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ORIGINAL PAPER

# Transesterification via Baeyer–Villiger oxidation utilizing potassium peroxydisulfate ($K_2S_2O_8$) in acidic media

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**Abstract** Baeyer–Villiger oxidation of ketones with potassium peroxydisulfate ($K_2S_2O_8$) and sulfuric acid generates the anticipated esters or lactones. These products are transformed into new esters (or hydroxy esters) in the presence of alcohols via transesterification under Baeyer–Villiger reaction conditions in one pot.

**Keywords** Potassium peroxydisulfate ($K_2S_2O_8$) · Transesterification · Baeyer–Villiger oxidation · Hydroxy esters

## Introduction

Transesterification is an equilibrium process in which an existing ester is transformed into a desired one through interchange of the alkoxy group [1]. Since transesterification is an equilibrium process, an acidic [2, 3] or basic [4, 5] catalyst is usually required to promote the desired reaction. Transesterification occurs by mechanisms [6] that are identical to those of ester hydrolysis (by the acyl-oxygen fission mechanisms) and frequently fail when the alkoxy group is tertiary due to steric hindrance. This process generates a new ester, and if lactones are used as starting material they are easily opened by treatment with alcohols to give open-chain hydroxy esters [7, 8].

Baeyer–Villiger reaction involves formation of esters (from acyclic ketones) or lactones (from cyclic ketones), so its products can be used for transesterification under appropriate conditions. Baeyer–Villiger oxidation is usually carried out with peroxy compounds such as peracids [9–11] and ROOH [12, 13]. Acids, bases, enzymes, and metal-containing reagents are known to catalyze Baeyer–Villiger oxidation [14, 15].

## Results and discussion

Recently, we reported a general route for direct synthesis of lactones by utilizing a peroxydisulfate oxidative system [16–20]. Herein we describe an application of potassium peroxydisulfate ($K_2S_2O_8$) in sulfuric acid solution in the presence of ketones and excess alcohols to prepare the relevant esters (or hydroxy esters) via transesterification of Baeyer–Villiger oxidation products (Scheme 1).

Peroxydisulfate salts are powerful and useful oxidizing agents [21, 22]. Potassium peroxydisulfate (also known as potassium persulfate) in acidic solution generates peroxodisulfuric acid with the chemical formula $H_2S_2O_8$. Hydrolysis of peroxodisulfuric acid gives peroxomonosulfuric acid ($H_2SO_5$), which is often called Caro's acid and is the real oxidant in this reaction [23]. The mechanism of Baeyer–Villiger oxidation involves nucleophilic addition of the peroxymonosulfate anion to the protonated carbonyl group, formation of a Criegee intermediate, loss

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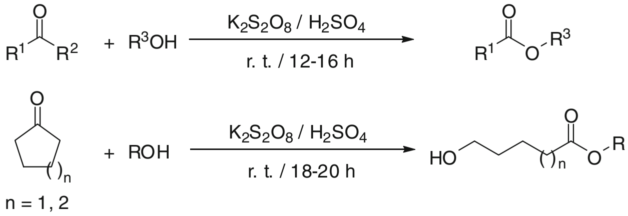


**Scheme 1**

of $HSO_4^-$ with simultaneous formation of a dioxirane ring [24], and finally intramolecular rearrangement to give an ester or lactone [25, 26] (Scheme 2).

Because of the presence of excess alcohol and acidic conditions, esters and lactones undergo transesterification to produce the relevant new esters and hydroxy esters, respectively. By use of different ketones and alcohols, various esters were obtained in high yields except with *t*-butanol because of steric hindrance (Table 1).

Herein is described an efficient and mild method for the oxidation and transesterification of ketones to the relevant esters in one step at room temperature using $K_2S_2O_8$ and 40% sulfuric acid in the presence of alcohols. This procedure affords high product yields, especially of hydroxy esters, in a clean one-pot reaction using readily available reagents.

**Scheme 2**

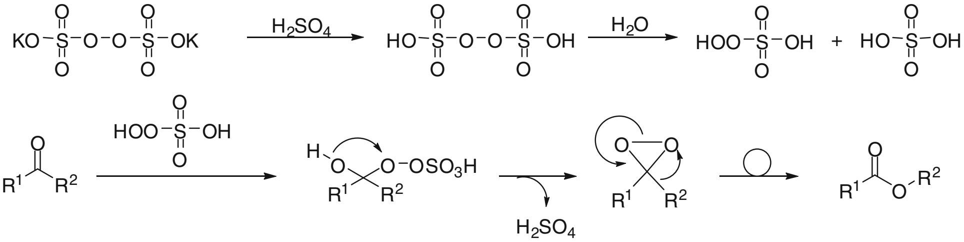
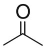
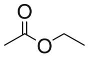
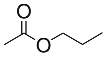
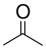
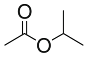
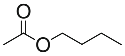
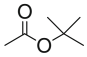
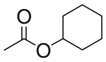
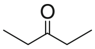
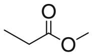
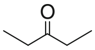
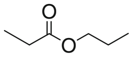
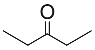
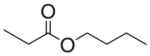
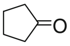
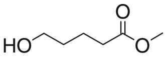
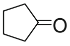
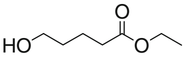
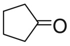
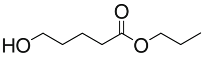
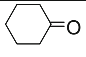
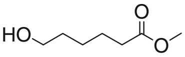
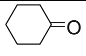
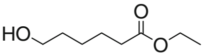
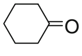
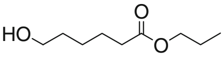


**Table 1** Baeyer–Villiger oxidation of linear and cyclic ketones utilizing $K_2S_2O_8/H_2SO_4$ and subsequence transesterification in the presence of different alcohols

| Entry | Ketone | Alcohol | Product | Time (h) | Yield[c] (%) |
|---|---|---|---|---|---|
| 1[a] |  | EtOH |  | 12 | 84 |
| 2[a] |  | *n*-PrOH |  | 12 | 92 |
| 3[a] |  | *i*-PrOH |  | 14 | 98 |
| 4[a] |  | *n*-BuOH |  | 12 | 97 |
| 5[a] |  | *t*-BuOH |  | 20 | 54 |
| 6[a] |  | Cyclohexanol |  | 14 | 95 |
| 7[a] |  | MeOH |  | 12 | 98 |
| 8[a] |  | *n*-PrOH |  | 15 | 97 |
| 9[a] |  | *n*-BuOH |  | 15 | 97 |
| 10[b] |  | MeOH |  | 18 | 81 |
| 11[b] |  | EtOH |  | 18 | 97 |
| 12[b] |  | *n*-PrOH |  | 18 | 98 |
| 13[b] |  | MeOH |  | 20 | 95 |
| 14[b] |  | EtOH |  | 20 | 99 |
| 15[b] |  | *n*-PrOH |  | 20 | 96 |

[a] The reaction products were identified by GC–MS analysis [27]

[b] Identification of products was done by comparison of their IR, $^1$H NMR, and mass spectra with data in Refs. [28–32]

[c] Determined by GC analysis of the reaction mixture

## Experimental

### *General procedure for the Baeyer–Villiger oxidation*

The oxidizing agent was prepared by adding potassium peroxydisulfate (4.32 g, 16 mmol) to sulfuric acid (40%, 15 $cm^3$) under stirring at room temperature. The ketone (8 mmol) and excess alcohol (5 $cm^3$) were added to the oxidant and the reaction mixture was stirred for 12–20 h. After the completion of the reaction (monitored by GC), the solution was diluted with 15 $cm^3$ water, filtered, and extracted with diethyl ether (2 × 20 $cm^3$). The organic layer was washed with 5% sodium bicarbonate, then with distilled water, dried over magnesium sulfate, filtered, and concentrated in vacuum. Simple esters (Table 1, entries 1–9) were injected into the GC–MS system without further purification, but hydroxy esters (entries 10–15) were first purified by using a short silica gel column (eluent: *n*-hexane/ethyl acetate 9:1). Pure hydroxy esters were obtained after evaporation of the solvent.

The relevant products were detected via their retention times as measured by GC–MS analysis on a Hewlett-Packard 6890 GC instrument (helium as carrier gas) furnished with an HP-5MS (30 m × 0.25 mm × 0.25 μm) column and Hewlett-Packard 5973N MSD instrument. The IR spectra were recorded on an FTIR-8900S spectrophotometer as neat films on sodium chloride plates. The $^1$H NMR spectra were recorded on a Bruker 500 MHz instrument. The structures of simple esters (entries 1–9) were determined by comparing their mass spectra and fragmentation patterns with a GC–MS instrument library search (Wiley 275) and those of the authentic compounds [27]. The structures of hydroxy esters (entries 10–15) were determined by their IR, $^1$H NMR, and mass spectra fragmentation pattern [28–32].

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