

An efficient preparation of α -diketones.

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Keywords: Lewis acid, 1,3-diketone and 1,2-diketone

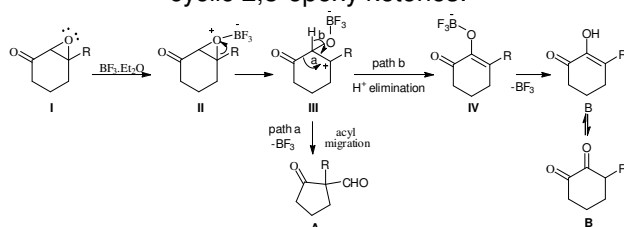
INTRODUCTION

Cyclic α,β -epoxy ketones are valuable synthetic intermediates due to their high reactivity. Various products resulting from rearrangements of cyclic 2,3-epoxy ketones are important starting materials for the synthesis of perfumes, synthetic food flavorings, and pharmaceuticals.¹

Lewis acid catalyzed ring opening of these epoxides usually follow some well defined paths: the intermediate carbocation is always formed in the carbon atom farther from the carbonyl group (III) (Scheme 1), because this group destabilizes positive charges in α -position.

The carbocation can either undergo acyl migration or H^+ elimination (or hydrogen migration) to form a ring-contracted aldehyde (A) or an α -diketone (B) (Scheme 1).

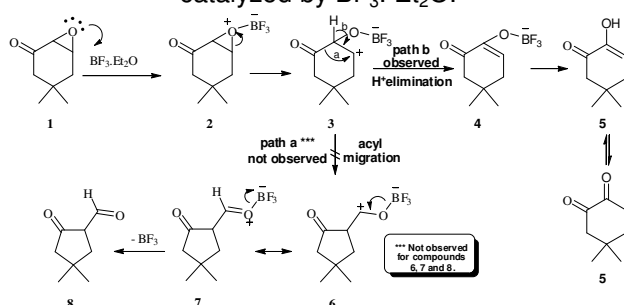
Scheme 1: Lewis acid catalyzed rearrangement of cyclic 2,3-epoxy ketones.



RESULTS AND DISCUSSION

As part of an ongoing research project, we have studied the epoxide-ring opening of ketone **1** catalyzed by $BF_3 \cdot Et_2O$. The usual preference for the ring contraction path was not observed however, and we obtained only the *vic*-diketone **5** (90% yield) (Scheme 2).

Scheme 2: Ring opening of 2,3-epoxy ketone **1** catalyzed by $BF_3 \cdot Et_2O$.

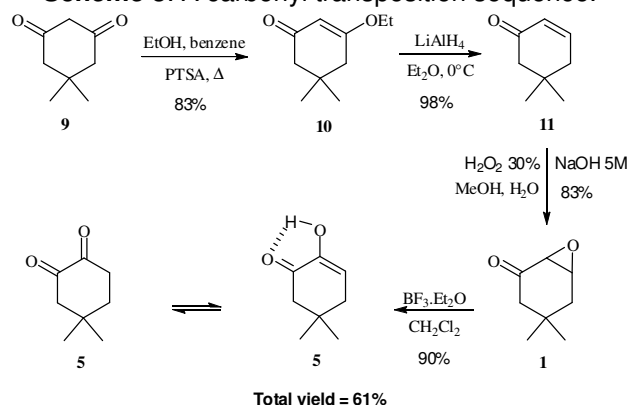


Comparing this result with others described in the literature² we can conclude what the ring contraction is favored if an additional substituent is present at the β -position, otherwise the formation of β -diketone is the preferred path. This opens the possibility to convert 1,3-diketones into 1,2-diketones, since 1,3-diketones can be easily converted to α,β -epoxy ketones deprived of β -substituents.

As can be seen in scheme 3, the intermediate **1** can be easily obtained from 5,5-dimethylcyclohexane-1,3-dione (**9**), a commercially available starting material.

For this purpose 5,5-dimethylcyclohexane-1,3-dione (**9**) was converted to intermediate **10** by esterification³ (83% yield), followed by reduction⁴ with $LiAlH_4$, furnishing the enone **11** (98% yield). Treatment with alkaline solution of hydrogen peroxide⁴ converts the enone **11** into the epoxy ketone **1** with good yield (83%).

Scheme 3: A carbonyl transposition sequence.



CONCLUSION

The carbonyl transposition sequence presented in this communication is an easy and efficient method to obtain 1,2-diketones from readily available 1,3-diketones such as dimedone.

ACKNOWLEDGEMENTS

FAPESP, CNPq and CAPES.

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