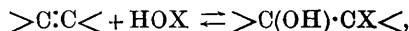


XXVI.—*The Action of Bromine Water on Ethylene.*

By JOHN READ and MARGARET MARY WILLIAMS.

ALTHOUGH chloro- and bromo-hydrins may often be produced by direct addition of hypochlorous and hypobromous acid to the corresponding unsaturated compound, according to the general scheme



the method does not appear to have found any very extensive use. This fact is probably due as much to the tedious nature of the operations involved as to the unsatisfactory yields afforded by the method. In the latter connexion, it may be noted that the material resulting from the reaction appears always to include a certain amount of the dihalogen additive product, formed through the partial decomposition of the hypochlorous or hypobromous acid with production of free halogen.

The acid employed in the reaction is usually prepared by the action of the free halogen on freshly precipitated mercuric oxide in the presence of water, and, as a rule, the most favourable conditions are secured by working in the dark or in diffused light with ice-cooled acid varying in strength from 1 to 3 per cent.

In the important and interesting case of ethylene, Carius (*Annalen*, 1863, **126**, 197) found that alkaline hypochlorite has little action, whereas aqueous hypochlorous acid reacts rapidly, giving a yield of ethylene chlorohydrin with Butlerow (*Annalen*, 1866, **144**, 40) estimated at 33 per cent. of the amount theoretically possible. Subsequent investigations by Mokiewsky (*J. Russ. Chem. Soc.*, 1898, **30**, 900) indicate that hypobromous acid reacts

more rapidly and gives a better yield than hypochlorous acid, amounting in some instances to as much as 60 per cent. of the quantity theoretically possible.

In view of the satisfactory yield of ethylene bromohydrin furnished by the direct addition, under appropriate conditions, of hypobromous acid to ethylene, it appeared important to ascertain whether the objectionable features of the method could be overcome. The work described in this paper was accordingly carried out with a view to avoid the use of mercuric oxide in the preparation of the requisite hypobromous acid, and thus eliminating the subsequent precipitation of the mercury with potassium sulphide; and, in addition, it was sought to reduce the large quantities of liquid rendered necessary by the employment of previously prepared solutions of the acid at the high dilutions indicated above.

In seeking to arrive at a suitable modification of the process, a reaction utilised by Pope and Read (T., 1912, 101, 760) for the preparation of bromohydroxyhydrindene from indene was recalled. This amounted, in effect, to the addition of hypobromous acid to indene by agitating the hydrocarbon with successive quantities of bromine water, a yield of 85 per cent. of the additive product being readily obtained in this simple manner.

It appears doubtful whether the action of bromine water on ethylene has been previously investigated; in all the available references to the reaction, the assumption seems to be that the sole product is ethylene dibromide. The experiments outlined below, however, demonstrate that when ethylene is passed through bromine water cooled to about 0°, a yield of ethylene bromohydrin is obtained practically equal to that quoted by Mokiewsky as furnished by the cumbersome mercuric oxide method. As an example, in one experiment, in which the volume of water employed was only 500 c.c., 200 grams of bromine gave 85 grams of ethylene bromohydrin and 88 grams of ethylene dibromide, the yield of the former substance being 54.4 per cent. of the amount theoretically possible. The two products are easily separable in presence of water, and the reaction thus provides a very effective and expeditious method for the preparation of ethylene bromohydrin.

#### EXPERIMENTAL.

1. The well-washed ethylene, generated from alcohol and syrupy phosphoric acid, was passed into an ordinary wash-bottle cooled in ice-water and containing 7.2 grams of bromine dissolved in 500 c.c. of water. After complete absorption of the bromine, a fresh portion, equal in amount to the first, was added; the process was con-

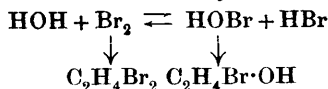
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tinued, with frequent and vigorous agitation, until a total weight of 200 grams of bromine had reacted. The lower layer of ethylene dibromide which was formed during the process was separated, washed with water, and dried over sodium sulphate. It weighed 88 grams, and on distillation passed over between 129° and 135°. After neutralising with sodium carbonate and saturating the aqueous layer with common salt, the ethylene bromohydrin was extracted from it by shaking with two successive quantities of 100 c.c. of ether; from the extract, dried over sodium sulphate, the ether was distilled through a column. The bulk of the residual liquid, which weighed 85 grams, distilled between 145° and 149°. The identity of the two products was checked by means of bromine estimations.

Assuming that hypobromous acid is produced in accordance with the scheme  $\text{HOH} + \text{Br}_2 \rightleftharpoons \text{HBr} + \text{HOBr}$ , it follows that 54.4 per cent. of the bromine is utilised in the formation of ethylene bromohydrin, and that 37.5 per cent. is converted into ethylene dibromide. The total amount of hydrogen bromide produced in the reaction, as ascertained by titration with silver solution, was 70.0 grams; it thus appears that practically the whole of the remaining 8.1 per cent. of bromine is accounted for by the decomposition of hypobromous acid into hydrogen bromide and oxygen.

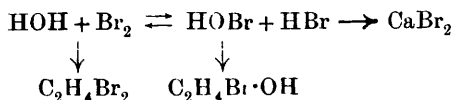
2. Decomposition of the hypobromous acid in the manner indicated would probably be avoided to some extent by using bromine at greater dilutions; but, as the percentage of free bromine to water was never above 1.5, it appeared undesirable to dilute further. The point was tested, however, by adding the bromine in identical amounts (7.2 grams) to half the amount of water (250 c.c.), the concentration of bromine being thus doubled; in this case only 45 per cent. of the bromine was utilised for the production of bromohydrin and 35 per cent. for dibromide, whilst practically the whole of the remaining 20 per cent. was converted into hydrogen bromide as before. Concentrating the bromine water, therefore, results in diminishing the yield of bromohydrin, whilst the amount of dibromide produced is substantially the same as before.,

3. A prime factor governing the ratio between the amounts of bromohydrin and dibromide produced in any particular case will be the relative ease with which the unsaturated compound unites with hypobromous acid and bromine respectively. The relationships may be represented schematically in the following manner:



In the case of indene, which readily yields a high percentage of bromohydrin, it is evident that the ratio of the two reaction velocities involved is more favourable to bromohydrin formation than in the case of ethylene.

4. Connected with the foregoing consideration is the question of the velocity of formation of hypobromous acid from bromine and water, and the consequent removal of free bromine from the sphere of action. It seemed possible that the addition of calcium carbonate, by promoting the formation of hypobromous acid, might enhance the yield of bromohydrin. The relationships concerned are illustrated below:



Under the conditions laid down in (2), however, although the addition of calcium carbonate resulted in a more rapid absorption of the ethylene, the yield of bromohydrin fell from 45 to 32 per cent., whilst the yield of dibromide remained almost unaltered at 34 per cent.

Similarly, under the conditions obtaining in (1), the addition of a molecular proportion of sodium hydrogen carbonate with the bromine depressed the yield of bromohydrin from 54.4 to 34 per cent. The yield of dibromide simultaneously produced was 37 per cent. In both cases the balance of the bromine was found in the aqueous layer as bromide.

It would thus appear that any attempt to accelerate the rate of formation of the hypobromous acid is ineffective in increasing the yield of bromohydrin, owing to the increased tendency of the acid to decompose into hydrogen bromide and water. It is conceivable, however, that an acceleration of the rate of formation of the hypobromous acid might be rendered effective by accelerating in turn the gross rate of absorption of the ethylene, as, for example, by dispersing the gas in the liquid so as to obtain a much larger active surface.

5. The yield of bromohydrin was materially less when the operation was conducted at the ordinary temperature; the process is thus favoured by working in the cold.

6. During the course of the work, it was noticed that solid calcium chloride was dissolved when allowed to remain in contact with the bromohydrin. The observation suggested the existence of a compound of calcium chloride with the bromohydrin which might possibly be of use in purifying the substance. When a quantity of the bromohydrin is saturated with calcium chloride

at the water-bath temperature, and then allowed to cool, crystals of the supposed additive product separate from the solution, but owing to the extreme ease with which the material is decomposed by moist air, no satisfactory analytical results were obtainable. The substance is decomposed by water, with production of the bromohydrin; when free from water, it does not appear to undergo decomposition at 100°.

Further investigations of a related character are in progress.

DEPARTMENT OF ORGANIC CHEMISTRY,  
UNIVERSITY OF SYDNEY.

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