting butyl alcohol into butyl chloride, (2) chlorinating butyl chloride to dichlorobutane and (3) converting dichlorobutane into butadiene by passing it over heated soda lime.

(1) *n*-Butyl alcohol was converted into *n*-butyl chloride according to the method of Norris[6] by heating the alcohol with concentrated hydrochloric acid and anhydrous zinc chloride.

(2) The pure butyl chloride was then chlorinated to the dichloride by allowing the vapors of butyl chloride to react with chlorine gas under the influence of light. Perkin[5] describes an apparatus, which he used for this purpose, but we have remodeled and improved this apparatus so that it gives a much better yield of the chlorinated product and requires very little attention. In Fig. 1 is shown the chlorinating apparatus that was

used. A is a three-liter round-bottomed flask which contains two liters of butyl chloride heated on an electric plate. A thermometer B is immersed in the liquid in flask A; this gives the distillation temperature of the liquid. As the chlorination proceeds the distillation temperature of the liquid rises, and it is thus possible to follow the extent of the reaction. C is a heat insulated Vigreux column (about 40 cm. long), and D is the reaction tube where the chlorine gas and the vapors of the butyl chloride are mixed. The mixed vapors are carried on up the tube and are exposed to the light coming from a 1000-watt lamp placed at X. Under the influence of the light reaction occurs with the formation of the higher-boiling dichlorobutane. F is a bulb reflux condenser so designed that the openings of the bulbs are large at the bottom, where most of the condensation occurs, and become gradually smaller as they approach the top, where the condensate is slight. This type of condenser is very efficient for any purpose in which a great deal of condensate is formed. The hydrogen chloride vapors pass through the reflux condenser F and are absorbed over water. The butyl chloride in A is heated to boiling; when the butyl chloride vapors have filled tube D, the chlorine is allowed to pass in through E and the 1000-watt lamp is turned on. The chlorine is passed in through a flowmeter and a sulfuric acid wash-bottle at a rate, calculated for standard conditions, of 1120 cc. of chlorine per minute. The course of the reaction is followed by the thermometer B. At the beginning of the chlorination the temperature is 77°, the boiling point of butyl chloride. As the distillation proceeds the distillation temperature of the liquid in A rises. The chlorination is allowed to proceed until the temperature reaches 115°. This requires about six hours. If the temperature is allowed to go much higher than 115° some higher chlorinated products are formed. The time could be reduced even more if the reflux condenser F was made larger than the one we actually used. After the reaction was over the chlorinated mixture was roughly fractionated through a column one meter long filled with glass beads. The results of four such runs are recorded in Table I. In each run 2000 cc. (about 1775 g.) of butyl chloride was used. and the chlorination was continued at a constant rate for about six hours, allowing the distillation temperature to rise to 115°.

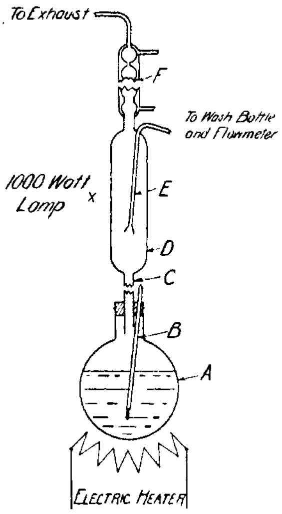


Fig. 1.

TABLE I

CHLORINATION EXPERIMENTS ON BUTYL CHLORIDE

Run no.	1 77–110°, g.	2 110–120°, g.	3 120–130°, g.	4 130–140°, g.	5 140–150°, g.	6 150–165°, g.	Residue, g.
1	242	330	503	546	166	132	100
2	382	300	472	552	191	127	114
3	392	252	418	516	169	138	100
4	292	345	500	540	207	122	107

Fraction 1 (77–110°) contains mostly unreacted butyl chloride and some of the lower dichlorides. Fraction 2 (110–120°) may very likely contain α,α-dichlorobutane, b. p. 114°. Fraction 3 (120–130°) contains most of the α,β-dichlorobutane, b. p. 125°. Fraction 4 (130–140°) contains most of the α,γ-dichlorobutane, b. p. 134–137°. Fraction 6 (150–165°) contains most of the α,δ-dichlorobutane, b. p. 161–163°. Fraction 5 (140–150°) is probably a mixture of fractions 4 and 6.

It is interesting to note that in the chlorination of butyl chloride α,γ- and α,β-dichlorobutanes are the main products. There is some α,δ- and probably some α,α-dichlorobutane formed.

(3) The different fractions of dichlorobutane were now distilled over heated soda lime, which removed two moles of hydrogen chloride to give butadiene. The apparatus that was used for this purpose is illustrated in Fig. 2. The dichlorobutane was placed in the separatory funnel A and it was allowed to flow through a tube one meter long (in order to give sufficient pressure to force the vapors through the apparatus) into the round-bottomed flask (500-cc.) B, which was heated on an electric plate. The rate of flow of the dichlorobutane and the temperature of the flask B were so controlled that the process was essentially a flash distillation. The dichlorobutane then passed into the steel tube D, which contained coarse soda lime (about 450 g.). The tube was heated to about 700–730° by means of the electric oven E. At this temperature the soda lime removed two moles of hydrogen chloride from the dichlorobutane to give butadiene.

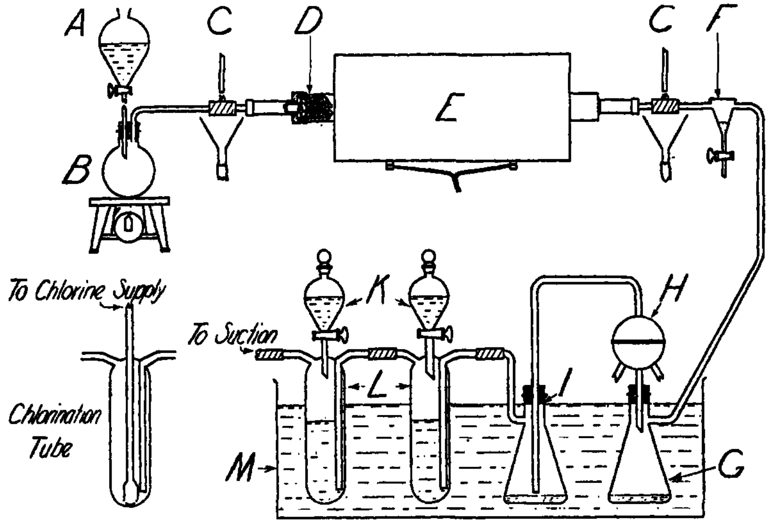


Fig. 2.

The vapors were then passed in succession through the flasks G, ball condenser H and flask I. These flasks were immersed in an ice–salt bath M and served to free the butadiene gas from water, unreacted dichlorobutane and resinous decomposition products. At C water was allowed to run over the rubber connections joining the hot steel tube D to the rest of the apparatus. F is a trap which served to collect a great deal of the water and resinous decomposition products. The butadiene coming from flask I was sufficiently pure to use in our work.

In order to determine which fraction of the dichlorobutane gave the best yield of butadiene, a number of runs were made with each of the fractions of the dichlorides. The butadiene formed was collected as the tetrabromide. For this purpose the butadiene coming from I was passed into the bromination flasks L, which were immersed in the ice–salt bath M. These flasks were about half-filled with chloroform and the bromine was added from the separatory funnels K so that an excess of bromine was always present. Usually the absorption was complete in the first flask but the second flask was used in order to prevent any possible loss of butadiene. In order to overcome the pressure in the system, a slight suction was applied at the end of the second bromination flask. At the completion of the run the brominated mixture was removed from the flasks and warmed under diminished pressure to remove any excess bromine and chloroform. At this stage some solid butadiene tetrabromide would crystallize out of solution. This was removed and the filtrate was subjected to fractional distillation under 50 mm. pressure. From the lower-boiling fractions of the chlorinated butyl chloride considerable dibromobutane distilled over at 75–82° under 50 mm. pressure. This is no doubt due to some unchanged butyl chloride still present in the chlorinated mixture, which is converted into 1-butene by the hot soda lime and which in turn is brominated to 1,2-dibromobutane. After all of the dibromobutane had distilled over, the temperature rose quickly to about 145°, at which temperature the lower-boiling stereoisomeric tetrabromide of butadiene distilled over. The temperature then rose to 175°, at which temperature the pure solid tetrabromide, m. p. 117°, distilled. The fraction from 145–175° consisted of a mixture of the two tetrabromides. From the higher-boiling fractions of the chlorinated butyl chloride the two stereoisomeric tetrabromides alone were obtained. From the combined filtered and distilled butadiene tetrabromides the yield of butadiene was calculated. In Table II are recorded the yields of butadiene obtained from 200 g. of each of the chlorinated fractions. About one hour was required for each run. Two runs were made on each fraction.

TABLE II

PERCENTAGE OF BUTADIENE OBTAINED FROM EACH OF THE CHLORINATED FRACTIONS

	1 75–110° g.	2 110–120°, g.	3 120–130°, g.	4 130–140°, g.	5 140–150°, g.	6 150–165°, g.
Butadiene tetrabromide obtained, g..........	40	118	148	174	139	146
	41	104	144	174	...	157
Yield of butadiene, %..	6.9	18.8	24.8	29.6	23.6	25.6

It is thus seen that the α,γ-dichlorobutane gave the best yield of butadiene, 29.6% of the theoretical.

The Chlorination of Butadiene.—The butadiene coming from I was passed into the chlorination tube shown in the diagram. Usually two such chlorination tubes were used and these were immersed in the ice–salt bath M. The tubes were about half filled with carbon disulfide and a slow stream of chlorine gas was passed in. At the completion of the run (about one hour for 200 g. of dichlorobutane) the chlorinated mixture was removed and freed from carbon disulfide by means of suction. The residual oil was subjected to fractional distillation. After several redistillations four fractions were collected under 40 mm. pressure: (a) 45–45.5°, (b) 75–76°, (c) 110–111°, (d) 130–134°. Each fraction was analyzed for chlorine; the first two fractions proved to be dichloro addition compounds of butadiene, while the last two fractions proved to be tetrachloro addition compounds of butadiene.

It was possible to control the chlorination of butadiene so that the dichlorides were formed almost exclusively. This was accomplished by allowing the butadiene to pass into the chlorination tubes at a more rapid rate than the chlorine. This was usually accompanied by a loss of some of the butadiene. If the chlorine was allowed to pass in at a fairly rapid rate, or if the reaction was allowed to warm up, the tetrachlorides of butadiene were formed exclusively. In one experiment the pure butadiene was chlorinated directly, without any solvent, at about −75° and the same products were formed.

1,2-Dichlorobutadiene.—The lower-boiling dichloride is a colorless oil. It distils at 45–45.5° under 40 mm. pressure and at 115° under atmospheric pressure, without decomposition. Its refractive index was determined with an Abbé refractometer; at 30.5° its refractive index is 1.4550.

Anal. Calcd. for $C_4H_6Cl_2$: Cl, 56.75. Found: Cl, 56.73, 56.80.

The structure of the lower-boiling dichloride (a) was determined by ozonization. Considerable difficulty was experienced in isolating the oxidized fragments. Its identification was finally effected by ozonizing the pure dichloride, without any solvent, and keeping the temperature of the oxidation reaction at about 0°. After the ozonization was complete, water was added to the viscous ozonide, and it was warmed on the water-bath to decompose it. The aldehydes were taken up in ether and washed several times with dilute alkali to remove any acids. If the ozonization was not allowed to continue too long, only negligible quantities of acids were formed. The ethereal solution was dried over sodium sulfate, the ether removed by suction, and the residual oil was distilled under diminished pressure. Most of it distilled over at 73° under 50 mm. pressure, the boiling point of α,β-dichloropropionic aldehyde. This was further identified by treating with sodium acetate according to the method of Piloty and Stock,[21] which converted the dichloride into α-chloro-acrolein. This distilled over at 40° under 30 mm. pressure, the recorded boiling point of α-chloro-acrolein. The water solution remaining from the ethereal extract gave the usual color tests for formaldehyde. This proved that the lower-boiling dichloride (a) has the 1,2-structure, $CH_2ClCHClCH{=}CH_2$.

This structure was further confirmed by oxidizing the lower dichloride with potassium permanganate in dilute alcoholic solution. An acidic oil was obtained which crystallized on standing to a solid melting at 50°, the recorded melting point of α,β-dichloropropionic acid.

1,4-Dichlorobutadiene.—The higher-boiling dichloride (b), when first distilled, is a yellow oil with a pungent odor, but after several distillations it is obtained as a colorless oil with a very faint odor. It distils at 75–76° under 40 mm. pressure and at about 145° under atmospheric pressure without decomposition. Its refractive index was determined with an Abbé refractometer; its refractive index is 1.4745 at 30.5°.

Anal. Calcd. for $C_4H_6Cl_2$: Cl, 56.75. Found: Cl, 56.84, 56.97.

The structure of the higher-boiling dichloride (b) was determined in a manner entirely analogous to the method used for the lower-boiling dichloride. However, in this case, no difficulty was encountered in working up the products of oxidation. A number of oxidation experiments were carried out both with ozone and potassium permanganate and in every case a good yield of chloro-acetic acid was isolated. This was identified by its melting point, 62°, and the melting point of a mixture with a sample of known origin. This proves that the higher-boiling dichloride has the 1,4-structure, CH_2Cl-$CH{=}CHCH_2Cl$.

Tetrachlorobutanes.—Fractions (c) and (d) are the two stereoisomeric tetrachlorobutanes. Fraction (c) is a colorless oil with a faint odor. It distils at 110–111° under 40 mm. pressure.

Anal. Calcd. for $C_4H_6Cl_4$: Cl, 72.41. Found: Cl, 72.49, 72.57.

Fraction (d) crystallized to a solid which melted at 72°.

Anal. Calcd. for $C_4H_6Cl_4$: Cl, 72.41. Found: Cl, 72.64. 72.55.

Reduction of the Di- and Tetrachlorides of Butadiene.—Samples of each of the dichlorides and of the tetrachlorides were reduced with powdered zinc and alcohol according to the method of Thiele.[8] In each case butadiene was formed, which was identified as the tetrabromide, m. p. 114°. This proves that these chlorides are true addition products of butadiene.

1-Chlorobutadiene.—If either of the dichlorides, the 1,2- or 1,4-isomer, is heated to about 90° with twice its weight of powdered potassium hydroxide, a vigorous reaction occurs, and a lower-boiling chloride is formed and distils over through a condenser which is attached to the reaction flask. After several fractionations a colorless liquid is ob-

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[21] Piloty and Stock, *Ber.*, 31, 1385 (1898).

tained which boils at 85° under atmospheric pressure. It polymerized on standing to a dark resinous mass. It was analyzed for chlorine and proved to be the monochloride, CHCl=CHCH=CH_2.

Anal. Calcd. for C_4H_5Cl: Cl, 40.07. Found: Cl, 39.99, 40.08.

Attempted Rearrangements of the Two Dichlorides.—Samples of each of the dichlorides, the 1,2- and 1,4-isomers, were allowed to stand for several weeks at room temperature (about 25–30°) but no change in their refractive indices occurred. They were then redistilled several times at atmospheric pressure, and their refractive indices were again measured, but no change could be detected. Finally, samples of each were sealed in bomb tubes and heated for four hours at 90°. There was no change in the index of refraction of either of the two dichlorides and we must therefore conclude that even at 90° and under pressure the dichlorides are stable and do not rearrange into one another.

Summary

1. An improved method for the preparation of butadiene starting from *n*-butyl alcohol is given, including a detailed description of the apparatus used.
2. On chlorinating butadiene a mixture of two dichlorides and two tetrachlorides is obtained. The structures of the two dichlorides were proved by oxidation experiments: the lower-boiling dichloride, b. p. 45–45.5° under 40 mm. pressure, is a 1,2-dichloride—$CH_2ClCHClCH{=}CH_2$; the higher-boiling dichloride, b. p. 75–76°, is a 1,4-dichloride—$CHClCH{=}CHCH_2Cl$. The two stereoisomeric tetrachlorides distilled at 110–111° and 130–134°, respectively. The latter crystallized to a solid, m. p. 72°.
3. It was definitely established that the two dichlorides did not rearrange into each other even at 90° and under pressure.
4. On heating either of the dichlorides with solid potassium hydroxide a monochloride, b. p. 85° under atmospheric pressure, is formed. Its structure is $CHCl{=}CHCH{=}CH_2$.
5. A theory to interpret the addition reactions of conjugated systems without recourse to any special hypothesis of conjugation is presented.

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