

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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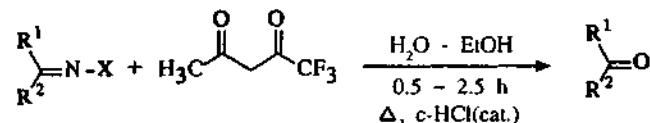
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Deblocking methods of oximes and hydrazones have received much attention to organic chemists¹. Recently, we have reported an efficient regeneration method of carbonyl compounds from their oximes and hydrazones including *N,N*-dimethylhydrazones and 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**.

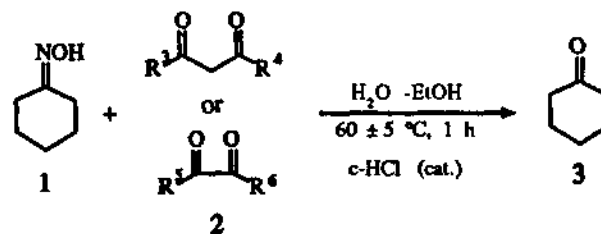
In a typical run, to a stirred solution or a suspension of cyclohexanone oxime (**1**, 226 mg, 2 mmol) and dicarbonyl compound **2** (4 mmol) in 50% aq. EtOH (10 ml), a catalytic amount of *c*-HCl (100 μ l) was added, and the mixture warmed for 1 h. Conversion yield of cyclohexanone (**3**) was determined 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-



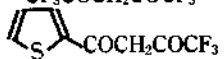
X = OH, NH₂, NMe₂, NHSO₂C₆H₅

Scheme 1.



Scheme 2.

Table 1. Regeneration of Cyclohexanone from Cyclohexanone Oxime

Entry	Dicarbonyl Compound	Conversion Yield ^a (%)
1	CH ₃ COCH ₂ COCF ₃	100
2	PhCOCH ₂ COCF ₃	100
3	CF ₃ COCH ₂ COCF ₃	100
4	 COCH ₂ COCF ₃	82
5	CH ₃ COCH ₂ COCO ₂ CH ₃	100
6	CH ₃ COCH ₂ COCO ₂ Et	100
7	EtCOCH ₂ COCO ₂ CH ₃	100
8	PhCOCH ₂ COCO ₂ CH ₃	100
9	CH ₃ COCOCH ₃	100
10	PhCOCOCH ₃	100
11	PhCOCOPh	64
12	PhCOCHO	88
13	EtO ₂ CCOCO ₂ Et	100
14	CH ₃ COCH ₃	55
15	CH ₃ COCH ₂ CH ₂ CO ₂ H	40
16	CH ₃ COCH ₂ COCH ₃	100
17	CH ₃ COCO ₂ H	100

^aDetermined by GC of the reaction mixture, area percentage.

tone (entry 16) and pyruvic acid (entry 17). However, thioyltrifluoroacetone (entry 4), benzil (entry 11), and phenylglyoxal (entry 12) gave somewhat lower yield due to its poor solubility in aq. EtOH. Acetone (entry 14) and levulinic acid (entry 15) were poorly effective under the present reaction conditions.

In conclusion, we found that certain dicarbonyl compounds such as β -diketones substituted with electron withdrawing group or α -diketones, can convert effectively cyclohexanone oxime to cyclohexanone. Thereby, these methods could also be applied conveniently to the deoximation reaction of other oxime compounds.

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A Convenient Method for Esterification over Perfluorinated Resinsulfonic Acid (Nafion-H)

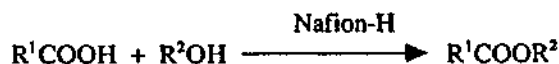
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Nafion-H is perfluorinated resinsulfonic acid having sulfonic acid group in the amount of 0.01 to 5 mequiv/gram resin. The estimated H_0 value for Nafion-H is comparable to or larger than that of 96 to 100% sulfuric acid¹⁻³. Nafion-H in contact with solvent system affects only the surface acidity (the solvent phase directly in contact with the catalytic surface). Nafion-H and related perfluoroalkanesulfonic acids are also stable in corrosive environment and at temperatures up to 210 $^{\circ}$ C. These unique properties have led to an extensive development of various acid catalyzed reactions such as alkylation, transalkylation, nitration, polymerization, ether and ester formation, rearrangement, etc⁴⁻⁷.

In this paper we wish to report our results of convenient esterification reaction catalyzed by Nafion-H. The esterification experiment was carried out by refluxing a mixture of carboxylic acid (1.0 g), alcohol (5.0 ml), Nafion-H (0.2 g), and 3-nitrotoluene (0.02 g, internal standard for GC analysis) for 8 hours.



Water was removed with small amount of silica gel in a soxhlet thimble suspended just below refluxing condenser. The mixture was analyzed with gas chromatography on a 25 m capillary column of 5% phenylmethylsilicon. The yields are corrected for the molar response of the authentic esters to internal standard. The results are summarized in Table

Table 1. Yields^a of Esterification of Carboxylic acids (R¹COOH) with Alcohols (R²OH) using Nafion-H^b

R ¹	R ²	C ₂ H ₅	n-C ₄ H ₉	n-C ₆ H ₁₃	cy-Hexyl ^c	t-C ₄ H ₉
CH ₃		92.9	100	90.0	20.4(47.8)	27.0
C ₂ H ₅		92.6	85.4	92.7	33.1(46.3)	18.4
n-C ₃ H ₇		100	100	100	40.5(33.5)	8.7
i-C ₃ H ₇		97.4	92.1	98.3	46.2(43.2)	14.0
cy-Hexyl		96.0	100	96.5	45.5(61.5)	6.8

^aPercent yield based on the starting carboxylic acids, ^bReaction condition, reflux for 8 hours, ^cThe number in parenthesis is the yield of cyclohexene based on cyclohexanol.