An efficient preparation of α-diketones.

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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.

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 BF₃. Et₂O. 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 BF₃. Et₂O.

Comparing this result with others described in the literature, 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 silylation with LiAlH₄, furnishing the enone 11 (98% yield). Treatment with alkaline solution of hydrogen peroxide 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.

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REFERENCES