[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Butylacetylene with Hydrogen Bromide[1]

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Although it is a problem of much interest, relatively little attention has been directed toward the addition of hydrogen bromide to acetylene compounds. Bauer[2] obtained vinyl bromide and ethylene dibromide from acetylene and hydrogen bromide in the presence of gaseous oxidizing agents. Using catalysts such as mercuric bromide on asbestos, Wibaut[3] obtained from acetylene and hydrogen bromide a mixture of ethylidene dibromide and ethylene dibromide, the latter compound being formed in the larger amount. Réboul[4] found that aqueous hydrogen bromide and methylacetylene reacted to form 2,2-dibromopropane and a small amount of 2-bromopropene.

During the course of the investigation in this Laboratory, there appeared two papers which furnished further data on the addition of hydrogen bromide to acetylene compounds. Harris and Smith[5] found that in the presence of perbenzoic acid hydrogen bromide added to 10-undecynoic acid to yield the 11-bromo acid, while in the absence of peroxides the 10-bromo acid was formed. Only one molecule of hydrogen bromide was added. On adding hydrogen bromide to methylacetylene Kharasch, McNab and McNab[6] obtained 1,2-dibromopropane in the presence of ascaridole, and 2,2-dibromopropane in the absence of peroxides. No monobromopropenes were obtained. The results of these two papers agree with certain portions of the present communication.

The existence of peroxides in many acetylene derivatives has been demonstrated by Young, Vogt and Nieuwland.[7] In view of the importance in the field of olefins of the peroxide effect discovered by Kharasch and Mayo,[8] it has been deemed advisable to study carefully the influence of peroxides on the addition of hydrogen bromide to some convenient member of the acetylene series. For this purpose butylacetylene has been chosen.

When hydrogen bromide is passed into butylacetylene containing an appreciable amount of peroxides, there is formed a mixture of 1-bromo-1-hexene and 1,2-dibromohexane in quantities depending on the conditions of the experiment. At 0° the hydrogen bromide is absorbed very rapidly and at the end of an hour only a small amount of unreacted butylacetylene remains. The product of the reaction is 1-bromo-1-hexene, together with a small amount of 1,2-dibromohexane. If the reaction is carried out for a longer period of time, greater amounts of 1,2-dibromohexane are formed. There is no formation of 2-bromo-1-hexene in the presence of peroxides.

The reaction of hydrogen bromide with butylacetylene in the absence of peroxides occurs at a very much slower rate. In order to accelerate the addition the reaction was carried out at 15°. In one experiment using hydroquinone as the inhibitor and toluene as a solvent, less than one-half of the butylacetylene reacted in six hours, and the products of the reaction consisted of about one-sixth 2-bromo-1-hexene and about five-sixths 1-bromo-1-hexene. Since the hydrogen bromide was not completely free from oxygen, the 1-bromo-1-hexene was probably produced by the formation of a trace of peroxide in the reaction mixture.

It has been found that ferrous salts rapidly destroy the peroxides which are formed in butylacetylene. Consequently, in attempting to add hydrogen bromide to butylacetylene in the absence of peroxides, both hydroquinone and ferrous bromide were finally used as inhibitors. No solvent was used, and the reaction was carried out at 15°. At the end of twelve hours about one-half of the butylacetylene had not yet reacted, and the remainder of the butylacetylene had been converted to 2-bromo-1-hexene and 2,2-dibromohexane, together with a small quantity of 1-bromo-1-hexene.

The addition of hydrogen bromide to butylacetylene in the presence and in the absence of peroxides has therefore been shown to be similar

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(1) Fourteenth paper of a recent series on the reactions of alkylacetylenes; previous paper, *J. Org. Chem.*, **1**, 163 (1936). Original manuscript received January 20, 1936.

(2) Bauer, U. S. Patent 1,414,852; *C. A.*, **16**, 2150 (1922); U. S. Patent 1,540,748; *C. A.*, **19**, 2210 (1925).

(3) Wibaut, *Rec. trav. chim.*, **50**, 313 (1931).

(4) Réboul, *Ann. chim. phys.*, [5] **14**; 465 (1878).

(5) Harris and Smith, *J. Chem. Soc.*, 1572 (1935).

(6) Kharasch, McNab and McNab, THIS JOURNAL, **57**, 2463 (1935).

(7) Young, Vogt and Nieuwland, *ibid.*, **56**, 1822 (1934); *ibid.*, **58**, 55 (1936); *J. Chem. Soc.*, 115 (1935).

(8) Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933).

to the additions of hydrogen bromide which numerous workers have obtained with olefins having a terminal double bond. However, the results with butylacetylene are particularly interesting because the peroxide effect is shown in the addition of both one and two molecules of hydrogen bromide.

In order to obtain further information concerning the manner in which the dibromohexanes were formed, hydrogen bromide was added to 1-bromo-1-hexene and to 2-bromo-1-hexene, both in the presence and in the absence of peroxides. With 1-bromo-1-hexene containing a small amount of peroxide, hydrogen bromide reacted rapidly at 10°, giving at the end of one and one-half hours a 75% yield of 1,2-dibromohexane. No 1,1-dibromohexane was formed. Using hydroquinone and ferrous bromide as inhibitors, hydrogen bromide was passed for one hundred and twenty hours into 1-bromo-1-hexene at room temperature. The only reaction product was a small quantity of 1,2-dibromohexane. It is evident that the "normal" addition to form 1,1-dibromohexane occurs very slowly, if at all, under the conditions used.

In the presence of peroxides hydrogen bromide reacted readily with 2-bromo-1-hexene at 25°, most of the olefin being converted to 1,2-dibromohexane in four hours. No 2,2-dibromohexane was formed. On the other hand, the addition of hydrogen bromide to 2-bromo-1-hexene in the absence of peroxides, using hydroquinone and ferrous bromide as inhibitors, was considerably slower. At a temperature of 23° about two-thirds of the olefin had reacted at the end of nine hours. The product was mainly 2,2-dibromohexane, but a small amount of 1,2-dibromohexane was also formed.

Experimental

Butylacetylene.—The butylacetylene, b. p. 70.5–70.7°, corr., (747 mm.), was prepared from sodium acetylide and butyl bromide in liquid ammonia by a modification of the method described by Lebeau and Picon.[9]

Detection of Peroxides.—In all cases where peroxides were used, they were formed by the unsaturated compounds themselves. The peroxides were estimated colorimetrically, using as the reagent an acidified solution of ferrous ammonium sulfate and ammonium thiocyanate in absolute methyl alcohol. Details of this method are to be published elsewhere.

Addition to Butylacetylene in the Presence of Peroxides.—Two typical experiments will be reported. The reactions were carried out in all experiments in a 500-cc. three-necked flask equipped with an efficient mechanical stirrer, an inlet tube and a reflux condenser. In all cases the products of the reactions were washed with aqueous sodium carbonate and then with water. The products were dried with anhydrous sodium sulfate or with calcium chloride.

In one experiment 1.5 moles of dry hydrogen bromide was passed rapidly into 82 g. (1 mole) of butylacetylene containing a fairly good quantity of peroxides (about 0.8 mole %). The reaction flask was cooled with an ice-bath. At the end of one hour the reaction was stopped. Upon distillation of the reaction mixture through an efficient column there were obtained 5 g. of unreacted butylacetylene, 120 g. of 1-bromo-1-hexene and 3 g. of 1,2-dibromohexane.

In another experiment 2 moles of hydrogen bromide was passed for three hours into 82 g. of butylacetylene containing a fair amount (about 0.6 mole %) of peroxides. The reaction flask was cooled with an ice-bath. From the reaction mixture there were obtained 85 g. of 1-bromo-1-hexene and 91 g. of 1,2-dibromohexane.

Addition to Butylacetylene in the Absence of Peroxides.—Two moles of hydrogen bromide was added to a solution of 102 g. of peroxide-free butylacetylene in 138 g. of toluene to which had been added 0.5 g. of hydroquinone. The toluene facilitated somewhat the absorption of the hydrogen bromide. The reaction flask was maintained at 17°. At the end of six hours the reaction was stopped, and the product washed and dried in the usual manner. Upon distillation of the product there were obtained 67 g. of unreacted butylacetylene, 8 g. of 2-bromo-1-hexene and 38 g. of 1-bromo-1-hexene.

Using 0.25 g. of hydroquinone and 0.5 g. of ferrous bromide as inhibitors, 4 moles of hydrogen bromide was passed into 156 g. of peroxide-free butylacetylene without any solvent. The temperature was kept at 15°, and the reaction continued for twelve hours. There were obtained on distilling the reaction product 42 g. of butylacetylene, 135 g. of 2-bromo-1-hexene, 6 g. of 1-bromo-1-hexene and 39 g. of 2,2-dibromohexane.

Addition to 1-Bromo-1-hexene.—One-half mole of hydrogen bromide was passed during a period of one and one-half hours into 54 g. (1/3 mole) of 1-bromo-1-hexene containing a trace of peroxides. The reaction temperature was 10°. On distilling the reaction product there were obtained 11 g. of unreacted 1-bromo-1-hexene and 60 g. of 1,2-dibromohexane.

A solution of 138 g. of peroxide-free 1-bromo-1-hexene, 78 g. of benzene, 0.5 g. of hydroquinone and 1 g. of ferrous bromide was kept saturated with hydrogen bromide for one hundred twenty hours at room temperature. Three moles of hydrogen bromide was used. After removing the benzene from the reaction product, there were obtained 120 g. of unreacted 1-bromo-1-hexene and 5 g. of 1,2-dibromohexane. The distillation curve gave no indication of 1,1-dibromohexane.

Addition to 2-Bromo-1-hexene.—In the presence of a small quantity of peroxide 0.4 mole of hydrogen bromide was passed into a solution of 32.6 g. (0.2 mole) of 2-bromo-1-hexene in 39 g. of benzene. The solution was kept at 25°. The reaction was continued for four hours. The

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(9) Lebeau and Picon, *Compt. rend.*, **156**, 1077 (1913); Picon, *ibid.*, **158**, 1346 (1914); *ibid.*, **169**, 32 (1919).

reaction product consisted of 3.5 g. of 2-bromo-1-hexene and 41 g. of 1,2-dibromohexane.

One-half mole of hydrogen bromide was passed for nine hours into a solution of 32.6 g. of peroxide-free 2-bromo-1-hexene in 39 g. of benzene; 0.2 g. each of hydroquinone and ferrous bromide were used to inhibit peroxide formation. The temperature of the reaction was 23°. The reaction product contained 10 g. of unreacted 2-bromo-1-hexene, 24 g. of 2,2-dibromohexane and 4 g. of 1,2-dibromohexane.

Identification of Products.—The properties of 2-bromo-1-hexene, b. p. 132.5–133.5° (740 mm.), n^{19}_D 1.4555, d_{20} 1.1960, agree closely with those reported by Bourguel:[10] b. p. 134° (760 mm.), n^{19}_D 1.455, d_{19} 1.203.

The 1-bromo-1-hexene had the properties: b. p. 139–141° (751 mm.), n^{20}_D 1.4596, d_{21} 1.1998. Bachman[11] reported for this compound: b. p. 138–140° (747 mm.), n^{20}_D 1.4584, d^{20}_{20} 1.1910. The slight discrepancy in these physical constants may be caused by a difference in the ratio of *cis-trans* isomers obtained in the two cases. The 1-bromo-1-hexene was analyzed for bromine by the method of Chablay, as modified by Vaughn and Nieuwland:[12] calcd. for $C_6H_{11}Br$, 49.0; found, Br, 49.1.

The properties of the 1,2-dibromohexane, b. p. 89–90° (18 mm.), n^{20}_D 1.5023, d_{21} 1.5767, agree well with those reported by Schmitt and Boord:[13] b. p. 89–90° (18 mm.), n^{20}_D 1.5024, d_{20} 1.5774.

The 2,2-dibromohexane has not been reported previously. The following physical constants were obtained: b. p. 83.5–84.0° (24 mm.), n^{22}_D 1.4930, calcd. MR_D 45.45, found MR_D 45.57, d_{22} 1.5463. *Anal.*:[12] calcd. for $C_6H_{12}Br_2$: Br, 65.5; found: Br, 65.4. The identity of the 2,2-dibromohexane was established by hydrolyzing it to 2-hexanone. This was accomplished by refluxing with silver sulfate in 10% sulfuric acid. The 2-hexanone boiled at 126.1° (747 mm.), reported b. p. 126.0–126.5° (760 mm.),[14] and the semicarbazone melted at 118°, reported m. p. 118°.[15]

Summary

1. The addition of hydrogen bromide to butylacetylene in the presence of peroxides derived from butylacetylene yielded 1-bromo-1-hexene and 1,2-dibromohexane.
2. In the absence of peroxides hydrogen bromide yielded mainly 2-bromo-1-hexene and 2,2-dibromohexane.
3. The addition of hydrogen bromide was much more rapid in the presence of peroxides than in their absence.
4. The addition of hydrogen bromide to 1-bromo-1-hexene in the presence of peroxides formed only 1,2-dibromohexane, while in the absence of peroxides scarcely any reaction occurred under the conditions used. No 1,1-dibromohexane was formed in either case.
5. In the presence of peroxides 2-bromo-1-hexene yielded with hydrogen bromide only 1,2-dibromohexane; under peroxide-free conditions the chief product was 2,2-dibromohexane, the other product being 1,2-dibromohexane.

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[10] Bourguel, *Compt. rend.*, **177**, 688 (1923).

[11] Bachman, THIS JOURNAL, **55**, 4282 (1933).

[12] Vaughn and Nieuwland, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 274 (1931).

[13] Schmitt and Boord, THIS JOURNAL, **54**, 760 (1932).

[14] Clarke, *ibid.*, **34**, 681 (1912).

[15] Michael, *ibid.*, **41**, 416 (1919).

[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

Extensions of the Leuckart Synthesis of Amines

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The conversion of certain ketones (and aldehydes) to the corresponding amines by heating with excess ammonium formate was described by Leuckart[1] as early as 1885. The mechanism of the reaction has been discussed by Wallach,[2c] but is not definitely known. The equation

$$R—CO—R' + 2HCO_2NH_4 \longrightarrow R—CH(NHCHO)R' + 2H_2O + NH_3 + CO_2$$

appears to summarize the primary reaction, although formamide is doubtless an intermediate and may be used instead of ammonium formate. The amine is formed by subsequent hydrolysis of the formyl derivative.

Although Leuckart's method has been applied by Wallach[2] to a number of alicyclic and terpenoid ketones, and appears to be rather general, it has found little use by others. Possibly the obvious advantages of economy and simplicity have appeared to be outweighed by the unsatisfactory procedures that have so far been suggested. Leuckart himself, and also Wallach, ordinarily heated the reagents in a sealed tube at 210–240°. In some instances, however, Wallach[2b,2c] and others[3] have shown that the primary reaction

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[1] Leuckart, *et al.*, *Ber.*, **18**, 2341 (1885); **19**, 2128 (1886); **20**, 104 (1887); **22**, 1409, 1851 (1889).

[2] Wallach, *et al.*, (a) *ibid.*, **24**, 3992 (1891); *Ann.*, **269**, 347 (1892); **276**, 306 (1893); (b) *ibid.*, **300**, 283 (1898); (c) *ibid.*, **343**, 54 (1905).

[3] (a) Freylon, *Ann. Chim.*, [8] **15**, 141 (1908); (b) Read and Robertson, *J. Chem. Soc.*, 2217 (1926); (c) Read and Johnston, *ibid.*, 231 (1934).