Tetrahedron 139 (2023) 133450

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Simple metal-free oxidative cleavage of 1,2-diols

Vicente Dorado, Clara I. Herrerías**, José M. Fraile*

Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Facultad de Ciencias, CSIC-Universidad de Zaragoza, C/ Pedro Cerbuna 12, E-50009, Zaragoza, Spain

ARTICLE INFO

Article history:
Received 20 February 2023
Received in revised form
20 April 2023
Accepted 2 May 2023
Available online 3 May 2023

Keywords:
Oxidative cleavage
Oxone
Azelaic acid
Adipic acid

ABSTRACT

Cleavage of 1,2-diols is easily carried out under mild conditions with the Oxone/KBr (or Oxone/NaCl) method in either acetonitrile/water or tert-butanol/water medium at room temperature. This procedure is highly efficient for the cleavage of dihydroxyfatty esters and acids. The reaction takes place through a double oxidation of the 1,2-diol, leading to the 1,2-diketone that undergoes a Baeyer-Villiger oxidation, with a final hydrolysis of the generated anhydride. The application to other diols, including simple internal and terminal diols, is also possible, but the nature of the diol substrate conditions the optimal halide/solvent system, given that important differences in reactivity are observed. These differences are ascribed to the change in the rate limiting step depending on the substrate/halide/solvent combination.

1. Introduction

The oxidative cleavage of 1,2-diols [1] is a very useful synthetic organic reaction, whose research still deserves an active interest, in aspects such as the finding of more sustainable methods or the scope of the reaction. One example is the cleavage of diols derived from fatty acids, to produce shorter acids and diacids, such as pelargonic (nonanoic) and azelaic (nonanodioic) acids from 9,10-dihydroxystearate [2], considered as a safe alternative for the risky ozonolysis.

In some cases, the oxidative cleavage has been coupled to the dihydroxylation reaction. For example the classical dihydroxylation methods were modified to promote the cleavage, by using a large excess of $KMnO_4$ in basic medium in combination with an emulsifier [3], or by using an additional oxidant, such as Jones reagent (CrO_3/H_2SO_4) [4] or Oxone [5], with OsO_4 as catalyst. Other examples include the addition of $Co(OAc)_2$ as a second catalyst in the reaction mixture containing H_2O_2 and H_2WO_4 [6], or the use of a stoichiometric oxidant, such as $NaIO_4$ [7] or NaOCl [8]. The oxidative cleavage of 9,10-dihydroxystearate with O_2 and NaOH has been reported with supported gold nanoparticles as catalyst [2,9]. The corresponding aldehydes (nonanal and 9-oxononanoic acid) can be obtained by cleavage of 9,10-dihydroxystearate with H_2O_2 catalysed by WO_3/MCM-41 [10], or by cleavage of 9,10-epoxystearate with H_2O_2 catalysed by WO_3/mesoporous-SnO_2 in a release-and-capture catalytic system [11]. Some stepwise cleavage methods have been also described, for example using thiazolydinene as catalyst [12], or with a combination of Ni/SiO_2 and *in situ* formed performic acid [13]. Therefore, the oxidation methods with environmentally friendly oxidants require the use of heavy metal catalysts, whereas the metal-free methods use rather expensive or environmentally unfriendly oxidants.

Recently, other methods for oxidative cleavage of different *vic*-diols have been reported. Some of them use molecular oxygen as an oxidant with either homogeneous catalysts, such as AgOTf in basic (NaOMe) medium [14], or heterogeneous catalysts, for example a mixture of Pt/C and V_2O_5 [15], a Mn layered mixed oxide [16], or atomically dispersed Co on N-doped carbon [17]. Other oxidants have been used in combination with metal catalysts, such as NMO with perruthenate [18], or DMSO with MoO_2Cl_2 [19]. However, metal-free methods are scarce, including the use of hypervalent iodine oxidants and nitroxyl radicals as catalysts [20], and the O_2/NaO^tBu system [21]. As can be seen, the described methods suffer from the need for costly reagents or the poor performance with aliphatic diols. Hence, the development of new metal-free methods of oxidative cleavage of diols, using cheap and environmentally friendly oxidants, and suitable for aliphatic diols is still a problem to be solved.

In our currently ongoing research project about transformations of fatty esters under environmentally friendly conditions [22,23],

* Corresponding author.
** Corresponding author.
E-mail addresses: clarah@unizar.es (C.I. Herrerías), josem.fraile@csic.es, jmfraile@unizar.es (J.M. Fraile).

https://doi.org/10.1016/j.tet.2023.133450

the application of two methods for oxidation of alcohols [24], namely H_2O_2/KBr/*p*-toluenesulfonic acid and Oxone/KBr, to a *vic*-diol led to a significant amount of the cleavage products. We report here the optimization of the oxidative cleavage of *vic*-diols, without using any transition metal catalyst.

2. Results and discussion

2.1. Oxidative cleavage of dihydroxyfatty esters and acids

The two oxidation methods were compared with methyl *syn*-9,10-dihydroxystearate (Table 1). In the first one, H_2O_2 is used as an oxidant together with a mixture of KBr and *p*-toluenesulfonic acid (pTosOH) as catalyst. Aqueous H_2O_2 (60%) in a molar ratio of 3 was used in combination with a mixture of KBr (40 mol%) and pTosOH (40 mol%) in a biphasic dichloromethane/water medium (entry 1). However, only 55% conversion was obtained and the detected products were methyl 9 (10)-hydroxy-10 (9)-oxostearate (hydroxyketones HK), as a result of one single alcohol oxidation, and methyl 9,10-dioxostearate (diketone DK), as a result of the oxidation of both alcohols (Scheme 1). When 1,2-dichloroethane (DCE) was used instead of dichloromethane to increase the reaction temperature to 60 °C, conversion raised to 90%, but no cleavage products were detected after 24 h (entry 2). High selectivity (90%) to cleavage products (CP), pelargonic acid and azelaic acid monomethyl ester (in 1:1 M ratio), at total conversion was only obtained by using double amount of catalysts (80 mol% KBr and 80 mol% pTosOH) and a very large excess of H_2O_2 (molar ratio = 21) after a very long reaction time (1 week) (entry 3).

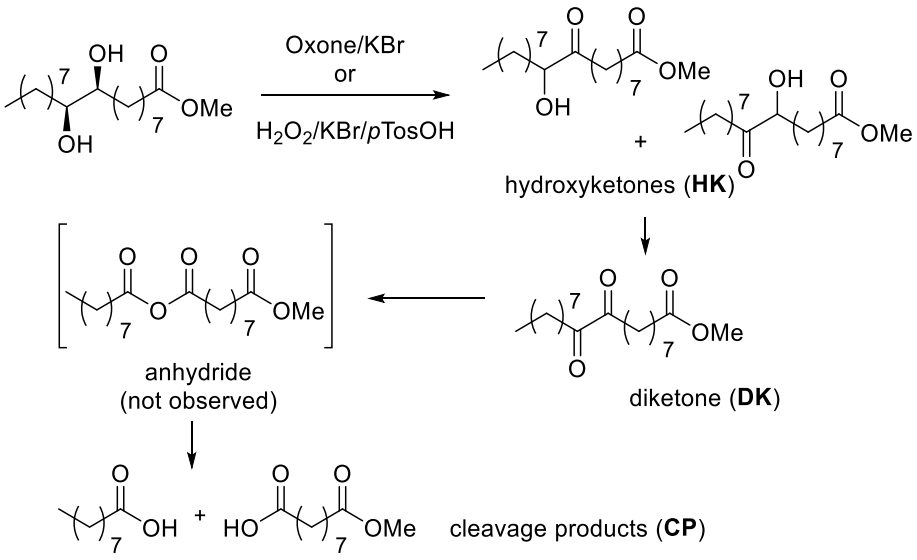
In the second oxidation method, Oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) is used as an oxidant with KBr as catalyst. The use of Oxone in a molar ratio of 4, with 20 mol% of KBr as catalyst in acetonitrile/water (9:1) at room temperature, led to 90% conversion of dihydroxystearate with pelargonic acid and azelaic acid monomethyl ester as the only products after 24 h (entry 4). In *tert*-butanol/water, the result was even improved (entry 6), with 98% conversion and total selectivity to the cleavage products (CP). The role of KBr was shown to be essential, as no conversion was observed without this catalyst under the same conditions (entry 5). Thus, it can be assumed the participation of an oxidized bromine species, most likely HOBr [25], as pointed in the case of degradation of pollutants by a similar method [26,27]. Although Oxone had been used as a selective oxidant in a large variety of oxidation reactions [28], the cleavage of *vic*-diols had been only described with very variable yields in combination of iodobenzoic acid through the *in situ* formation of a iodoxy derivative [29], whereas α-hydroxyketones were obtained in the oxidation of *vic*-diols with Oxone/RuO_4 [30]. On the other hand, Oxone had been reported as an efficient oxidant for the cleavage of α-hydroxyketones and α-diketones in methanol [31], and even 1,3-dicarbonyl compounds [31,32]. The direct oxidative cleavage of alkenes, presumably through the *vic*-diol formation, had been described using OsO_4 as catalyst [5].

At shorter reaction times with the Oxone/KBr procedure the reaction mixture also contained hydroxyketones (HK) and diketone (DK) in addition of cleavage products (CP) (Scheme 1), indicating that the reaction takes place through successive oxidations of the two alcohols to ketones. The catalytic cycle for these first two steps should involve repeated oxidations of the bromide (Br^-) to

Table 1
Oxidative cleavage of methyl *syn*-9,10-dihydroxystearate.

Entry	Oxidant (molar ratio[a])	Catalyst (mol%[b])	Solvent[c]	T (°C)	Time (h)	Conv. (%)	Products[d] (selectivity)
1	H_2O_2 60% (3)	KBr (40) + *p*TosOH (40)	CH_2Cl_2/H_2O (9:1)	r.t.	24	55	HK (85) + DK (15)
2	H_2O_2 60% (3)	KBr (40) + *p*TosOH (40)	DCE/H_2O (9:1)	60	24	90	HK (38) + DK (26) + others (36)
3	H_2O_2 60% (3x7[e])	KBr (80) + *p*TosOH (80)	DCE/H_2O (9:1)	60	168	>99	Others (10) + <B>CP (90)</B>
4	Oxone (4)	KBr (20)	MeCN/H_2O (9:1)	r.t.	24	90	<B>CP (100)</B>
5	Oxone (4)	none	MeCN/H_2O (9:1)	r.t.	24	0	–
6	Oxone (4)	KBr (20)	^{t}BuOH/H_2O (3:1)[f]	r.t.	24	98	<B>CP (100)</B>

Reaction conditions: 0.5 mmol of diol, 10 mL solvent. [a] Oxidant/diol molar ratio. [b] mol% with respect to diol. [c] DCE = 1,2-dichloroethane. [d] HK = hydroxyketones; DK = diketone; CP = cleavage products (pelargonic acid and azelaic acid monomethyl ester, 1:1 ratio); others = 1 or 2 unidentified peaks in GC. [e] One addition of 3 equivalents each 24 h. Seven total additions. [h] With 4 mL of solvent.

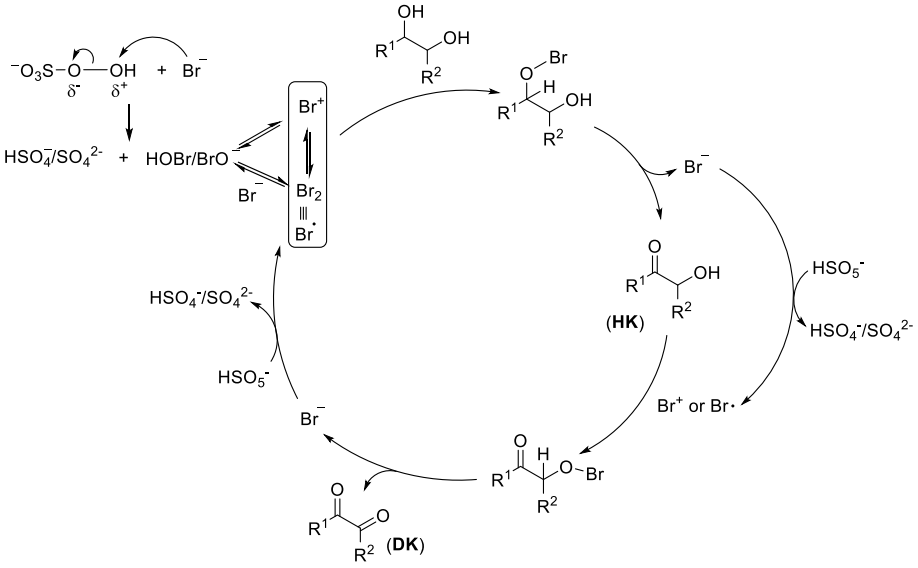


Scheme 1. Oxidative cleavage of methyl *syn*-9,10-dihydroxystearate and proposed reaction pathway.

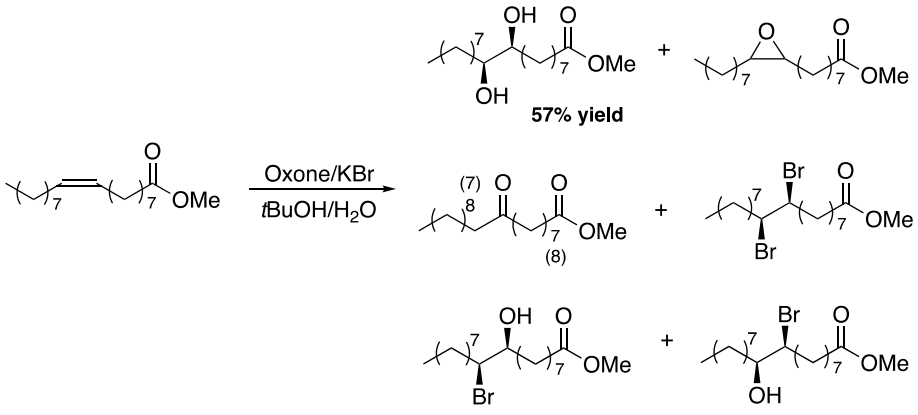
activated bromine species, either to a bromonium ion (Br^+) or to a bromo radical ($Br^\bullet$) (Scheme 2). Both species react in a competitive way with the alcohol groups following ionic o radical pathways [24], but with no difference in the intermediate products (HK and DK).

After the formation of the diketone, a Baeyer-Villiger reaction should give the anhydride (not detected), which would be rapidly hydrolyzed to the CP. In fact, Oxone has been described as an efficient oxidant for Baeyer-Villiger reaction of α,β-unsaturated ketones, under similar conditions and in the absence of KBr [33,34]. This cleavage mechanism is different from that proposed for the oxidative cleavage of aryl-alkenes with Oxone in the absence of KBr [35,36]. It was proposed that the formed 1,2-diol was cleaved through the formation of a six-membered cyclic hypervalent sulphur intermediate and subsequent collapse to the aldehydes. In our case, nonanal and methyl 9-oxononanoate were not detected in any of the reactions. In fact, when that method [35] was tested with methyl oleate, a complex mixture of products was obtained (ESI), including several cleavage products different from those obtained from the diol with the Oxone/KBr method. On the other hand, the Oxone/KBr system did not produce the cleavage of methyl oleate, and in the reaction mixture only dihydroxystearate (57% yield) together with other minor compounds such as epoxystearate and ketostearate (obtained through epoxide rearrangement), dibromostearate or hidroxybromostearate were detected (Scheme 3). The presence of bromine in the aliphatic chain must be due to the direct addition of Br_2 (or the HOBr species) to the double bond, and also to the epoxide opening by a nucleophilic attack of the Br^-. In this way, Br^- is eliminated from the reaction medium, avoiding the oxidation of the *vic*-diol and its subsequent reactions.

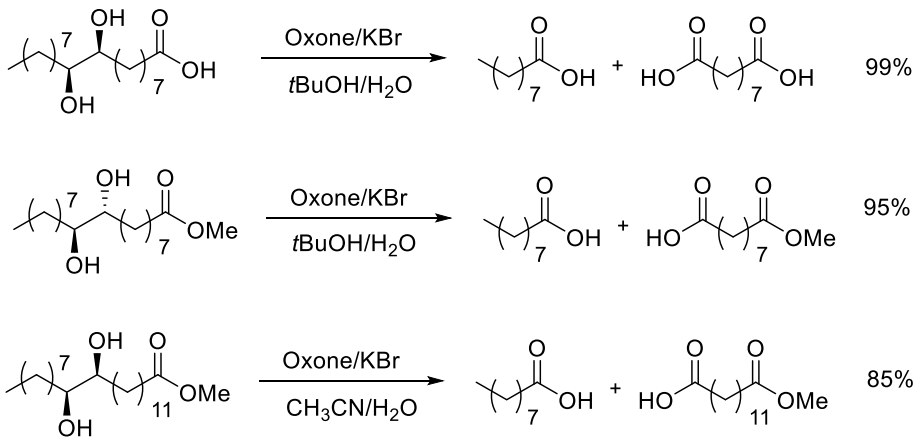
The cleavage of three other fatty acid derivatives was tested with the system Oxone/KBr (Scheme 4) in *t*BuOH/H_2O. The reaction was very efficient (total conversion) with *syn*-9,10-dihydroxystearic acid to get pelargonic and azelaic acids as the only products. Methyl *anti*-9,10-dihydroxystearate behaved similarly to the *syn* isomer (95% yield), indicating that the relative configuration of the diol has no significant effect on the reactivity. Finally, the reaction with methyl *syn*-13,14-dihydroxy-docosanoate was slightly less efficient (75% conversion) than the reaction with methyl 9,10-dihydroxystearate, probably due to solubility problems of the more hydrophobic diol. The use of acetonitrile/water (9:1) slightly improved this result (85% yield). Only pelargonic acid and tridecanedioic acid monomethyl ester were detected in both solvents.



Scheme 2. Mechanism proposal for the KBr catalysed oxidation of *vic*-diols to diketones.



Scheme 3. Reaction of methyl oleate with Oxone/KBr.



Scheme 4. Oxidative cleavage of fatty acid derivatives.

2.2. Oxidative cleavage of 1,2-cyclohexanediol: effect of stereochemistry, solvent and halide

Next, the Oxone/KBr method was applied to another interesting *vic*-diol, *trans*-1,2-cyclohexanediol, to obtain adipic acid (Table 2).

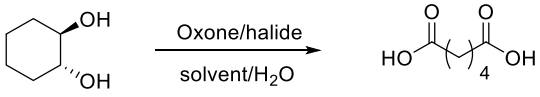
The optimal conditions gave only a moderate result (59% yield, entry 1), whereas the use of acetonitrile/water led to much higher yield (94%, entry 2). This improvement was not an effect of volume and solvent/water ratio (entry 3). *Tert*-Butanol is considered a quite green solvent (preferred by Pfizer [37], recommended by CHEM21 [38], and with some problems for GSK [39] and Sanofi [40]), whereas the discrepancies are important in the classification of acetonitrile, recommended by Sanofi [40], useable for Pfizer [37], problematic for CHEM21 [38] and GSK [39], and even hazardous for AstraZeneca [41]. In an attempt to improve the sustainability of the process, dimethyl carbonate (entry 4) and diethyl carbonate (entry 5) were used as greener alternatives to acetonitrile [39,41]. The existence of a solvent effect was clear (acetonitrile > dimethyl carbonate > diethyl carbonate > *tert*-butanol), that seems to be related with Kamlet-Taft solvation parameters [42,43], as better results are obtained with low β and high π* solvents. Given that this effect is dependent on the nature of the diol, it might be related to its solubility in the organic phase, although the true reason is still unclear.

Additionally, the effect of the catalyst was tested, and no significant differences were observed with NaBr, KCl and NaCl in acetonitrile/water (entries 6–8), with total conversion to adipic acid with both chlorides. The poor performance in *tert*-butanol was again confirmed with NaCl (entry 9). In the case of the optimal solvent, acetonitrile/water, the volume can be significantly reduced (entry 10), improving the sustainability of the process. In none of the reactions, any other products were detected, indicating the fast oxidation of the probable hydroxyketone and diketone intermediates. The need for a halide as catalyst was confirmed again, as no conversion was detected without it (entry 11).

On the contrary, the solvent effect is less important in the case of *cis*-1,2-cyclohexanediol. Whereas the results are identical to those of the *trans* isomer in acetonitrile/water with either KBr (entry 12) or NaCl (entry 14), the results in *tert*-butanol/water are significantly better. 73% yield was obtained with KBr, and total conversion with NaCl.

The effect of the solvent/halide combination was checked in the case of 9,10-dihydroxystearic acid. Both KBr/tBuOH and NaCl/acetonitrile led to total conversion and quantitative yield of azelaic and pelargonic acids. The other two combinations, KBr/acetonitrile and NaCl/acetonitrile, produced a slightly lower yield (90–91%) with conversions in the range of 93–98%. Thus, this effect was not so important with this dihydroxy fatty acid, demonstrating again to be highly dependent on the nature of the substrate, in an unpredictable way.

Table 2
Oxidative cleavage of 1,2-cyclohexanediols.



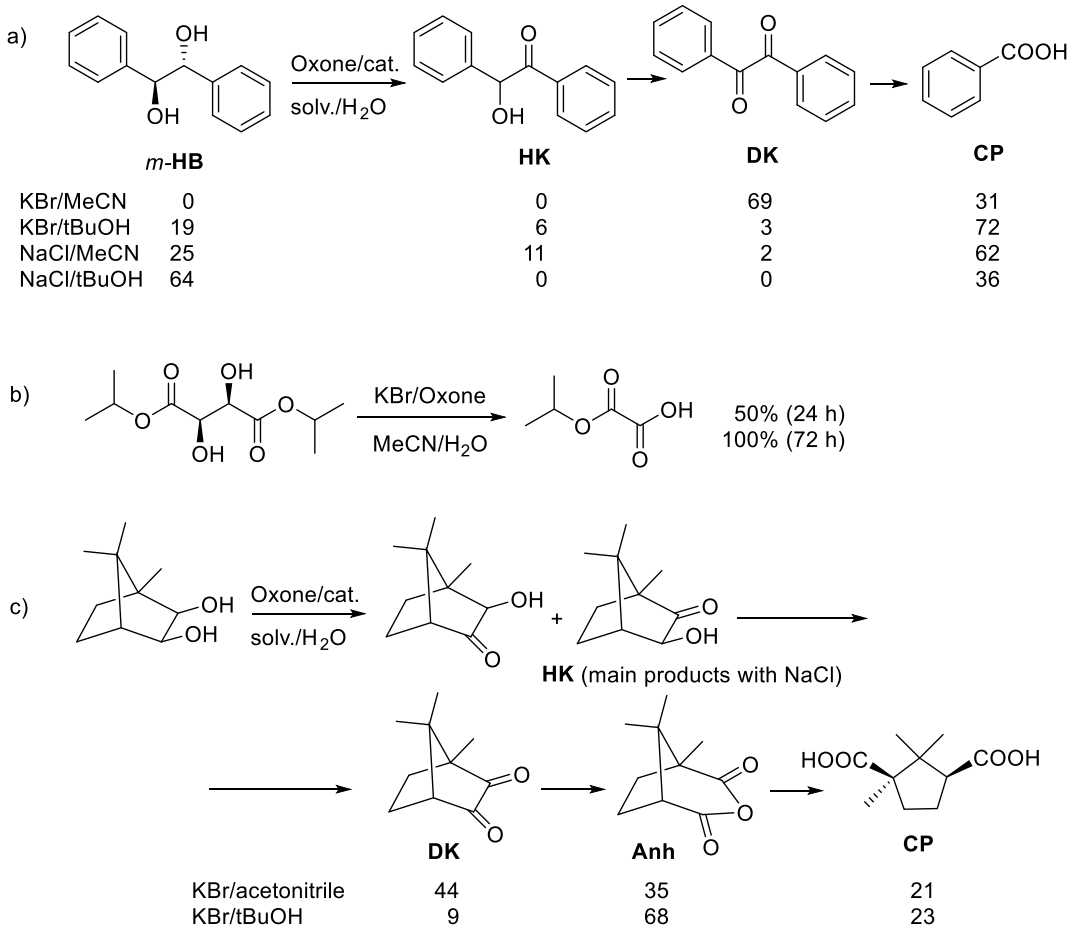
Entry	Catalyst	Solvent	Volume (mL)	Yield[a] (%)
trans-1,2-cyclohexanediol				
1	KBr	*t*BuOH/H_2O (3:1)	4	59
2	KBr	MeCN/H_2O (9:1)	10	94
3	KBr	*t*BuOH/H_2O (9:1)	10	33
4	KBr	DMC[b]/H_2O (9:1)	10	63
5	KBr	DEC[c]/H_2O (9:1)	10	57
6	NaBr	MeCN/H_2O (9:1)	10	90
7	KCl	MeCN/H_2O (9:1)	10	99
8	NaCl	MeCN/H_2O (9:1)	10	99
9	NaCl	*t*BuOH/H_2O (3:1)	4	31
10	NaCl	MeCN/H_2O (9:1)	5	99
11	none	MeCN/H_2O (9:1)	10	0
cis-1,2-cyclohexanediol				
12	KBr	MeCN/H_2O (9:1)	10	94
13	KBr	*t*BuOH/H_2O (3:1)	4	73
14	NaCl	MeCN/H_2O (9:1)	10	99
15	NaCl	*t*BuOH/H_2O (3:1)	4	99

Reaction conditions: 0.5 mmol of diol, 2 mmol of Oxone, 0.1 mmol of catalyst, r.t., 24 h [a] Only adipic acid and unconverted diol were detected. [b] DMC = dimethyl carbonate. [c] DEC = diethyl carbonate.

2.3. Oxidative cleavage of other vic-diols

From these results, we checked the scope of this reaction by testing secondary *vic*-diols with different structural features (Scheme 5). In all the cases both solvent systems (acetonitrile/water and *tert*-butanol/water) and both halides (KBr and NaCl) were tested in the search for the optimal procedure for each diol.

In the case of *meso*-hydrobenzoin (*m*-HB, Scheme 5a), the behaviour with the different catalyst/solvent combinations is very different. In the KBr/acetonitrile system, the main product is the diketone (DK), showing that the limiting step in the process is the Baeyer-Villiger oxidation. On the contrary, in the NaCl/*tert*-butanol system, the limiting step is the first alcohol oxidation, as shown by the low conversion, whereas the oxidized intermediate products



Scheme 5. Oxidative cleavage of secondary *vic*-diols and composition of the reaction mixtures.

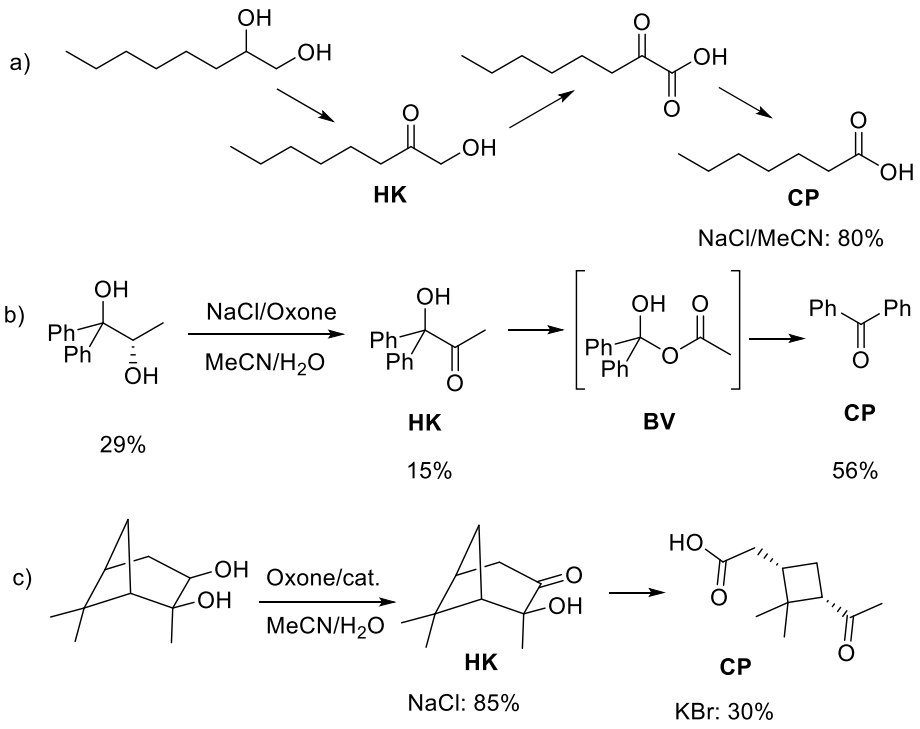
(HK and DK) are not detectable, indicating a faster reaction. The cleavage is favoured in the other two systems, mainly with KBr/*tert*-butanol, where the reaction mixture contains 72 mol% of the cleavage product (CP, benzoic acid). In any case, the aromatic groups seem to be detrimental for the reactivity of the diol.

In the case of diisopropyl tartrate (Scheme 5b), NaCl was not active, with conversions below 10% in both solvents. On the contrary, KBr was active in both solvents with conversions around 50% to monoisopropyl oxalate due to a slower kinetics. Total conversion was reached at longer reaction time (72 h).

The results in the oxidative cleavage of a bicyclic terpenic diol, such as *exo*,*exo*-2,3-camphanediol (Scheme 5c), confirm the proposed mechanism and clearly show the role of the halide/solvent system on the change in rate limiting step of the process. With NaCl, total conversion of the diol was obtained and the two hydroxyketones (HK) were the main products. The other two products were the anhydride (**Anh**) and camphoric acid as the final cleavage product (CP). The absence of diketone (DK) in the reaction mixture indicates a fast Baeyer-Viller oxidation, whereas the presence of HK points to its oxidation as the limiting step. The presence of the bicyclic anhydride also indicates a slower hydrolysis than in the case of the open chain ones. On the contrary, HK were not detected with KBr, showing a change in the limiting step. In acetonitrile/water, a significant amount of DK remained unconverted due to a slower Baeyer-Villiger oxidation. However, in *tert*-butanol/water the Baeyer-Villiger oxidation was faster, leading to 91% of **Anh** + CP. Dimethyl camphorate was obtained with 90% yield by direct esterification of this mixture in methanol.

Then, *vic*-diols with one primary or tertiary alcohol were tested (Scheme 6). The effect of one primary alcohol was checked using 1,2-octanediol (Scheme 6a). Only two of the possible intermediate products were detected in very low amounts, 1-hydroxy-2-octanone (HK) and 2-oxo-octanoic acid, as a result of the oxidation of secondary and primary alcohols. The results were strongly dependent on the halide/solvent system. At best, 80% yield of heptanoic acid was obtained with NaCl/acetonitrile, whereas the yields were much lower with KBr/acetonitrile (47%), KBr/*tert*-butanol (39%) and NaCl/*tert*-butanol (18%).

As a tertiary diol cannot be oxidized to ketone, the secondary-tertiary *vic*-diols would not be cleaved through the proposed pathway. As expected, the cleavage of 1,1-diphenyl-1,2-propanediol (Scheme 6b) was less efficient, but a significant amount of benzophenone (12–21%) was obtained with the four halide/solvent combinations. The diol conversion was increased up to 71% with 56% yield of benzophenone by using 40 mol% of NaCl and Oxone/diol molar ratio of 6 in acetonitrile/water. 1,1-Diphenyl-1-hydroxy-2-propanone was also obtained in 15% yield. In some of the reaction mixtures, small amounts of the Baeyer-Villiger product (BV) were detected. In the oxidation of 2,3-pinanediol (Scheme 6c), the hydroxyketone (HK) was the major product with the NaCl/acetonitrile system, up to 85% yield with 40 mol% of NaCl and Oxone/diol molar ratio of 6. However, small amounts of pinonic acid, the



Scheme 6. Oxidative cleavage of *vic*-diols with one primary or tertiary alcohol.

cleavage product (CP), were also obtained, up to 30% with KBr in acetonitrile/water under the same conditions. These results seem to indicate that the Baeyer-Villiger reaction of tertiary-hydroxy ketones is possible, although less favourable than the reaction from diketones.

3. Conclusions

This work describes an easy and environmentally friendly procedure for the cleavage of 1,2-diols under mild conditions. The yield in cleavage products ranges from moderate to high on almost all substrates tested, including aliphatic linear and cyclic, aromatic and functionalized diols, showing the efficacy and versatility of this method. The right combinations of Oxone as oxidant, together with several halides, such KBr or NaCl, as catalysts, and mixtures of acetonitrile/water or *tert*-butanol/water as solvents, are the key to obtain the best results for each type of substrate. The analysis of the intermediates has shown that the reactions steps consist in a double oxidation of the *vic*-diol to hydroxyketone and diketone, followed by a Baeyer-Villiger oxidation leading to an anhydride, and a final *in situ* hydrolysis. However, the limiting step in this sequence is not only depending on the diol but also on the combination halide/solvent. The non-predictable suitable combination for each substrate requires a deeper study of the reaction mechanism and the role played by each component of this system.

4. Experimental

4.1. General procedure

To a solution of 1,2-diol (0.5 mmol) in 4 mL *t*BuOH/H_2O (3:1 v:v) or 10 mL acetonitrile/water (9:1 v:v), were added 12 mg of KBr (0.1 mmol, 20 mol%) or 5.9 mg of NaCl (0.1 mmol, 20 mol%) and 614.7 mg of Oxone (2.0 mmol) and the mixture was stirred at room temperature for 24 h. The reaction crude was diluted with distilled water (15 mL) and the products were extracted with ethyl acetate (3×10 mL). The combined organic phases were washed with brine (10 mL), dried with anhydrous $MgSO_4$, and filtered. The solvents were evaporated under reduced pressure. The results were determined by NMR and/or GC analysis, as detailed in the Supporting Information.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interestsJM Fraile reports financial support was provided by Agencia Estatal de Investigación. JM Fraile reports financial support was provided by Government of Aragón.

Data availability

Data will be made available on request.

Acknowledgment

This work was financially supported by the Spanish Agencia Estatal de Investigación (projects RTI2018-093431-B-I00 and PID2021-125762NB-I00), the Gobierno de Aragón (E37_20R group) and co-financed with Feder 2014–2020 “Construyendo Europa desde Aragón”.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2023.133450.

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