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REDUCTION OF ESTERS OF CARBOXYLIC ACIDS INTO ALDEHYDES WITH DIISOBUTYLALUMINIUM HYDRIDE*

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REDUCTION of esters of carboxylic acids directly to aldehydes is of great synthetic interest. We have previously shown that commercially available diisobutylaluminium hydride could be very useful in reducing nitriles[1] and N,N-dialkylamides[2] into aldehydes.

We have found that at low temperatures (about -70°) diisobutylaluminium hydride reduces in high yields various esters of aliphatic and aromatic acids into aldehydes, the reaction proceeding as follows:

$$RCOOR' + (i\text{-}C_4H_9)_2AlH \longrightarrow R\text{-}CH(OR')(OAl(i\text{-}C_4H_9)_2) \xrightarrow{H_2O} RCHO.$$

To a solution of ester in toluene, hexane and ether is added an equimolecular amount of diisobutylaluminium hydride in the same solvent at -70°. In 0.5-1 hr the mixture is decomposed either with an excess of a saturated solution of sodium bisulphite or with a saturated solution of ammonium chloride. In the former case a bisulphite derivative of aldehyde is produced and the aldehyde is isolated in a conventional manner. The experimental results are summarized in Table 1. In some runs the yield of

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* Translated by A.L. Pumpiansky, Moscow.

1 L.I. Zakharkin and I.M. Khorlina, Dokl. Akad. Nauk SSSR 116, 422 (1957).

2 L.I. Zakharkin and I.M. Khorlina, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk 2146 (1959).

TABLE 1

The Yield of Aldehydes on Reduction of Ethers of Carboxylic Acids with Diisobutylaluminium Hydride

Ester	Yield aldehydes (%)
1. Ethylbutyrate	88
2. Ethyl-iso-butyrate	80
3. Methylcapronate	85
4. Ethyl-ω-ethoxyheptanoate	82
5. Methyl-δ-chlorovaleriate	78
6. Ethyllaurinate	88
7. Ethylstearate	50
8. Dimethylsebacinate	90
9. Ethylbenzoate	62.5
10. Isopropylbenzoate	74
11. Ethyl p-methoxybenzoate	70
12. Ethyl p-nitrobenzoate	48
13. Propylphenylacetate	86
14. Diisobutylphtalate	86

aldehydes was determined in terms of 2,4-dinitrophenylhydrazones.

In most cases aliphatic aldehydes are obtained in higher yields than aromatic aldehydes. Solvents affect reduction; thus, in toluene and hexane the yields of aldehydes exceed by 10-15 per cent those in ether.

We have also found that the reduction of esters with sodium diisobutylaluminium dihydride, readily available from sodium hydride and diisobutylaluminium hydride,[3] in diethyl ether solution at -70° also leads to the formation of aldehydes in a high yield. Thus ethylbutyrate, methylcapronate and ethylbenzoate yielded respective aldehydes in amounts 80, 72 and 60 per cent of theory.

The investigation of the reaction is being carried on so as to establish its full range of application.

[3] L.I. Zakharkin and V.V. Gavrilenko, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk 2245 (1960).