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# One Pot Conversion of Carboxylic Acids to Aldehydes with DIBAL-H

**S. Chandrasekhar,* M. Suresh Kumar and B. Muralidhar**

Indian Institute of Chemical Technology, Hyderabad-500 007, India.

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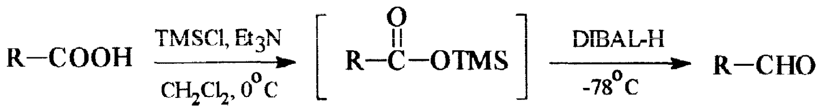
***Abstract*** : A mild and selective reduction of carboxylic acids to aldehydes is described. This process involves *in situ* protection of carboxylic acid as its TMS ester which was reduced to aldehyde using stoichiometric amounts of DIBAL-H.

Undoubtedly, aldehyde functionality occupies a central position of all the groups because of their ability not only to accept electrophiles but also for its ability to reverse the polarity (*umpolung*) after derivatisation with sulphur reagents. It is not surprising therefore, that a good number of procedures[1] have been introduced to generate this functionality ranging from oxidation of benzylic and allylic sites, alcohols, ethers, halides, to reduction of carboxylic acids and their derivatives. Of these, the direct reduction of carboxylic acids to aldehydes is rather poorly addressed. The few literature reagents described includes lithium in dimethyl amine,[2] thexyl borane,[3] 2-thiazoline-2-thiol,[4] isobutylmagnesium bromide/dichloro bis (η-cyclo pentadienyl) titanium,[5] bis(4-methyl piperazinyl)-aluminium hydride[6] and $BH_3:S(CH_3)_2/PCC$,[7] only the last one being practical. However this also suffers drawbacks especially when the olefin is a part structure. Thus efforts are still directed towards the development of selective and more convenient methods. One such method, the direct conversion of carboxylic acids to aldehydes by chemoselective reduction of their corresponding TMS esters[8] (*in situ* generated) using DIBAL-H[9] in a single pot is described herein.



$$R{-}COOH \xrightarrow[CH_2Cl_2,\ 0^{\circ}C]{TMSCl,\ Et_3N} \left[ R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OTMS \right] \xrightarrow[-78^{\circ}C]{DIBAL\text{-}H} R{-}CHO$$

The readily available phenylacetic acid **1a** was treated with 1 equivalent each of triethylamine and $(CH_3)_3SiCl$ at 0°C followed by cooling to -78°C and addition of 1 eq of DIBAL-H for 30 minutes allowed clean formation of phenylacetaldehyde **1b** in 83% isolated yield. This encouraging result prompted us to study some other commercial acids for a similar transformation, and indeed excellent yields of the corresponding aldehydes were obtained (Table-

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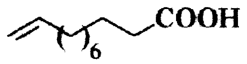
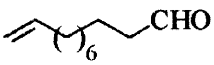
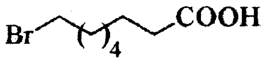
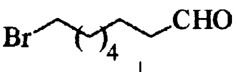
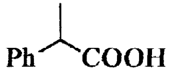
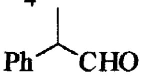
**Table-1 : Reduction carboxylic acids to aldehydes**

| Entry | Starting compound | | Product | | Yield%[a] |
|---|---|---|---|---|---|
| 1. |  | 1a |  | 1b | 83 |
| 2. |  | 2a |  | 2b | 85 |
| 3. |  | 3a |  | 3b | 82 |
| 4. |  | 4a |  | 4b | 80 |
| 5. | o,m-$(OCH_3)_2C_6H_3COOH$ | 5a | o,m-$(OCH_3)_2C_6H_3CHO$ | 5b | 63[b] |
| 6. | m-$ClC_6H_4COOH$ | 6a | m-$ClC_6H_4CHO$ | 6b | 67[b] |
| 7. | o-$CH_3C_6H_4COOH$ | 7a | o-$CH_3C_6H_4CHO$ | 7b | 70[b] |
| 8. | m-$NO_2C_6H_4COOH$ | 8a | m-$NO_2C_6H_4CHO$ | 8b | 65[b] |

a : Yields based on isolation of chromatographically homogenous products
b : 5-8% of alcohols were also isolated

1). 11-Undecenoic acid (entry 2) was also reduced to 11-undecenal **2a** in 85% yield. This substrate is sensitive to $BH_3{:}S(CH_3)_2$/PCC protocol, wherein olefin hydroboration is competetive. The 8-bromooctanoic acid (entry 3) was reduced to 8-bromooctanal **3b** and no bromo reduction product was noticed under the described procedure. A noteworthy feature of the present protocol is that aromatic benzoic acids (entries 5,6,7 and 8) were also reduced smoothly to corresponding aldehydes albeit in moderate yields.

The method reported herein has the advantage over existing borane based reagents especially when substrates contain olefins. Also the reaction procedure is simple, convenient and involves commercial reagents and an easy workup.

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8. Kabalka, G.W.; Bierer, D.E. *Synthetic Comm.*, **1989**, *19*, 2783.
9. DIBAL-H has been previously used to reduce acids to aldehydes, However excess reagent, longer reaction hours required and invariably alcohol is formed in substantial amounts. See Zakharkin, L.I.; Khorlina, I. M. *J. Gen. Chem.* USSR, **1964**, *34*, 1029.