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A NEW SYNTHESIS OF ALDEHYDES FROM ACIDS *via* REDUCTION OF N-ACYL SACCHARINS USING SODIUM DIHYDRO BIS-(2-METHOXY-ETHOXY) ALUMINATE

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Abstract—Synthesis of certain aldehydes from the carboxylic acids has been carried by reduction of the corresponding N-acyl saccharins using SDA. The N-acyl saccharins are easily prepared by reaction of an acid with γ-saccharin chloride, which can be used for the next step of reduction without isolation and purification. This provides a convenient and one step synthesis of aldehydes by combining the two reactions, *viz.*, preparation of the N-acyl compound and its reduction. The method has been successfully applied for the reduction of aliphatic, alicyclic, aromatic, and α,β-unsaturated acids to the corresponding aldehydes and the yields obtained are quite satisfactory.

Numerous synthetic routes to aldehydes from carboxylic acid derivatives are known.[1,2] The recent methods of aldehyde synthesis from the acids or their derivatives utilise metal hydride reduction. Normally the metal hydride reduction of acid derivatives, e.g., the esters or acid chlorides gives the corresponding alcohols while the amide derivatives are reduced to amines or alcohols, but during the reduction of tertiary amides and in case of certain phenolic esters, the rupture of —CO—N< or —CO—O— bond has frequently been observed, which results in N— or O— deacetylation, respectively. If the hydride is not used in excess, the acyl function can be isolated as the corresponding aldehyde, particularly if the reduction is carried out at a low temperature. A comprehensive survey of such methods of aldehyde synthesis has recently been made by Smith[3] and Weygand.[4-6]

In many of these methods, the N-acyl compound is derived from more acidic >NH groups such as those in carbazole,[7] 3,5-dimethyl pyrazole,[8,9] imidazole and pyrrole. This is to be expected because such N-acyl compounds are active trans-acylating reagents and the amine component in such compounds can act as a good leaving group, resulting in easy cleavage of —CO—N< bond. The same is true of phenolic esters.

An aldehyde synthesis introduced by Staab[10] involves the reduction of N-acylimidazole. Recently the trans-acylation reactions of N-acylsaccharin were reported from these laboratories[11] and the reactivity of N-acyl saccharin has been found to be comparable to that of N-acyl imidazole. It has now been found that the N-acyl saccharin can be synthesised in one-step from the carboxylic acid and γ-saccharin chloride which is easily prepared.[9] N-Acyl saccharins thus synthesised can be reduced in high yield to the corresponding aldehydes by sodium bis-(2-methoxy-ethoxy) aluminium hydride (SDA). This provides a convenient and one-step synthesis of aldehyde from the carboxylic acid. The main advantage of the proposed method is combining of the two reactions, i.e., the preparation of N-acyl compound and its reduction in one step. The reductions are successfully carried at 0 to 5°, whereas in many other cases, temperatures as low as −70° have to be employed. The method has been successfully applied for the reduction of aliphatic, alicyclic, aromatic and α,β-unsaturated acids to the corresponding aldehydes.

EXPERIMENTAL

Reagents and material. Sodium bis(2-methoxy-ethoxy) aluminium hydride (SDA) used in the present investigation was obtained as a 70% benzene solution (supplied by The Institute of Inorganic Synthesis, Czechoslovak Academy of Sciences, Prague), used as such or after proper dilution with dry benzene.

'AnalaR' benzene used as the solvent was dried by distillation over SDA.

Preparation of N-Acyl Saccharins

(a) *Via carboxylic acid chloride.* A mixture of the acid chloride (1 mol) and sodium salt of saccharin (1·5 mol) was melted together for a few min. The products obtained as such were washed with $NaHCO_3$aq and finally recrystallised from ethyl methyl ketone or THF.

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Table 1

S. No.	N-acyl-saccharin	Aldehyde	b.p. (°C)	Yield (%)
1.	N-Acetyl-saccharin	Acetaldehyde	18(20)	76
2.	N-Propyl-saccharin	Propionaldehyde	53(49)	78
3.	N-Butyryl-saccharin	Butyraldehyde	72(75)	78
4.	N-Cyclohexanecarbonyl-saccharin	Cyclohexane aldehyde	66(63)	75
5.	N-Benzoyl-saccharin	Benzaldehyde	182(179)	80
6.	N(o-Chlorobenzoyl) saccharin	*o*-Chlorobenzaldehyde	210(213)	65
7.	N(*p*-Chlorobenzoyl) saccharin	*p*-Chlorobenzaldehyde	212(214)	72
8.	N(*o*-Toluoyl) saccharin	*o*-Tolualdehyde	201(200)	63
9.	N(*p*-Toluoyl) saccharin	*p*-Tolualdehyde	206(204)	70
10.	N(*p*-Nitrobenzoyl) saccharin	*p*-Nitrobenzaldehyde	103*(106)	75
11.	N-Cinnamoyl-saccharin	Cinnamaldehyde	253(252)	77

*m.p. of *p*-nitrobenzaldehyde.

(b) *From γ-saccharin chloride.* To a soln of γ-saccharin chloride (1 mol) in methylene chloride was added the carboxylic acid (1 mol) at 0°.[12] The mixture was kept at this temp for 10 min or such time till the completion of reaction which was ascertained by TLC. Finally the methylene chloride was distilled off and the N-acyl saccharin obtained was subjected to reduction.

Reduction of N*-acyl saccharins by SDA.* To a suspension of the N-acyl saccharin (1 mol) in dry benzene, was added with stirring, a soln of SDA (0·5 mol) in benzene, in small portions, during 5–10 min at 0 to 5°. The stirring was continued at this temp for about 2 h, and the product was subsequently decomposed with little water. The benzene layer was separated and the ppt of saccharin and the metal hydroxide was filtered off and washed with benzene.

The aqueous layer was extracted several times with benzene and all the benzene extractions were combined and subjected to reduced pressure distillation using rotary vacuum flash evaporator. In this manner, the aldehydes were separately collected. The yield of aldehydes was found to be in the range of 70 to 80%. Alternatively the combined benzene solution may be treated with a soln of 2,4-dinitrophenyl hydrazine and the precipitated hydrazones can be weighed. The results obtained by the reduction of various N-acyl saccharins with SDA are given in Table 1.

A controlled experiment between saccharin and SDA showed that saccharin was not reduced by SDA.

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