Tetrahedron Letters No. 29, pp. 2087-2090, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THE PREPARATION OF ALDEHYDES BY REDUCTION OF ESTERS OF CARBOXYLIC ACIDS WITH SODIUM ALUMINIUM HYDRIDE*

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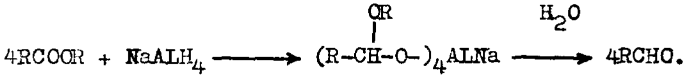
(Received 21 October 1963)

REDUCTION of esters of carboxylic acids to aldehydes is of considerable synthetic interest. It has been recently shown I) that such a reduction may be effectively carried out by diisobutylaluminium hydride or its complex with sodium hydride. We have now found that reduction of esters of carboxylic acids can be effected also by sodium aluminium hydride that has recently become readily available 2,3,4). The reduction proceeds by the following scheme:



$$4RCOOR + NaALH_4 \longrightarrow (R\text{-}\overset{\overset{OR}{|}}{CH}\text{-}O\text{-})_4ALNa \xrightarrow{H_2O} 4RCHO.$$

The reaction is carried out in tetrahydrofuran solution or in tetrahydrofuran and pyridine mixture at low temperature ($-65 - -45^{o}$). The temperature must be carefully controlled as rising temperature leads to sharp decrease in yield. The aldehydes are isolated as already described I). The results obtained are listed in Table I. It will be seen that the yields are essentially good, aliphatic aldehydes being obtained in higher yields than aromatic ones.

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* Translated by A.L. Pumpiansky, Moscow.

Reduction of esters of aromatic acids needs lower temperature and more time (5 to 7 hrs) than of esters of aliphatic acids (2 to 5 hrs).

TABLE I

The Yield of Aldehydes on Reduction of Esters of Carboxylic Acids with Sodium Aluminium Hydride*

Ester	Yield aldehydes (%)
I. Methylbytirate	8I
2. Methylcapronate	85
3. Ethyl-α,α,ω-trichlorocapronate	66
4. Ethylnicotinate	8I
5. Ethylbenzoate	48
6. Methyl o-chlorobenzoate	43
7. Dimethylphtalate	52
8. Methylcinnamate	46
9. Methylhydrocinnamate	88
I0. Dimethylsebacinate	74
II. Ethylundecylenate	60
I2. Ethyllaurinate	76
I3. Methyloleinate	66
I4. Ethyl-δ-cyanovaleriate	25
I5. δ-valerolactone	75
I6. Tridecanolide	72

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* The yield of aldehydes was accounted for by 2,4,-dinitrophenylhydrazones.

To a solution of methylhydrocinnamate (I6 g) in tetrahydrofuran (I00 ml) at)-45 - -60° sodium aluminium hydride (I.45 g) in tetrahydrofuran (20 ml) is gradually added. After three hour's stirring the reaction mass is poured in an excess cold solution of sodium bisulphite. The bisulphite compounds of hydrocinnamic aldehyde are decomposed by 5% sulphuric acid solution to yield hydrocinnamic aldehyde (I0.4 g or 80% of theory). Lactones are also reduced by sodium aluminium hydride to corresponding hydroxyaldehydes in a good yield (Table I).

We have also found that low temperature reduction of esters of carboxylic acids by lithium aluminium hydride in tetrahydrofuran or in the mixtures tetrahydrofuran with pyridine instead of ether gives in some cases rise to aldehydes in fair yield. Thus reduction of methylcapronate by lithium aluminium hydride in tetrahydrofuran at -78° led to capronic aldehyde in 49% yield together with 22% of hexyl alcohol whereas reduction of methylcapronate in diethyl ether in similar conditions resulted in less than I0% of capronic aldehyde and in 55% of hexyl alcohol. Reducing ethyllaurinate at -75° in tetrahydrofuran by lithium aluminium hydride resulted in 45% of laurinic aldehyde whereas with methylbenzoate no aldehyde was formed.

Esters of carboxylic acids may be also reduced in some cases in fair yield to aldehydes also by potassium aluminium hydride in diglime solution through at higher temperature than with sodium aluminium hydride. Thus reduction of methylbytirate at -I5° and dimethylsuccinate at -5° led to aldehydes in a 54 and 5I% yield respectively.

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