

A NOTE ON THE ACTION OF *N*-BROMOSUCCINIMIDE ON ALIPHATIC DICARBOXYLIC ACIDS

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THE reaction mentioned in the title does not appear to have been previously investigated.

Saturated Aliphatic Dicarboxylic Acids. *N*-Bromosuccinimide reacts with oxalic, malonic and succinic acids in aqueous solution on heating at the temperature of a boiling water-bath, forming carbon dioxide hydrogen bromide and succinimide. With acids other than oxalic acid, an olefine is obtained. The reaction proceeds easily at room temperature on shaking an aqueous solution of oxalic acid and *N*-bromosuccinimide, but with homologues of oxalic acid, heat is necessary to effect the reaction. Compared with the fatty acids the dicarboxylic acids possess higher dissociation constants, and are therefore stronger acids. This is especially so in the case of oxalic acid. This fact illustrates why such a reaction takes place. Succinimide has been isolated in the reaction with oxalic and malonic acids, and the formation of ethylene with malonic and succinic acids has been proved.

Unsaturated Aliphatic Dicarboxylic Acids. Maleic acid is a stronger acid than its isomer. On the other hand the hydrogen atom of the second carboxyl group of fumaric acid is more easily dissociated than that of maleic acid (Ostwald). Of the two stereoisomeric acids, fumaric acid is the more stable. *N*-Bromosuccinimide reacts with maleic and fumaric acids in boiling aqueous solution to give succinimide, carbon dioxide, hydrogen bromide and acetaldehyde. No free acetylene could be detected, but the presence of acetaldehyde was proved by the isolation of acetaldehyde 2:4-dinitrophenylhydrazone. The addition of water to acetylene to form acetaldehyde is well known. The behaviour of the two stereoisomeric acids towards *N*-bromosuccinimide is very much the same, except for the fact that in the case of maleic acid, a portion (about 10 per cent.) is converted into the more stable fumaric acid.

EXPERIMENTAL

N-Bromosuccinimide and Oxalic Acid. To a cold solution of 1.26 g. (1 mol.) of crystalline oxalic acid in 25 ml. of distilled water, 1.78 g. (1 mol.) of powdered *N*-bromosuccinimide was added and the solution was shaken, vigorously. A reaction proceeded instantaneously at room temperature the solution assumed a brown-red colour, and carbon dioxide and hydrogen bromide were evolved. In about an hour nearly all the *N*-bromosuccinimide had gone into solution, The brown-red solution was filtered and the filtrate was concentrated to about 5 ml. Colourless crystals separated

N-BROMOSUCCINIMIDE

out on cooling and were recrystallised from methanol, giving succinimide, m.pt. 125° to 126° C.

N-Bromosuccinimide and Malonic Acid. Malonic acid 1.04 g. (1 mol.) and powdered *N*-bromosuccinimide 1.78 g. (1 mol.) were heated with 25 ml. of water in a boiling water bath. The *N*-bromosuccinimide gradually dissolved and the solution became yellow. The gases evolved were removed in a current of nitrogen and found to be carbon dioxide, hydrogen bromide and ethylene. After one hour's heating in the water bath, the reaction mixture was filtered and from the filtrate 0.6 g. of succinimide was obtained. With *N*-bromosuccinimide and succinic acid similar results were obtained.

N-Bromosuccinimide and Maleic Acid. Maleic acid 1.16 g. (1 mol.) and powdered *N*-bromosuccinimide 1.78 g. (1 mol.) were heated with 35 ml. of water on the electric plate for one hour. A vigorous reaction took place, carbon dioxide and hydrogen bromide being evolved. From the reaction mixture, which had a conspicuous paraldehyde odour, 0.12 g. of fumaric acid, m.pt. 302° to 304° C. was isolated. From the filtrate 0.6 g. of succinimide was isolated.

In a second experiment the evolving gases were removed by a current of nitrogen and were passed, after washing with sodium hydroxide solution into ammoniacal cuprous chloride solution, but no acetylene could be detected. The sodium hydroxide solution became turbid and on heating a portion of this solution a yellowish precipitate of aldehyde resin was observed.

In a third experiment maleic acid 2.32 g., and *N*-bromosuccinimide 3.56 g., with 50 ml. of water were refluxed in a boiling water bath for one hour. On cooling the solution the odour of paraldehyde was perceptible. Dilute sulphuric acid (5 ml.) was added, the reaction mixture was heated and the gases evolved were received in 2:4-dinitrophenylhydrazine sulphate solution in methanol. The orange crystals formed were identified as acetaldehyde 2:4-dinitrophenylhydrazone by m.pt. and mixed m.pt.

N-Bromosuccinimide and Fumaric acid. Equimolecular quantities of *N*-bromosuccinimide and fumaric acid were used. The same results as in the case of maleic acid were recorded; again no free acetylene could be detected.

SUMMARY

1. *N*-Bromosuccinimide reacts with saturated aliphatic dicarboxylic acids such as oxalic acid in aqueous solution at room temperature evolving carbon dioxide with the formation of hydrogen bromide and succinimide. With homologues of oxalic acid heat is necessary to effect the reaction.

2. *N*-Bromosuccinimide reacts with unsaturated aliphatic dicarboxylic acids such as maleic and fumaric acids in boiling aqueous solution giving carbon dioxide, hydrogen bromide and succinimide. The acetylene which is expected in the reaction is converted into acetaldehyde.

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