

LVII.—*Action of Hydrogen Bromide in Presence of Ether on Carbohydrates and certain Organic Acids.*

By HENRY J. HORSTMAN FENTON, M.A., and Miss MILDRED GOSTLING, B.Sc., Lond.

IT has been shown by one of the authors (Trans., 1896, 553) that the ethylic salt of dihydroxymaleic acid can readily be obtained by the interaction of the free acid with anhydrous ethylic ether in presence of dry hydrogen bromide at the ordinary temperature. The product is identical in every respect with that obtained from the acid and ethylic alcohol in presence of hydrogen chloride, and the yield appears to be about the same. A similar result cannot be effected by substituting hydrogen chloride for hydrogen bromide. Ethylic ether is known, of course, to react with sulphuric, hydrochloric, and a few other inorganic acids, under certain conditions, to form ethylic salts, but no such behaviour towards organic acids appears to have been observed.

It was therefore considered advisable to extend the observations to some other acids, in order to ascertain whether the reaction is one of general application. Accordingly, experiments were made with oxalic, acetic, benzoic, stearic, and boric acids. In every case examined, the ethylic salt of the acid was readily obtained, the yield being generally good.

The acid was in each case covered with anhydrous ether purified carefully from alcohol and water as previously described, dry hydrogen bromide was passed into the mixture until it was saturated or nearly saturated, and it was then left for some days. The product was separated and purified by the ordinary methods.

*Oxalic Acid.*—Twenty grams of the pure dry acid were covered with about 200 c.c. of ether, saturated with dry hydrogen bromide, and after three days the mixture was treated with water; the heavy liquid which separated was purified by washing with dilute sodium carbonate solution, dried over calcium chloride, and distilled. The portion distilling between  $178^{\circ}$  and  $182^{\circ}$  weighed 15 grams, and had all the properties of ethylic oxalate, as recognised by its boiling point, odour, action on aqueous ammonia, and action on alcoholic potash.

*Acetic Acid.*—Twenty grams of glacial acetic acid were covered with about 150 c.c. of ether and saturated with dry hydrogen bromide; after three days, it was treated in exactly the same way as the ethylic oxalate. The portion distilling between  $75^{\circ}$  and  $82^{\circ}$  was collected, and was readily recognised as ethylic acetate by its characteristic odour. The yield was about 9 grams.

*Benzoic Acid.*—Twenty grams of benzoic acid covered with pure dry ether were saturated with gaseous hydrogen bromide and allowed to stand for a few days. It was then heated for some time on a water bath to free it from hydrogen bromide, shaken with excess of sodium carbonate solution to remove any free benzoic acid, extracted with ether, dried over calcium chloride, and distilled. The portions distilling between  $209^{\circ}$  and  $212^{\circ}$  weighed 11 grams.

*Stearic Acid.*—Some stearic acid was treated in exactly the same manner with ether and hydrogen bromide, and after a few days shaken up with a dilute sodium carbonate solution, the ether evaporated, and the waxy-looking residue crystallised from alcohol. The crystals, dried and freed from alcohol in a vacuum desiccator, were recognised as ethylic stearate by their appearance and melting point ( $33^{\circ}$ ).

*Boric Acid.*—Crystallised boric acid was covered with ether, saturated with hydrogen bromide, and after being allowed to stand for two days was distilled under reduced pressure to remove free hydrogen bromide and ether. The portions collected between  $115^{\circ}$  and  $120^{\circ}$  were redistilled under atmospheric pressure.

The product burnt with a green flame, and was quickly decomposed

by water, giving boric acid and ethylic alcohol. The quantity obtained, however, was but small.

The yields appear to be fairly good in most instances, and the process may, in certain special cases, have a practical advantage over the usual methods of preparing ethylic salts; the principal object of this part of the investigation, however, was to demonstrate that the change is a general one, that is to say, that the acid interacts with ether in presence of dry hydrogen bromide to form an ethylic salt.

Experiments were then made with a view of ascertaining the behaviour of organic compounds other than acids when submitted to a similar treatment; the first group of substances selected was that of the carbohydrates and some of the allied alcohols.

*Cane-sugar.*—The powdered substance was covered with anhydrous ether, and dry hydrogen bromide was passed into the mixture nearly to saturation, the vessel being surrounded by cold water. At first, only a yellow coloration was produced, but after the mixture had been allowed to stand for about an hour at the ordinary temperature, a beautiful and intense *purple colour* was developed, both in the solution and in the undissolved solid, and remained permanent for some days.

On adding water, the colour is immediately discharged, and a greenish-black precipitate separates which dissolves in concentrated sulphuric acid with a purple colour.

On evaporating the purple ethereal solution in a vacuum over sulphuric acid and solid potash, a purplish-black, gummy mass remains, and a similar effect is produced by precipitation with light petroleum. If the purple solution is treated with excess of anhydrous sodium carbonate, a yellow mass is obtained from which ether extracts a substance that gives the purple coloration with concentrated sulphuric acid. It is left as a yellow gum on evaporating the ether, but on adding light petroleum it is partially precipitated in yellow flocks which dry up in a vacuum to a buff-yellow powder. This again gives the purple colour with sulphuric acid.

The properties of this substance seem closely to resemble those of the compound which has been described by Stenhouse and others as 'metafurfurol,' which is obtained in small quantity in the ordinary preparation of furfuraldehyde. It does not appear, however, to be volatile, as it could not be detected in the distillate when either the acid or alkaline mixtures, above referred to, were distilled under reduced pressure or in a current of steam. The nature of this substance is still under investigation.

A similar colour reaction cannot be obtained by substituting *hydrogen chloride* for *hydrogen bromide*, only a slight reddish coloration being obtained even after long standing; and hydrogen iodide merely gives

a separation of iodine. Subsequent experiments have shown, however, that the *ether* is not essential. If powdered cane-sugar be shaken in a stoppered bottle filled with dry hydrogen bromide, the gas is slowly absorbed, and the solid becomes first pink and then deep purple. The colour, however, is not so permanent as when ether is employed, being changed to black after some hours.

In order to compare the behaviour of other carbohydrates, &c., with that of cane-sugar under uniform conditions, about 0.5 gram of the powdered substance was placed in a stoppered bottle and covered with 7.5 c.c. of anhydrous ether which had previously been saturated with dry hydrogen bromide at about 15°. With these proportions, cane-sugar gives an intense purple colour in about an hour and a half.

*Milk-sugar, maltose, dextrose, galactose, xylose*, and the *synthetical sugar* obtained by condensation of glycollic aldehyde (Trans., 1897, 71, 377) give only varying shades of yellow, brown, or red, even after standing for several hours, but after the mixtures have remained for periods of about 24 hours a certain amount of *purple* colour is obtained in each case. The intensity and brilliancy of this colour, however, even after standing for several days, never even distantly approaches that obtained with cane-sugar after it has stood for about an hour and a half. The colour obtained with xylose is more intense than that given with the other substances mentioned in this group, and appears rather more quickly.

*Lævulose* (crystallised), on the other hand, when treated in a similar way, gives a much more energetic reaction than cane-sugar, a red colour being developed after a minute or two, and becoming intensely purple after about half an hour. The dry substance absorbs hydrogen bromide, almost instantaneously becoming deep purple. The absorption of the gas is extremely rapid, and forms a striking experiment when the powdered substance is placed in a jar of hydrogen bromide over mercury; a small jar is completely filled in about 5—10 minutes, whilst in the case of cane-sugar a similar absorption takes about 5 hours.

Dry hydrogen chloride also gives a certain amount of purple colour with lævulose, which is soon changed to black; and an ethereal solution of hydrogen chloride gives a red colour after the lapse of some hours.

*Glycollic aldehyde* (Trans., 1895, 67, 774) and *arabinose* give only various shades of orange and brownish-red, without any trace of purple, even on long standing.

*Starch, glycogen, cellulose, gum, mannitol, dulcitol, sorbitol, erythritol, and glycerol* all produce merely a yellow colour.

*Dextrin* gives no colour until after the mixture has stood for about 24 hours, when a very faint trace of purple colour becomes apparent.

*Inulin*, however, after standing for about 1—2 hours, gives an *intense purple colour* resembling that from cane-sugar or lævulose.

*Sorbose* behaves exactly like *lævulose*, giving an intense purple colour after about half an hour.

*Rhamnose* behaves in the first instance like *arabinose*, giving only an orange or red colour after about 24 hours; but on longer standing a certain amount of purple colour is obtained.

Mucic, saccharic and manno-saccharic acids give no colour.

The carbohydrates which have so far been examined may conveniently be classified with regard to their behaviour towards hydrogen bromide in ethereal solution in the following manner.

*a.* Those which give an *intense* purple coloration after standing for *two hours* or less.

*b.* Those which give a purple colour of relatively moderate intensity only after standing for *a day or two*.

*c.* Those which give a deep red or brown colour without any tinge of purple, even on long standing, and

*d.* Those which remain unaffected, or give only a yellow colour.

On reference to the examples given, it will be observed that the substances which behave as in *a* are either *ketoheoses* or are carbohydrates capable of producing these on hydrolysis.

Substances which behave as in *b* are *hexaldoses* or carbohydrates which give rise to them, whilst glycollic aldehyde (dialdose) and *arabinose* (pentaldose), behave according to *c*. The behaviour of *rhamnose* (methylpentose) appears to be intermediate between *b* and *c*. *Xylose* (pentaldose), however, shows a behaviour similar to the *hexaldoses*; with this exception, it would appear that the production of any purple colour, either quickly or slowly, is indicative of *ketoheoses*, *hexaldoses*, or substances which give rise to these. It is of course possible that this exception is due to impurity in the *xylose* employed. It was, however, the purest obtainable specimen, recrystallised.

This colour reaction may be of service as a general method of distinguishing certain types of carbohydrates, especially those which behave as in *a*, the reaction for which is very characteristic; and it may, perhaps, be employed for showing the presence of such carbohydrates in natural products, &c.

*Cork* and *bran* become purple-violet after the mixture has remained for a few hours, whilst unripe fruits (*gooseberries* and *currants*, for example) give the coloration after a few minutes.

NOTE.—Professor Tilden has called our attention to the fact that *terpineol*, and also many essential oils, give a purple coloration when treated with gaseous hydrogen chloride (*Trans.*, 1879, 35, 286), and we find that a somewhat similar effect is produced by a solution of hydrogen bromide in ether. This colour does not, however, appear to have

any connection with that which is obtained with carbohydrates, and the effects are easily distinguished. In the case of terpeneol, the maximum colour-intensity, which is relatively very slight, is obtained immediately and fades on adding more of the reagent.

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