

trans-1,2-dibromocyclohexane was produced in an almost quantitative yield. TMSCl+NaClO₃ pair were found very efficient for α -chlorination of ketones.

A New Aldehyde Synthesis From Carboxylic Acid Esters With Sodium Diethylpiperidino-hydroaluminate¹

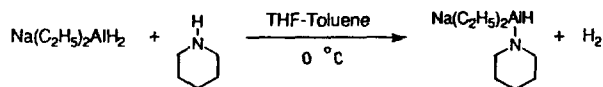
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Partial reduction of carboxylic acid esters to the corresponding aldehydes have been accomplished successfully with various substituted metal hydrides, such as diisobutylaluminum hydride (DIBAH)², lithium tri-*t*-butoxyaluminum hydride (LTBA)³ and diaminoaluminum hydride⁴. Of these reagents, LTBA can be applied only for phenyl esters of aliphatic acids and diaminoaluminum hydride requires longer reaction time (6-10 h), usually at elevated temperature (65°C). On the other hand, DIBAH has been generally utilized for the aldehyde synthesis from esters. However, the yields of aromatic aldehydes (48-70%) are considerably lower than those of aliphatic aldehydes (80-88%). Recently we have improved considerably (10-28%) the yields of aromatic aldehydes by adding *o*-anisidine to the reaction mixture⁵. But the very low temperature (-70°C) required for the DIBAH reduction is still a considerable handicap, especially for larger samples.

Recently we have found that sodium diethylpiperidino-hydroaluminate (SDPA) could be prepared conveniently by reacting equimolar amount of piperidine with sodium diethyldihydroaluminate (OMH-1) in THF-toluene (1:1) cosolvent at 0°C. Reaction of excess SDPA (4 eq) with esters at 0°C showed a distinct rate break after one hydride uptake, suggesting a possibility of aldehyde synthesis (Fig. 1). Indeed we could apply this substituted aluminohydride successfully for the synthesis of aldehydes from the corresponding carboxylic acid esters. The results for representative carboxylic acid esters are summarized in Table 1.



As shown in Table 1, aromatic esters were reduced almost quantitatively to the corresponding aldehydes, using 1.1 eq of SDPA. This is contrasted to the very low yield by OMH-1, as shown in the reduction of ethyl benzoate. *t*-Butyl benzoate was reduced very slowly, in rather lower yield (85%) presumably due to the bulky *t*-butyl group. The yields of aldehydes from aliphatic esters were somewhat low compared with the aromatic aldehydes, yet the yields are comparable to the other known methods. The yields of aldehydes

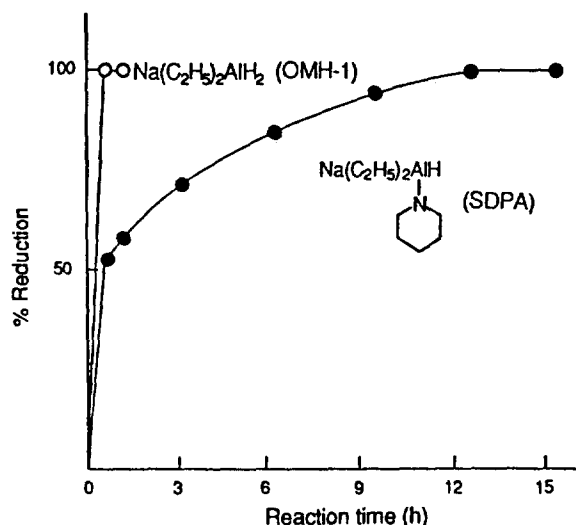


Figure 1. Reaction of OMH-1 and SDPA with Ethyl Benzoate in THF-Toluene at 0°C. ([Hydride]=0.8 M, and [Ester]=0.2 M).

Table 1. Partial Reduction of Esters to the Corresponding Aldehydes with SDPA in THF-Toluene at 0°C

| Esters | Ratio of hydride/compd. | Reaction time(h) | Yield ^b of aldehyde(%) |
|---------------------------------|-------------------------|------------------|-----------------------------------|
| methyl benzoate | 1.1 ^c | 0.5 | 98 |
| ethyl benzoate | 1.1 | 0.5 | 99 |
| | (1.1) | (0.5) | (22) ^d |
| isopropyl benzoate | 1.1 | 1.0 | 97 |
| <i>t</i> -butyl benzoate | 4.0 | 3.0 | 85 ^d |
| phenyl benzoate | 1.1 | 0.5 | 97 |
| ethyl <i>o</i> -toluate | 1.1 | 1.0 | 60 |
| | 1.5 | 1.0 | 92 |
| | (1.1) | (1.0) | (27) ^d |
| ethyl <i>m</i> -toluate | 1.1 | 1.0 | 94 |
| ethyl <i>p</i> -toluate | 1.1 | 1.0 | 94 |
| ethyl <i>o</i> -methoxybenzoate | 1.5 | 1.0 | 96 |
| ethyl <i>p</i> -methoxybenzoate | 1.1 | 1.0 | 94 |
| methyl <i>o</i> -chlorobenzoate | 1.1 | 3.0 | 93 |
| methyl <i>m</i> -chlorobenzoate | 1.1 | 0.5 | 99 |
| ethyl <i>p</i> -chlorobenzoate | 1.1 | 0.5 | 96, 79 ^d |
| ethyl <i>p</i> -nitrobenzoate | 1.1 | 0.5 | 98, 77 ^d |
| ethyl caproate | 1.1 | 1.0 | 85 |
| ethyl decanoate | 1.1 | 1.0 | 90 |
| isopropyl caproate | 1.1 | 1.0 | 63 |
| | 1.1 | 3.0 | 52 |
| | 1.5 | 2.0 | 77 |
| ethyl cyclohexanecarboxylate | 1.1 | 3.0 | 47 |
| | 1.5 | 3.0 | 61 |
| ethyl cinnamate | 1.1 | 1.0 | 65 |

^a1.1 Equiv. of SDPA was added to esters in THF-Toluene at 0°C. ^bYields were estimated by GLC. ^cYields obtained by OMH-1 alone are shown in parenthesis. ^dIsolated yield.

from linear unhindered esters such as ethyl caproate or ethyl decanoate were good, however hindered esters such as isopropyl caproate and ethyl cyclohexanecarboxylate, and α , β -

unsaturated ester, ethyl cinnamate gave only moderate yields. Overall the yields of aldehydes are better than those with the other methods²⁻⁴. Another big advantage of this reagent is that this aldehyde synthesis can be carried out at 0°C instead of the very low temperature (-70°C). Therefore, SDPA is believed to be a reagent of choice for the synthesis of aldehydes from esters.

The following reduction is representative. [Reagent] Into a 500 ml flask, which was thoroughly dried in an oven and cooled down under nitrogen, 150 ml (300 mmol) of 2 M OMH-1 solution in toluene and 150 ml of THF were introduced. The solution was cooled to 0°C, and then 32.6 ml (330 mmol) of distilled piperidine was added with vigorous stirring. Stirring was continued for additional 3 h for complete hydrogen evolution. The SDPA solution thus prepared was 0.88 M in hydride as standardized by hydrolyzing SDPA with *t*-BuOH-THF (1:1) mixture, [Reduction] Into a 50 ml flask, was introduced 2.8 ml of THF, followed by 1.0 ml (1.0 mmol) of ethyl 4-nitrobenzoate solution in THF containing mesitylene as an internal standard. The solution was maintained at 0°C, and 1.25 ml (1.1 mmol) of 0.88 M solution of SDPA in THF-toluene (1:1) was added. After 0.5 h, the reaction mixture was hydrolyzed with 10 ml of 1 N sulfuric acid and the product was extracted with 10 ml of ethyl ether. The ether layer was dried over anhydrous potassium carbonate, and analyzed by GLC on a FFAP 50 m capillary column; which showed a 98% yield of 4-nitrobenzaldehyde. For the isolation of aldehyde (50 mmol scale), the ether layer was poured into 150 ml of saturated aqueous sodium bisulfite solution. To this solution was added 100 ml of THF and the mixture was stirred for 2 h. At this time the crystalline bisulfite adduct of 4-nitrobenzaldehyde was apparent. The solution was cooled in an ice bath to ensure complete crystallization of the adduct. The adduct was collected by filtration, washed with pentane (3×50 ml), and dried. The adduct was placed in 100 ml of saturated aqueous magnesium sulfate solution, and 100 ml of pentane and 20 ml of a 37% formaldehyde solution were added. The mixture was stirred for 1 h. The pentane layer was separated and dried over anhydrous magnesium sulfate. Evaporation of all volatile materials gave a 77% yield of pure 4-nitrobenzaldehyde, mp 107°C (lit. 106-107°C).

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Regeneration of Cyclohexanone From Its Oxime With Various Dicarboxyl Compounds

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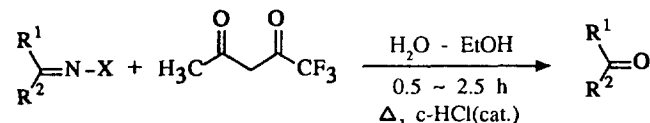
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Deblocking methods of oximes and hydrazones have received much attention to organic chemists¹. Recently, we have reported an efficient regeneration method of carbonyl compounds from their oximes and hydrazones including *N,N*-dimethylhydrazones and tosylhydrazones by the exchange reaction with 1,1,1-trifluoro-2,4-pentanedione (TPD) under mild conditions as outlined in **Scheme 1**².

In connection with our studies on the exchange reaction, our endeavor was focused on finding new alternatives to TPD. We have explored the exchange reactions with various dicarbonyl compounds **2** with cyclohexanone oxime (**1**) as the common substrate to regenerate cyclohexanone (**3**). To trap effectively the hydroxylamine liberated³ from the exchange reaction, we examined dicarbonyl compounds which were activated with electron withdrawing substituent such as trifluoromethylated β -diketones, β -acylpyruvates⁴, and α -diketones as shown in **Scheme 2**.

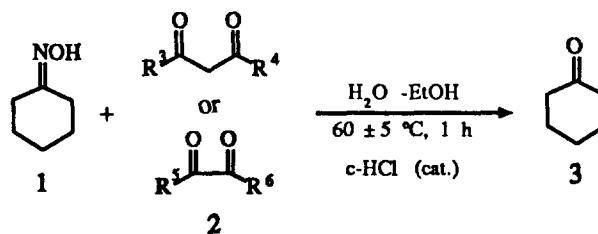
In a typical run, to a stirred solution or a suspension of cyclohexanone oxime (**1**, 226 mg, 2 mmol) and dicarbonyl compound **2** (4 mmol) in 50% aq. EtOH (10 ml), a catalytic amount of *c*-HCl (100 μ l) was added, and the mixture warmed for 1 h. Conversion yield of cyclohexanone (**3**) was determined by GC⁵ and the results were summarized in **Table 1**. And for comparison, we utilized acetone⁶, levulinic acid⁷, acetylacetone⁸, and pyruvic acid⁹ (entry 14-17).

In addition to the β -diketones containing trifluoromethyl group as described previously², conversion of **1** into **3** was also found to be cleanly effected by using 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (entry 3), β -acylpyruvates (entry 5-8), α -dicarbonyl compounds (entry 9,10,13), which have appreciable solubility in the reaction medium, as well as acetylac-



X = OH, NH₂, NMe₂, NHSO₂C₆H₅

Scheme 1.



Scheme 2.