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SELECTIVE DEACETYLATION OF AROMATIC ACETATES BY AMINOLYSIS

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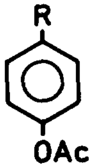
Abstract. Pyrrolidine was shown to deacetylate aromatic acetyl groups considerably faster than aliphatic groups.

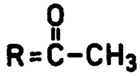
Acetyl groups are often used to protect hydroxyl functions in organic syntheses It is sometimes desirable to deacetylate aromatic acetates without affecting aliphatic acetates. Preliminary experiments showed that neither base hydrolysis (OH^-), alcoholysis (sodium isopropylate/isopropyl alcohol) nor reduction ($LiAlH_4$) was sufficiently selective for our purpose. Recently[1] a selective deacetylation method has been reported, which is based on a catalytic type of methanolysis of aromatic acetates using activated zink in methanol Previously we have reported deacetylation of cellulosic esters by aminolysis using pyrrolidine as the amine[2,3]. In this paper a new, simple method is presented for the selective deacetylation of aromatic acetates by aminolysis. A series of acetylated phenols (I - XIV) were treated with pyrrolidine Quantitative determination (GC)[2,3] of 1-acetylpyrrolidine formed in the reaction showed that phenolic acetyl groups reacted quantitatively within a few minutes.

In a typical deacetylation procedure, the acetylated phenol was dissolved in pyrrolidine or in a mixture of pyrrolidine and another solvent e.g. dichloromethane or dioxane After three minutes at room temperature, dichloromethane or ethylacetate was added and the solution was subsequently extracted with HCl (2 M) several times. The organic layer was dried and the solvent evaporated in vacuo to yield the deacetylated product which was identified by ^{1}H-NMR (isolated yield > 80 %) According to NMR the excess of pyrrolidine and the 1-acetylpyrrolidine formed were completely removed from the organic phase in the extraction step.

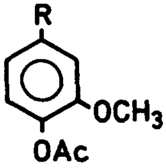
The following generalisations can be made (1) The aminolysis of unhindered aromatic acetates is quantitative and very fast. (2) Hindered acetates (e.g VIII) require a longer reaction time. (3) There is a pronounced difference in the aminolysis rate between the aromatic acetyl groups and the aliphatic acetyl groups in IV, V, VII, XII and XIV The aromatic acetyl groups were removed within a few minutes (1 - 15 min, RT), whereas the aliphatic acetyl groups in the molecules generally required several hours, often at elevated temperatures. This suggested that aminolysis also may be utilized in a new method for the quantitative determination of phenolic groups in various compounds, e.g. in lignin, an essential component of wood The 1-acetylpyrrolidine, formed in the reaction, is easily determined by GC[3] Investigations of such a method are under way and the results will be published shortly[4].



I $R=CH_3$

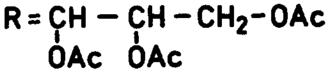


II $R=\overset{O}{\overset{\|}{C}}-CH_3$



III $R=H$

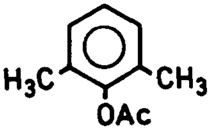
IV $R=CH_2-CH_2-CH_2-OAc$



V $R=\underset{OAc}{CH}-\underset{OAc}{CH}-CH_2-OAc$

VI $R=CH_2-CH=CH_2$

VII $R=CH=CH-CH_2-OAc$



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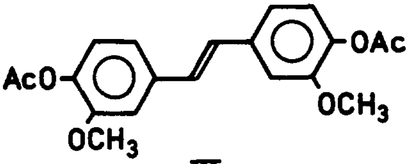

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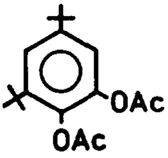

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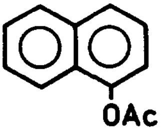

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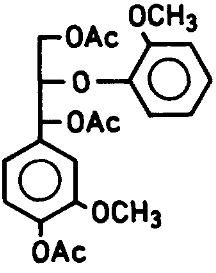

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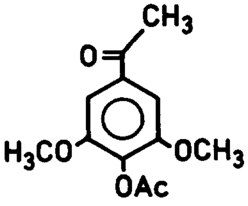

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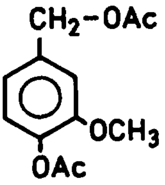

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4. P. Månsson, to be published.

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