Tertiary cyclopropanol systems as synthetic intermediates: novel ring-cleavage of tertiary cyclopropanol systems using vanadyl acetylacetonate

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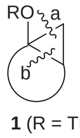
Tertiary cyclopropanol systems react with a catalytic amount of vanadyl acetylacetonate under an oxygen atmosphere to afford β-hydroxyketones and β-diketones.

Tertiary cyclopropyl silyl ethers (**1**), readily available from the cyclopropanation of enol silyl ethers, are important synthetic intermediates due to their high reactivity,[1] and simple fragmentation at their cyclopropanol system is familiar as the procedure for the α-homologation of ketones. Several methods have been developed to achieve specific cleavage at bond ‘a’[2] or ‘b’.[3] The methods of bond cleavage at both ‘a’ and ‘b’ have been reported by Rubottom and co-workers[4] and ourselves.[5]



a: $Hg(OAc)_2$, ZnI_2, base, halogen, $AgBF_4$, $Cu(BF_4)_2$, $SnCl_4$, PhPdOTf, $[Pt(C_2H_4)Cl_2]_2$
b: $FeCl_3$, $Mn(pic)_3$, electrolysis
a & b: $PhI(OAc)_2$, $Pb(OAc)_4$

1 (R = TMS, H)

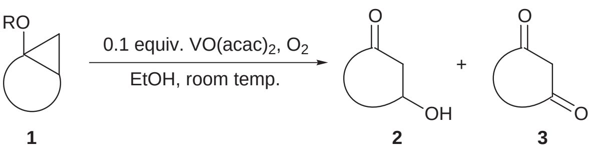
Here we describe a novel reaction involving the treatment of tertiary cyclopropyl silyl ethers or tertiary cyclopropanols (**1**) with a catalytic amount of vanadyl actylacetonate‡ under an O_2 atmosphere in EtOH to cause a ring fragmentation resulting in the formation of β-hydroxy ketones and β-diketones§ (Scheme 1). These results are summarised in Table 1. In the case of 1-(trimethylsiloxy)bicyclo[*n*.1.0]alkanes or bicyclo[*n*.1.0]alkanols (entries 1–6), the ‘b’ bond was specifically cleaved to afford ring-enlarged β-hydroxy ketones and β-diketones. As noted in entry 6, the cyclopropane ring without oxygen-functionality did not react under these reaction conditions.

β-Diketones were not obtained by the reaction of β-hydroxy ketones with $VO(acac)_2$. These results mean that β-diketones were directly produced from the cyclopropanol systems. Molecular oxygen acts as the co-oxidant and reoxidises the low valent vanadium compound formed, thus a stoichiometric amount of $VO(acac)_2$ reacted with 1-(trimethylsiloxy)-bicyclo[4.1.0]heptane in the absence of oxygen (Scheme 2).

Although $VO(acac)_2$ did not react with **1** in an aprotic solvent (*e.g.* CH_2Cl_2), it reacted with **1** in trifluoroethanol to afford β-diketones (**3**) predominantly (Scheme 3).

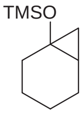
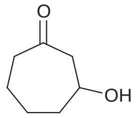
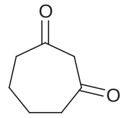
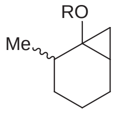
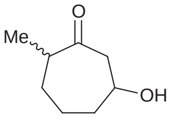
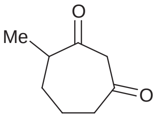
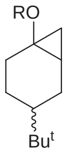
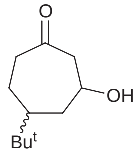
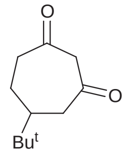
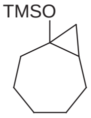
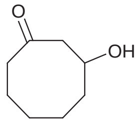
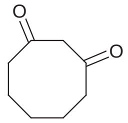
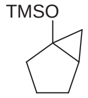
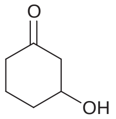
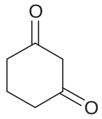
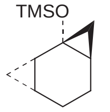
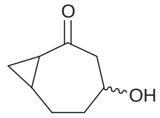
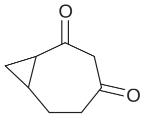
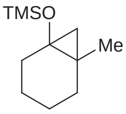
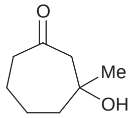
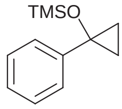
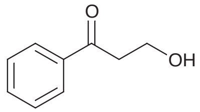
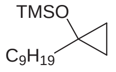
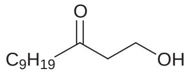
Interestingly, 5-but-3-enylbicyclo[4.1.0]heptan-1-ol (**4**) did not cause tandem ring expansion–cyclisation but caused simple ring expansion to afford **5** and **6**. This result is in sharp contrast to iron(III) chloride[3c,d] or manganese(III) picolinate[3g] that causes the tandem reaction (Scheme 4). We also found that a radical inhibitor [2,6-di(*tert*-butyl)-*p*-cresol] did not interfere with the reaction of $VO(acac)_2$ with **1**.

Although the reaction mechanism is unknown, these results suggest that this reaction is different from the other specific ‘b’

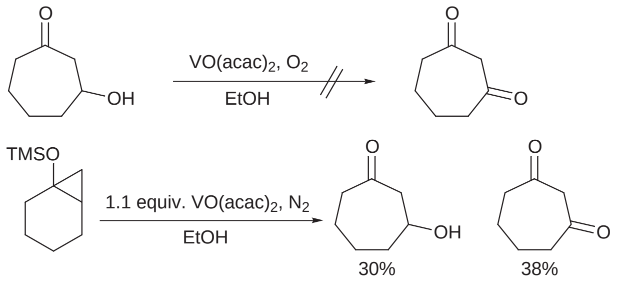


Scheme 1

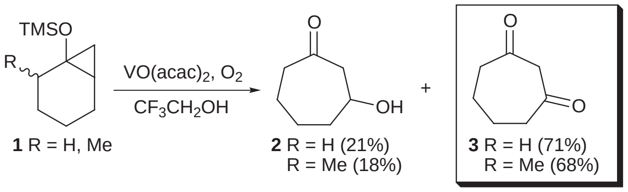
Table 1 Results of ring-cleavage reactions[a]

Entry	Starting Material	Products	
1		 41%	 24%
2		 R = TMS (40%) R = H (36%)	 R = TMS (25%) R = H (39%)
3		 R = TMS (25%) R = H (21%)	 R = TMS (30%) R = H (35%)
4		 31%	 33%
5		 75%	 10%
6		 29%	 31%
7		 53%	
8		 47%	
9		 46%	

[a] All known products were identifed by comparison with authentic samples, and new compounds were characterized on the basis of mass, IR, and NMR spectral data.



Scheme 2



Scheme 3

bond cleavage reactions[3] which proceed through a simple radical oxidation. Further details of the mechanism are currently under investigation.

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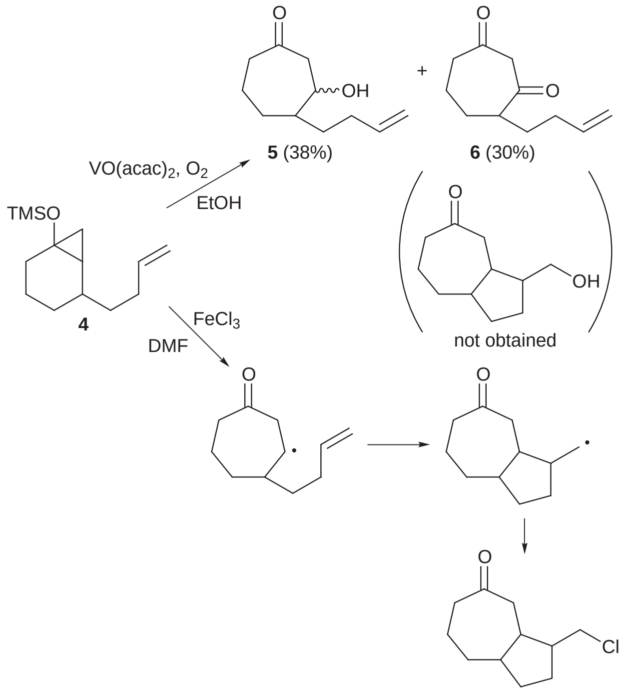

Scheme 4

Notes and References

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‡ The reaction with pentavalent vanadium compounds [*e.g.* dichloro(ethoxy)(oxy)vanadium] did not afford β-hydroxy ketones or β-diketones, giving instead complex mixtures.

§ A typical experimental procedure is as follows: a mixture containing tertiary cyclopropyl silyl ethers (or tertiary cyclopropanols) (0.5 mmol), VO(acac)$_2$ (0.05 mmol) and EtOH (5 ml) was stirred at room temperature under an oxygen atmosphere for 1.5–35 h. Water (3 ml) was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate (20 ml × 3). The combined organic extracts were washed with brine, dried over magnesium sulfate, and evaporated to afford the crude mixture of β-hydroxy ketones and β-diketones. Separation and purification by chromatography (silica gel, hexane–ethyl acetate) gave pure samples.

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