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Oxidative cleavage of aryl epoxides to benzaldehydes catalyzed by $VO(acac)_2$



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ABSTRACT

to good yields.

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Introduction

Epoxides are one of the most useful and versatile substrates in organic synthesis due to their high reactivity and easy availability through a wide variety of methods. Although, there are few methods reported in the literature for oxidative cleavage of epoxides to aldehydes,¹ these methodologies include the reaction with aqueous sodium periodate² or aqueous sodium paraperiodate (Na₃H₂IO₆)³ or iodosylbenzene (PhIO).⁴ In contrast, several procedures have been developed for the conversion of epoxides to aldehydes or ketones by rearrangement catalyzed by Lewis acids.^{5–10}

High valent oxo-complexes have an extreme relevance to oxidation catalysis,¹¹⁻¹⁴ such as in epoxidation of olefins, and more recently they have been also successfully applied in the reduction or deoxygenation of a large variety of organic compounds.^{13–16}

In 2011, we reported a novel method for the deoxygenation of several epoxides to the corresponding olefins in moderate to good vields catalyzed by oxo-rhenium complexes without adding any reducing agents.¹⁷ In continuation of our work on the use of oxo-complexes for the deoxygenation of organic compounds, we decided to investigate the deoxygenation of aryl epoxides catalyzed by high valent oxo-vanadium, oxo-molybdenum and oxo-tungsten complexes.

Results and discussion

This work reports a novel method for the oxidative cleavage of aryl epoxides to the corresponding

aldehydes, catalyzed by the complex vanadyl acetylacetonate, VO(acac)₂, without adding any oxidizing

agent. This complex proved to be efficient for the oxidative cleavage of several aryl epoxides in moderate

In order to compare the catalytic activity of several oxo-complexes, the oxidative cleavage of 4-chlorostyrene oxide was carried out in the presence of the catalysts $VO(acac)_2$, MoO_2Cl_2 , WO_2Cl_2 , $MoO_2Cl_2(H_2O)_2$,¹⁸ $MoO_2Cl_2(dmso)_2$,¹⁸ $MoO_2Cl_2(acac)_2$ and $MoO_2Cl_2(dmf)_2^{18}$ in reflux of toluene under air atmosphere (Table 1). The reactions performed with the catalysts MoO_2Cl_2 , $MoO_2(acac)_2$ and WoO₂Cl₂ were carried out under nitrogen atmosphere and in reflux of dry toluene. The progress of the reactions was monitored by thin layer chromatography and by ¹H NMR.

The best result was obtained using the catalyst VO(acac)₂ (10 mol %), affording the 4-chlorobenzaldehyde in 57% yield after 24 h (Table 1, entry 1). Using only 5 mol % of this catalyst, the aldehyde was obtained in 15% yield, after 24 h (Table 1, entry 2). The oxo-molybdenum and oxo-tungsten complexes catalyzed the oxidative cleavage of 4-chlorostyrene oxide in moderate to low yields (Table 1, entries 3-8). No reaction occurs in the absence of catalyst (Table 1, entry 9).

The influence of the solvent on the oxidative cleavage of epoxides catalyzed by VO(acac)₂ (10 mol %) was also explored using trans-stilbene oxide as the test substrate. Toluene was the best solvent at reflux temperature, affording the benzaldehyde in 85% yield after 6 h (Table 2, entry 1). At room temperature, no reaction was observed (Table 2, entry 2). The reaction performed in acetonitrile gave moderate yield of benzaldehyde, but the reaction required 24 h (Table 2, entry 3). In benzene, p-xylene, tetrahydrofuran, dichloromethane and chloroform, the aldehyde was obtained in low yields (Table 2, entries 4-8).





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Table 1

Oxidative cleavage of 4-chlorostyrene oxide by different oxo-complexes^a



^a All reactions were carried out with 1.0 mmol of 4-chlorostyrene oxide. ^b Yield determined by ¹H NMR.

To evaluate the general applicability of this methodology, the oxidative cleavage of several epoxides catalyzed by 10 mol % of VO(acac)₂ in refluxing toluene under air atmosphere was explored (Table 3).¹⁹ The best result was obtained in the oxidative cleavage of *trans*-stilbene oxide, affording the benzaldehyde in 85% yield after 6 h (Table 3, entry 1). The reaction of *trans*-stilbene oxide catalyzed by 10 mol % of VO(acac)₂ was also carried out under inert atmosphere (6 h, 83% yield) and with bubbling air (5 h 45 min 84% yield). In both cases the results obtained are similar.

Good yields of benzaldehyde were also observed in the reaction of ethyl 3-phenylglycidate and *trans*-1,3-diphenyl-2,3-epoxypropan-1-one (83–79%), but these reactions required longer reaction times (24 h) (Table 3, entries 2 and 3).

In contrast to the good yield of aldehyde obtained in the reaction of *trans*-stilbene, the benzaldehyde was formed in 68% yield in the reaction of *cis*-stilbene after 24 h (Table 3, entry 4). 4-Chlorobenzaldehyde, benzaldehyde and 4-fluorobenzaldehyde were obtained in moderate yields (57–46%) from the oxidative cleavage of 4-chlorostyrene oxide, styrene oxide and 4-fluorostyrene oxide, respectively (Table 3, entries 5–7).

Finally, we observed that these reaction conditions were not efficient for the deoxygenation of the aliphatic epoxide 1,2-epoxy-hexane, cyclohexene oxide and 4-chlorophenylglycidyl ether that produced a residual amount of the corresponding aldehyde.

To evaluate the scalability of the present protocol, the oxidative cleavage of *trans*-stilbene oxide was performed on a 10 mmol scale

 Table 2

 Oxidative cleavage of trans-stilbene oxide catalyzed by VO(acac)₂ in different solvents^a



^a All reactions were carried out with 1.0 mmol of *trans*-stilbene oxide. ^b Yield determined by ¹H NMR.

Table 3

Oxidative cleavage of epoxides catalyzed by VO(acac)2^a



^a All reactions were carried out with 1.0 mmol of epoxide.

^b Yield determined by ¹H NMR.

using 10 mol % of VO(acac)₂, producing the benzaldehyde in 74% yield after purification by silica gel column chromatography.

Conclusion

In conclusion, we developed a novel, practical and efficient method for the oxidative cleavage of aryl epoxides to the corresponding aldehydes, catalyzed by the oxo-vanadium complex VO(acac)₂ without adding any oxidizing agent. The advantages of this methodology are: (a) the absence of an oxidizing agent; (b) moderate to good yields of aldehydes; (c) applicability to a variety of aryl epoxides; (d) use of a commercial and easy-to-handle catalyst; (e) easy procedure (the reactions can be carried out under air atmosphere with readily available equipment).

All these features make this procedure one of the easiest, practical and eco-friendly procedures for the oxidative cleavage of aryl epoxides reported in the literature, minimizing the use and generation of hazardous substances than traditional methods.

Further studies to improve the yields of the oxidative cleavage through catalyst modifications and mechanistic studies, including computational studies, are now in progress in our group.

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- 19. In a typical experiment, the mixture of aryl epoxide (1.0 mmol) and VO(acac)₂ (10 mol %) in toluene (3 ml) was stirred at reflux temperature under air atmosphere, and the progress of the reaction was monitored by TLC or ¹H NMR spectroscopy (the reaction times are indicated in Tables 1–3). Upon completion, the yields of the aldehydes were determined by ¹H NMR.