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

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. VI. The Addition of Hydrogen Bromide to Isobutylene

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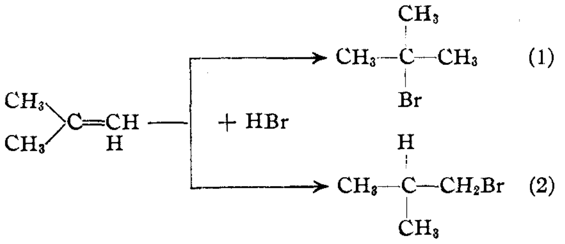
It has been shown by one of us and collaborators[1] that in the presence of antioxidants, or in air, propylene and butene-1 yield isopropyl and *s*-butyl bromide, respectively. On the other hand, in the presence of peroxides the normal bromides are obtained. The fact that in the presence of air or oxygen the secondary bromides were obtained was explained on the basis that propylene and butene-1 do not form peroxides readily. In an attempt to determine the scope of the effect of peroxides, the addition of hydrogen bromide to isobutylene was undertaken. This molecule was of particular interest, for in accordance with the postulates of one of us and collaborators,[2] the valence electrons of the double bond of this molecule are much displaced in the direction of the $-CH_2$ carbon atom. Therefore, the normal product of addition of halogen acids to that substance should lead to the formation of the tertiary butyl halide.

Our work indicates that while hydrogen bromide may add to isobutylene in two ways



the first product of the reaction, namely, the tertiary butyl bromide, is the normal product of the reaction, while isobutyl bromide is the peroxide catalyzed reaction product.

Previous Work.—Previous work[3] upon the addition of halogen acids to isobutylene showed complete agreement in that the only product of the reaction was tertiary butyl halide. It is true that Ipatieff and Ogonowsky[3] state that the direction of addition is influenced by glacial acetic acid. These investigators report that two separate additions of hydrogen bromide to isobutylene in glacial acetic acid showed, respectively, the presence of 5 and 15% of isobutyl bromide. The authors attach a great deal of significance to their findings in that they believe that a real change in the direction of addition has been accomplished by them. However, as will be shown later in our article, these results are of doubtful value, and if true must be due to impurities in the starting material. In all of our additions in glacial acetic acid, using very pure isobutylene, we have been able to obtain one product only, tertiary butyl bromide. It is true that the limit of accuracy of our analysis of mixtures is ±5%, but within those limits we have been unable to detect any isobutyl bromide in experiments which led to quantitative yields of the tertiary butyl bromide on the basis of the isobutylene used.

The work of all other investigators and particularly that of Michael and Brunel[3] can be interpreted most readily in the light of our findings on the effect of peroxides on the direction of addition, and the low susceptibility of isobutylene to the effect of peroxides.

Factors Influencing the Addition of Hydrogen Bromide to Isobutylene.—We have evaluated very carefully the addition of hydrogen bromide to isobutylene in an attempt to determine whether such factors as time of addition, light, solvent, temperature, metallic catalysts, had any effect upon the direction of addition of the hydrogen bromide to isobutylene. Some of these results are reproduced in Table I. As may be noted by an examination of that table, all of those factors have no effect upon the direction of addition of the hydrogen bromide to isobutylene: tertiary butyl bromide was obtained in practically quantitative yields irrespective of the experimental conditions. These facts are very striking for they indicate once more that in systems which are not very sensitive to peroxides (and to which halogen acids add very rapidly), the external con-

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(1) Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933); Kharasch, McNab and Mayo, *ibid.*, **55**, 2521, 2531 (1933); Kharasch and Hannum, *ibid.*, **56**, 712 (1934); Kharasch and Hinckley, *ibid.*, **56**, 1212 (1934).

(2) Kharasch and Darkis, *Chem. Reviews*, **5**, 571 (1928); Kharasch and Reinmuth, *J. Chem. Ed.*, **8**, 1703 (1931).

(3) Butlerow, *Ann.*, **144**, 1 ff. (1867); Roozeboom, *Ber.*, **14**, 2396 (1881); Chechoukoff, *Bull. soc. chim.*, [2] **46**, 823 (1886); Ipatieff and Ogonowsky, *Ber.*, **36**, 1988 (1903); Michael and Zeidler, *Ann.*, **393**, 109 (1912); LeBel, *Bull. soc. chim.*, [2] **28**, 460 (1877); Puchot *Ann. chim. phys.*, [5] **28**, 508, 549 (1883); Michael and Brunel, *Am. Chem. J.*, **48**, 267 (1912); Brunel, THIS JOURNAL, **39**, 1990 (1917); Coffin, Sutherland and Maass, *Canadian J. Res.*, **2**, 267 (1930).

TABLE I

ADDITION OF HYDROGEN BROMIDE TO ISOBUTYLENE[a,b,c]

No.	Experimental conditions	Gas in bomb	Total yield, %	n^{20}_{D}	Bromide, % Isobutyl	Bromide, % t-butyl
1	Peroxide-free isobutylene[a]	None	95	1.4278[d]	..	100
2	See[a]	Air	90	1.4279	..	100
3	Same as 2 except light (500-w. lamp)	Air	95	1.4277	..	100
4	Same as 2 except oxygen bubbled through material	Oxygen	90	1.4276	..	100
5	Same as 1	Nitrogen	90	1.4277	..	100
6	Same as 1 except heated at 76°	None	85	1.4276	..	100
7	Same as 1 except reaction allowed to go to completion at −10°	None	80	1.4275	..	100
8	95% glacial acetic used as solvent (1.5 moles). Reaction allowed to go to completion in the dark	None	90	1.4277	..	100
9	Same as 8 except use of light (500-w. lamp)	None	95	1.4275	..	100
10	Glacial acetic used as solvent (1.5 moles)[b]	None	90	1.4278	..	100
11	Same as 1 except that 0.04 mole of *p*-thiocresol was used	None	85	1.4273	..	100
12	Same as 1 except glacial acetic (1.5 moles) and 0.03 mole of diphenylamine added	None	85	1.4280	..	100
13	Same as 1 except xylene (1.5 moles) used as solvent	None	92	Estimated by b. p.		100
14	Same as 1 except added 0.2% of water	None	95	....	..	100
15	Same as 1 except diphenylamine (0.03 mole) added	None	91	1.4275	..	100[h]
16	Same as 1 except $FeCl_3$ used	None	90	1.4277	..	100
17	Same as 1 except 0.04 mole of ascaridol added	Air	92	1.4347	89[e]	11
18	Same as 17, except 0.03 mole of ascaridol added	Air	91	1.4335	80[f]	20
	Same as 17, except larger quantity of isobutylene (46.4 g.) used	Air	96	1.4350	94[g]	6

[a] The technique of additions was the same as described by Kharasch and Mayo.[1] Unless otherwise specified the reactions were allowed to go to completion at room temperature. The reaction is known to be very fast and proceeds within a few hours even at −80°. The yields were excellent in all cases.

[b] The results reported are the mean of two or more additions, and in some cases of as many as ten. They never varied by more than ±2%.

[c] The hydrogen bromide was always present in excess. Usually 1.5 moles of hydrogen bromide was used. (The limits were 1.18–1.68 moles of hydrogen bromide.)

[d] The indices of refraction of the *t*-butyl bromide used by us were 1.4275–1.4277 and the index of the iso compound 1.4355. A maximum error of five per cent. is admitted.

[e] This material all boiled within the range of 87.2–91.5°.

[f] Eighty per cent. of this material boiled at 87–91.3°.

[g] Ninety-six per cent. of this material boiled from 87–91.2°.

[h] This material all boiled from 73.0–73.4°.

ditions have no effect upon the direction of addition of hydrogen bromide. Isobutylene is apparently not very sensitive to peroxides for additions carried out in air and even in the presence of oxygen yielded the tertiary butyl bromide only. Runs 17, 18 and 19, however, indicate that the direction of addition may be influenced by the addition of peroxides to isobutylene, and under those conditions excellent yields of the isobutyl bromide were obtained. The yield of the isobutyl bromide on the basis of the isobutylene amounted to at least 80%. This is an exceptionally large yield if one bears in mind that the addition of hydrogen bromide to isobutylene, leading to the formation of tertiary butyl bromide, is very fast and will proceed to completion within an hour. The peroxide-catalyzed reaction must therefore be a very much faster reaction if it is to "outrun" the normal addition and yield such large quantities of the isobutyl bromide.

These results in conjunction with our work on propylene, butylene-1 and neopentylethylene (4,4′-dimethylpentene-1) indicate the tremendous importance of evaluating the peroxide effect in regard to the normal and abnormal addition of halogen acids to unsaturated compounds. While propylene, butene-1 and isobutylene are not very sensitive to peroxides, and even additions carried out in air yield the normal compounds, neopentylethylene is very sensitive to peroxides, and additions of hydrogen bromide to that molecule in air yield the abnormal product of the reaction.[4] It

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(4) Kharasch, Hannum and Gladstone, THIS JOURNAL, **56**, 244 (1934).

is under antioxidant conditions only and *in vacuo* that neopentylethylene yields the normal product of the reaction. It is thus obvious that although the empirical rule of Markownikoff[5] when first advanced had no broad experimental basis, it must have a far reaching theoretical significance. The significance of this rule we believe to be due to the lower electronegativity of a hydrogen atom as compared with an organic radical as discussed fully by one of us in previous articles.[2]

Experimental Part

The method of carrying out the addition of hydrogen bromide to unsaturated compounds has been described by one of us and collaborators. The same technique was employed in the addition of hydrogen bromide to isobutylene. Whenever the addition was carried out *in vacuo*, the tubes were evacuated to 10^{-4} mm. For the exact method of carrying out these additions the reader is referred to some of our previous articles.[1] The method of analysis to determine the relative amount of tertiary butyl bromide and isobutyl bromide involved both the boiling points and refractive indices of the compounds. We have established experimentally that the index of refraction of the mixture is a linear function of the composition. As a final proof of the composition of the mixture, whenever the isobutyl bromide was formed along with the tertiary, the material was repeatedly shaken with water and sodium carbonate solution, to remove the tertiary butyl bromide, and the constants of the compound thus freed from the tertiary butyl bromide were determined. In all cases there was an exact correspondence in the percentage of the isobutyl bromide calculated from the index of refraction and the amount obtained after separation of the tertiary butyl bromide. The boiling point and the index of refraction were the two criteria employed in the identification of the isobutyl bromide.

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Summary

1. It has been demonstrated that the normal product of addition of hydrogen bromide to isobutylene is tertiary butyl bromide.

2. It has been shown that tertiary butyl bromide is the only product of the reaction of isobutylene and hydrogen bromide, and that a variety of experimental conditions such as temperature, light or solvent have no effect on the direction of addition of hydrogen bromide to isobutylene.

3. It has been shown that in the presence of peroxides, isobutylene will add hydrogen bromide to give at least 80% of isobutyl bromide.

4. The value of the Markownikoff rule has been further extended, and it is suggested that the significance of it is due to the lower electronegativity of a hydrogen atom as compared with many organic radicals.

5. The work of previous investigators can be correlated readily if one bears in mind the facts that isobutylene is a molecule which does not form peroxides readily, and that in the presence of peroxides the abnormal addition product, isobutyl bromide, is formed.

6. The work is being continued.

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(5) Markownikoff, *Ann.*, **153**, 256 (1870).