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THE REACTION OF CARBONATES WITH AMMONIA

A thesis presented in partial fulfilment of the degree of Master of Science in Chemistry at Massey University

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1969
A feature of typical carbohydrates/ammonia reactions is the formation of complex mixtures of imidazoles (among other products). These imidazole mixtures have proved difficult to separate in many cases. A theory for cation exchange chromatography of bases has been developed in this work and applied to the separation of imidazole mixtures. The technique used appears to be capable of separating mixtures of imidazoles more effectively than other previously used.

D-Glucosone (D-arabino-hexosulose) was prepared by the action of benzaldehyde on glucosazonel (D-arabino-hexosephylosazone) and its reaction with ammonia investigated. It was found that the reaction mixture included a number of imidazoles. These imidazoles were separated by the ion exchange technique developed earlier and a total of sixteen compounds giving a positive reaction with the imidazole-specific. Pauly reagent (diazotised sulphanilic acid) were detected. Fifteen of these compounds were isolated and six were identified by mass spectrometry and/or nuclear magnetic resonance spectrometry.

It was also intended to investigate the reaction of 4-O-methyl-D-glucose and ammonia. It was proposed to prepare this compound by methylation of methyl-2,3,4-tri-O-acetyl-\(\alpha\)-D-glucopyranoside with methyl iodide in the presence of silver oxide. Under these conditions an acetyl migration from the 4-O to 6-O position occurs with the methylation to give methyl-2,3,5-tri-O-acetyl-4-O-methyl-\(\beta\)-D-glucopyranoside which may be hydrolysed to give 4-O-methyl-D-glucose. It was intended to prepare the starting material for this reaction (methyl-2,3,4-tri-O-acetyl-\(\alpha\)-D-glucopyranoside) from D-glucose by the following steps.

1. Ketohexolysis of D-glucose catalysed by an H\(^+\) cation exchange resin to give methyl-\(\beta\)-D-glucopyranoside.
2. Blocking of the 6-O position with triphenylchloromethane.
3. Acetylation with acetic anhydride to give methyl-6-O-triphenylmethyl-2,3,4-tri-O-acetyl-\(\alpha\)-D-glucopyranoside.
4. Removal of the triphenylmethyl blocking group to give the required methyl-2,3,4-tri-O-acetyl-\(\beta\)-D-glucopyranoside.

In fact at the time of this writing the first three steps had been accomplished but attempts to remove the triphenylmethyl blocking group while leaving the acetyl groups intact had proved unsuccessful.
ACKNOWLEDGEMENT

The author wishes to thank Dr. E.H. Richards
for encouragement and advice.
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