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

Studies of Conjugated Systems. XII. The Addition of Bromine, Hydrogen Bromide and Hypobromous Acid to 1-Bromobutadiene

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In the course of an extended investigation of the properties and reactions of conjugated systems Muskat and his co-workers[1] have developed a theory of the electronic configuration and addition reactions of conjugated compounds which has proved very useful in interpreting a large number of heretofore anomalous reactions of these compounds. This theory is based on the supposition that conjugated systems differ from non-conjugated systems only in so far as the former may exhibit 1,3-rearrangement, while the latter cannot exhibit this phenomenon. It further assumes that the addition of both components of the addendum to an ethylenic double bond need not occur simultaneously, but rather, as has been suggested by Stieglitz,[2] that the essential feature is the attraction of the positive substituting group to the negative carbon valencies irrespective of complete saturation.[3]

Ingold and his collaborators[4] have developed a somewhat similar theory to interpret the addition reactions of conjugated systems. As a direct consequence of their theory Ingold and Smith[5] predicted that 1-bromobutadiene would add halogens and halogen acids in the 3,4-positions similar to 1-phenylbutadiene. Consequently they studied the addition of bromine and hydrogen bromide to 1-bromobutadiene and reported that 3,4-addition had taken place in each instance. Previous to the publication of this work we had begun an investigation of the addition of bromine, hydrogen bromide, and hypobromous acid to 1-bromobutadiene. Our results are in contradiction to those reported by Ingold and Smith, for we were able to prove definitely that bromine, hydrogen bromide, and hypobromous acid add to 1-bromobutadiene in the 1,4-positions.

Applying the principles developed by Muskat and Northrup[6] for the addition reactions of conjugated systems, to the bromination of 1-bromobutadiene, we would have as the first step of the reaction the addition of

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[1] Muskat and Becker, THIS JOURNAL, **52**, 812 (1930); Muskat and Northrup, *ibid.*, **52**, 4043 (1930); Muskat and Knapp, *Ber.*, **64**, 779 (1931); Muskat and Hudson, THIS JOURNAL, **53**, 3178 (1931); Muskat and Herrman, *ibid.*, **54**, 2001 (1932).

[2] Stieglitz, *ibid.*, **44**, 1304 (1922).

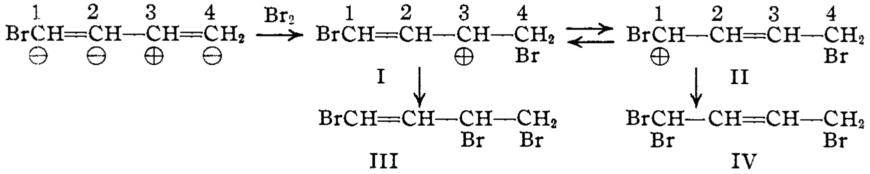
[3] In some cases, as in the reduction of conjugated compounds with sodium amalgam and similar reducing agents [see Muskat and Knapp, *Ber.*, **64**, 779 (1931)], it is the negative valencies which are first attacked.

[4] Ingold, *et al.*, *J. Chem. Soc.*, 910 (1928); *ibid.*, 2022 (1929); *ibid.*, 2752 (1931).

[5] Ingold and Smith, *ibid.*, 2752 (1931).

[6] Muskat and Northrup, THIS JOURNAL, **52**, 4049 (1930).

the positive bromine atom to the 4-carbon atom to give I.[7] In the second phase of this reaction the negative bromine atom may satisfy the positive charge on carbon atom 3 to give III, 3,4-dibromide of 1-bromobutadiene, in a manner normal to ordinary ethylenic compounds; or the intermediate I may undergo a typical 1,3-rearrangement to II, and the negative bromine atom could now add to the 1-carbon atom to give IV, 1,4-dibromide of 1-bromobutadiene. The formation of either the 1,4- or 3,4-isomer depends on the equilibrium of the two intermediates, I and II. This equilibrium in turn depends on the relative effects of the groups Br- and CH_2Br-, and upon the experimental environment in promoting or hindering this 1,3-rearrangement. Now if the effect of the CH_2Br group in promoting such a rearrangement is greater than the effect of the Br group in retarding this rearrangement, then we should expect bromination to occur mostly in the 1,4-positions. These are exactly the results we obtained. Of course the addition of hydrogen bromide and hypobromous acid may be explained in a similar manner.



$$\begin{array}{ccccc}
\overset{1}{\underset{\ominus}{\mathrm{BrCH}}}=\overset{2}{\underset{\ominus}{\mathrm{CH}}}-\overset{3}{\underset{\oplus}{\mathrm{CH}}}=\overset{4}{\underset{\ominus}{\mathrm{CH_2}}} & \xrightarrow{\mathrm{Br_2}} & \overset{1}{\mathrm{BrCH}}=\overset{2}{\mathrm{CH}}-\overset{3}{\underset{\oplus}{\mathrm{CH}}}-\overset{4}{\underset{\mathrm{Br}}{\mathrm{CH_2}}} & \rightleftarrows & \overset{1}{\underset{\oplus}{\mathrm{BrCH}}}-\overset{2}{\mathrm{CH}}=\overset{3}{\mathrm{CH}}-\overset{4}{\underset{\mathrm{Br}}{\mathrm{CH_2}}} \\
 & & \mathrm{I}\ \downarrow & & \downarrow\ \mathrm{II} \\
 & & \mathrm{BrCH}=\mathrm{CH}-\underset{\mathrm{Br}}{\mathrm{CH}}-\underset{\mathrm{Br}}{\mathrm{CH_2}} & & \underset{\mathrm{Br}}{\mathrm{BrCH}}-\mathrm{CH}=\mathrm{CH}-\underset{\mathrm{Br}}{\mathrm{CH_2}} \\
 & & \mathrm{III} & & \mathrm{IV}
\end{array}$$

The addition of bromine to 1-bromobutadiene was studied first. It was found that one mole of bromine was readily absorbed to give a dibromide addition product distilling at 94° under 8 mm. pressure. The bromination was effected in ligroin, chloroform and acetic acid solutions and in each case the same dibromide addition product was isolated. The structure of the dibromide addition product was determined by oxidation. Three dibromide addition products are theoretically possible, depending on whether 1,2-, 1,4-, or 3,4-addition takes place. If 1,2-addition occurs then on ozonization and subsequent hydrolysis formaldehyde, 1,2,2'-tribromopropionic aldehyde or their respective acids should be formed. If 1,4-addition occurs then on ozonization and subsequent hydrolysis bromoacetaldehyde, dibromoacetaldehyde (or rather, its hydrolysis and oxidation products, glyoxalic acid and oxalic acid) or their respective acids should be formed. If 3,4-addition occurs then bromoformaldehyde (or rather its decomposition products), 1,2-dibromopropionic aldehyde or their respective acids should be formed.

The dibromide addition product was oxidized both with ozone and potassium permanganate in acetone solution, and in each case bromoacetic acid was the main product. Oxalic acid was also isolated in some of the

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(7) The plus and minus signs do not imply a complete transfer of an electron from one atom to another. They indicate merely a displacement of the electrons from their central positions. We propose to use the encircled plus and minus signs to differentiate them from ionic charges.

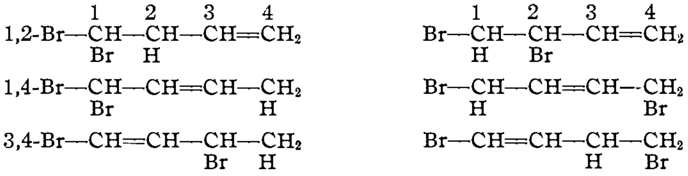
ozonization experiments, and qualitative tests for glyoxalic acid were obtained. In not one of the large number of oxidation experiments that were performed were we able to detect any formaldehyde, 1,2-dibromopropionic aldehyde or bromoacraldehyde. This proves that 1-bromobutadiene absorbs bromine in the 1,4-positions to give 1,1′,4-tribromo-Δ^2-butene, rather than in the 3,4-positions to give 1,3,4-tribromo-Δ^1-butene as claimed by Ingold and Smith. As evidence for their structure Ingold and Smith state that they obtained carbon monoxide, hydrogen bromide and 1-bromoacraldehyde. The 1-bromoacraldehyde was identified by its carbon and hydrogen analysis (no bromine analysis is given), which is the same for oxalic acid, one of the products we isolated. However, they prepared a semicarbazone derivative which melted at 160°, the melting point of the semicarbazone of 1-bromoacraldehyde, and a mixture with the known semicarbazone also melted at 160°. This evidence is not so conclusive since the semicarbazone of 1-bromoacraldehyde melts with decomposition.[8]

In order to make certain that no rearrangement occurred during the distillation, the bromination of the 1-bromobutadiene was effected at about −20° in low-boiling ligroin and the brominated product was immediately subjected to ozonization in the ligroin solution, the temperature being kept at −20° until the ozonization was completed. The same results reported above for the distilled product were again obtained.

The 1,1′,4-tribromo-Δ^2-butene absorbs a mole of bromine to give the same mixture of pentabromobutanes as reported by Willstätter and Bruce.[9]

The addition of hydrogen bromide to 1-bromobutadiene was then studied. The structure of the product was determined by ozonization. In this case six hydrogen bromide addition products are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place and also on the relative positions taken by the hydrogen and bromine groups.

I II



I

$\text{1,2-Br—}\underset{\text{Br}}{\overset{1}{\text{CH}}}\text{—}\underset{\text{H}}{\overset{2}{\text{CH}}}\text{—}\overset{3}{\text{CH}}\text{=}\overset{4}{\text{CH}_2}$

$\text{1,4-Br—}\underset{\text{Br}}{\text{CH}}\text{—CH=CH—}\underset{\text{H}}{\text{CH}_2}$

$\text{3,4-Br—CH=CH—}\underset{\text{Br}}{\text{CH}}\text{—}\underset{\text{H}}{\text{CH}_2}$

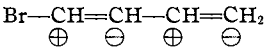
II

$\text{Br—}\underset{\text{H}}{\overset{1}{\text{CH}}}\text{—}\underset{\text{Br}}{\overset{2}{\text{CH}}}\text{—}\overset{3}{\text{CH}}\text{=}\overset{4}{\text{CH}_2}$

$\text{Br—}\underset{\text{H}}{\text{CH}}\text{—CH=CH—}\underset{\text{Br}}{\text{CH}_2}$

$\text{Br—CH=CH—}\underset{\text{H}}{\text{CH}}\text{—}\underset{\text{Br}}{\text{CH}_2}$

Since 1-bromobutadiene most likely has the structure



$$\text{Br—}\underset{\oplus}{\text{CH}}\text{=}\underset{\ominus}{\text{CH}}\text{—}\underset{\oplus}{\text{CH}}\text{=}\underset{\ominus}{\text{CH}_2}$$

we should expect that the hydrogen bromide addition product would have a structure as represented in Series I rather than in Series II. Also, as a result of our theoretical developments with regard to the addition

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(8) Von Auwers and Müller, *Ann.*, **434**, 168 (1923).

(9) Willstätter and Bruce, *Ber.*, **40**, 3994 (1907).

reactions of conjugated systems, we should expect 1,4-addition to take place. The final proof of the structure of the hydrogen bromide addition product fully confirmed these views. On ozonizing the hydrogen bromide addition product it was possible to isolate both oxalic and acetic acids from the ozonized product. These acids could only result from the oxidation of a 1,4-addition product as represented in Series I. No trace of formaldehyde or brominated propionic acid derivatives which would result from the oxidation of 1,2- or 3,4-addition products, could be obtained. This proves that hydrogen bromide is absorbed in the 1,4-positions to give 1,1′-dibromo-Δ^2-butene, rather than in the 3,4-positions to give 1,3-dibromo-Δ^1-butene as claimed by Ingold and Smith.

The crude hydrogen bromide addition product was subjected to ozonization without any preliminary distillation in order to eliminate the possibility of rearrangement. The same oxidation products were isolated as with the pure distilled 1,1′-dibromo-Δ^2-butene reported above.

The 1,1′-dibromo-Δ^2-butene was dissolved in chloroform and one mole of bromine was added. The reaction was quite rapid. A product was obtained which distilled at 148–150° under 25 mm. pressure, and analysis showed it to be 1,1′,2,3-tetrabromobutane.

Finally the addition of hypobromous acid to 1-bromobutadiene was studied. It was found that one mole of hypobromous acid was readily absorbed to give a product which upon analysis proved to be a monohypobromous acid addition product. Its structure was determined by ozonization. Again, as above with the hydrogen bromide addition product, six mono-addition products are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place and also on the relative positions taken by the bromine and hydroxyl groups. In this case 1,4-addition was expected to give 1,4-dibromo-1-hydroxy-Δ^2-butene. This structure was fully confirmed by the isolation of oxalic acid and bromoacetic acid, which could only have resulted from the oxidation of this compound. No trace of any products which might have resulted from the 1,2- or 3,4-addition of hypobromous acid to 1-bromobutadiene were found.

These results on the addition of bromine, hydrogen bromide and hypobromous acid to 1-bromobutadiene, although in contradiction with the results of Ingold and Smith, are in full accord with the theoretical developments of Muskat and Northrup.[6]

Experimental Part

The Bromination of 1-Bromobutadiene.—1-Bromobutadiene was prepared according to the method of Willstätter and Bruce[9] by the dry distillation of the 1,4-dibromide of butadiene with pulverized potassium hydroxide.[10] The pure 1-bromobutadiene dis-

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(10) Muskat and Northrup [THIS JOURNAL, **52**, 4055 (1930)] used the same method for the preparation of 1-chlorobutadiene. The boiling point of the 1-chlorobutadiene is 65–67° rather than 85° as stated on page 4055.

tils at 92–94° under atmospheric pressure. The theoretical amount of bromine (one mole) dissolved in low-boiling ligroin was added to the 1-bromobutadiene dissolved in ligroin. Absorption took place fairly rapidly and the reaction mixture became warm. The ligroin was removed by means of suction and the resulting oil was distilled under reduced pressure. A light colored oil was distilled over at 94° under 8 mm. pressure.

Anal. Calcd. for $C_4H_5Br_3$: Br, 81.91. Found: Br, 81.87, 82.20.

The conditions under which the 1-bromobutadiene was brominated were varied considerably. Various solvents such as ligroin, chloroform and glacial acetic acid were used and the temperature was varied from about −20° to about 50°. However, in all cases only one dibromide was obtained, regardless of the experimental conditions employed.

The 1-bromobutadiene dibromide, dissolved in dry carbon tetrachloride, was subjected to ozonization and the ozonide was decomposed with water. To assure complete decomposition, it was warmed on the water-bath for a short time. The mixture was free of aldehydes, as was shown by a negative fuchsin test. The water solution was extracted with ether a number of times, the ether extract was dried over anhydrous sodium sulfate and the ether was removed by means of suction. An oil remained which crystallized on standing. The crystals melted at 50°, the melting point of bromoacetic acid. A mixture with known bromoacetic acid also melted at 50°. The aqueous solution remaining from the ether extraction was carefully evaporated to dryness and further heated in the oven to 110° for several hours. The residue melted at 187°, the melting point of anhydrous oxalic acid. A mixture with pure oxalic acid also melted at 187°. The oxalic acid was further identified by a quantitative titration with standard potassium permanganate. A 43% yield of oxalic acid was isolated in one experiment. In some of the ozonization experiments color tests for glyoxalic acid with concentrated sulfuric acid were obtained.

The 1-bromobutadiene dibromide was also oxidized with potassium permanganate in acetone solution according to the method of Staudinger.[11] On working up the oxidized products as described by Staudinger, a considerable amount of bromoacetic acid was obtained which was identified as above.

In one experiment the 1-bromobutadiene was brominated in ligroin solution at −20°, and the ligroin solution at that temperature was directly subjected to ozonization without preliminary distillation. At no time was the temperature allowed to rise above −20°. On working up the oxidized product, both bromoacetic and oxalic acids were isolated and identified as above.

The 1-bromobutadiene dibromide absorbs one mole of bromine to give a mixture of pentabromobutanes. This mixture was identical with a mixture of pentabromobutanes obtained by Willstätter and Bruce by treating 1-bromobutadiene with an excess of bromine.[9]

The Addition of Hydrogen Bromide to 1-Bromobutadiene.—Dry hydrogen bromide, free from bromine, was passed directly into 1-bromobutadiene without the use of any solvent. Absorption took place fairly readily. If ether is used as a solvent, the absorption is very slow and incomplete. After one mole of hydrogen bromide had been absorbed, the dissolved hydrogen bromide was removed by means of suction and the resulting oil was distilled under atmospheric pressure. The largest part of the distillate came over at 155–157°. It was redistilled under 24 mm. pressure, the entire product distilling over at 71–72°. The product was analyzed soon after distillation, for decomposition occurs on standing.

Anal. Calcd. for $C_4H_6Br_2$: Br, 74.77. Found: Br, 74.54, 74.51.

The dibromobutene was dissolved in chloroform and subjected to ozonization. The

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[11] Staudinger, *Helv. Chim. Acta*, **5**, 766 (1922).

ozonized product was worked up in a manner entirely analogous to the method described above for the 1-bromobutadiene dibromide. Both oxalic and acetic acids were isolated from the ozonized product. The oxalic acid was identified by its calcium salt and by titration with standard potassium permanganate. A 30% yield of oxalic acid was isolated in one experiment. The acetic acid was identified by its boiling point, formation of ethyl acetate with ethyl alcohol and sulfuric acid, the cacodyl test, and by the preparation of the *p*-toluide of acetic acid, m. p. 146°, which is the melting point of aceto-*p*-toluide. A mixture with a known product also melted at 146°.

In one experiment the crude hydrogen bromide addition product was subjected to ozonization without any preliminary distillation. At no time was the temperature allowed to rise above 0°. On working up the oxidized product, both acetic and oxalic acids were isolated and identified as above.

The 1,1′-dibromo-Δ^2-butene was dissolved in chloroform and one mole of bromine was added. The reaction was quite rapid. The chloroform was removed by means of suction and the resulting oil was distilled under reduced pressure. The major portion distilled over at 148–150° under 25 mm. pressure. Its analysis showed it to be 1,1′,2,3-tetrabromobutane.

Anal. Calcd. for $C_4H_6Br_4$: Br, 85.56. Found: Br, 85.32, 85.47.

The Addition of Hypobromous Acid to 1-Bromobutadiene.—The hypobromous acid was prepared by allowing bromine to drop slowly into a finely divided suspension of mercuric oxide in water at about −5°. A 1–2% solution of hypobromous acid, free from bromine, was used in these experiments.

1-Bromobutadiene was treated with the theoretical quantity of hypobromous acid solution. Absorption took place quite readily. The reaction product was extracted with ether, the solution was washed free of halides and dried over anhydrous sodium sulfate, and the ether was removed by means of suction. The resulting oil was analyzed and proved to be the bromohydrin of 1-bromobutadiene.

Anal. Calcd. for $C_4H_6OBr_2$: Br, 69.56. Found: Br, 69.56, 69.73.

The bromohydrin was dissolved in chloroform and subjected to ozonization. The ozonized product was worked up in a manner entirely analogous to the method described above. Both oxalic acid and bromoacetic acid were isolated from the ozonized product and they were identified exactly as described above for the 1-bromobutadiene dibromide.

Summary

1-Bromobutadiene absorbs bromine, hydrogen bromide and hypobromous acid in the 1,4-positions and not in the 3,4-positions as stated by Ingold and Smith. This is in direct accord with the theoretical developments of Muskat and his collaborators.

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