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Baeyer–Villiger oxidation of cyclic ketones utilizing potassium peroxydisulfate ($K_2S_2O_8$) or sodium perborate ($NaBO_3$) in acidic media

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Abstract

The efficient, green, facile, mild and straightforward conversion procedure for the oxidation of cyclic ketones to lactones at room temperature utilizing potassium peroxydisulfate ($K_2S_2O_8$) in acidic media is satisfactory to high yields without using traditional chlorinated solvents is reported. This oxidative reagent is cheap and friendly environmental procedure for industrial purposes than use of organic peracids.

Keywords: Baeyer–Villiger oxidation; Cyclic ketones; Potassium peroxydisulfate ($K_2S_2O_8$); Acidic media; Sodium perborate ($NaBO_3$)

The Baeyer–Villiger (B–V) reaction has been widely employed in organic synthesis by virtue of the unique transformation. An oxygen atom can be inserted into a carbon–carbon single bond by an oxidant [1–3]. Hydrogen peroxide has several disadvantages: less reactivity, formation of the regioisomeric mixtures from α-substituted cyclopentenone substrates in particular, and hydrolysis of the esters or lactones product particularly in the presence of strong acids [4]. To overcome these disadvantages, a wide variety of homogeneous and heterogeneous metal catalysts have been developed for the B–V oxidation [1,5].

Several excellent reviews on the subject are available [6–8]. In the laboratory, reagents typically used to carry out this reaction are organic peroxyacids such as meta-chloroperoxybenzoic acid (m-CPBA) [9] (most common reagent because it is commercially available), peroxytrifluoroacetic acid [10] and other peracids which are unstable in solutions and typically require chlorinated solvents such as CH_2Cl_2 or $CHCl_3$ for optimum performance. On an industrial scale, usually hydrogen peroxide with a catalyst is preferred on the grounds of cost and process intensification. The reaction has considerable industrial importance for the manufacture of fine chemicals, in particular, lactones, which are key fragrance ingredients [11–13].

Although more than a century has gone since its discovery, the B–V reaction is far from being at the end of its development. A wide range of oxidants may be used with their activity decreasing in the order: CF_3CO_3H > monopermaleic acid > monoperphthalic acid > 3,5-dinitroperbenzoic acid > p-nitroperbenzoic

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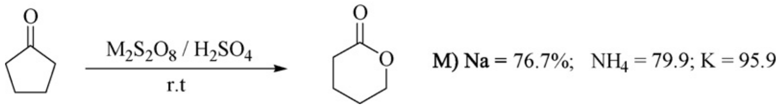
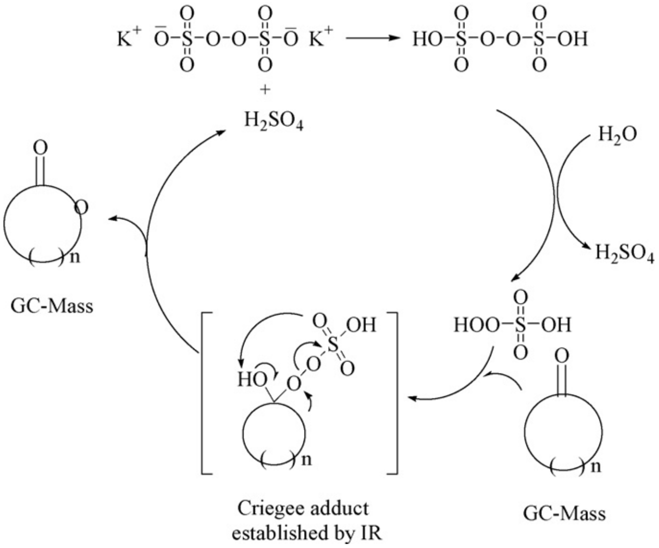


Scheme 1.



Scheme 2. Catalytic cycles of potassium peroxydisulfate ($K_2S_2O_8$) in acidic media in Baeyer–Villiger oxidation.

acid > m-CPBA ~ HCO_3H > $C_6H_5CO_3H$ > CH_3CO_3H >> H_2O_2 > t-BuOOH. Recently, the use of biotransformation and enzymatic methods by recombinant whole-cell increased [14,15]. Lately, we have been able to establish a general route for the direct synthesis of several γ-butyrolactones mediated via benzyl radical cyclization utilizing oxidative system such as $S_2O_8^{2-}/Cu^{2+}$ [16–19].

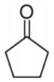
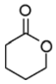
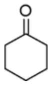
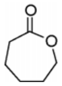
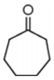
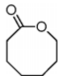
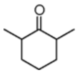
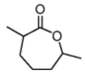
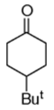
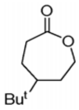
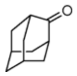
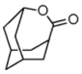
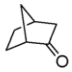
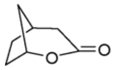
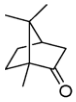
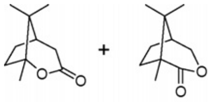
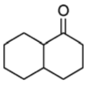
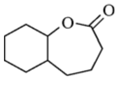
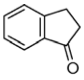
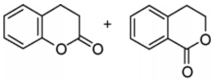
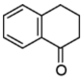
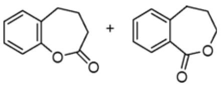
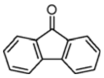
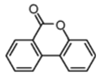
We herein present direct lactonization of cyclic ketones in satisfactory to high yield in aqueous sulfuric acid utilizing stable source of oxygen donor such as potassium peroxydisulfate ($K_2S_2O_8$). The peroxy solution disulfuric acid ($H_2S_2O_8$) that appears to be more widely used as its alkali metal salts generated in situ in the presence of aqueous acid (40% H_2SO_4). Our overall methodology is schematically illustrated in Schemes 1 and 2. Commercially compounds containing peroxodisulfate are $Na_2S_2O_8$, $K_2S_2O_8$ and $(NH_4)_2S_2O_8$, they are all used as strong oxidizing agents. In order to select appropriate reagent, cyclopentanone as substrate with different peroxodisulfate salts in 40% sulfuric acid was utilized. Reaction mixture stirs for 24 h at room temperature.

The lactonization result for cyclopentanone utilizing these commercial compounds is depicted in Scheme 1.

The solubility of potassium salt (5.2 g in 100 mL H_2O) compared to the sodium and ammonium salts (70 and 80 g in 100 mL H_2O, respectively) is very low but its conversion is more than two others (Scheme 1). In the light of this estimation the solution of $K_2S_2O_8$ (16 mmol, 2 equiv.) and 40% H_2SO_4 (15 mL) for synthesis of target lactones **1b**–**12b**, **8c**, **10c**, **11c** from starting cyclic ketones **1a**–**12a** (8 mmol, 1 equiv.) was utilized [20]. The results are summarized in Table 1. In each case while the substrate solubility in aqueous media is low, use of dioxane is appropriate. All yields are good except 2-adamantanone (entry **6**), probably it is due to the bulky and rigidity of the structure.

The mechanism of Baeyer–Villiger reaction in the presence of potassium peroxydisulfate ($K_2S_2O_8$) in acidic media involves nucleophilic addition of in situ prepared persulfuric acid to the carbonyl group of substrate. The prepared Criegee tetrahedral adducts intermediate immediately undergoes intramolecular migration of a substituent from carbon to oxygen with cleavage of the peroxide bond and simultaneous loss of HSO_4^- to generate corresponding lactones (Scheme 2). The rearrangement step is usually, but not always considered as a rate limiting step. The

Table 1
$K_2S_2O_8/H_2SO_4$ Baeyer–Villiger oxidation of cyclic ketones.

Entry	Substrate (a)	Product[a] (b) + (c)	Yield (%)	Solvent[b]	Selectivity[c]	Temp (°C)
1			96	H_2O	100	RT
2			100	H_2O	100	RT
3			98	H_2O	100	RT
4			97	H_2O	100	RT
5			59	H_2O	100	RT
6			41.5	H_2O + dioxane		
7			96	H_2O + dioxane	100	RT
8			97	H_2O + dioxane	83:14	RT
9			98	H_2O + dioxane	100	RT
10			55	H_2O	84:16	RT
11			99	H_2O	77:22	RT
12			20	H_2O + dioxane	100	RT

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[a] Reaction conditions: substrate (8 mmol), potassium peroxydisulfate (16 mmol), 40% H_2SO_4 (15 mL), stirred 24 h, rt.

[b] In each case that carbonyl compounds solubility was low, dioxane as co-solvent (5–10 mL) was added.

[c] Selectivity to the mentioned product listed in the sixth column [23].

migratory ability being: tertiary alkyl > cyclohexyl > secondary alkyl > benzyl > phenyl > primary alkyl > CH_3 [21]. The possibility of H_2O_2 as a real oxidant is excluded, because the large scale production of Caro's acid (H_2SO_5) is usually produced by reaction of 85% sulfuric acid and 50% hydrogen peroxide (called Piranha solution). The reverse reaction producing H_2O_2 is extremely slow [22].

In other efforts replacing potassium peroxydisulfate:40% H_2SO_4 with sodium perborate ($NaBO_3$):20% H_2SO_4 and stirring the resulted mixture at rt for one day, leads to ~4–8% less yields for lactones **1–12** (Table 1). Utilizing potassium peroxydisulfate:20% H_2SO_4 instead of potassium peroxydisulfate:40% H_2SO_4 the desired lactones with 2.5–4% lower yields was achieved. In other efforts replacing of $K_2S_2O_8$:40% H_2SO_4 or $K_2S_2O_8$:20% H_2SO_4 with $K_2S_2O_8$:glacial acetic acid was failed. Baeyer–Villiger reaction of either of these reagents $K_2S_2O_8$:40% H_2SO_4 or $K_2S_2O_8$:20% H_2SO_4 with 4-hydroxybenzaldehyde even after 7 days at rt was not successful. While Baeyer–Villiger reaction of same aldehyde utilizing $K_2S_2O_8$:urea:H_2O_2, 2:1:1 and refluxed over 23 h worked excellent. The reaction of 4-hydroxybenzaldehyde and $NaBO_3$:glacial acetic acid 1:3, reflux for 2 days following by 10 s in Microwave successfully gave desired hydroquinone. In conclusion we have demonstrated an efficient and mild protocol for the oxidation of cyclic ketones to the corresponding lactones at room temperature in high yields utilizing $K_2S_2O_8$:40% sulfuric acid without using any traditional chlorinated solvents. Therefore in the commercial scale this oxidative reagent is cheap and friendly environmental procedure.

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[19] N.O. Mahmoodi, K. Tabatabaeian, M. Kosari, S. Zarrabi, Chin. Chem. Lett. 19 (2008) 1431.
[20] The oxidizing agent is prepared by adding potassium peroxydisulfate (4.32 g, 16 mmol) to sulfuric acid (40%, 15 mL) and stirring for several minutes at room temperature. Then carbonyl compound (8 mmol) was added over a period of 30 min [in each case that carbonyl compounds solubility was low, dioxane as co-solvent (5–10 mL) was added]. After the addition has been completed, reaction mixture stirred for 24 h in room temperature. After the completion of reaction, solution is diluted with 15 mL of water and after filtering, extracted with Et_2O (2 mL × 20 mL). The organic layer washed at first with sodium bicarbonate 5%, then with distilled water and finally dried over $MgSO_4$, filtered and concentrated in vacuum. Products were detected from their retention times as measured by GC–MS analysis on a Hewlett-Packard 6890 GC instrument (gas carrier He) furnished with a HP-5MS (30 m × 0.25 mm) column and Hewlett-Packard 5973N MSD instrument. Identification of products was made by comparison of their mass spectrums with authentic samples and IR, ^1H and ^{13}C NMR; 2-oxocanone **3b**: ^1H NMR ($CDCl_3$, 500 MHz, δ ppm): 1.55 (m, 4H), 1.73 (m, 4H), 2.44 (t, 2H), 4.32 (t, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, δ ppm): 24.93, 26.16, 29.05, 31.64, 32.64, 68.45, 177.43. MS (EI): Exact Mass: (M+): Calcd. 128.0837; Found 128.0834.128, 110, 100, 98, 83, 82, 80, 69, 55 (100), 42; 2-oxo-tricyclo[4,3,1,$1^{4,8}$]dudecane-3-one **6b**: ^1H NMR ($CDCl_3$, 500 MHz, δ ppm): 1.72–2.21 (m, 12H), 3.03 (bs, 1H), 4.44 (bs, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, δ ppm): 26.43, 31.28, 34.16, 35.92, 41.65, 73.64, 179.04. MS (EI): Exact Mass: (M+): Calcd. 166.0994; Found 166.0991,166, 122, 107, 93, 80 (100), 67, 53, 41; 2-oxabicyclo[3.2.1]octan-3-one **7b**: ^1H NMR ($CDCl_3$, 500 MHz, δ ppm): 1.54–2.25 (m, 7H),

2.43–2.76 (m, 2H), 4.88 (bs, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, δ ppm): 29.85, 32.25, 32.83, 35.75, 41.11, 81.43, 171.22. MS (EI): Exact Mass $C_7H_{10}O_2$: (M+): Calcd. 126.0681; Found. 126.0680, 126, 111, 98, 82, 67 (100), 55.

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[23] The selectivity in Table 1 was defined from their chromatograms, e.g. for symmetry starting material ketones was chosen as 100% while the selectivity of unsymmetrical ketones determined from integration of lactone peaks.