Summary

Hexamethylethane can be prepared readily in 10% yield by adding magnesium to a refluxing ether solution of t-butyl chloride.

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

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. V. The Addition of Hydrogen Bromide to Butene-1

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Introduction

It has been stressed in previous communications from this Laboratory[1] that the direction of addition of hydrogen bromide to some unsaturated compounds is controlled by the peroxide content of the material. Of particular importance was the observation that the product of the reaction of hydrogen bromide and propylene in the presence of peroxides (benzoyl peroxide, ascaridole, etc.) was normal propyl bromide, a product never heretofore obtained under any experimental conditions. Under peroxide-free conditions isopropyl bromide was obtained in quantitative yields. The latter product was therefore called by us the normal product and the normal propyl bromide was considered the abnormal (peroxide catalyzed) product.

The necessity of further extension of these studies in the aliphatic field is self-evident. This paper records our observations on the addition of hydrogen bromide to butene-1.

Previous Work.—It was surprising to the authors to find so little in the literature about the addition of halogen acids to butene-1. Except for the recent work of Lucas and collaborators,[2] the only other observations recorded are those of Saytzeff[3] and of Lieben and Rossi.[4] The early investigators are in accord that the addition of hydrogen iodide to butene-1 leads to the formation of secondary butyl iodide. Mental reservation regarding the value of these results is in order, however, for undoubtedly these investigators used mixtures of butene-1 and butene-2 of various compositions.

Lucas and his collaborators, in a search for a method of analysis of mixtures of butene-1 and butene-2, investigated the addition of hydrogen bromide to butene-1 in glacial acetic acid. In view of the fact, however, that secondary butyl bromide was the only product, the reaction could not be employed as an analytical method, for both isomeric butenes yielded the same product.

Factors Influencing the Addition of Hydrogen Bromide to Butene-1.—Our results on the directed addition of hydrogen bromide to butene-1 indicate that this compound may be added to the list of compounds previously described in which the addition of hydrogen bromide is profoundly affected by the peroxide content of the material. Thus Table I proves quite conclusively that the addition of hydrogen bromide to butene-1 in air leads to practically quantitative yields of the secondary butyl bromide. The same results are obtained in solvents such as glacial acetic acid, nitrobenzene, dilute acetic acid, etc. The same product results also if the additions are carried out *in "vacuo"*[5] with samples of butene-1 from which air has been excluded rigorously during the preparation of the material. The effect of antioxidants of the type of diphenylamine and thiocresol is also to produce secondary butyl bromide.

The fact that in the presence of air and under antioxidant conditions the same product is obtained, can be correlated on the basis that butene-1 either is not sensitive to the peroxide effect, or the total amounts of peroxides present in butene-1 are very small. The correctness of this latter assumption can be demonstrated most readily by the ordinary peroxide test,[1] which shows that if air or oxygen is allowed to bubble through butene-1 at −80° for two hours, the material still fails to give any appreciable per-

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[1] Kharasch and collaborators, THIS JOURNAL, **55**, 2468, 2521, 2531 (1933); **56**, 712 (1934).

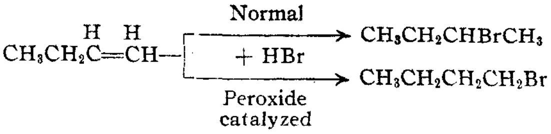
[2] Lucas, Dillon and Young, *ibid.*, **52**, 1949 (1930).

[3] Saytzeff, *J. prakt. Chem.*, **111**, 88 (1871).

[4] Lieben and Rossi, *Ann.*, **158**, 164 (1871).

[5] By "vacuo" we imply that the reagents were held at liquid air temperature while the residual gases in the bomb tubes were removed before the tubes were sealed off. Naturally as the tubes containing the addition mixture were sealed and allowed to come to room temperature, there is considerable pressure developed.

oxide test, and the addition of hydrogen bromide to such a material gives exclusively secondary butyl bromide. It appeared, therefore, that butene-1 is much less sensitive to peroxides than propylene, and it was clear that in order to change the direction of addition much more drastic means would need to be employed. Our assumption was fully justified for when the butene-1 was treated with fairly large quantities of benzoyl peroxide or ascaridole (0.05–0.1 mole), quantitative yields of normal butyl bromide were obtained. This latter product, therefore, is the abnormal product of the reaction, while the secondary butyl bromide may be considered the normal product of the reaction.



$$CH_3CH_2\overset{H}{C}{=}\overset{H}{C}H - \left[\begin{array}{l} \xrightarrow[]{\text{Normal}} CH_3CH_2CHBrCH_3 \\ \quad + HBr \\ \xrightarrow[\text{Peroxide catalyzed}]{} CH_3CH_2CH_2CH_2Br \end{array}\right.$$

The effects of other experimental conditions on the direction of addition were noted by us, and we have again established quite definitely that external conditions such as solvent, temperature or light, affect only those reactions which are peroxide-catalyzed, but have no effect on the reactions which are little sensitive to peroxides. In the case of butene-1, since the material is very little sensitive to peroxides, no change in the

TABLE I

ADDITION OF HYDROGEN BROMIDE TO BUTENE-1[a,b,i]

No.	HBr, moles	Antioxidant or peroxide, moles	Solvent, moles	Reaction time in hours	Total yield, %	B. p., °C.	n_D^{20} [c]	Normal butyl bromide, %
1	1.56	None	None	24	90	89–90	1.4979	0
2	1.45	None	Gl. HAc	24	80	89–90	1.4968	0
3	1.57	0.05 Thiocresol	Gl. HAc*[i]	24	80	89–90	1.4968	0
4	1.53	None	None*[i]	18	85	89–90	1.4968	0
5	1.72	0.06 Thiocresol + 0.001 $MnCl_2$	2.64(*) Ligroin[i]	90	69	87.0–91.5	1.4361[d]	0
6	1.74	0.06 Ascaridole	0.7 Ligroin	3.5	76	101.0–101.5	1.4396[e]	100
7	1.68	0.1 Ascaridole	None	3.5	95	99.5–100.3	1.4395	100
8	1.12	Small amts. ozone[f]	None	3	42	90.0–95.0[f] 75% 90–91.6		10
9	1.64	0.1 Ascaridole	None	17	89	97.5–102.6 82% 97.5–101.4	1.4391	85
10	1.79	0.05 Ascaridole	None	4	80	93.5–101.0 95% 96–101	1.4392	90
11	1.79	Oxygen passed through butene for 2.5 hrs. before addn. of HBr	None	4	37	89.5–90.4[g] 80% at 90.4	1.4369	0
12	1.54	0.032 Benzoyl peroxide	None	4	80	90.0–100.7[h] 72% 97.7–100.7	1.4390	82
13	1.50	0.027 Diphenyl amine	None(*)[i]	5.5	64	90.4–90.6	1.4369	0
14	1.83	0.038 Dicyclohexylamine oxide	None	4.5	51	90.5–90.8	1.4368	0

[a] The bombs were all kept at −80° during the introduction of hydrogen bromide. They were then sealed off and the final addition allowed to take place at room temperature.

[b] The results recorded in this table are the averages of at least two or more experiments none of which differed by more than 5%.

[c] The index of refraction for the best grade of Eastman *n*-butyl bromide which boiled within a range of 101.0–101.1° was 1.4395. The index for the secondary bromide was 1.4369. While the absolute values differed from those given by Lucas and collaborators (*loc. cit.*), the difference between the indices of primary and secondary butyl bromides is the same.

[d] Low refractive index due to the difficulty of removing last traces of ligroin.

[e] The mercury compound (C_4H_4HgBr) was prepared by the usual method; without crystallization it melted at 125°. M. p. of *n*-butyl mercuric bromide 128°, secondary butyl mercuric bromide 39°.

[f] There was a flash of light in the tube before it was sealed and again after it was sealed. A deposit of carbon formed in the tube. Contents of tube lost before index of refraction was determined.

[g] About 25% of contents of bomb did not distil during vacuum distillation. This residue was clear and colorless. It is being investigated.

[h] A low boiling, red, fluorescent substance passed over in first cc. of distillate.

[i] All the additions were carried out in the presence of air except those marked with an asterisk which were evacuated.

direction of addition could be accomplished by any of the experimental conditions mentioned above. The only factor that changed the order of addition of hydrogen bromide to butene-1 was the presence of a fairly large quantity of organic peroxides.

An appreciation of the facts mentioned above is of tremendous significance, for it can be seen that in discussing the effects of external conditions on the direction of addition, one must know beforehand whether the material is or is not sensitive to peroxides. In the former case the external conditions show a tremendous effect through their effect on the peroxides. On the other hand, if the system is little sensitive to peroxides, the external conditions play a very small part in determining the direction of addition of the halogen acid.

It is noteworthy that peroxides have no effect on the final products of addition once they are formed. Numerous experimental variations were tried to test the validity of this statement. In all cases, however, except for small losses, the starting materials were recovered unchanged. The peroxides must therefore exert their peculiar effect on the direction of addition through their effect on the hydrogen bromide or the unsaturated compound or both before addition has actually taken place.

Experimental Part

The method of working up a product of the reaction of butene-1 and hydrogen bromide was the same as described in some of our previous publications.[1] The determination of the relative amounts of the addition products was made by index of refraction. Previous work by us has shown that this method is a reliable one for a semi-quantitative estimation of the relative amounts of the two addition products. As a final proof of the structure of the final product, mercury compounds were made. In all cases perfect agreement was noted between the boiling points, indices of refraction and the melting points (before crystallization) of the mercury compounds.

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Summary

1. It has been shown that butene-1 will add hydrogen bromide under antioxidant conditions to give quantitative yields of secondary butyl bromide.

2. It has been shown that in the presence of air secondary butyl bromide is formed.

3. It has been shown that in the presence of peroxides the addition of hydrogen bromide to butene-1 is reversed and normal butyl bromide is formed.

4. The conclusion is drawn that butene-1 is less sensitive to peroxides than allyl bromide, allyl chloride, vinyl chloride and vinyl bromide. This conclusion is based upon the fact that in air butene-1 adds hydrogen bromide to give a normal product, *i. e.*, secondary butyl bromide.

5. It has been pointed out that external conditions such as solvent, temperature, light, etc., have a very powerful effect on those systems which are very sensitive to peroxides, but practically no effect on unsaturated systems which are not sensitive to peroxides. This observation clarifies many so-called "abnormal reactions" recorded in the literature for unsaturated compounds.

6. Work on other unsaturated compounds is under way in this Laboratory.

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