

A NOVEL PROCESS FOR THE EPIMERIZATION OF GLUCOSEPENTAACETATE
INVOLVING IMIDAZOLE CATALYZED ACYL TRANSFER

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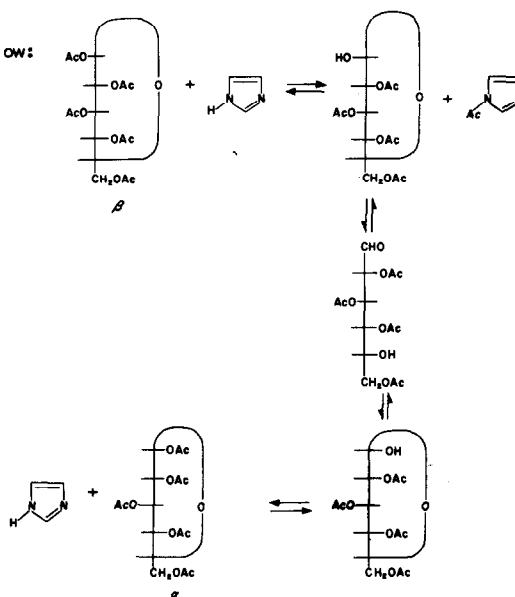
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The processes of acyl-transfer and hydrolysis are fundamental to many biochemical pathways. This communication describes a new acyl transfer system and its application to acylation of alcohols, amines, mercaptans, and an interesting epimerization of glucosepentaacetate.

Alpha-glucosepentaacetate was found to acetylate methanol, *n*-amylamine and *n*-amylmercaptan in dilute deuteriochloroform solution at room temperature if the reaction is catalyzed by imidazole. The kinetics were conveniently determined via nmr spectroscopy, which method allowed further the demonstration that it is specifically the 1-acetate of the sugar that is involved in the acyl-transfer process. The rate of acetylation of methanol is dependent on the concentration of imidazole at low concentrations of imidazole and is faster with imidazole than with the more basic, albeit more hindered, 2-methylimidazole. This suggests the direct intervention of *N*-acetylimidazole in the transfer process. Confirmation of this was obtained by the surprisingly facile epimerization of the less stable β -glucosepentaacetate to the more stable α -glucosepentaacetate by treating it in dilute deuteriochloroform solution at room temperature with imidazole. This isomerization must involve the formation of

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N-acetylimidazole as shown below:



Finally, it was found that histamine was acetylated at the primary amino group by α -glucosepentaacetate in dilute deuteriochloroform at room temperature. Since we have shown that the transacetylation under these conditions requires imidazole catalysis, we postulate first the imidazole moiety of histamine receiving an acetyl group and thence transfer of the acetyl group, either via an inter- or intra-molecular process to the primary amine.

We plan to elaborate the applications of this process to selective acetylation.

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