Green Oxidation of Ketones to Lactones with Oxone in Water

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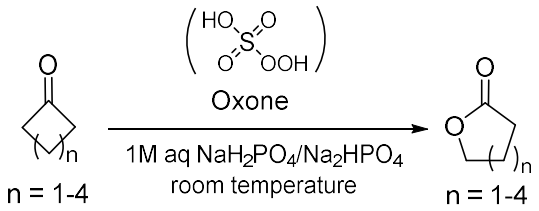


ABSTRACT: Cyclic ketones were quickly and quantitatively converted to 5-, 6- and 7-membered lactones, very important synthons, by treatment with Oxone, a cheap, stable, and non-pollutant oxidizing reagent, in 1M NaH_2PO_4/Na_2HPO_4 water solution (pH 7). Under such simple and green conditions, no hydroxyacid was formed thus making unnecessary the adoption of more complex and non-ecofriendly procedures previously developed to avoid lactone hydrolysis. With some changes, the method was successfully applied also to water insoluble ketones such as adamantanone, acetophenone, 2-indanone and challenging cycloheptanone.

The Baeyer-Villiger (BV) oxidation of carbonyl to ester or lactone function, first accomplished on menthone in 1899,[1] is one of the most important transformations in organic chemistry. Its continuing success is due to a combination of factors, the main ones of which are large variety of the substrates, multiple applications of the products and many options for oxidizing agents and reaction conditions.[2,3] However, the development of greener BV procedures remains a current challenge. Revealingly, the most recurrent subject in the last three years literature on BV oxidation is the replacement of expensive, hazardous and not environmentally benign peracids with the clean oxidant hydrogen peroxide. Nevertheless, according to the most recent BV procedures, hydrogen peroxide needs to be used, due to its weak oxidant power, in combination with purposely prepared catalysts and sometimes in problematic, or even undesirable, solvents.[4] Alongside, potassium peroxomonosulphate ($KHSO_5$), dismissed for decades after the initial use of persulfuric acid (Caro's acid) by Baeyer and Villiger,[1] is witnessing a sort of renaissance due to its many advantages. Commercially available as the stable triple salt $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$ (Oxone, caroate), it is a versatile, easy to handle and non-toxic oxidizing agent, which generates non-polluting by-products. Oxone requires to be dissolved in an aqueous medium, in which carbonyl substrates are sometimes insoluble and their oxidation products are hydrolysable. Therefore, many research efforts have addressed the development of procedures avoiding the use of water or minimizing its drawbacks. Examples include the use of wet-alumina or silica gel supported $KHSO_5$ in DCM,[5] of oxone in ionic liquids, followed by treatment with DCM,[6] in DMF,[7] in water and DCM in the presence of a phase transfer catalyst (PTC),[8] or in trifluoroethanol.[9] As can be seen, despite the employment of a clean oxidant, replacement of water is not accomplished according to principles of sustainable and scalable procedures.

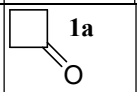
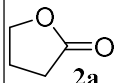
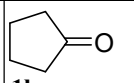
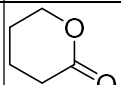
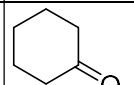
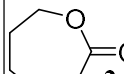
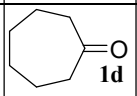
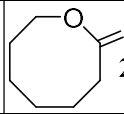
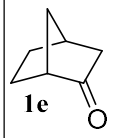
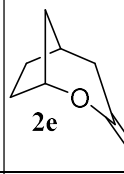
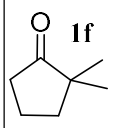
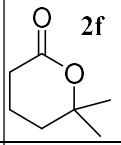
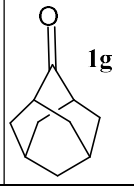
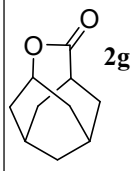
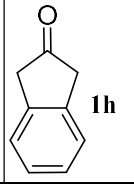
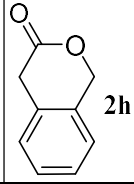
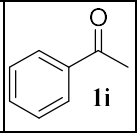
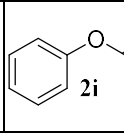
One of the most important applications of BV oxidation is the conversion of cyclic ketones into lactones, for which it is a very attractive synthetic option, as cyclic ketones are largely available and only the net insertion of a single oxygen atom is required. Furthermore, lactones are important synthons with a myriad of applications, one on all the ring opening polymerization of ε-caprolactone and δ-valerolactone to give biodegradable polyesters.[10]

Interested in this application of BV oxidation, we have intended to develop an oxone-based green protocol that was as simple as possible. Literature unanimously indicates oxone's strong acidity, due to $KHSO_4$ component, as helpful for ketone activation to nucleophilic attack by the hydroperoxide group, but contra-indicated in aqueous medium, which is necessary to dissolve oxone, by lactone hydrolysis.[5b,6] That's why measures have been taken to preserve both catalytic and oxidant functions of oxone avoiding hydrolysis, such as replacement of water with other solvents (ionic liquids, DMF, trifluoroethanol) able to partially solubilize oxone or the use of oxone in biphasic systems in the presence of PTCs or deposited on solid supports in apolar solvents. Indeed, our initial attempts to convert cyclopentanone and cyclohexanone into δ-valerolactone and ε-caprolactone, respectively, by treatment with oxone in water at room temperature resulted in quantitative oxidation and hydrolysis to 5-hydroxyvaleric acid and 6-hydroxcaproic acid.

The currently accepted mechanism for the BV reaction involves two main steps: (a) the addition of peroxyacid to protonated carbonyl of ketone to give the cationic tetrahedral adduct known as the Criegee intermediate and (b) the migration of one of the two carbonyl substituent, preferentially the one that best stabilizes the positive charge in unsymmetrical ketones, to the nearest peracid oxygen atom with the simultaneous dissociation of the O-O bond.[3,11] Nevertheless, formation of ionic intermediates is proposed in highly acid media.[12] Alternatively, in non-

polar environments or in a neutral aqueous environment, a neutral and concerted mechanism without ions formation is possible for the BV reaction.[11] In particular, under neutral conditions, a molecule of water, which is a proton donor and acceptor, could act as a catalyst leading to the formation of a non-ionic Criegee intermediate and, successively, to a concerted non-ionic migration step. Relying on the reliability of such a reaction mechanism without acid catalysis, we tried the conversion of cyclic ketones into lactones by treatment with oxone at room temperature in NaH_2PO_4/Na_2HPO_4 water solution (pH 7). We reasoned that, under these conditions, according to literature data,[12] hydrolysis of γ and larger lactones should not take place or it should be very slow, while oxone should maintain its oxidant component HSO_5^- unaltered, as the pK_2 of Caro's acid, related to the hydrogen peroxide proton, is higher than 9.[13] To our knowledge, such simple conditions for BV oxidation with oxone had no precedents in the literature and were worth testing. Eight ketones were selected: cyclobutanone (**1a**), cyclopentanone (**1b**), cyclohexanone (**1c**), cycloheptanone (**1d**), norcamphor (**1e**), 2,2-dimethylcyclopentanone (**1f**), adamantanone (**1g**) and 2-indanone (**1h**). We decided to use 2.0 mmol of oxone per mmol of substrate. The oxidations were performed on 10 mmol of ketone in 40 mL of 1M NaH_2PO_4/Na_2HPO_4 water solution (pH=7). Oxone was dissolved into the buffer and then ketone was added to the resultant solution. The mixture was vigorously stirred at room temperature for ten minutes. The aqueous phase was extracted with ethyl acetate three times. The organic extracts were dried and concentrated to give the desired lactone. According to such a procedure, **1a**, **1b**, **1c** and **1e** were quantitatively converted into γ-butyrolactone (**2a**), δ-valerolactone (**2b**), ε-caprolactone (**2c**) and the lactone of 3-hydroxycyclopentaneacetic acid (**2e**), which were then isolated with yields ranging between 85 and 92% by distillation (**2a** and **2b**) or by chromatography on silica gel (**2c** and **2e**) (Table 1, runs 1-3 and 5). The substrate **1f**, whose expected product was the tertiary alcohol cyclic ester 6,6-dimethyltetrahydro-2*H*-pyran-2-one (**2f**), showed a different behaviour from **1a**-**1c** and **1e**. In fact, it took four hours to achieve a 2:1 **2f**/**1f** ratio in the reaction mixture and during this time a significant portion of substrate (~40%) underwent, presumably after conversion into lactone, to lactone ring opening despite buffering at neutral pH. This was attributable to the easy alkyl-oxygen bond cleavage favoured by tertiary alkyl nature because resulting in a stable leaving tertiary carbocation. Therefore, under these conditions, **2f** was obtained in 40% yield after ethyl acetate extraction of the aqueous reaction mixture and subsequent separation from unreacted **1f** (20%) by distillation (Table 1, run 6). On the other hand, without buffering, namely under acidic conditions, the ethyl acetate extract contained only residual unreacted **1f**, while **2f** was completely absent according to the reported high lability of tertiary alcohol cyclic esters in even slightly acidic aqueous medium.[14] This proved that neutral buffering, even if not able to completely avoid **2f** degradation, could at least slow it enough to isolate a significant amount of **2f** at a high conversion degree of **1f**. Overall, these results indicated that ring expansion to 5-, 6-, and 7-membered lactones was not problematic as well as the stability of the ester function, partially excluding **2f**, under the selected reaction conditions. Hydrolysis did not occur even prolonging the reaction times. Furthermore, the oxidation of the non-symmetric cyclic ketones **1e** and **1f** showed the expected BV regioselectivity univocally providing the lactones **2e** and **2f** respectively.

Table 1. Oxone-Promoted Oxidation of Ketones to Lactones and Esters in Water.[a]

run	substrate	product	time	conv.[b] (%)	yield[c] (%)
1	 **1a**	 **2a**	10 min	100	86
2	 **1b**	 **2b**	10 min	100	88
3	 **1c**	 **2c**	10 min	100	92
4[d]	 **1d**	 **2d**	24 h	85	52
5	 **1e**	 **2e**	10 min	100	85
6	 **1f**	 **2f**	4 h	80	40
7[e]	 **1g**	 **2g**	8 h	100	83
8[f]	 **1h**	 **2h**	24 h	90	72
9[g]	 **1i**	 **2i**	36 h	83	76

[a] General reaction conditions: ketone (10 mmol), Oxone (20 mmol), 1M NaH_2PO_4/Na_2HPO_4 water solution (pH=7) (40 mL), room temperature. [b] Determined by ^1H NMR. [c] Isolated yield by distillation (**2a**, **2b**, **2d**, and **2f**) or chromatography on silica gel (**2c**, **2e**, **2g**, and **2i**) or crystallization (**2h**). [d] Oxone (30 mmol), 1M NaH_2PO_4/Na_2HPO_4 water solution (pH=7) (60 mL), room temperature. [e] In water (75 mL) and acetonitrile (10 mL) without buffering. [f] Oxone (30 mmol) in water (40 mL) without buffering at 70 °C. [g] Oxone (30 mmol) in water (30 mL) without buffering at 40 °C.

In the case of the cage ketone **1g** and of the aralkyl ketone 2-indanone (**1h**), high water insolubility hampered oxidation. Increase of water volume (75 mL) and addition of acetonitrile (10 mL) promoted the solubilization of the substrate **1g**, which was quantitatively converted into 2-oxahomoadamantan-3-one **2g** in

eight hours at room temperature and then isolated by chromatography with 83% yield (Table 1, run 7). For the substrate **1h**, 90% conversion into desired lactone 3-isochromanone (**2h**) was achieved without increasing the water volume and without adding acetonitrile, but only using 3.0 mmol of oxone per mmol of substrate, instead of 2.0 mmol, at room temperature for 48 hours or, alternatively, at 70 °C for 24 hours (Table 1, run 8). Under these conditions, **2h** was isolated by crystallization from diethyl ether with 72% yield. Notably, the oxidation of both **1g** and **1h** was accomplished in water and not in aqueous phosphate buffer, as the caged ε-caprolactone ring of **2g** [15] and the cyclic benzyl ester **2h** are resistant to acidic hydrolysis.

Separate discussion should be done for the BV oxidation of cycloheptanone (**1d**) to eight membered ζ-enanthiolactone (**2d**). Medium-ring (8-11 membered) lactones are significantly more challenging synthetic targets than small- and large-ring compounds. Due to transannular strain, eight membered lactones are more difficult to be constructed and easier to be opened by hydrolysis. Revealingly, investigations on new procedures for BV oxidation of cyclic ketones are often limited to 5-7 membered lactones [6a,16] or admit their failure when applying the developed general method to **1d**.[17] On the other hand, except for the use of peracids in halogenated solvents, reports claiming oxidation of **1d** to **2d** with high conversion degrees and yields are elusive on **2d** isolation or describe very small-scale procedures.[5b,18] And as far as oxone, **1d** is reported to be oxidized to **2d** by oxone supplorted on silica gel in DCM with 93% conversion, but **2d** is isolated, impure, without specifying procedure and yield.[5b] The same reaction, accomplished with oxone and wet-alumina in DCM, affords **2d** with an isolated yield (23%) much lower than those obtained oxidizing 5- and 6-membered cyclic ketones and experimental details are not given.[5a] Water insoluble like **1g** and **1h**, but not so refractory to hydrolysis as **2g** and **2h** after conversion into lactone, ketone **1d** presented itself as a problematic substrate to be oxidized in water. Indeed, we saw that it was necessary to prolong the reaction to 24 hours and to use 3.0 mmol of oxone per mmol of substrate to achieve 85% conversion and that $H_2PO_4^-/HPO_4^=$ buffering was essential to limit hydrolysis, otherwise complete, to 7-hydroxyenanthic acid. Under these conditions, **2d** was isolated by extraction with ethyl acetate of the reaction mixture and successive distillation with 52% yield, which is a valuable result in the light of the above considerations (Table 1, run 4).

Lastly, although we designed the above simple procedure to convert cyclic ketones into lactones, we explored the possibility of applying it also to the oxidation of an aromatic ketone to phenyl ester. We are long interested in this kind of oxidation because it gives access, upon ester hydrolysis, to phenols useful for the construction of benzodioxane scaffolds.[19] For acetophenone (**1i**), the literature methods of conversion into phenyl acetate (**2i**) are mainly based on the use of perbenzoic acids or hydrogen peroxide in water or in halogenated solvents and acid catalysis plays an important role as aromatic ketones are less reactive than aliphatic ones.[16d,20] On the other hand, hydrolysis of resulting phenyl acetate is predictably slow in a dilute aqueous solution of bisulphate at room temperature. These factors combined to indicate the feasibility of oxidation of **1i** to **2i** by treatment with oxone in water without buffering oxone acidity, the main uncertainty being due to the very poor hydrosolubility of **1i**. To our knowledge, the only examples of conversion of **1i** to **2i** with oxone are in non-aqueous medium, such as dichloromethane or ionic liquids.[5b,6a] Indeed, **1i** could be oxidized to **2i** by three equivalents of oxone in water at 40 °C. It took 36 hours to achieve a high conversion degree (83%), but hydrolysis did not occur (76% yield; Table 1, entry 9).

In conclusion, we have developed a novel, simple procedure to obtain γ-, δ- and ε-lactones by oxidation of ketones with the green oxidant oxone in a pH 7 1M NaH_2PO_4/Na_2HPO_4 water solution, thus demonstrating that products hydrolysis can be avoided without using unsustainable solvents, such as DMF or trifluoroethanol, or adopting complex reaction conditions, such as the use of PTCs in biphasic systems, ILs or supported oxidant in organic solvents. With some changes, the procedure was successfully applied also to poorly hydrosoluble or water insoluble ketones, such as acetophenone, adamantanone, 2-indanone and cycloheptanone.

EXPERIMENTAL SECTION

General experimental details. Ketones **1a**-**1h** were purchased from commercial sources. ^{1}H-NMR and ^{13}C-NMR spectrums were recorded in $CDCl_3$ at 300 MHz and 75 MHz respectively, with Varian Mercury 300 Spectrometer and elaborated with Mnova software. Chemical shifts are reported in ppm relative to residual solvent as internal standard. The percent of conversion was evaluated by NMR analysis.

General procedure for oxidation of cyclic ketones. In a single neck round bottom flask, oxone (20 mmol) was added to a NaH_2PO_4/Na_2HPO_4 buffer solution (1 M, 40 mL, pH=7) and the resulting suspension was vigorously stirred until oxone dissolved. Ketone (10 mmol) was added and the reaction mixture was stirred at room temperature for 10 minutes. The aqueous phase was extracted with EtOAc (3 x 80mL). The combined organic layers were collected, dried over Na_2SO_4 and concentrated under vacuum to give the desired product, which was purified as detailed below. For substrates **1d** and **1f**-**1i**, the conditions of the above general procedure were modified as follows. In the case of ketone **1d**, the oxone amount was increased to 30 mmol, the buffer solution volume was increased to 60 mL and the reaction time was protracted to 24 hours. For ketone **1f**, the time was increased to 4 hours. For ketone **1g**, the reaction was accomplished in water (75 mL) and acetonitrile (10 mL) for 8 hours. For ketone **1h**, the reaction was accomplished with 30 mmol of oxone in water (40 mL) for 24 hours at 70 °C or for 48 hours at room temperature. For ketone **1i**, the reaction was accomplished with 30 mmol of oxone in water (30 mL) at 40 °C for 36 hours.

*γ-Butyrolactone (**2a**).*[21] Obtained as a colorless liquid after distillation; yield 86%; bp 80 °C/10 mbar; Rf (cyclohexane/ethyl acetate 6:4) = 0.26; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.25 (t, J = 8.0 Hz, 2H), 2.49–2.28 (m, 2H), 2.28 – 2.06 (m, 2H). ^{13}C{^{1}H}-NMR (CDCl3) δ 177.8, 68.5, 27.7, 22.1.

*δ-Valerolactone (**2b**).*[22] Obtained as a colorless liquid after distillation; yield 88%; bp 100 °C/10 mbar; Rf (cyclohexane/ethyl acetate 6:4) = 0.22; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.29 (m, 2H), 2.49 (m, 2H), 1.92-1.74 (m, 4H). ^{13}C{^{1}H}-NMR (75 MHz, CDCl3) δ 171.4, 69.4, 29.8, 22.3, 19.0.

*ε-Caprolactone (**2c**).*[22] Obtained as a colorless liquid after chromatography on silica gel (cyclohexane/ethyl acetate 6:4); yield 92%; Rf (cyclohexane/ethyl acetate 6:4) = 0.26; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 (m, 2H), 2.61 (m, 2H), 1.87 (m, 2H), 1.71

(m, 4H). $^{13}C\{^{1}H\}$-NMR (75 MHz, CDCl3) δ 176.2, 69.3, 34.5, 29.3, 28.9, 22.9.

*ζ-Enanthiolactone (**2d**)*.[23] Obtained as a colorless liquid after distillation; yield 52%; bp 90 °C/10 mbar; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34 (t, *J* = 5.6 Hz, 2H), 2.54 (t, *J* = 6.5 Hz, 2H), 1.97 – 1.72 (m, 4H), 1.73 – 1.43 (m, 4H). $^{13}C\{^{1}H\}$-NMR (75 MHz, CDCl3) δ 176.7, 67.9, 31.2, 30.9, 28.3, 25.8, 23.9.

*2-Oxabicyclo[3.2.1]octan-3-one (**2e**)*.[5b] Obtained as a white solid after chromatography on silica gel (cyclohexane/ethyl acetate 6:4); yield 85%; mp 66.5 °C; Rf (cyclohexane/ethyl acetate 6:4) = 0.43; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.85 (m, 1H), 2.76-2.41 (m, 2H), 2.18-1.43 (m, 7H). $^{13}C\{^{1}H\}$-NMR (75 MHz, CDCl3) δ 170.8, 81.0, 40.7, 35.8, 32.5, 31.8, 29.3.

*6,6-Dimethyltetrahydro-2H-pyran-2-one (**2f**)*.[24] Obtained as a colorless liquid after distillation; yield 40%; bp 90 °C/10 mbar, Rf (cyclohexane/ethyl acetate 7:3) = 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (t, *J* = 6.9 Hz, 2H), 1.85 (m, 2H), 1.71 (m, 2H), 1.36 (s, 6H); $^{13}C\{^{1}H\}$-NMR (75 MHz, CDCl3) δ 171.2, 82.14, 33.8, 29.0, 28.7, 16.8.

*2-Oxahomoadamantan-3-one (**2g**)*.[5b] Obtained as a white solid after chromatography on silica gel (cyclohexane/ethyl acetate 6:4); yield 83%; mp 281.5 °C; Rf (cyclohexane/ethyl acetate 6:4) = 0.49; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.45 (m, 1H), 3.04 (m, 1H), 2.12-1.69 (m, 12H); $^{13}C\{^{1}H\}$-NMR (75 MHz, CDCl3) δ 178.9, 73.1, 41.2, 35.7, 33.7, 30.9, 25.8.

*3-Isochromanone (**2h**)*.[25] Obtained as a white solid after crystallization from diethyl ether; yield 72%; mp 79 °C, Rf (DCM) = 0.35; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (m, 4H), 5.32 (s, 2H), 3.71 (s, 2H); $^{13}C\{^{1}H\}$-NMR (75 MHz, CDCl3) δ 170.7, 131.5, 130.9, 128.8, 127.4, 127.1, 124.7, 70.1, 36.2.

*Phenyl acetate (**2i**)*.[26] Obtained as a colorless liquid after chromatography on silica gel eluting with DCM (Rf = 0.74); yield 76%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.23 (m, 1H), 7.10 (m, 2H), 2.30 (m, 3H). $^{13}C\{^{1}H\}$-NMR (75 MHz, CDCl3) δ 169.5, 150.7, 129.4, 125.8, 121.5, 21.1.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H and ^{13}C NMR spectra for the isolated products.

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Notes

The authors declare no competing financial interest.

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