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Tetrahedron
Tetrahedron 61 (2005) 4831–4839

Fragmentation of tertiary cyclopropanol compounds catalyzed by vanadyl acetylacetonate

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Received 30 August 2004; accepted 4 March 2005

Available online 11 April 2005

Abstract—Tertiary cyclopropanol compounds react with a catalytic amount of vanadyl acetylacetonate in the presence of oxygen affording β-hydroxyketones and β-diketones. For 3-substituted-bicyclo[4.1.0]alkanols, peroxides are obtained, as are the β-hydroxyketones. Conversely, 2-ethoxycarbonylcyclopropyl silyl ethers produce ethyl γ-oxocarboxylate derivatives given the same reaction conditions.

1. Introduction

Tertiary cyclopropanol compounds (**1**) are important synthetic intermediates owing to their great reactivity. Many different reactions have been developed using derivatives of **1** as reagents,[1] including those whose purpose is to specifically cleave at bonds 'a' and/or 'b'[2–4] (Scheme 1).

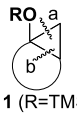
We found that when tertiary cyclopropyl silyl ethers or tertiary cyclopropanols (**1**) are treated with a catalytic amount of vanadyl acetylacetonate under oxygen and in ethanol, the cyclopropyl ring fragments and β-hydroxyketones (**2**) and β-diketones (**3**) are produced (Scheme 2). We described these findings in a preliminary communication.[5] We have further investigated the properties of the reactions and report full experimental details herein.

2. Results and discussion

To begin, we aerobically reacted ethanolic **1a** with 1.0 equiv of vanadyl acetylacetonate [$VO(acac)_2$][6] at room temperature and obtained as products, β-hydroxyketone (**2a**) and β-diketone (**3a**). The reaction also occurred in the presence of a catalytic amount of $VO(acac)_2$ (0.1 equiv; Scheme 3). β-Diketone (**3a**) was the major product when a stoichiometric amount of $VO(acac)_2$ was present. However, β-hydroxyketone (**2a**) predominated when a catalytic amount of $VO(acac)_2$ was used.

Generally, reactions involving derivatives of **1** and 0.1 equiv of $VO(acac)_2$ under oxygen and in ethanol caused the cyclopropane ring to fragment and produced β-hydroxy ketones and β-diketones (Table 1). For 1-(trimethylsiloxy)bicyclo[*n*.1.0]alkanes or bicyclo[n.1.0]alkanols (entries 1–6), the 'b' bond was specifically cleaved yielding ring-enlarged β-hydroxyketones and β-diketones. With $VO(acac)_2$ present, silyl ethers hydrolyzed immediately upon dissolution into ethanol and the corresponding alcohols were formed. Here, the reactive species are the tertiary cyclopropanols rather than the starting materials. When the cyclopropane ring lacked an oxygen functionality, the reaction did not occur (entry 6, Table 1).

Although vanadyl acetylacetonate did not react with **1a** or **1b** in an aprotic solvent (e.g., dichloromethane), it did



1 (R=TMS, H)

a: $Hg(OAc)_2$,[2e] ZnI_2,[2a] base,[2b] Br_2,[2d] $AgBF_4$,[2f,g] $Cu(BF_4)_2$,[2f,g] $SnCl_4$,[2h,l] PhPdOTf,[2i] $[Pt(C_2H_4)Cl_2]_2$,[2j] $TeCl_4$[2k]
b: $FeCl_3$,[3a-e] $Mn(pic)_3$,[3g-i] electrolysis[3f]
a & b: $Pb(OAc)_4$,[4a,b] $PhI(OAc)_2$[4c-h]

Scheme 1.

Keywords: Fragmentation reactions; Cyclopropanes; Peroxides; Vanadium compounds.
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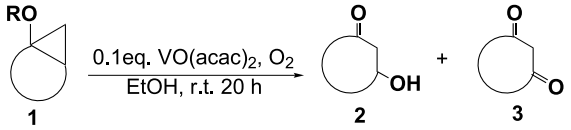
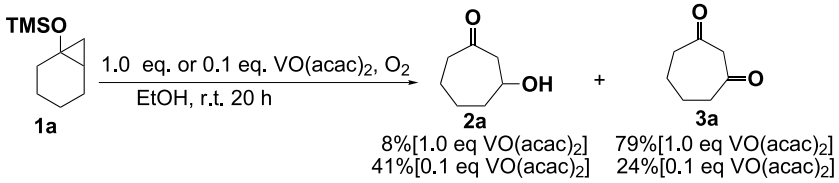
doi:10.1016/j.tet.2005.03.033



Scheme 2.

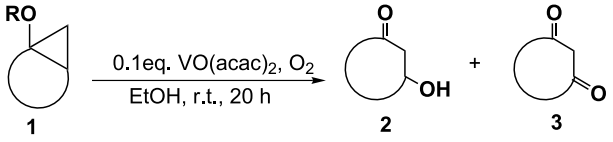
react with those compounds in trifluoroethanol with the β-diketones (**3a** and **3b**) as the main products (Scheme 4).

Interestingly, reaction of 5-but-3-enylbicyclo[4.1.0]heptane-1-ol (**1i**) did not result in a tandem ring expansion and cyclization, but instead a simple ring expansion

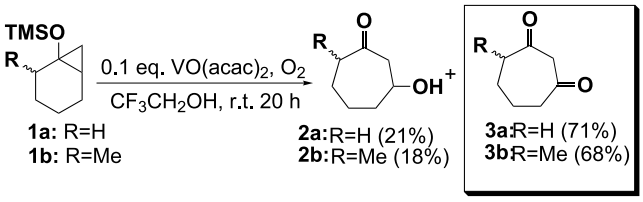


Scheme 3.

Table 1.



Entry	Starting material	Products	
1	TMSO **1a**	**2a** 41%	**3a** 24%
2	RO, Me **1b** (R=TMS) **1b′** (R=H)	**2b** R=TMS (40%) R=H (36%)	**3b** R=TMS (25%) R=H (39%)
3	RO, *t*-Bu **1c** (R=TMS) **1c′** (R=H)	**2c** R=TMS (25%) R=H (21%)	**3c** R=TMS (30%) R=H (35%)
4	TMSO **1d**	**2d** 31%	**3d** 33%
5	TMSO **1e**	**2e** 75%	**3e** 10%
6	TMSO **1f**	**2f** 29%	**3f** 31%
7	TMSO **1g**	**2g** 47%	
8	TMSO, C_9H_{19} **1h**	C_9H_{19} **2h** 80%	

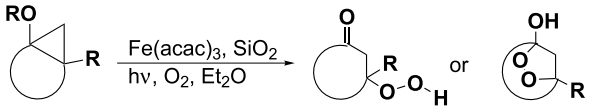


Scheme 4.

occurred giving **2i** and **3i**. This result contrasts sharply with the reaction of **1i** with an equimolar or excess amount of iron(III) chloride[3c,d] or manganese(III) picolinate[3g] under an inert atmosphere. For the latter, a radical tandem reaction occurs (Scheme 5).

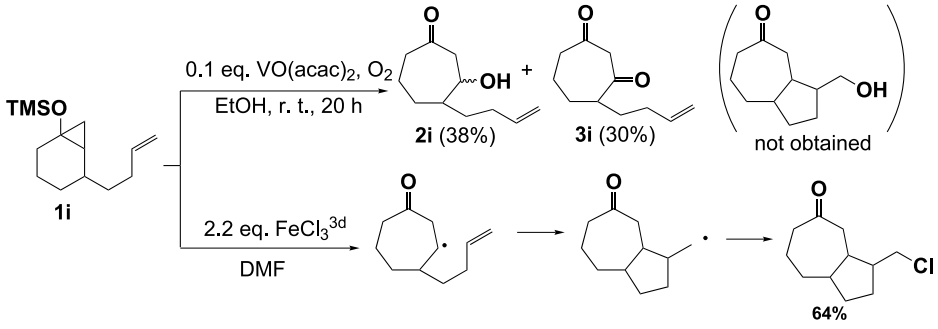
We assumed that the reaction of $VO(acac)_2$ is a radical reaction and molecular oxygen reacted with the radical faster than the radical reacted with the alkene. Actually, in the presence of oxygen, the cyclopropanol (**1i'**)[†] reacted with Fe(III) or Mn(II) producing **2i** and **3i** (Scheme 6).

Recently, Blanco and co-workers reported that ether solutions of 3-alkylbicyclo[*n*.1.0]alkanols when treated with ferric acetylacetonate and light in the presence of oxygen and silica gel produced peroxidated compounds (Scheme 8).[7]

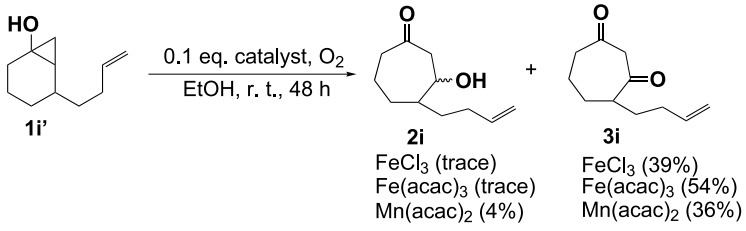


Scheme 8.

We also found that both peroxidated compounds (**4**) and β-hydroxyketones (**2**) were produced when 3-substituted bicyclo[4.1.0]alkanols (**1j**, **1k**, and **1l**) were treated with a catalytic amount of $VO(acac)_2$ under oxygen. Peroxides **4** were the principal products when trifluoroethanol was the solvent (Table 2).

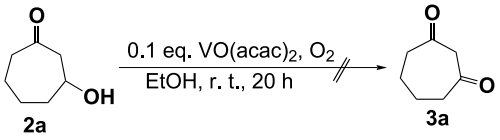


Scheme 5.



Scheme 6.

The β-diketone (**3a**) was not obtained by reaction of the β-hydroxyketone (**2a**) with $VO(acac)_2$ (Scheme 7). Therefore, most likely, β-diketones are directly produced from cyclopropanol derivatives.



Scheme 7.

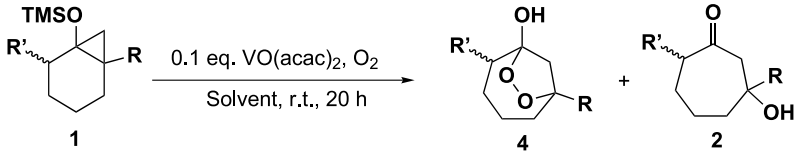
[†] The tertiary cyclopropyl silyl ether (**1i**) did not react under the same reaction condition.

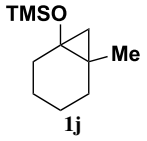
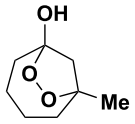
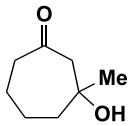
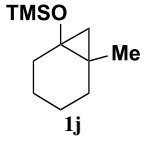
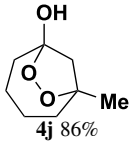
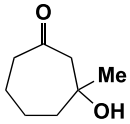
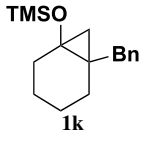
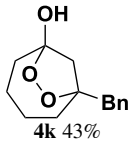
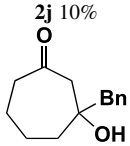
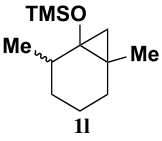
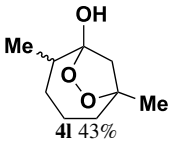
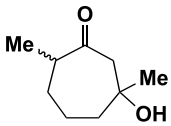
The structure of **4j** was determined by X-ray crystallography. The ORTEP plot shows the X-ray structure of **4j** (Scheme 9).

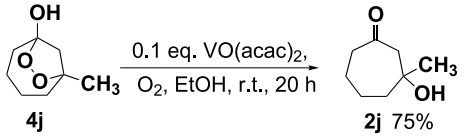
Treatment of **4j** with a catalytic amount of $VO(acac)_2$ in ethanol and oxygen afforded β-hydroxyketone **2j** at 75% yield (Scheme 10). Therefore, peroxide derivatives are probably reaction intermediates formed during production of β-hydroxyketones and β-diketones from cyclopropyl compounds. For 3-unsubstituted bicyclo[4.1.0]alkanols (**1**), peroxidated species might be unstable reaction intermediates and immediately form β-hydroxyketones and β-diketones.

A plausible reaction mechanism is depicted in Scheme 11. Tertiary cyclopropyl silyl ethers are immediately

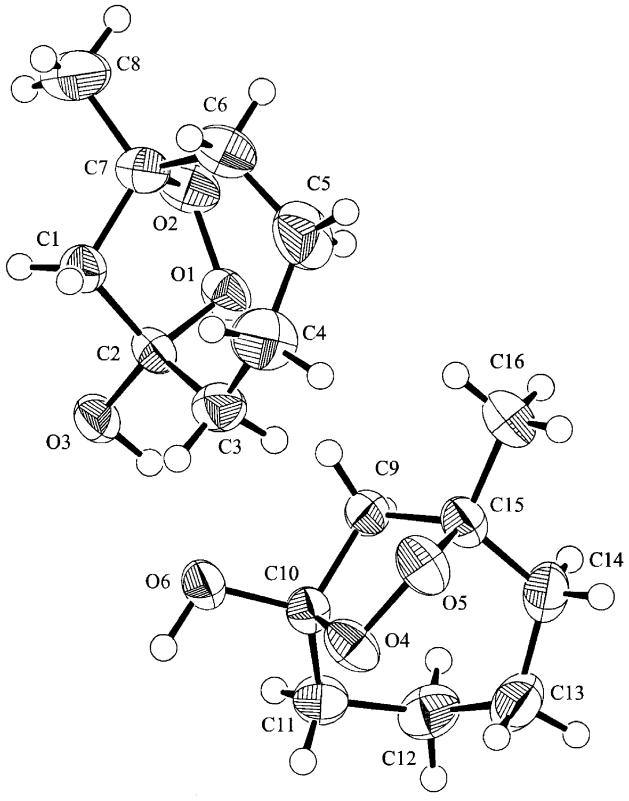
Table 2.



Entry	Starting material	Solvent	Products	
1	 **1j**	EtOH	 **4j** 45%	 **2j** 53%
2	 **1j**	CF_3CH_2OH	 **4j** 86%	 **2j** 10%
3	 **1k**	CF_3CH_2OH	 **4k** 43%	 **2k** trace
4	 **1l**	CF_3CH_2OH	 **4l** 43%	 **2l** 26%



Scheme 10.

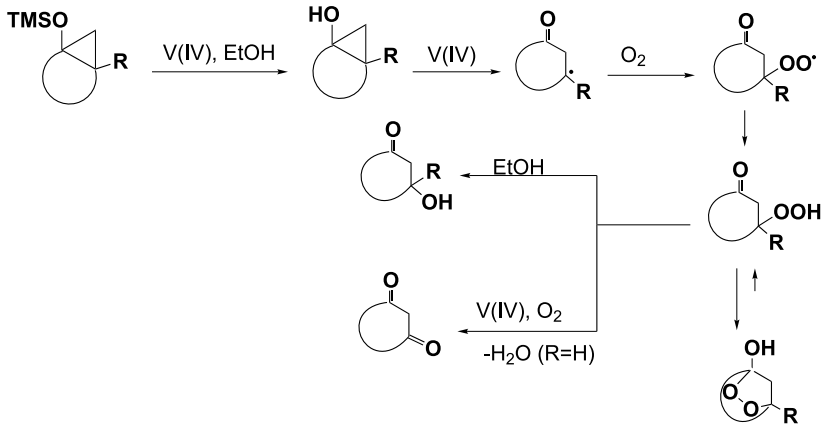


Scheme 9.

hydrolyzed into the corresponding alcohols by V(IV) in ethanol. The resulting cyclopropanols react with V(IV) resulting in the ring expansion and free radical formation. The radical then reacts with molecular oxygen to provide β-perhydroxyketones which are, in turn, transformed into endoperoxide compounds.[‡] The peroxy compounds then react with ethanol to provide β-hydroxyketones. β-Diketones might be obtained by reaction of the peroxy compounds with V(IV) and molecular oxygen, because a β-diketone was the main product a stoichiometric amount of $VO(acac)_2$.

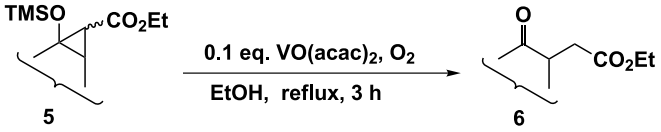
We also examined the reaction of 1-(trimethylsiloxy)bicyclo[*n*.1.0]alkanes bearing an ethoxycarbonyl group (**5**) at the 2-position and found that the 'a' bond was specifically cleaved to provide non-oxygenated compounds (**6**; Table 3). The same result was obtained when **5b** reacted in the absence of oxygen (Scheme 12). In these cases, $VO(acac)_2$ might act as a simple Lewis Acid.

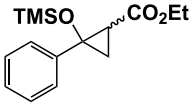
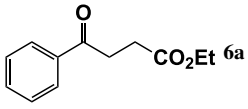
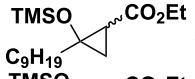
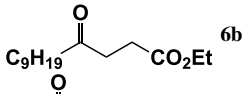
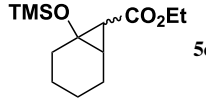
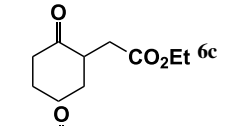
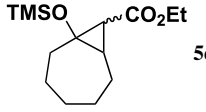
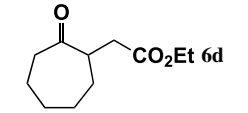
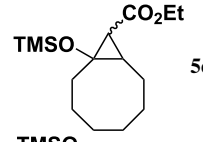
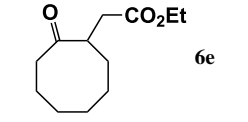
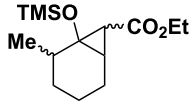
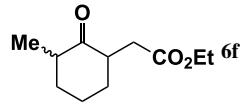
[‡] Although we reported previously that a stoichiometric amount of $VO(acac)_2$ reacted with 1-(trimethylsiloxy)bicyclo[4.1.0]heptane in the absence of oxygen,[5] it is possible that a trace amount of oxygen that was dissolved in the solvent might have reacted with 1-(trimethylsiloxy)bicyclo[4.1.0]heptane.

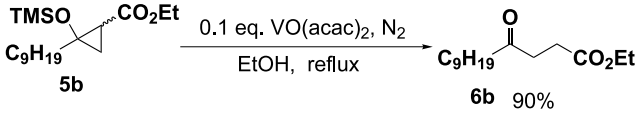


Scheme 11.

Table 3.



Entry	Starting material	Products	Yield (%)
1			84
2			82
3			86
4			90
5			90
6			88



Scheme 12.

3. Conclusions

Tertiary cyclopropyl silyl ethers react with a catalytic amount of $VO(acac)_2$ to provide β-hydroxyketones and β-diketones. For 3-substituted-bicyclo[*n*.1.0]alkanol derivatives, peroxides and with β-hydroxyketones are produced. The β-hydroxyketones and β-diketones obtained from the tertiary cyclopropyl silyl ethers must be derived from peroxide intermediates. Conversely, 2-ethoxycarbonyl-cyclopropyl silyl ethers afford ethyl γ-oxocarboxylate given the same conditions. In these cases, $VO(acac)_2$ probably acts as a Lewis acid.

4. Experimental

4.1. General

IR spectra were recorded using a Perkin–Elmer 1600 FT-IR or a Jasco IR-8300 FT-IR spectrophotometer. NMR spectra acquired using a Varian Gemini 300, a JEOL JNM-400, or a Varian UNITY plus 500 spectrometer. All NMR samples

were dissolved in $CDCl_3$ containing tetramethylsilane as an internal standard. Coupling constants (J) are given in hertz (Hz). Low-resolution and high-resolution mass spectra (electron impact) were recorded on using a JEOL D-200, a JEOL JMS D-200 or a JEOL AX505 spectrometer. Melting points were determined using a Yanagimoto micro-melting point apparatus and are reported as uncorrected values. For column chromatography, silica gel (Merck Kieselger 60) was the support.

Tertiary cyclopropyl silyl ethers and tertiary cyclopropanols were prepared according to reported methods.[1b,8]

4.2. General procedure for the syntheses of β-hydroxy ketones and β-diketones from tertiary cyclopropyl silyl ethers using vanadyl acetylacetonate

A mixture of a tertiary cyclopropyl silyl ether (or a tertiary cyclopropanol) (**1**) (0.50 mmol), vanadyl acetylacetonate (0.50 mmol or 0.05 mmol) and ethanol (5 ml) was stirred at room temperature under an oxygen atmosphere for 20 h. Saturated aqueous sodium bicarbonate (3 ml) was added to the mixture, and that was then extracted with ethyl acetate (20 ml $\times 3$). The combined organic extracts were washed with brine, dried over magnesium sulfate, and evaporated to give a crude mixture of a β-hydroxy ketone (**2**) and a β-diketone (**3**). Separation and purification by column chromatography (hexane-ethyl acetate) gave pure samples.

4.2.1. 3-Hydroxycycloheptanone (2a). IR (neat) cm^{-1}: 3420, 1696; ^1H NMR ($CDCl_3$) δ: 1.67–1.93 (4H, m), 1.94–2.03 (2H, m), 2.46–2.56 (2H, m), 2.75–2.83 (2H, m) 4.08–4.14 (1H, m); MS (m/z) 128 (M^+); HRMS calcd for $C_7H_{12}O_2$ (M^+): 128.0837, found 128.0840.

4.2.2. Cyclohepta-1,3-dione (3a). IR (neat) cm^{-1}: 1670; ^1H NMR ($CDCl_3$) δ: 1.97–2.04 (4H, m), 2.57–2.60 (4H, m), 3.60 (2H, s); MS (m/z) 126 (M^+); HRMS calcd for $C_7H_{10}O_2$ (M^+): 126.0681, found 126.0685.

4.2.3. 6-Hydroxy-2-methylcycloheptanone (3:1 mixture of stereoisomers) (2b). IR (neat) cm^{-1}: 3427, 1694; ^1H NMR ($CDCl_3$) δ: 1.03 (3H, d, $J=6.8$ Hz), 1.36–1.47 (2H, m), 1.56–1.70 (2H, m), 1.89–2.02 (1H, m), 2.39–2.44 (1H, m), 2.60–2.80 (3H, m), 3.96–4.06 (3/4H, m), 4.08–4.16 (1/3H, m); MS (m/z) 142 (M^+); HRMS calcd for $C_8H_{14}O_2$ (M^+): 142.0995, found 142.0994.

4.2.4. 4-Methylcyclohepta-1,3-dione (3b). IR (neat) cm^{-1}: 1698; ^1H NMR ($CDCl_3$) δ: 1.08 (3H, d, $J=6.6$ Hz), 1.57–1.63 (1H, m), 1.89–1.97 (1H, m), 1.98–2.03 (2H, m), 2.44–2.50 (1H, m), 2.52–2.58 (1H, m), 2.69–2.73 (1H, m), 3.53 (1H, d, $J=15.0$ Hz), 3.60 (1H, d, $J=15.0$ Hz); MS (m/z) 140 (M^+); HRMS calcd for $C_8H_{12}O_2$ (M^+): 140.0995, found 140.0994.

4.2.5. 5-*t*-Butyl-3-hydroxycycloheptanone (2.7:1 mixture of stereoisomers) (2c). IR (neat) cm^{-1}: 3420, 1698; ^1H NMR ($CDCl_3$) δ: 0.98 (9H, s), 1.08–1.11 (1H, m), 1.38–1.48 (2H, m), 1.95–2.01 (1H, m), 2.28–2.32 (2H, m), 2.51–2.60 (1H, m), 2.65–2.74 (1H, m), 2.80–2.92 (1H, m), 3.90–3.95 (2.7/3.7H, m), 4.30–4.35 (1/3.7H; MS (m/z) 184 (M^+); HRMS calcd for $C_{11}H_{20}O_2$ (M^+): 184.1444, found 184.1468.

4.2.6. 5-*t*-Butylcyclohepta-1,3-dione (3c). IR (neat) cm^{-1}: 1699; ^1H NMR ($CDCl_3$) δ: 0.91 (9H, s), 1.59–1.71 (2H, m), 2.08–2.16 (1H, m), 2.38–2.51 (2H, m), 2.60–2.67 (2H, m), 3.56 (2H, s); MS (m/z) 182 (M^+); HRMS calcd for $C_{11}H_{18}O_2$ (M^+): 182.1326, found 182.1303.

4.2.7. 3-Hydroxycyclooctanone (2d). IR (neat) cm^{-1}: 3420, 1696; ^1H NMR ($CDCl_3$) δ: 1.23–1.29 (1H, m), 1.46–1.67 (4H, m), 1.80–1.82 (1H, m), 1.84–2.03 (2H, m), 2.33–2.42 (2H, m), 2.66–2.70 (1H, m), 2.78–2.81 (1H, m), 4.05–4.10 (1H, m); MS (m/z) 142 (M^+); HRMS calcd for $C_8H_{14}O_2$ (M^+): 142.0994, found 142.1001.

4.2.8. Cycloocta-1,3-dione (3d). IR (neat) cm^{-1}: 1700; ^1H NMR ($CDCl_3$) δ: 1.62–1.70 (2H, m), 1.80–1.84 (4H, m), 2.50 (4H, t, $J=6.5$ Hz), 3.52 (2H, s); MS (m/z) 140 (M^+); HRMS calcd for $C_8H_{12}O_2$ (M^+): 140.0837, found 140.0812.

4.2.9. 3-Hydroxycyclohexanone (2e). IR (neat) cm^{-1}: 3420, 1696; ^1H NMR ($CDCl_3$) δ: 1.66–1.82 (2H, m), 1.99–2.16 (2H, m), 2.31 (2H, t, $J=6.7$ Hz), 2.40 (1H, dd, $J=14.1$, 7.5 Hz), 2.65 (1H, dd, $J=14.1$, 3.2 Hz), 4.19 (1H, heptet, $J=3.7$ Hz); MS (m/z) 114 (M^+); HRMS calcd for $C_6H_{10}O_2$ (M^+): 114.0681, found 114.0622.

4.2.10. 4-Hydroxybicyclo[5.1.0]octan-2-one (2:1 mixture of stereoisomers) (2f). IR (neat) cm^{-1}: 3405, 1665; ^1H NMR ($CDCl_3$) δ: 1.04–1.19 (1H, m), 1.24–1.38 (1H, m), 1.41–1.54 (1H, m), 1.66–2.37 (5H, m), 2.52–2.71 (2H, m), 3.70–3.78 (2/3H, m), 3.94–3.98 (1/3H, m); MS (m/z) 140 (M^+); HRMS calcd for $C_8H_{12}O_2$ (M^+): 140.0837, found 140.0852.

4.2.11. Bicyclo[5.1.0]octane-2,4-dione (3f). IR (neat) cm^{-1}: 1698, 1676; ^1H NMR ($CDCl_3$) δ: 1.19–1.28 (5H, m), 2.40–2.52 (3H, m), 3.79 (2H, s); MS (m/z) 138 (M^+); HRMS calcd for $C_8H_{10}O_2$ (M^+): 138.0681, found 138.0686.

4.2.12. 3-Hydroxy-1-phenylpropan-1-one (2g). IR (neat) cm^{-1}: 3422, 1680; ^1H NMR ($CDCl_3$) δ: 2.78 (1H, s), 3.15 (2H, t, $J=5.4$ Hz), 3.95 (2H, t, $J=5.4$ Hz), 7.36–7.53 (3H, m), 7.86–7.90 (2H, m); MS (m/z) 150 (M^+); HRMS calcd for $C_9H_{10}O_2$ (M^+): 150.0681, found 150.0622.

4.2.13. 1-Hydroxydodecan-3-one (2h). IR (neat) cm^{-1}: 3381, 1703; ^1H NMR ($CDCl_3$) δ: 0.81 (3H, t, $J=6.4$ Hz), 1.19–1.28 (14H, m), 2.37 (2H, t, $J=5.3$ Hz), 2.60 (2H, t, $J=5.5$ Hz), 3.81 (2H, t, $J=5.5$ Hz); MS (m/z) 200 (M^+); HRMS calcd for $C_{12}H_{24}O_2$ (M^+): 200.1776, found 200.1781.

4.2.14. 4-(3-Butenyl)-3-hydroxycycloheptanone (2i). IR (neat) cm^{-1}: 3417, 1694; ^1H NMR ($CDCl_3$) δ: 1.17–2.36 (7H, m), 2.83–2.88 (1H, m), 3.36–3.39 (2H, m), 3.43–3.49 (2H, m), 4.23–4.26 (2H, m), 4.92–5.03 (2H, m), 5.72–5.79 (1H, m); MS (m/z) 182 (M^+); HRMS calcd for $C_{11}H_{18}O_2$ (M^+): 182.1307, found 182.1320.

4.2.15. 4-(3-Butenyl)-3-hydroxycycloheptane-1,3-dione (3i). IR (neat) cm^{-1}: 1697; ^1H NMR ($CDCl_3$) δ: 1.20–1.35 (2H, m), 1.58–1.70 (2H, m), 1.75–1.99 (2H, m), 2.00–2.04 (2H, m), 2.49–2.59 (2H, m), 2.60–2.70 (1H, m), 3.53 (2H, s), 4.94–5.06 (2H, m), 5.65–5.80 (1H, m); MS (*m/z*) 180 (M^+); HRMS calcd for $C_{11}H_{16}O_2$ (M^+): 180.1158, found 180.1150.

4.3. General procedure for the syntheses of 2i and 3i from 1i using Fe(III) or Mn(II)

A mixture of the tertiary cyclopropanol (**1i**) (83.1 mg, 0.50 mmol), iron(III) chloride, iron(III) acetylacetonate or manganese(II) acetylacetonate (0.05 mmol) and ethanol (5 ml) was stirred at room temperature under an oxygen atmosphere for 48 h. Next, saturated aqueous sodium bicarbonate (3 ml) was added to the mixture, that was then extracted with ethyl acetate (20 ml ×3). The combined organic extracts were washed with brine, dried over magnesium sulfate, and evaporated to provide a crude mixture of **2i** and **3i**. Separation and purification by column chromatography (hexane–ethyl acetate) gave pure samples.

4.4. General procedure for the syntheses of β-hydroxyketones and peroxidated compounds from a tertiary cyclopropyl silyl ethers

A mixture of a tertiary cyclopropyl silyl ether (**1j**, **1k** or **1l**) (0.50 mmol), vanadyl acetylacetonate (0.05 mmol), and either ethanol or 2,2,2-trifluoroethanol (5 ml) was stirred at room temperature under an oxygen atmosphere for 20 h. Saturated aqueous sodium bicarbonate (3 ml) was added to the mixture, that was then extracted with ethyl acetate (20 ml×3). The combined organic extracts were washed with brine, dried over magnesium sulfate, and evaporated to afford a crude mixture of a β-hydroxy ketone and a peroxidated compound. Separation and purification by column chromatography (hexane-ethyl acetate) gave pure samples.

4.4.1. 6-Methyl-7,8-dioxabicyclo[4.2.1]nonan-1-ol (4j). Colorless crystals, Mp 85–86 °C (*n*-hexane–$CHCl_3$); IR (KBr) cm^{-1}: 3354, 2915; ^1H NMR ($CDCl_3$) δ: 1.30 (3H, s), 1.41–1.49 (1H, m), 1.51–1.74 (2H, m), 1.83–1.93 (4H, m), 1.99–2.03 (1H, m), 2.41 (1H, d, J=12.0 Hz), 2.79 (1H, d, J=12.0 Hz), 3.00–3.34 (1H, br); MS (*m/z*) 158 (M^+); HRMS calcd for $C_8H_{14}O_3$ (M^+): 158.0943, found 158.0923. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.70; H, 8.88.

X-ray crystallographic data for **4j**. Colorless prisms, $C_8H_{14}O_3$, M=158.20, monoclinic, a=5.665(1) Å, b=23.297(7) Å, c=14.969(5) Å, β=121.71(2)°, V=1680.8(8) $Å^3$, space group $P2_1/c$ (#14), Z=8, D_c=1.25 g cm^{-3}, $F(000)$=688.00, μ(Mo Kα)=0.94 cm^{-1}, R=0.046, Rw=0.064.

There are two independent molecules in the asymmetric unit of **4j**.

4.4.2. 3-Hydroxy-3-methylcycloheptanone (2j)

A colorless oil; IR (neat) cm^{-1}: 3854, 2932, 1696; ^1H NMR ($CDCl_3$) δ: 1.26 (3H, s), 1.56–1.74 (6H, m), 2.32–2.52 (3H, br), 2.60 (1H, dd, J=14.0, 1.7 Hz), 2.83 (1H, d, J=13.0 Hz); MS (*m/z*) 142 (M^+); HRMS calcd for $C_8H_{14}O_2$ (M^+): 142.0994, found 142.1003.

4.4.3. 6-Benzyl-7,8-dioxabicyclo[4.2.1]nonan-1-ol (4k)

Colorless crystals, Mp 89–91 °C (*n*-hexane–$CHCl_3$); IR (KBr) cm^{-1}: 3346, 2924; ^1H NMR ($CDCl_3$) δ: 1.35–1.64 (3H, m), 1.77–2.04 (5H, m), 2.45 (1H, d, J=13.0 Hz), 2.64–2.72 (2H, m), 2.88 (2H, d, J=4.0 Hz), 7.16–7.30 (5H, m); MS (*m/z*) 234 (M^+); HRMS calcd for $C_{14}H_{18}O_3$ (M^+): 234.1256, found 234.1212.

4.4.4. 2,6-Dimethyl-7,8-dioxabicyclo[4.2.1]nonan-1-ol (2:1 mixture of stereoisomers) (4l)

A colorless oil, IR (neat) cm^{-1}: 3447, 2919; ^1H NMR ($CDCl_3$) δ: 0.97 (3H×1/3, d, J=6.6 Hz), 1.04 (3H×2/3, d, J=7.1 Hz), 1.30 (3H×2/3, s), 1.32–2.13 (8H, m), 2.22 (1H×1/3, brd, J=13.0 Hz), 2.43 (1H×2/3, brd, J=13.0 Hz), 2.71 (1H×1/3, d, J=13.0 Hz), 2.86 (1H×2/3, d, J=13.0 Hz); MS (*m/z*) 172 (M^+); HRMS calcd for $C_9H_{16}O_3$ (M^+): 172.1099, found 172.1052.

4.4.5. 6-Hydroxy-2,6-dimethylcycloheptanone (4:1 mixture of stereoisomers) (2l)

A colorless oil, IR (neat) cm^{-1}: 3853, 2929, 1699; ^1H NMR ($CDCl_3$) δ: 1.08 (3H×1/5, d, J=6.3 Hz), 1.09 (3H×4/5, d, J=7.1 Hz), 1.30 (3H×4/5, s), 1.31 (3H×1/5, s), 1.36–2.57 (8H, m), 2.48 (1H×1/5, d, J=12.0 Hz), 2.62 (1H×4/5, d, J=12.0 Hz), 2.85 (1H×4/5, d, J=12.0 Hz), 2.93 (1H×1/5, d, J=13.0 Hz); MS (*m/z*) 156 (M^+); HRMS calcd for $C_9H_{16}O_2$ (M^+): 156.1150, found 156.1175.

4.5. General procedure for the syntheses of an ethyl γ-oxocarboxylates from a tertiary cyclopropyl silyl ethers

A mixture containing a tertiary cyclopropyl silyl ether (**5**) (0.50 mmol), vanadyl acetylacetonate (0.05 mmol) and ethanol (5 ml) was refluxed under an oxygen or a nitrogen atmosphere for 3 h. Next, saturated aqueous sodium bicarbonate (3 ml) was added to the mixture, that was then 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 product. Separation and purification by column chromatography (hexane-ethyl acetate) gave pure samples.

4.5.1. Ethyl 4-oxophenylbutanoate (6a)

A colorless oil, IR (neat) cm^{-1}: 1732, 1687; ^1H NMR ($CDCl_3$) δ: 1.20 (3H, t, J=7.1 Hz), 2.69 (2H, t, J=7.2 Hz), 3.25 (2H, t, J=7.2 Hz), 4.11 (2H, q, J=7.2 Hz), 7.37–7.42 (1H, m), 7.47–7.53 (2H, m), 7.90–7.94 (2H, m); MS (*m/z*) 206 (M^+); HRMS calcd for $C_{12}H_{14}O_3$ (M^+): 206.0943, found 206.0988.

4.5.2. Ethyl 4-oxotridecanoate (6b)

A colorless oil, IR (neat) cm^{-1}: 1736, 1717; ^1H NMR

($CDCl_3$) δ: 0.86 (3H, t, $J=6.6$ Hz), 1.19–1.26 (17H, m), 2.42 (2H, t, $J=7.3$ Hz), 2.55 (2H, t, $J=6.3$ Hz), 2.70 (2H, t, $J=6.3$ Hz), 4.10 (2H, q, $J=6.6$ Hz); MS (*m/z*) 256 (M^+); HRMS calcd for $C_{15}H_{28}O_3$ (M^+): 256.2038, found 256.2035.

4.5.3. Ethyl 2-(2-oxocyclohexyl)acetate (6c)

A colorless oil, IR (neat) cm^{-1}: 1734, 1713; ^1H NMR ($CDCl_3$) δ: 1.23 (3H, t, $J=7.3$ Hz), 1.36–1.83 (4H, m), 2.07–2.15 (2H, m), 2.33–2.40 (2H, m), 2.70–2.88 (3H, m), 4.11 (2H, q, $J=7.3$ Hz); MS (*m/z*) 184 (M^+); HRMS calcd for $C_{10}H_{16}O_3$ (M^+): 184.1099, found 184.2033.

4.5.4. Ethyl 2-(2-oxocycloheptyl)acetate (6d)

A colorless oil, IR (neat) cm^{-1}: 1732, 1704; ^1H NMR ($CDCl_3$) δ: 1.23 (3H, t, $J=7.0$ Hz), 1.28–1.85 (8H, m), 2.23–2.31 (1H, m), 2.37–2.48 (1H, m), 2.57–2.67 (1H, m), 2.74–2.84 (1H, m), 3.03–3.13 (1H, m), 4.80 (2H, q, $J=7.0$ Hz); MS (*m/z*) 198 (M^+); HRMS calcd for $C_{11}H_{18}O_3$ (M^+): 198.1256, found 198.1277.

4.5.5. Ethyl 2-(2-oxocyclooctyl)acetate (6e)

A colorless oil, IR (neat) cm^{-1}: 1732, 1704; ^1H NMR ($CDCl_3$) δ: 1.21 (3H, t, $J=7.2$ Hz), 1.36–1.87 (10H, m), 2.21–2.33 (2H, m), 2.64–2.73 (1H, m), 2.79–2.89 (1H, m), 3.17–3.28 (1H, m), 4.05 (2H, q, $J=7.2$ Hz); MS (*m/z*) 212 (M^+); HRMS calcd for $C_{12}H_{20}O_3$ (M^+): 212.1412, found 212.1444.

4.5.6. Ethyl 2-(3-methyl-2-oxocyclohexyl)acetate (6f)

A colorless oil, IR (neat) cm^{-1}: 1737, 1711; ^1H NMR ($CDCl_3$) δ: 1.00 (3H, d, $J=6.7$ Hz), 1.38–1.91 (6H, m), 1.17–1.26 (3H, m), 2.06–2.23 (2H, m), 2.66–2.79 (1H, m), 2.98–3.04 (1H, m), 4.11 (2H, q, $J=6.7$ Hz); MS (*m/z*) 198 (M^+); HRMS calcd for $C_{11}H_{18}O_3$ (M^+): 198.1256, found 198.1257.

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