V.—*w*-Bromocamphoric Acid.

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ALTHOUGH the bromocamphoric anhydride, which was first prepared by Wreden a long time ago (*Annalen*, 1872, **163**, 330), has been investigated by several chemists during recent years, the corresponding bromocamphoric acid has not hitherto been isolated. As is well known, the anhydride is slowly decomposed by boiling water, yielding, as principal product, camphanic acid,

the lactone of a hydroxycamphoric acid which, apparently, does not exist, except in the form of a salt. A similar change occurs when bromocamphoric anhydride is boiled with sodium carbonate solution, but, under these conditions, as Aschan has recently pointed out (*Ber.*, 1894, **27**, 2112), a much larger quantity of lauronic acid is formed than is the case when water alone is employed.

The fact that bromocamphoric acid has never been found amongst the various products obtained from the anhydride on treatment with water or alkalis, might be accounted for in one of two ways; it might be, as Aschan assumes (*loc. cit.*), because bromocamphoric acid, like dimethylfumaric acid (pyrocinchonic acid), and diethylfumaric acid (xeronic acid), for example, is actually incapable of existing under ordinary conditions, owing to the readiness with which anhydride formation takes place; or else because the acid loses hydrogen bromide and passes into camphanic acid with extreme facility.

In the course of an investigation of π -bromocamphoric acid (*Proc.*, 1895, 33, 88, and 210), the results of which will form the subject of a future paper, this question of the possible existence of a bromocamphoric acid, corresponding with Wreden's anhydride, came into prominence. π -Bromocamphoric acid, $\text{C}_{10}\text{H}_{15}\text{BrO}_4$, a structural isomeride of the unknown bromo-acid, was found to be stable under ordinary conditions, as was also π -dibromocamphoric acid, $\text{C}_{10}\text{H}_{14}\text{Br}_2\text{O}_4$, a compound in which one of the bromine atoms doubtless occupies the same relative position in the molecule as the halogen atom in Wreden's bromocamphoric anhydride.

These observations seemed to indicate that suitable conditions alone were required for the successful preparation of the bromocamphoric acid in question; this conclusion was ultimately verified by experiment.

On treating Wreden's bromocamphoric anhydride with concentrated nitric acid in the manner described below, it is partially transformed into the corresponding acid of the composition $\text{C}_{10}\text{H}_{15}\text{BrO}_4$;

this acid is a well-defined, crystalline, moderately stable compound, which closely resembles the π -bromo- and π -dibromocamphoric acids in ordinary properties.

As it is convenient to have some means of distinguishing by name the two structurally isomeric monobromocamphoric acids now known, the compound derived from Wreden's anhydride will subsequently be referred to as *w*-bromocamphoric acid; a purely arbitrary designation of this kind (the initial letter of Wreden's name), has, no doubt, its disadvantages, but is probably less misleading than any other.

In a recent paper (*Ber.*, 1894, **27**, 2112), Aschan describes the results of some experiments on *w*-bromocamphoric anhydride; on treating *l*-isocamphoric chloride with bromine, he obtained as principal product *w*-bromocamphoric anhydride, and in one experiment he also succeeded in isolating a very small quantity of a brominated acid, which separated from water in long needles, melting at 196°. Although unable to obtain sufficient for an analysis, he studied the action of sodium carbonate on this brominated acid, and, from its behaviour, concluded that it was probably a bromisocamphoric acid, $C_{10}H_{15}BrO_4$. In the last number of the *Berichte* (*Ber.*, 1895, **28**, Ref., 922), there is an abstract of another paper by the same author, and it is there stated that *l*-bromisocamphoric acid has been isolated from the products obtained on brominating *d*-camphoric acid and *l*-isocamphoric acid; this compound is described as separating from benzene in crystals of the composition $C_{10}H_{15}BrO_4 + \frac{1}{2}C_6H_6$, and melting at 196°. Unfortunately, the original publication (*Acta. soc. scient. fenn.*, **21**, No. 5, 1) is not yet accessible, so that it is impossible, from the data at hand, to say with certainty whether Aschan's acid, which appears to be the same as that mentioned by him in the earlier paper (*loc. cit.*), is identical with, or different from, the *w*-bromocamphoric acid described below. In his interesting paper (*Ber.*, **27**, 2001) on the relation between the various camphoric acids, Aschan himself has shown that the α -rotatory *w*-bromocamphoric anhydride is partially converted into *l*-isocamphoric acid on reduction with zinc dust and acetic acid, from which it would be concluded that simple hydrolysis of the α -rotatory *w*-bromo-anhydride should also afford *l*-bromisocamphoric acid. The properties of Aschan's *l*-bromisocamphoric acid, however, are certainly different from those of the compound obtained by the author; although, apparently, the two substances have practically the same melting point, *w*-bromocamphoric acid is insoluble, or nearly so, in benzene, and cannot be recrystallised from water; at ordinary temperatures it is practically insoluble in this liquid, and, even on boiling, it passes into solution only very slowly, being at the same time decomposed.

Preparation of w-Bromocamphoric Anhydride.—The preparation of the material required for this investigation was very kindly undertaken by Mr. Panisset, a student of the Chemical Department of the Central Technical College, the method adopted having been that described by Reyher (*Inaug. Diss.*, Leipzig, 1891), which seemed more convenient than Aschan's process when small quantities only are required.

The bromine having been added gradually to the mixture of pure *d*-camphoric acid and amorphous phosphorus, until the evolution of hydrogen bromide suddenly slackened, the heating on a water bath was continued for a short time, in order to volatilise the excess of halogen; water was then added, in small quantities at a time, cooling well, and later on a little alcohol, in order to dissolve the oil with which the crystals were mixed. The product was then separated by filtration, washed with a little alcohol, dried on porous earthenware, and purified by recrystallisation from chloroform; 8.5 grams of camphoric acid gave 7 grams of crude crystalline product, from which 5.4 grams of pure *w*-bromocamphoric anhydride were obtained; the yield was therefore about 50 per cent. of the theoretical, or much the same result as that obtained by Reyher and Aschan.

w-Bromocamphoric acid.

The pure *w*-bromocamphoric anhydride (m. p. 214°), in quantities of 2—5 grams, was placed in a small, glass, evaporating basin, and rather more than covered with concentrated nitric acid (sp. gr. 1.42); the basin was then covered with a clock-glass and heated on the water bath. The anhydride quickly passed into solution, especially on stirring, and a slight evolution of ruddy fumes was observed, but there was no odour of bromine. As soon as all had dissolved, the clock-glass was removed and the heating continued during two or three minutes longer; the solution was then allowed to cool, diluted with water, and the colourless, crystalline product separated by filtration, washed with water, and placed on porous earthenware. As soon as it appeared to be dry, it was treated with a relatively large quantity of cold chloroform; the greater part, consisting of large crystals of *w*-bromocamphoric anhydride, soon passed into solution, but a small portion of a crystalline powder did not dissolve; this was separated by filtration and washed repeatedly with chloroform, first on the filter and finally on unglazed earthenware.

This product was found to be an acid, and at first it seemed possible that it might be the isocamphanic acid, $C_{10}H_{14}O_4$, described by Reyher (*loc. cit.*), this substance being also practically insoluble in chloroform; as, however, the two compounds differed considerably in melting point, this possibility was excluded.

Camphanic acid, the formation of which under the above conditions was not improbable, is so readily soluble in chloroform that its presence was impossible; the compound obtained in the manner just described was therefore some new derivative of *w*-bromocamphoric anhydride.

As 5 grams of the anhydride had only afforded 0.2 to 0.3 gram of the new acid, a few attempts were now made to improve the method of preparation, but not with any success. On heating the bromo-anhydride with concentrated nitric acid during a longer time than 3—4 minutes, it undergoes oxidation to a greater extent, the yield of the desired product is no larger, and a greater proportion of the anhydride is wasted. The use of a larger quantity of nitric acid, with the object of preventing crystallisation until the solution had cooled to a temperature considerably below 100°, appeared also to give no better results.

The original method was, therefore, again adopted, the anhydride, which was recovered in a practically pure condition on evaporating the chloroform extract of the crude product, being continually used for a following experiment; working in this way, 4.7 grams of the anhydride, after three operations, gave rather more than 0.7 gram of the pure acid, and 3.8 grams of the anhydride were recovered; it is consequently an easy matter to prepare the acid in moderately large quantities.

The crude crystalline acid, freed from anhydride by repeatedly washing with chloroform, was dissolved in dry ether, the filtered solution evaporated to a small bulk, and mixed with a large quantity of chloroform; the crystals which were at once deposited from the hot solution were then separated by filtration, washed with chloroform, and heated for a short time in a water oven.

An analysis of this preparation gave results agreeing well with those required for a bromocamphoric acid.

0.1527 gave 0.2404 CO_2 and 0.0745 H_2O . $\text{C} = 42.93$; $\text{H} = 5.43$.

$\text{C}_{10}\text{H}_{15}\text{BrO}_4$ requires $\text{C} = 43.01$; $\text{H} = 5.37$ per cent.

That the substance is a bromocamphoric acid corresponding with Wreden's anhydride is amply proved by the experiments described below.

w-Bromocamphoric acid crystallises from a hot mixture of ether and chloroform in small, transparent prisms or plates, but, when crystallisation takes place slowly at ordinary temperatures, the acid is deposited in large, orthorhombic pyramids; it melts at 195—196°, at the same time effervescing violently and charring slightly. It is practically insoluble in chloroform and in benzene, but it dissolves freely in cold ether, acetone, and alcohol; in these respects, it resembles the π -bromo- and π -dibromo-camphoric acids (*Proc., loc. cit.*).

When a concentrated solution of the acid in sodium carbonate is warmed for a few minutes and then acidified, an oily or crystalline precipitate is produced; this product is formed with elimination of hydrogen bromide, and should, therefore, be ordinary camphanic acid. In order to prove this, some pure *w*-bromocamphoric anhydride was boiled for a short time with sodium carbonate and dilute alcohol, and the camphanic acid thus prepared was compared directly with the compound obtained in a similar way from the *w*-bromocamphoric acid. Both preparations crystallised from dilute alcohol in fern-like prisms, and in long needles, identical in appearance; these crystals in both cases melted in their water of crystallisation when suddenly heated at about 140°; but after recrystallisation from chloroform, in which they were readily soluble, both specimens melted, although not very sharply, at 198—200° (pure camphanic acid melts at 201°).

When finely divided *w*-bromocamphoric acid is shaken with a fairly large relative quantity of cold water, it does not dissolve to any appreciable extent, but on boiling it slowly passes into solution; this solution gives a precipitate immediately on the addition of a solution of silver nitrate, but it does not give a crystalline deposit on simply cooling, unless it has been previously concentrated to a very small bulk; the needles which then separate are readily soluble in cold chloroform, and melt at about 198—200° after recrystallisation.

w-Bromocamphoric acid is, therefore, decomposed by boiling water, giving camphanic acid and hydrogen bromide,

from cold alcohol and acetone, however, it is, apparently, deposited unchanged, as the crystals are insoluble in chloroform; it may also be inferred that the dry acid is stable at temperatures below about 180°, since melting point determinations, under different conditions as to the rate of heating, give concordant results.

A final proof that the compound here described is a bromocamphoric acid, corresponding with Wreden's anhydride, is afforded by its behaviour with acetyl chloride; it dissolves slowly in this liquid in the cold, and seems to be deposited unchanged on evaporating the solution at ordinary temperatures; when, however, the solution is warmed for a short time, the acid is converted into its anhydride. This anhydride is readily soluble in hot chloroform, but only sparingly in ether, and separates from a mixture of these solvents in colourless prisms melting at 214°, and identical in other respects with the crystals of *w*-bromocamphoric anhydride; a mixture of this preparation with some pure *w*-bromo-anhydride melted sharply at 214°.

The above account of the properties of *w*-bromocamphoric acid explains the difficulty met with in its preparation; on the one hand,

the anhydride is not very easily hydrolysed; on the other, the bromo-acid is readily converted into camphanic acid.

During this investigation it has often happened that solutions of *w*-bromocamphoric anhydride in chloroform have been rapidly evaporated on a water bath in order to recover the anhydride; in some cases, but by no means frequently, the solvent may be removed almost entirely before crystallisation commences, and a highly supersaturated solution results; when, finally, crystallisation occurs it is attended with a fairly loud report, and the liquid contents of the vessel are almost instantaneously transformed into a dry, rather bulky, mass of small crystals, free from any visible quantity of liquid chloroform, although still smelling slightly of the solvent.

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