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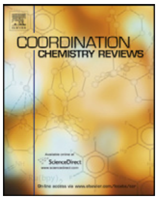

Review

Aerobic oxidation of organic compounds catalyzed by vanadium compounds

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Contents

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ABSTRACT

Aerobic oxidation of α-hydroxy ketones catalyzed by dichloroethoxyoxovanadium in ethanol causes a carbon–carbon bond cleavage that produces diesters or diketones. This reaction is highly chemoselective, and disecondary glycols do not react at all. However, ditertiary glycols effectively react with dichloroethoxyoxovanadium or trichlorooxovanadium to provide the corresponding ketones. Aerobic

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Disulfide

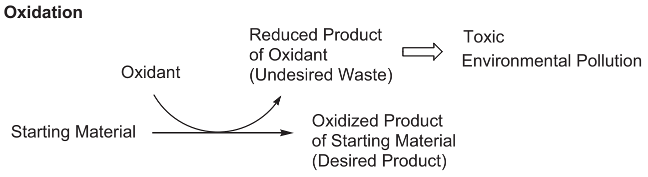
oxidation of α-hydroxy ketones catalyzed by dichloroethoxyoxovanadium or trichlorooxovanadium in aprotic solvents almost quantitatively affords the corresponding α-diketones. The reaction of tertiary cyclopropanol compounds with vanadyl acetylacetonate under an oxygen atmosphere causes fragmentation of the cyclopropane moiety to produce β-hydroxy ketones and β-diketones. For the 6-substituted bicyclo[4.1.0]heptanol derivatives, the endoperoxides are also obtained together with β-hydroxy ketones. Conversely, 2-ethoxycarbonylcyclopropyl silyl ethers produce γ-oxocarboxylate derivatives given the same reaction conditions. Monothioacetals are easily deprotected into carbonyls using a catalytic amount of trichlorooxovanadium in 2,2,2-trifluoroethanol under an oxygen atmosphere. Thiols are converted into the corresponding disulfides by the aerobic oxidation catalyzed by trichlorooxovanadium in the presence of molecular sieves 3A. Polymer-supported vanadium compounds are synthesized by the reaction of vanadium oxytrichloride with polymers bearing hydroxyl moieties. The catalyst prepared from TentaGel S OH was highly active and reusable for the aerobic oxidations.

1. Introduction

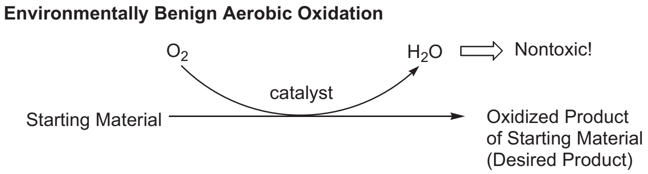
Needless to say, oxidation is one of the most important reactions in organic synthesis. However, oxidation reactions frequently become the source of environmental pollution. During the oxidation of organic compounds, the starting materials are oxidized to the desired compounds and the oxidants are simultaneously reduced. This means that a large amount of waste is produced when the starting materials are oxidized. The waste is sometimes toxic and the cause of environmental pollution (Scheme 1).

The effective method to prevent environmental pollution caused by oxidations is the use of aerobic oxidation. During aerobic oxidation, the oxidant is molecular oxygen, which is reduced to nontoxic water (Scheme 2). Catalysts are usually required for the aerobic oxidation of organic compounds, and vanadium compounds can serve this purpose [1,2].

In this review, the vanadium-catalyzed aerobic oxidations accomplished by our research group are summarized [3,9,12,16,22,26,34].



Scheme 1.



Scheme 2.

2. Oxidative cleavage of α-hydroxy ketones [3]

2.1. Traditional methods of oxidative cleavage of glycols and α-hydroxy ketones

The oxidative cleavage of carbon–carbon bonds in glycols and α-hydroxy ketones is a very important reaction which has frequently been utilized in organic syntheses. However, only a few methods for this oxidative cleavage have been developed [4]. Most organic chemists use classical sodium periodate ($NaIO_4$) [5] or lead tetraacetate [$Pb(OAc)_4$] [6] for this purpose (Scheme 3).

Although $NaIO_4$ effectively reacts with glycols and α-hydroxy ketones in many cases, the reaction does not proceed when using tertiary α-hydroxy ketones, ditertiary glycols, and *trans*-cyclic glycols [5]. On the other hand, $Pb(OAc)_4$ can react with these compounds; therefore, it has been used as a convenient oxidant for the cleavage of a carbon-carbon bond in glycols and α-hydroxy ketones. However, $Pb(OAc)_4$ is highly toxic and is reduced to lead diacetate which is also highly toxic, and therefore undesirable waste.

2.2. Aerobic cleavage of tertiary α-hydroxy ketones

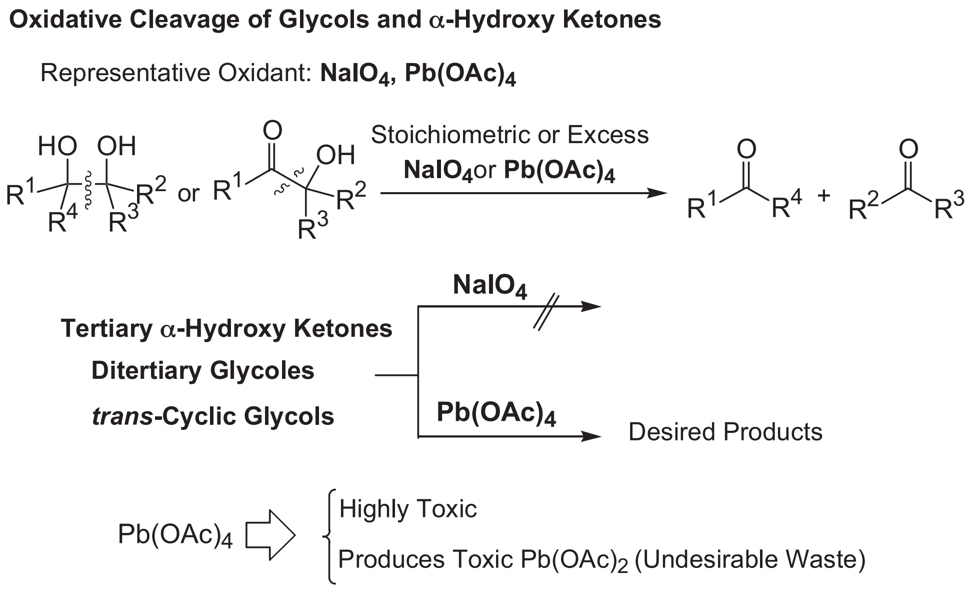
The synthetic studies of nitrogen containing heterocyclic compounds have been worked by our research group [7], and during the course of the study, $Pb(OAc)_4$ was utilized as the reagent for the oxidative cleavage of the tertiary α-hydroxy ketone (**1a**). Although the desired compound (**2a**) was obtained, the isolated yield of this compound was not very high (unpublished result). Furthermore, an excess amount of $Pb(OAc)_4$ was required to accomplish the reaction. Therefore, investigations were started to alternate reagents which could be used for the oxidative cleavage of **1a**. Several oxidants, which have been used as the glycol-cleavage reagent, were examined, for example $NaIO_4$ [8], calcium hypochlorite [4d], hypervalent iodines [4a], and organobismuth compounds [4h], however, **2a** was not obtained (Scheme 4).

Then, the vanadium-catalyzed aerobic cleavage of α-substituted ketones developed by Hirao's group [1p] was focused on. They reported that cyclic ketones bearing a methyl or chloro group at their α-positions reacted with a catalytic amount of dichloroethoxyoxovanadium [$VO(OEt)Cl_2$] in ethanol under an oxygen atmosphere to produce the ketoesters or diesters (Scheme 5) [1p].

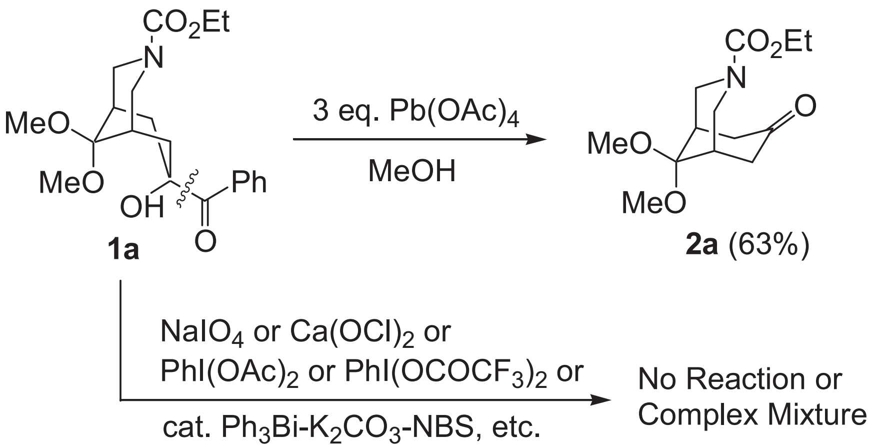
The reaction of the tertiary α-hydroxy ketone (**1a**) with 1 mol% $VO(OEt)Cl_2$ in refluxing ethanol under an oxygen atmosphere caused the desired oxidative cleavage to produce the ketone (**2a**) in 75% yield (Table 1, entry 1). Other tertiary α-hydroxy ketones (**1b**, **c**) also reacted under the same conditions to produce the desired ketones (**2b**, **c**) (Table 1) [3].

2.3. Aerobic cleavage of primary and secondary α-hydroxy ketones

Then the aerobic oxidative cleavage of primary and secondary α-hydroxy ketones catalyzed by $VO(OEt)Cl_2$ under oxygen was examined (Table 2) [3]. A primary α-hydroxy ketone (**1d**) was immediately oxidized at room temperature to produce ethyl benzoate (**2d**) in 74% yield (entry 1). Secondary α-hydroxy ketones (**1e**–**k**) were also smoothly cleaved at room temperature to provide the diesters (**2e**–**k**) in moderate to high yields in most cases (entries 2–8). The sterically hindered secondary α-hydroxy ketone (**1k**) required reflux conditions in order to obtain the diester (**2k**),



Scheme 3.



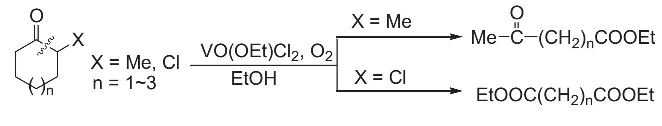
Scheme 4.

and furthermore, it took longer for the reaction to reach completion (entry 8).

2.4. Chemoselectivity

Hirao reported that 2-methylcyclohexanone reacted with $VO(OEt)Cl_2$ under oxygen to afford the ketoester [1p]. Therefore, the selectivity of this aerobic oxidation catalyzed by $VO(OEt)Cl_2$ was then examined. In the case of 2-hydroxy-6-methylcyclohexanone (**1l**), the C(1)–C(2)-bond was regioselectively cleaved to produce the diester (**2l**) (Scheme 6) [3].

Interestingly, glycols, an α-amino ketone, an α-acetoxy ketone, and an α-thiophnyl ketone are inert under the stated reaction conditions (Scheme 7). These results are in contrast to those with other reagents which cleave both α-hydroxy ketones and glycols [3].



Scheme 5.

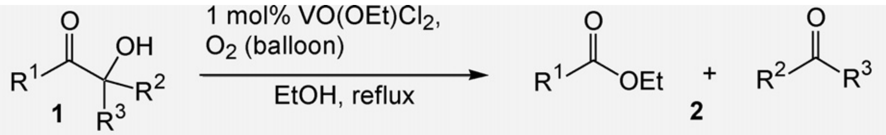
In the case of the compound having both the α-hydroxy ketone and glycol (**1m**), the α-hydroxy ketone was selectively cleaved by the aerobic oxidation catalyzed by $VO(OEt)Cl_2$ to produce the corresponding diester (**2m**) [3]. Conversely, phenyliodine diacetate [4a] reacted with that compound to selectively cause glycol-cleavage to produce the dialdehyde (**2m′**) (Scheme 8).

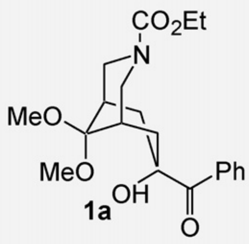
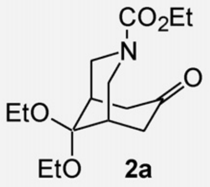
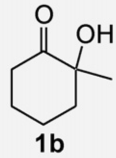
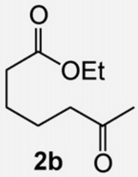
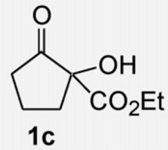
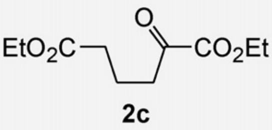
2.5. Investigation of reaction mechanism

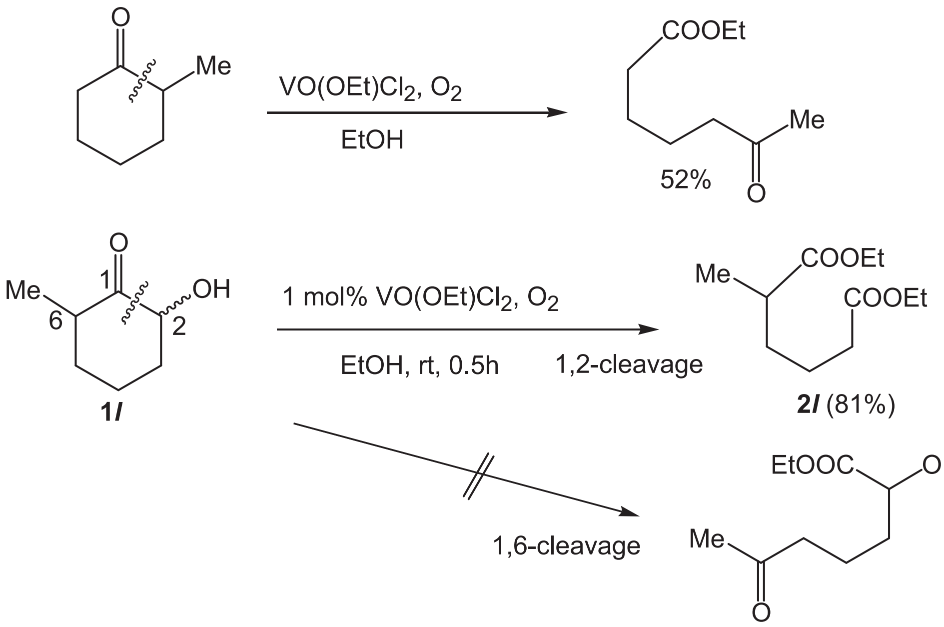
Even in the absence of oxygen, the α-hydroxy ketone (**1f**) reacted with 2 equiv. of $VO(OEt)Cl_2$ to produce the corresponding diester (**2f**) [3]. This result is in sharp contrast to the cleavage of the α-methyl ketone with $VO(OEt)Cl_2$ reported by Hirao's group [1p]. In that case, the reaction of 2-methylcyclohexanone with a stoichiometric of $VO(OEt)Cl_2$ afforded the corresponding ketoester at only 3% yield in the absence of oxygen. In the case of the cleavage of α-hydroxy ketone, molecular oxygen acts as the co-oxidant and reoxidized the formed low valent vanadium compound (Scheme 9).

In the presence of a radical inhibitor, the reaction of a ketone bearing a secondary α-hydroxy group (**1f**) did not give the diester (**2f**), but the α-diketone (**3f**). The same result was obtained when acetonitrile was used as the solvent instead of ethanol. Moreover, when the reaction proceeded at low temperature, only **3f**

Table 1
Vanadium(V)-catalyzed aerobic oxidative cleavage of tertiary α-hydroxy ketones [3].



entry	starting material	time (h)	product	yield (%)
1	 **1a**	24	 **2a**	75
2	 **1b**	25	 **2b**	64
3	 **1c**	48	 **2c**	73



Scheme 6.

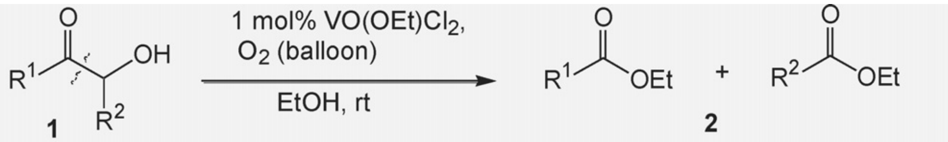
was obtained. The α-diketone (**3f**) was efficiently cleaved with $VO(OEt)Cl_2$ under an oxygen atmosphere. A ketone bearing a tertiary α-hydroxy group (**1b**) was inert under these reaction conditions. Although the reaction mechanism is unclear, these results suggest that secondary α-hydroxy ketones were oxidized to α-diketones in the first step and the resulting α-diketones are cleaved in the second step. The second step involves radical intermediates, and ethanol is essential to the cleavage [3] (Scheme 10).

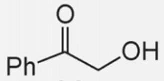
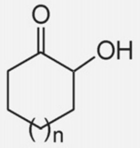
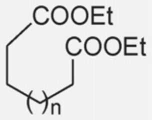
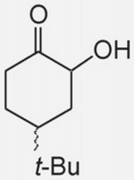
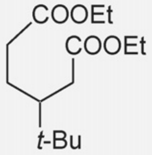
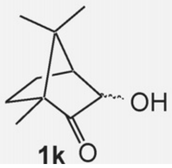
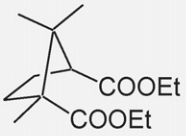
3. Oxidative cleavage of ditertiary glycols [9]

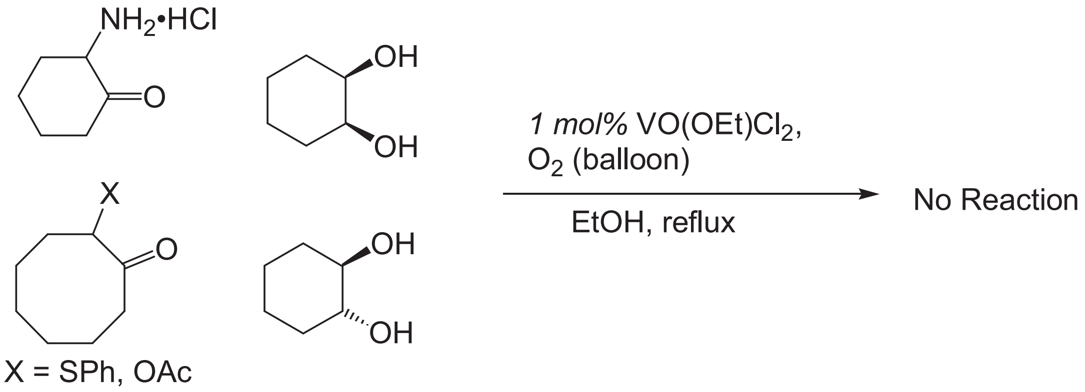
3.1. Vanadium mediated oxidative cleavage of glycols

As described in Section 2.4, glycols did not react with a vanadium catalyst under an oxygen atmosphere, however, we only examined the disecondary glycols [3]. However, ditertiary glycols can be cleaved by the reaction with a stoichiometric amount of vanadyl

Table 2
Vanadium(V)-catalyzed aerobic oxidative cleavage of primary and secondary α-hydroxy ketones [3].



entry	starting material	time (h)	product	yield (%)
1	 **1d**	0.25	PhCOOEt **2d**	74
2 3 4 5 6	 **1e~i**	0.5		**2e** (n = 1): 55 **2f** (n = 2): 71 **2g** (n = 3): 83 **2h** (n = 7): 87 **2i** (n = 10): 70
7	 **1j**	1	 **2j**	81
8	 **1k**	48	 **2k**	55 (reflux)

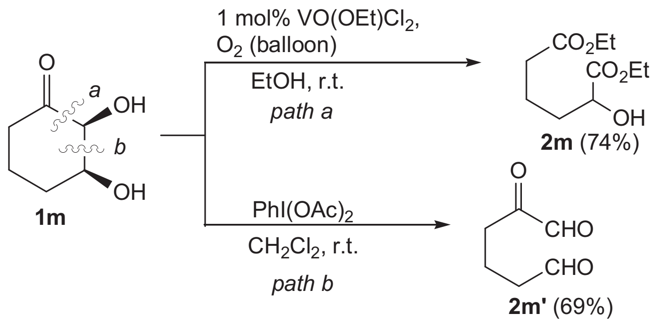


Scheme 7.

acetylacetonate [VO(acac)$_2$] or a catalytic amount of VO(acac)$_2$ in the presence of tertiary butyl hydroperoxide [10]. Disecondary glycols are inert under the stated reaction conditions [10]. Therefore, ditertiary glycols were expected to be cleaved to form ketones by the aerobic oxidation catalyzed by vanadium (Scheme 11). If the reaction worked, it would be a novel "green" reaction, because the standard oxidant for the cleavage of ditertiary glycols is the highly toxic Pb(OAc)$_4$.

3.2. *VOCl$_3$ catalyzed aerobic oxidative cleavage of ditertiary glycols*

Benzopinacol (**4a**) was chosen as the model compound of a ditertiary glycol, and the reaction conditions examined (vanadium catalysts, solvents, etc.). The best result was obtained in the case of the reaction of **4a** with 2.4 mol% of VOCl$_3$ in ethyl acetate at room temperature under an oxygen atmosphere [9]. The oxidative cleav-



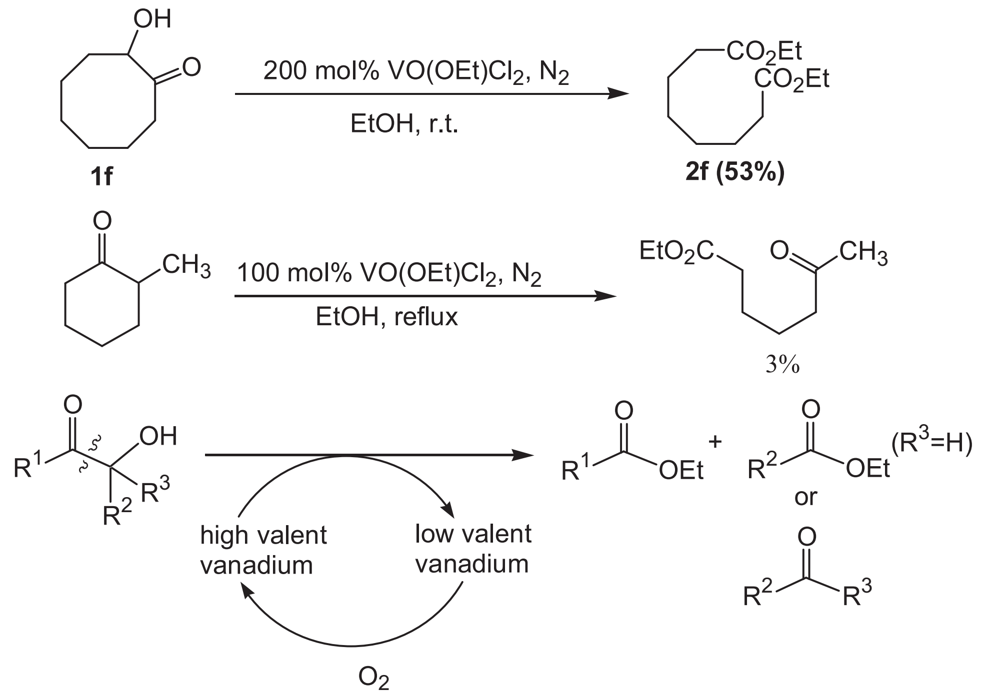
Scheme 8.

age of several ditertiary glycols (**4**) with 2.4 mol% $VOCl_3$ in ethyl acetate under an oxygen atmosphere at room temperature provided the desired ketones (**5**) in high yield in all cases (Table 3) [9].

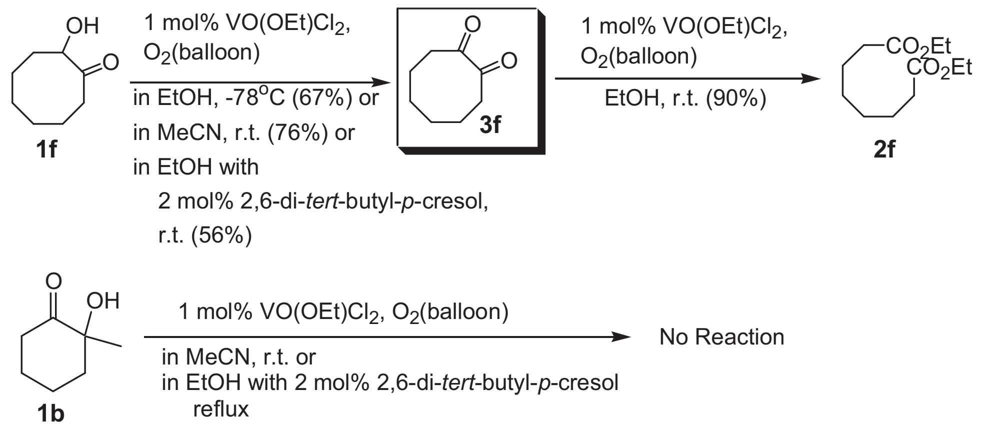
For the cyclic ditertiary glycols, the desired diketones were obtained in all cases (Table 4). Interestingly, both the *cis*- and *trans*-glycols similarly reacted. This is in sharp contrast to the oxidative cleavage of cyclic diols by $Pb(OAc)_4$ in which the *cis*-diols react much faster than the *trans*-diols, because the reaction proceeds via cyclic intermediates in the *cis*-diols [11]. Although the reaction mechanism is currently unknown, this vanadium-catalyzed aerobic cleavage of glycols does not pass through a cyclic intermediate.

3.3. *$VOCl_3$ catalyzed aerobic oxidative cleavage of secondary–tertiary glycols [3]*

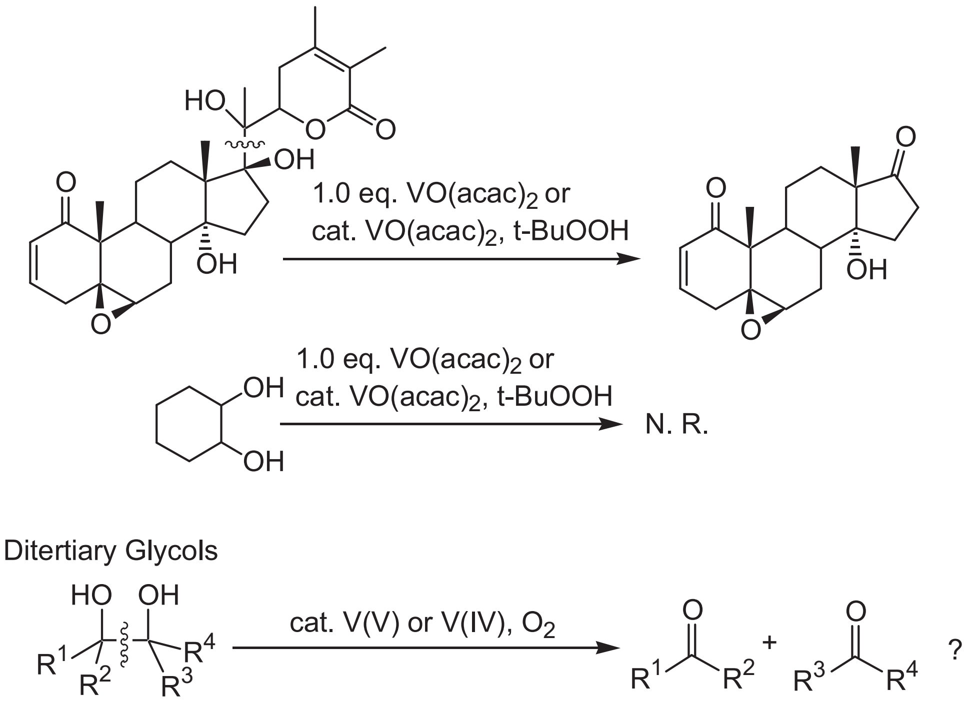
The reaction of secondary–tertiary glycols was then examined. Although the reaction proceeded, complex mixtures were obtained (Table 5) [9]. In the cases of an acyclic diol, the corresponding ketone was quantitatively obtained as part of the complex mixture. This result indicates that the tertiary alcohol portion of the reactant affords the ketone, and the secondary alcohol fragment yields complex mixtures [9].



Scheme 9.

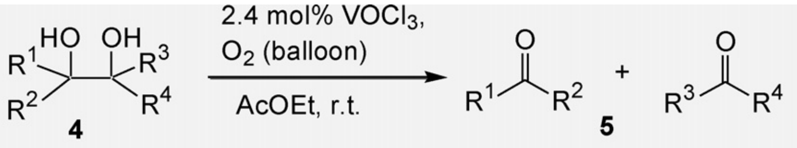


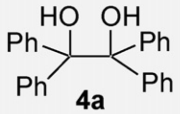
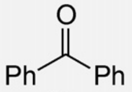
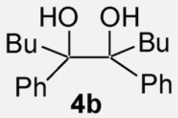
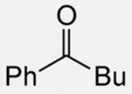
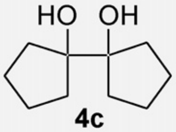
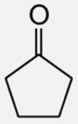
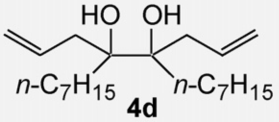
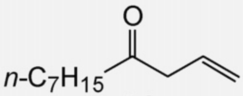
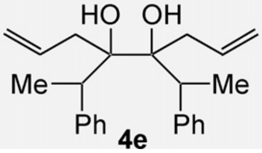
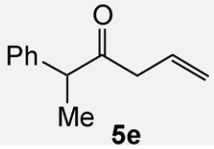
Scheme 10.



Scheme 11.

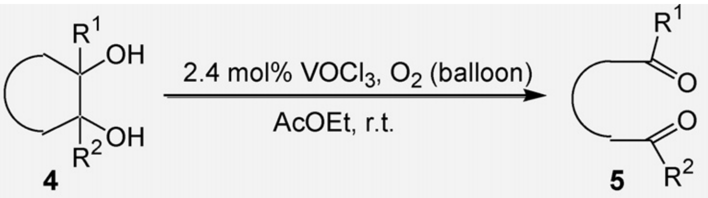
Table 3
Vanadium(V)-catalyzed aerobic oxidative cleavage of acyclic ditertiary glycols [9].

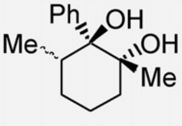
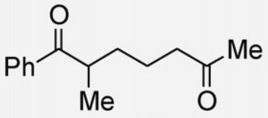
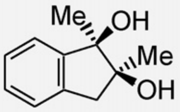
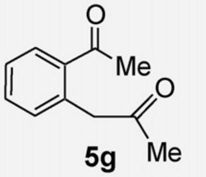
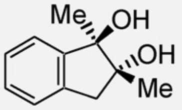
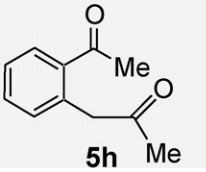


entry	diol	ketone	time (h)	yield (%)
1	 **4a**	 **5a**	0.5 0.2	quant. quant.*
2	 **4b**	 **5b**	0.5	91
3	 **4c**	 **5c**	0.5	85
4	 **4d**	 **5d**	2	74
5	 **4e**	 **5e**	3	76

*Reaction in refluxing AcOEt.

Table 4
Vanadium(V)-catalyzed aerobic oxidative cleavage of cyclic ditertiary glycols [9].



entry	diol	diketone	time (h)	yield (%)
1	 **4f**	 **5f**	0.5	97
2	 **4g**	 **5g**	8	40*
3	 **4h**	 **5h**	8	60*

*2-Methyl-1-methyleneindan-2-ol (24%) was obtained as a byproduct.

4. Oxidation of α-hydroxy carbonyls to α-dicarbonyls [12]

4.1. α-Dicarbonyls: important materials in organic synthesis

As shown in Section 2.5, several experiments were performed to investigate the reaction mechanism of the aerobic oxidative cleavage of α-hydroxy ketones, and the α-hydroxy ketones (**1**) did not give the diester (**2**), but rather the corresponding α-diketone (**3**) in an aprotic solvent (Scheme 12). Thus, this reaction was expected to be a procedure for the preparation of α-diketones (**3**).

α-Diketones (**3**) are important compounds in organic synthesis, because they have been used as substrates for the benzylic acid rearrangement [13] and starting materials for the syntheses of heterocyclic compounds [14]. α-Diketones (**3**) are frequently obtained by the oxidation of α-hydroxy ketones (**1**). Due to the sensitivity of α-diketones (**3**), special reagents and reaction conditions are required to prevent side reactions [15]. Although a number of methods have been developed to achieve this transformation, most of them suffer from drawbacks such as the use of stoichiometric amounts of toxic reagents.

4.2. Oxidation of α-hydroxy ketones and α-hydroxy esters

Benzoin (**1n**) was chosen as the model compound for an α-hydroxy ketone, and the reaction conditions were examined [12]. The corresponding benzil (**3n**) was obtained almost quantitatively by the reaction of **1n** with 1 mol% $VOCl_3$ in aprotic polar solvents (acetonitrile, acetone, and ethyl acetate) at room temperature under an oxygen atmosphere [12]. The reaction of several α-hydroxy ketones (**1**) with 1 mol% of $VOCl_3$ in acetonitrile under an oxygen atmosphere quantitatively provided the corresponding α-diketones (**3**) (Table 6) [12]. In all cases, the α-diketone (**3**) was the sole product and no by-products were observed. The reaction similarly proceeds in air. α-Hydroxy esters (**6**) were also efficiently oxidized to α-keto esters (**7**) in high yields (Scheme 13) [12].

4.3. Investigation of reaction mechanism and chemoselectivity

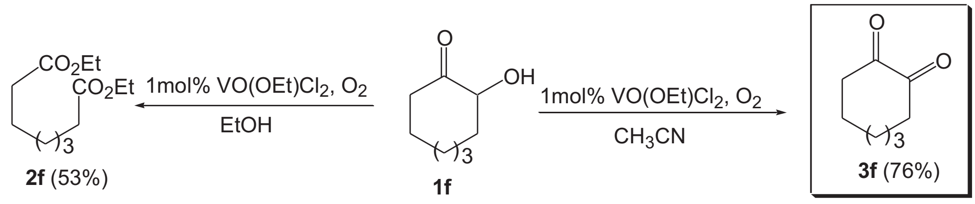
Even in the absence of molecular oxygen, **1n** reacted, with a shorter reaction time, with a stoichiometric amount of trichlorooxyvanadium to afford **3n** in a high yield. Although the reaction mechanism in not clear, this indicates that molecular oxygen acts as a co-oxidant, and reoxidized the formed low-valent vanadium compound. Alcohols without carbonyls at their α-position including β-hydroxy carbonyls are completely inert under the stated reaction conditions [12] (Scheme 14).

4.4. Similar reactions developed by other groups

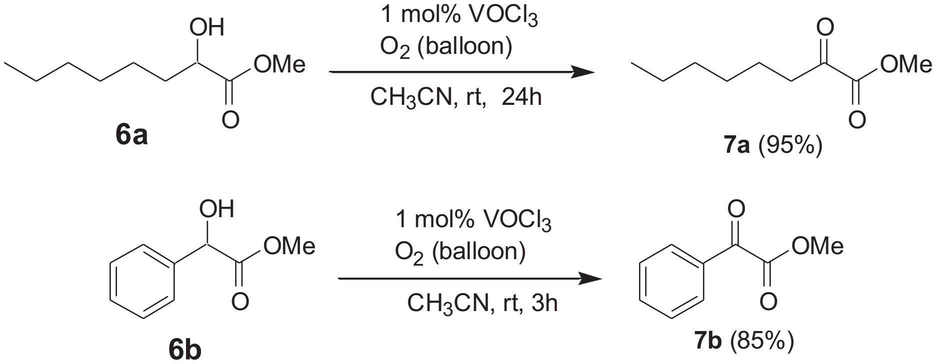
Propargilic alcohols (**8**) are oxidized to the corresponding carbonyls (**9**) in high yields by aerobic oxidation catalyzed by $VO(acac)_2$ in the presence of molecular sieves [1m,1n] (Scheme 15).

Kinetic resolutions of the racemic α-hydroxy carbonyls (**1**) using molecular oxygen and a catalytic amount of a chiral vanadium complex were achieved with a high enantiomeric excess [1k] (Scheme 16).

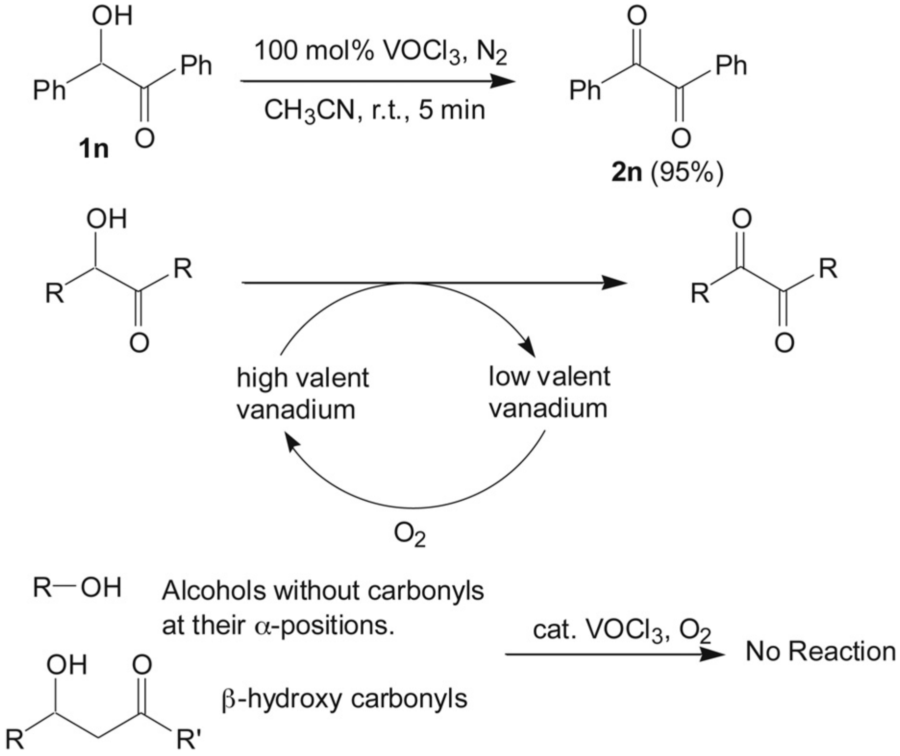
In our case, only the α-hydroxy carbonyls (**1**) can be oxidized and other alcohols are inert. However, several kinds of alcohols are oxidized to the corresponding carbonyls by the aerobic oxidation catalyzed by vanadium oxide in toluene [1m] (Scheme 17).



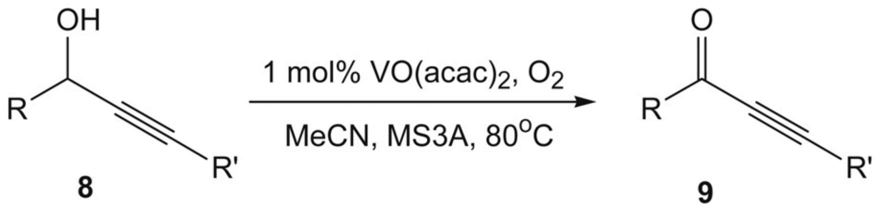
Scheme 12.



Scheme 13.

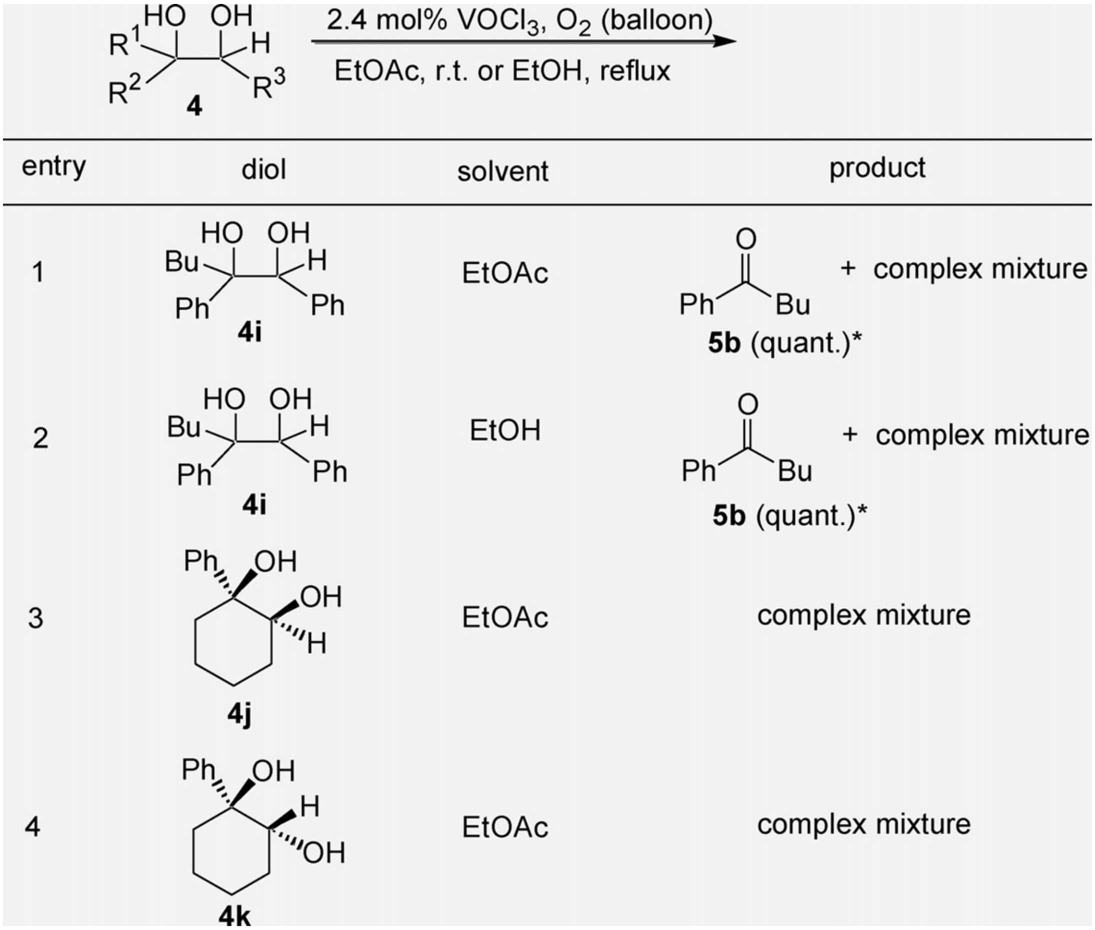


Scheme 14.



Scheme 15.

Table 5
Vanadium(V)-catalyzed aerobic oxidative cleavage of secondary-tertiary glycols [9].

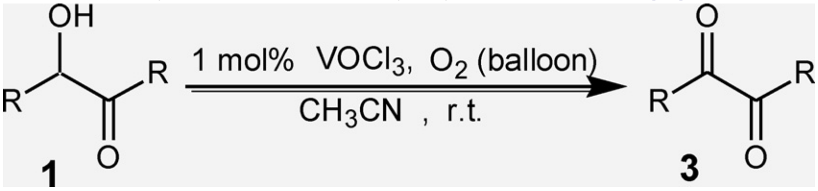


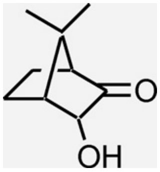
2.4 mol% $VOCl_3$, O_2 (balloon)
EtOAc, r.t. or EtOH, reflux

entry	diol	solvent	product
1	**4i**	EtOAc	**5b** (quant.)* + complex mixture
2	**4i**	EtOH	**5b** (quant.)* + complex mixture
3	**4j**	EtOAc	complex mixture
4	**4k**	EtOAc	complex mixture

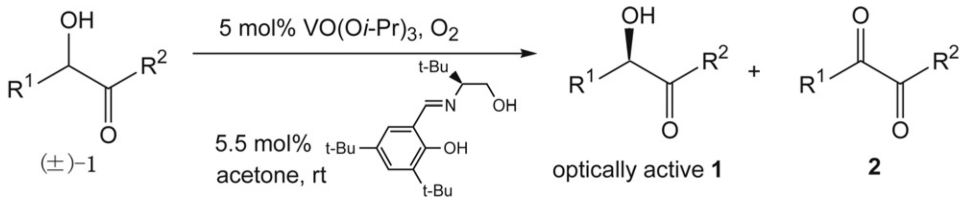
*Based on GC analysis.

Table 6
Vanadium(V)-catalyzed aerobic oxidation of α-hydroxy ketones to α-diketones [12].

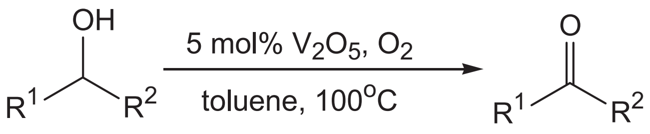


Entry	R	Time (h)	Yield (%)
1	Ph	1.5	95
2[a]	Ph	11	89
3	4-ClC_6H_4	1.5	Quant.
4	4-$MeOC_6H_4$	1.5	Quant.
5	Cyclohexyl	20	95
6	$CH_3(CH_2)_8$	12	Quant.
7	$CH_2{=}CH(CH_2)_7$	5.5	Quant.
8[b]	$CH_3(CH_2)_{14}$	13.5	Quant.
9	$-(CH_2)_{10}-$	8.5	Quant.
10	$-(CH_2)_{13}-$	22.5	95
11		114	Quant.

[a] The reaction was carried out in air.
[b] The reaction was carried out under reflux.

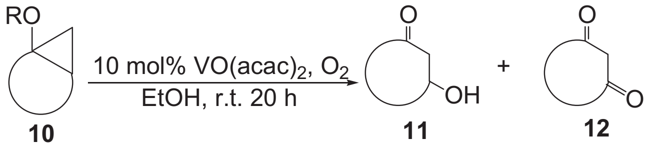


Scheme 16.



Scheme 17.

Scheme 18.



Scheme 19.

5. Cleavage of tertiary cyclopropanol compounds [16]

5.1. Tertiary cyclopropanol derivatives

Tertiary cyclopropanol compounds (**10**) are important materials in organic synthesis due to their significant reactivity, and many reactions have been developed using specifically the bonds ‘a’ and/or bond ‘b’ [17] (Scheme 18).

We have been working on developing new synthetic reactions by using tertiary cyclopropanols (**10**) [18], and found that when tertiary cyclopropyl silyl ethers or tertiary cyclopropanols (**10**) are treated with a catalytic amount of $VO(acac)_2$ under oxygen and in ethanol, the cyclopropyl ring fragments and β-hydroxy ketones (**11**) and β-diketones (**12**) are produced (Scheme 19) [16].

5.2. Cleavage of tertiary cyclopropanol derivatives by $VO(acac)_2$ in the presence of molecular oxygen

The reaction of a tertiary cyclopropyl silyl ether (**10a**) with 1.0 equiv. or 0.1 equiv. (10 mol%) of $VO(acac)_2$ examined at room temperature under an oxygen atmosphere (Scheme 20) [16]. Cleavage of the ‘b’ bond of the cyclopropane moiety produced the β-hydroxy ketone (**11a**) and the β-diketone (**12a**). β-Diketone (**12a**) was the major product when a stoichiometric amount of $VO(acac)_2$ was present. However, β-hydroxy ketone (**11a**) predominated when a catalytic amount of $VO(acac)_2$ was used.

Several tertiary cyclopropyl silyl ethers or cyclopropanols (**10**) similarly reacted with 10 mol% $VO(acac)_2$ in ethanol under an oxygen atmosphere to produce the β-hydroxy ketones (**11**) and β-diketones (**12**) (Table 7) [16]. With $VO(acac)_2$ present, the silyl ethers immediately hydrolyzed upon dissolution in ethanol and the corresponding alcohols were formed. Therefore, the reactive species are the tertiary cyclopropanols. When the cyclopropane ring lacked an oxygen functionality, the reaction did not occur (entry 6).

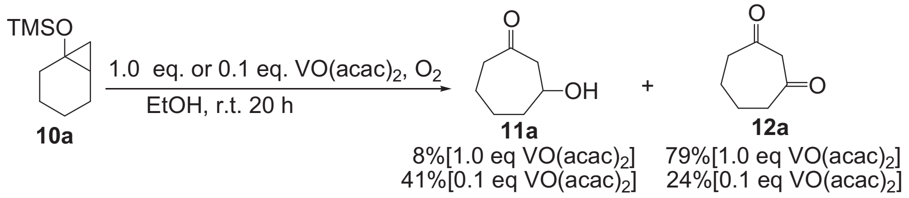
Although $VO(acac)_2$ did not react with **10a** or **10b** in an aprotic solvent (e.g., dichloromethane), it did react with these compounds in trifluoroethanol with the β-diketones (**12a** and **12b**) as the main products. The β-diketone (**12a**) was not obtained by the reaction of the β-hydroxy ketone (**11a**) with $VO(acac)_2$ (Scheme 21) [16]. Therefore, most likely, β-diketones (**12**) are directly produced from the cyclopropanol derivatives.

In the case of the 6-substituted bicyclo[4.1.0]heptanol (**10j** and **l**) derivatives, the reaction with 10 mol% $VO(acac)_2$ in ethanol under an oxygen atmosphere provided endoperoxides (**13**) together with β-hydroxy ketones (**11**) (Table 8) [16a]. Blanco and co-workers reported similar results for the reaction with ferric acetylacetonate and light in the presence of oxygen and silica gel [19].

Treatment of an endoperoxide (**13j**) with a catalytic amount of VO(acac)2 in ethanol and oxygen afforded the β-hydroxy ketone (**2j**) in 75% yield (Scheme 12) [16a]. Therefore, endoperoxides (**13**) might be the reaction intermediates formed during the production of β-hydroxy ketones (**11**) and β-diketones (**12**) from cyclopropanols (Scheme 22).

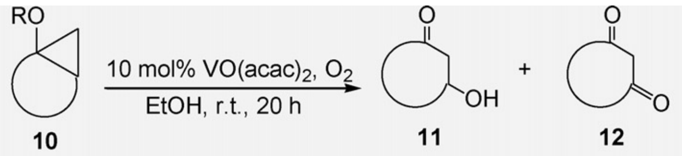
5.3. Investigation of reaction mechanism

Interestingly, the reaction of the 5-but-3-enylbicyclo[4.1.0]heptane-1-ol derivative (**10m**) did not result

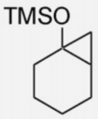
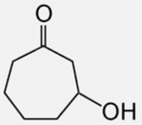
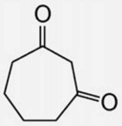
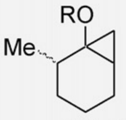
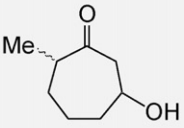
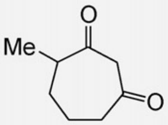
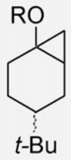
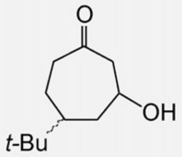
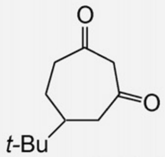
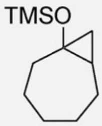
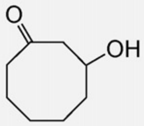
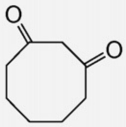
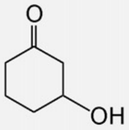
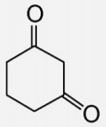
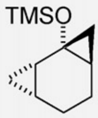
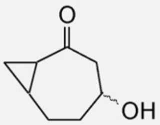
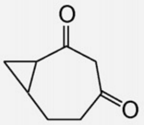
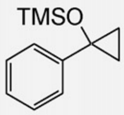
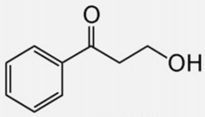
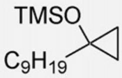
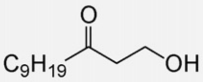


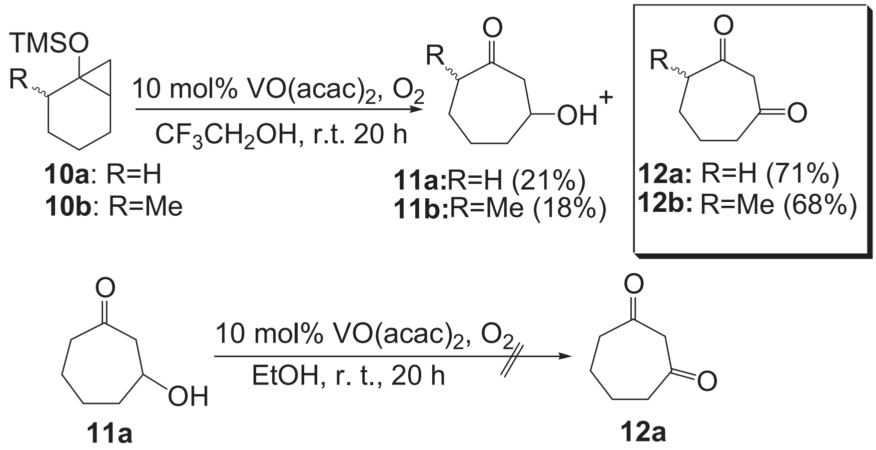
Scheme 20.

Table 7
VO(acac)$_2$-catalyzed aerobic cleavage of tertiary cyclopropanol systems [16].



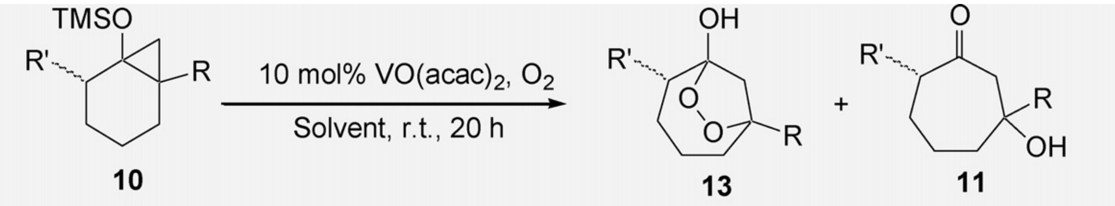
10 **11** **12**

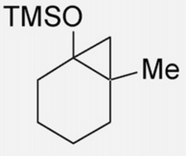
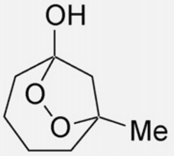
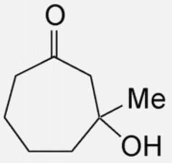
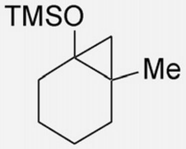
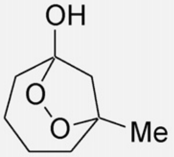
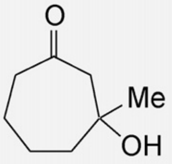
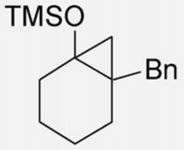
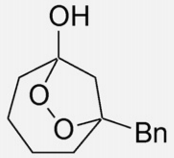
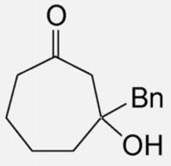
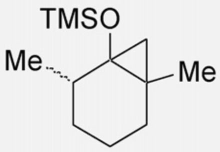
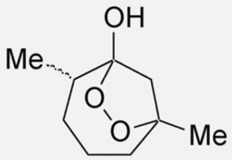
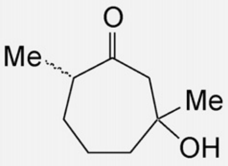
entry	starting material	products	
1	 **10a**	 **11a** (41%)	 **12a** (24%)
2	 **10b** (R=TMS) **10b'** (R=H)	 **11b** R=TMS (40%) R=H (36%)	 **12b** R=TMS (25%) R=H (39%)
3	 **10c** (R=TMS) **10c'** (R=H)	 **11c** R=TMS (25%) R=H (21%)	 **12c** R=TMS (30%) R=H (35%)
4	 **10d**	 **11d** (31%)	 **12d** (33%)
5	 **10e**	 **11e** (75%)	 **12e** (10%)
6	 **10f**	 **11f** (29%)	 **12f** (31%)
7	 **10g**	 **11g** (47%)	
8	 **10h**	 **11h** (80%)	

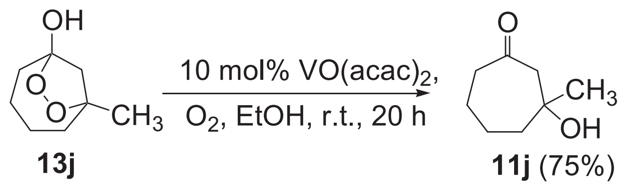


Scheme 21.

Table 8
VO(acac)$_2$-catalyzed aerobic oxidative cleavage of 6-substituted bicyclo[4.1.0]heptan-1-ol derivatives [16a].



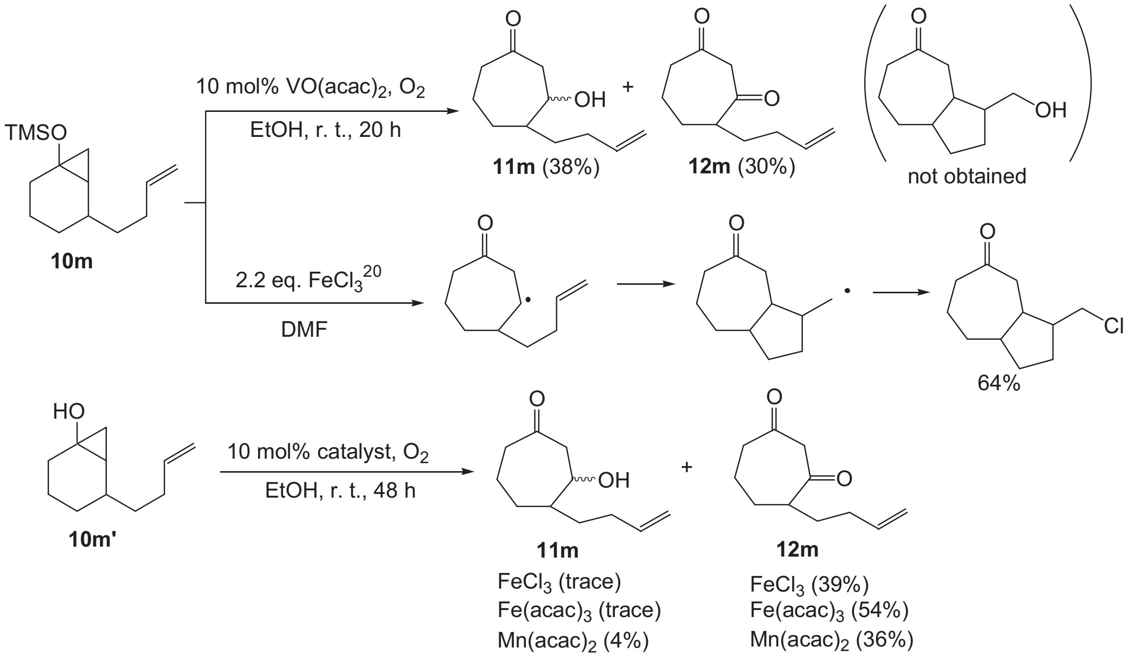
Entry	Starting Material	Solvent	Products	
1	 **10j**	EtOH	 **13j** (45%)	 **11j** (53%)
2	 **10j**	CF$_3$CH$_2$OH	 **13j** (86%)	 **11j** (10%)
3	 **10k**	CF$_3$CH$_2$OH	 **13k** (43%)	 **11k** (trace)
4	 **10*l***	CF$_3$CH$_2$OH	 **13*l*** (43%)	 **11*l*** (26%)



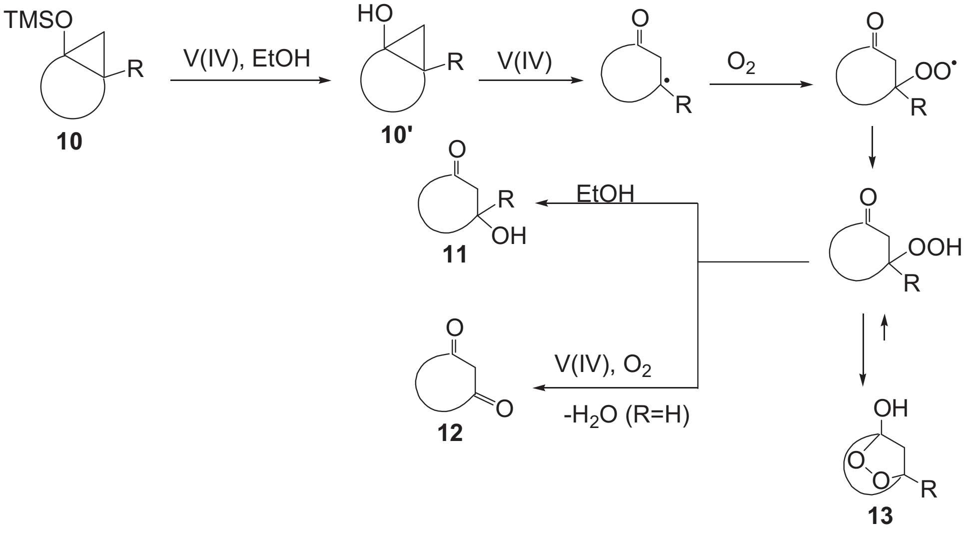
Scheme 22.

in a tandem ring expansion and cyclization, but instead a simple ring expansion occurred producing **11m** and **12m** [16]. This result sharply contrasts with the reaction of 5-but-3-enylbicyclo[4.1.0]heptane-1-ol (**10m**′) and its derivative (**10m**) with an equimolar or excess amount of iron(III) chloride [20] or manganese(III) picolinate [21] in an inert atmosphere. For the latter, a radical tandem reaction occurs. However, the reaction of 5-but-3-enylbicyclo[4.1.0]heptane-1-ol (**10m**′) with Fe(III) or Mn(III) in the presence of oxygen had not been reported. The reactions were examined and the corresponding β-hydroxy ketones (**11m**) and β-diketones (**12m**) were obtained [16a]. They mean that the tandem reaction did not occur (Scheme 23).

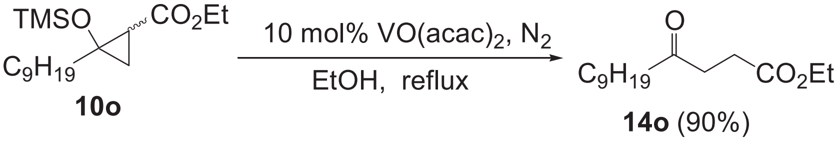
A plausible reaction mechanism is depicted in Scheme 24 [16a]. Tertiary cyclopropyl silyl ethers (**10**) are immediately hydrolyzed into the corresponding alcohols (**10**′) by V(IV) in ethanol. The resulting **10**′ reacted with V(IV) resulting in the ring expansion and free radical formation. The radical then reacts with molecular oxygen to provide the β-perhydroxy ketones which are, in turn, transformed into endoperoxide (**13**) compounds. In the case of **10m**, molecular oxygen reacted with the radical faster than the radical reacted



Scheme 23.



Scheme 24.



Scheme 25.

with the alkene. The peroxy compounds then react with ethanol to provide the β-hydroxy ketones (**11**). β-Diketones (**12**) might be obtained by the reaction of the peroxy compounds with V(IV) and molecular oxygen, because a β-diketone (**12**) was the main product using a stoichiometric amount of $VO(acac)_2$.

5.4. Reaction of cyclopropyl silyl ethers bearing an ethoxycarbonyl group on their cyclopropane ring [16a]

The reaction of cyclopropyl silyl ethers bearing an ethoxycarbonyl group on their cyclopropane ring (**10n–s**) with 10 mol% $VO(acac)_2$ in ethanol afforded γ-ketoesters (**14**) which were produced by the specific cleavage of the 'a' bond (Table 9). The same result was obtained in the absence of molecular oxygen (Scheme 25). In these cases, $VO(acac)_2$ might act as a simple Lewis acid [22].

6. Deprotection of monothioacetals [23]

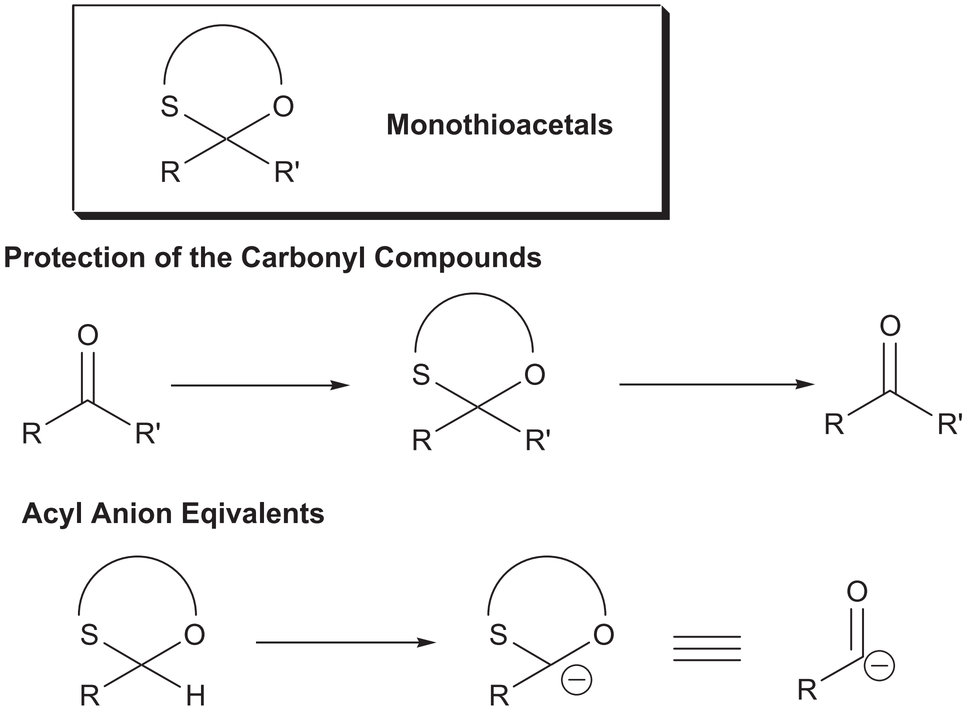
6.1. Monothioacetals: protective groups of carbonyl compounds

The *S*,*O*-acetals (monothioacetals) are widely used as a carbonyl protecting group in organic synthesis due to their stability under both acidic and basic conditions [24]. A cyclic monothioacetal, such as 1,3-oxathiane, is also used as an acyl anion equivalent precursor [25]. In spite of the synthetic importance of monothioacetals, there are not many methods for their deprotection. Furthermore, most of the reported deprotection methods require the use of a stoichiometric or an excess amount of reagent [26] (Scheme 26).

6.2. $VOCl_3$ catalyzed aerobic deprotection of monothioacetals [23]

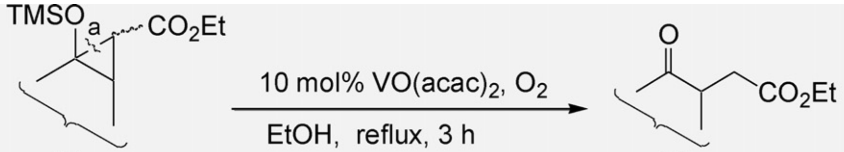
The reaction of monothioacetals (**15**) with 10 mol% of $VOCl_3$ in refluxing 2,2,2-trifluoroethanol under an oxygen atmosphere provided the corresponding carbonyls (**16**) in high yields (Table 10) [23]. Although the *S*,*S*-acetal (dithioacetal) (**15′**) was also deprotected under the same reaction conditions , it took much longer to complete the reaction (entry 8).

Interestingly, the deprotection of dithioacetal (**15′**) was promoted in the presence of equimolar amounts of the monothioacetals (**15**) (Scheme 27) [23]. The equimolar mixture of a dithioacetal (**15a′**) and a monothioacetal (**15b**) reacted with 10 mol% of $VOCl_3$ in refluxing 2,2,2-trifluoroethanol under an oxygen atmosphere to produce the corresponding ketones (**16a**, **b**), respectively, in 30 min. In the absence of a monothioacetal (**15b**), the dithioacetal (**15a′**) reacted to produce the corresponding ketone (**16a**) in only 7% yield under the same conditions.

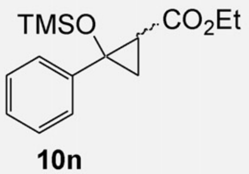
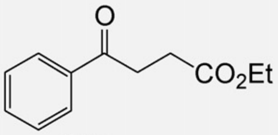
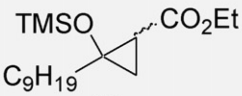
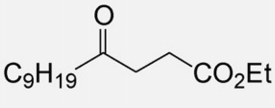
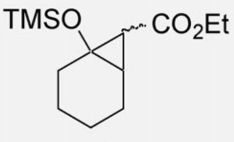
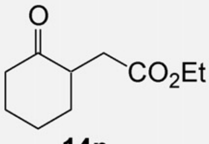
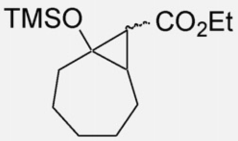
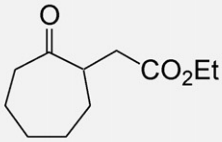
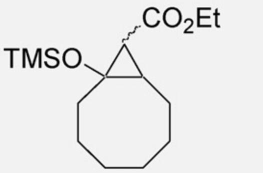
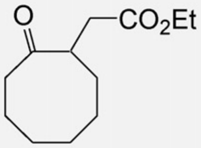
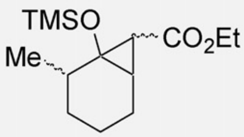
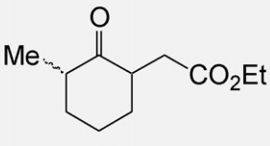


Scheme 26.

Table 9
Reaction of cyclopropyl silyl ethers bearing an ethoxycarbonyl group on their cyclopropane ring [16a].



10 **14**

entry	starting material	product	yield (%)
1	 **10n**	 **14n**	84
2	 **10o**	 **14o**	82
3	 **10p**	 **14p**	86
4	 **10q**	 **14q**	90
5	 **10r**	 **14r**	90
6	 **10s**	 **14s**	88

6.3. *A plausible reaction mechanism [23]*

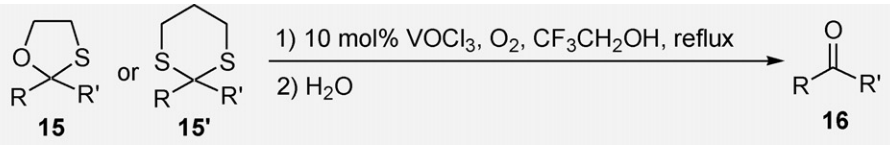
A plausible mechanism for the $VOCl_3$ catalyzed the aerobic deprotection of monothioacetals is shown in Scheme 28 [23]. The sulfur atom of the monothioacetal is oxidized to the sulfoxide ($n = 1$) or sulfone ($n = 2$). In this case, there are two possibilities: (1) vanadium compounds catalyze the oxidation with molecular oxygen; and (2) higher valent vanadium species directly oxidize the sulfur atom, and the resulting lower valent vanadium species are reoxidized into the higher valent vanadium by molecular oxygen. The acceleration mechanism of the dithioacetalization by a monothioacetal is not clear.

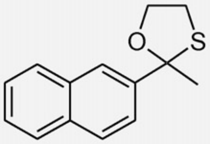
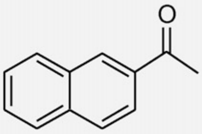
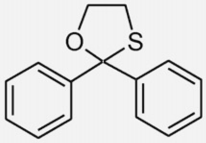
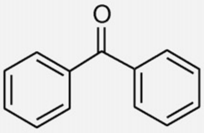
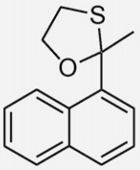
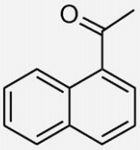
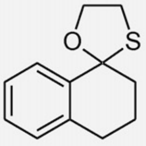
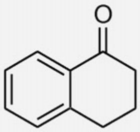
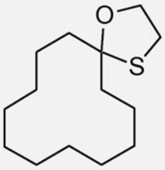
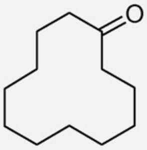
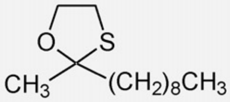
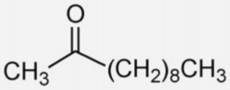
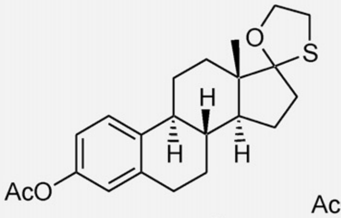
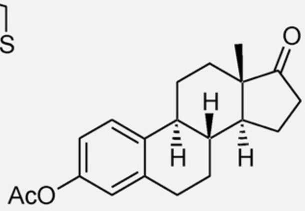
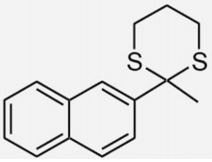
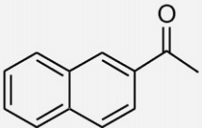
7. Oxidation of thiols to disulfides [27]

7.1. *Disulfides*

Disulfides are important compounds in both organic chemistry and the biosciences, because they are useful reagents in organic

Table 10
Vanadium(V)-catalyzed aerobic oxidative deprotection of thioacetals [22].

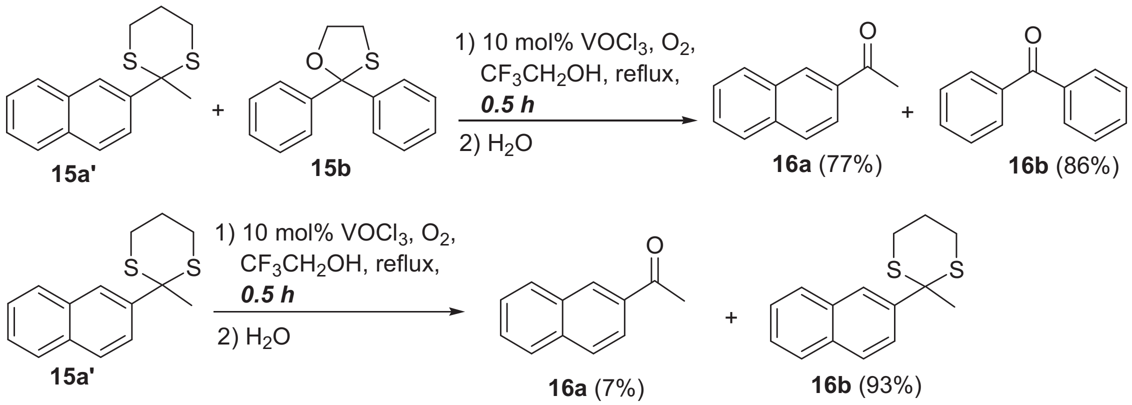


entry	starting material	product	time (h)	yield (%)
1			3.0	94
2			5.0	100
3			3.0	91
4			17.5	73
5			3.5	94
6			3.0	97
7			5.0	94
8			187 (7 days 14 hr)	85

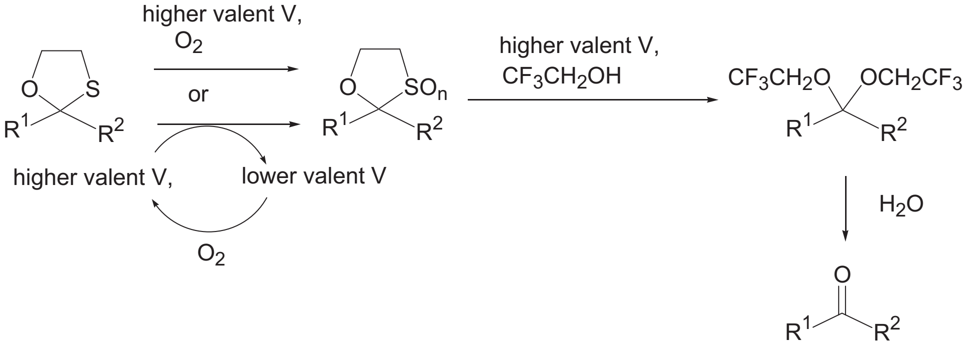
synthesis [28] and essential moieties of biologically active compounds for peptide and protein stabilization [29]. Thiols can be easily over-oxidized, and therefore, several selective methods of converting thiols into disulfides have been developed [30]. However, most of the existing methods suffer from drawbacks, such as the use of stoichiometric amounts of reagents that generate undesirable waste materials. To overcome these drawbacks, the aerobic oxidation of thiols to disulfides has been developed by several groups [31,32].

7.2. $VOCl_3$ catalyzed aerobic oxidation of thiols [27]

Stoichiometric higher valent vanadium compounds oxidize thiols to produce disulfides [33], and a catalytic amount of vanadyl



Scheme 27.



Scheme 28.

acetylacetonate causes the oxidative coupling of thiols in the presence of *t*-butylhydroperoxide [34]. However, there have been no reports about the aerobic oxidative coupling of thiols catalyzed by vanadium compounds.

The reaction conditions were examined, and the reaction with sulfides with 5 mol% of $VOCl_3$ in acetonitrile in the presence of molecular sieves 3 Å at room temperature under an oxygen atmosphere afforded the best results. Several thiols (**17**) were treated with 5 mol% of under the same conditions to provide the corresponding disulfides (**18**) in high yields (Table 11) [27].

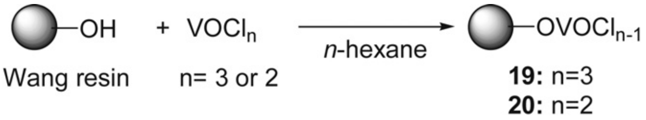
8. Polymer-supported vanadium catalysts [35]

8.1. A drawback of $VOCl_3$ catalyzed aerobic oxidations

As indicated in the previous chapters, $VOCl_3$ is a good catalyst for the aerobic oxidation of organic compounds. However, the catalyst is hard to recover after the reaction, because $VOCl_3$ is soluble in many organic solvents, and the reaction mixtures are homogeneous. A novel recyclable polymer-supported vanadium catalyst for the aerobic oxidation of organic compounds was strongly desired [36].

8.2. Wang resin-supported vanadium species [35]

Wang resin (polystyrene bounded 4-benzyloxybenzyl alcohol) reacts with $VOCl_3$ in refluxing acetonitrile or *n*-hexane to afford a blue-black solid (**19**). Wang resin reacts with vanadyl chloride ($VOCl_2$) in the same manner providing a blue-black solid (**20**) (Scheme 29) [35]. It is assumed that these solids are polymers supporting the vanadium compound.



Scheme 29.

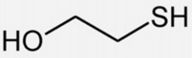
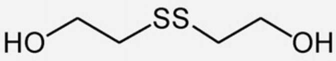
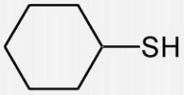
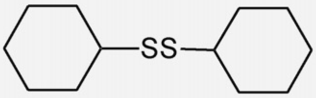
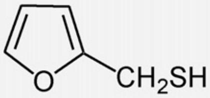
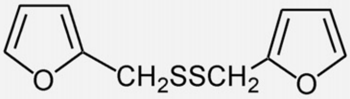
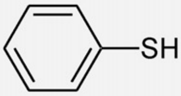
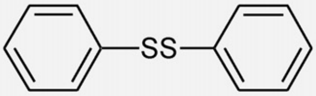
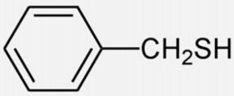
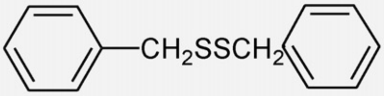
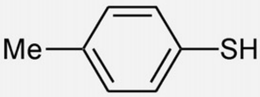
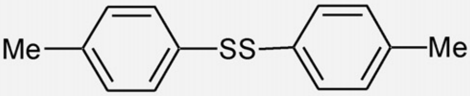
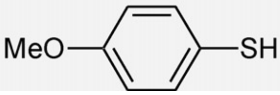
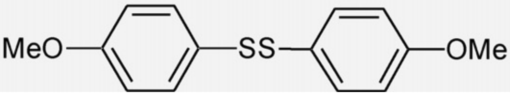
The aerobic oxidation of benzoin in ethyl acetate catalyzed by Wang resin-supported vanadium (**19**, **20**) was examined (Table 12) [35]. The polymer supported vanadium (**19**) obtained from $VOCl_3$ showed a highly catalytic activity for the aerobic oxidation of benzoin (**1n**). Benzoin (**1n**) was quantitatively oxidized into benzil (**3n**) at room temperature by the reaction catalyzed by **19** (run 1). On the other hand, the polymer supported vanadium (**20**) obtained from $VOCl_2$ was not an effective catalyst (run 3). Unfortunately, a significant amount of vanadium leached out from **19**, and the recovered catalyst did not show a sufficient catalytic activity (run 2). Based on these results, the Wang resin is not a good polymer for the immobilization of the vanadium compound.

8.3. Polystyrene A OH-supported $VOCl_3$ [35]

Polystyrene A OH (RAPP POLYMER) was treated with $VOCl_3$ in refluxing *n*-hexane to produce a polymer-supported vanadium compound (**21**) (Scheme 30) [35].

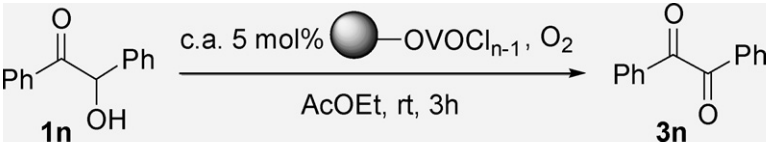
Table 11
Vanadium(V)-catalyzed aerobic oxidative coupling of thiols [26].

$$\underset{\textbf{17}}{\text{R·SH}} \xrightarrow[\text{molecular sieves 3A, rt}]{\text{5 mol\% VOCl}_3\text{, O}_2\text{, AcOEt}} \underset{\textbf{18}}{\text{1/2 RS—SR}}$$

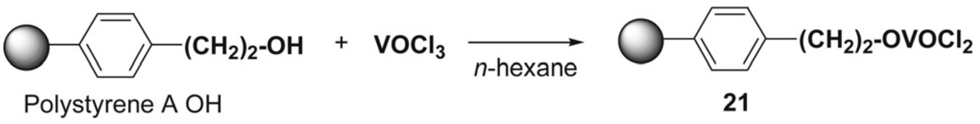
entry	thiol	product	time (h)	yield (%)
1	$CH_3(CH_2)_{11}SH$	$CH_3(CH_2)_{11}SS(CH_2)_{11}CH_3$	111 $(22)^a$	88 $(93)^a$
2	$CH_3(CH_2)_3SH$	$CH_3(CH_2)_3SS(CH_2)_3CH_3$	43 $(3)^a$	98 $(\text{quant})^a$
3			1.5 $(0.5)^a$	84 $(75)^a$
4			41 $(5)^a$	53^b $(93)^a$
5			109	80
6			52 $(22)^a$	93 $(99)^a$
7			74 $(4)^a$	91 $(99)^a$
8			20	96
9			66	98

[a] 0.4 equiv. of VOCl3 was used without molecular sieves 3A.
[b] Unidentified by-products were obtained.

Table 12
Wang resin-supported vanadium-catalyzed aerobic oxidation of benzoin (**1n**) [34].

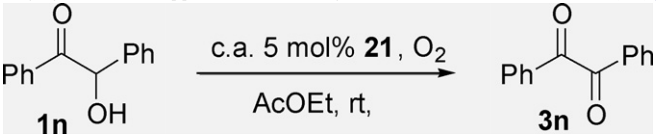


Run	Catalyst	Yield of benzil (%)	Recovery of the catalyst (%)
1	**19**: $n = 3$ (freshly prepared)	Quant.	62
2	**19**: $n = 3$ (recovered from run 1)	Reaction was not complete	83
3	**20**: $n = 2$ (freshly prepared)	12 (reaction was not complete)	82

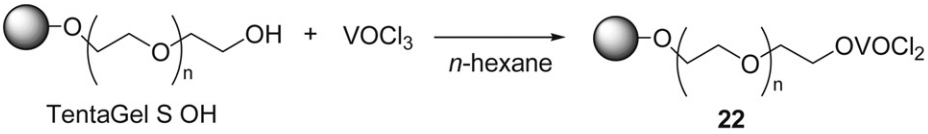


Scheme 30.

Table 13
Polystyrene A OH-supported $VOCl_3$-catalyzed aerobic oxidation of benzoin (**1n**) [34].



Run	Catalyst	Reaction time (h)	Yield of benzil (%)	Recovery of the catalyst (%)
1	**21** (freshly prepared)	3.5	88	83
2	**21** (recovered from run 1)	15.0	32 (reaction was not complete)	88



Scheme 31.

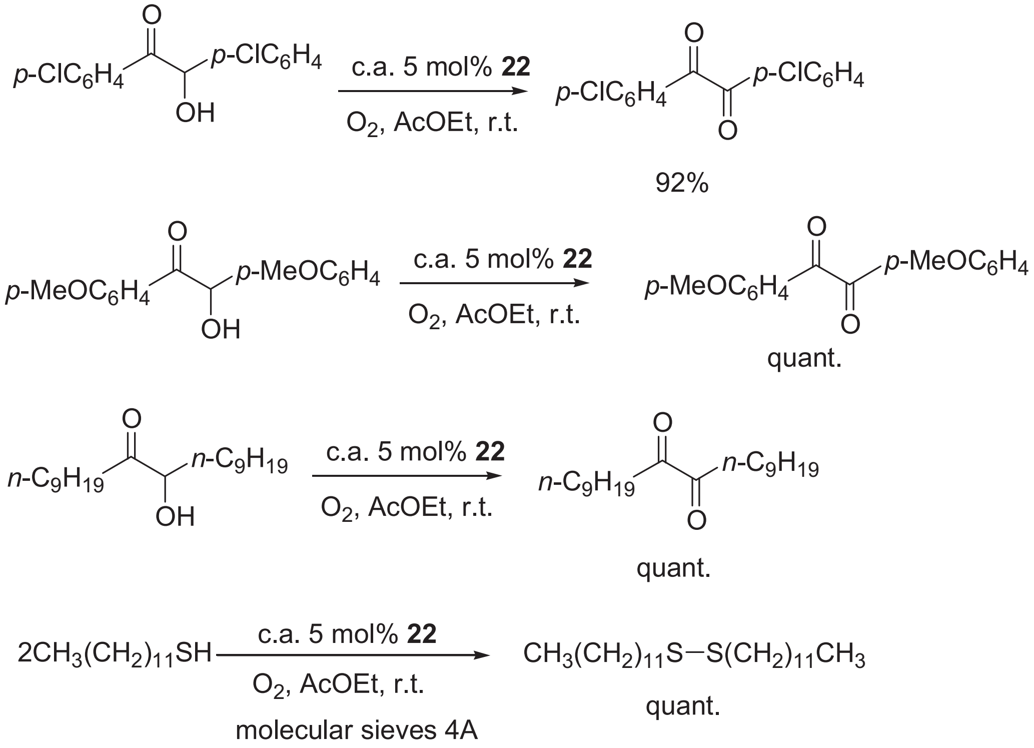
For the aerobic oxidation of benzoin (**1n**), the freshly prepared **21** exhibited a good catalytic activity, however, the recovered **21** did not have sufficient activity (Table 13) [35].

8.4. *TentaGel S OH-supported $VOCl_3$ [35]*

TentaGel S OH (RAPP POLYMER) reacts with $VOCl_3$ in refluxing *n*-hexane to afford a dark-green solid (**22**) (Scheme 31) [35].

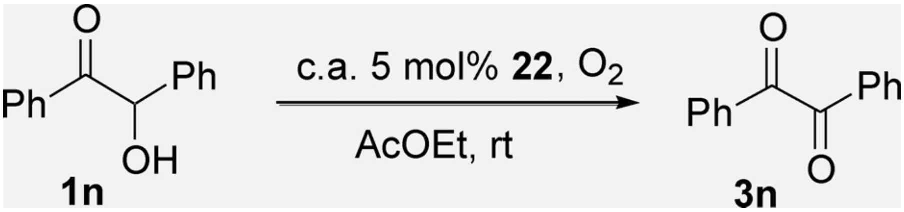
The reaction of benzoin (**1n**) with a catalytic amount of the polymer-supported vanadium (**22**) in ethyl acetate under an oxygen atmosphere quantitatively provided benzil (**3n**). Although a slight amount of vanadium was leached out of **22**, the recovered catalyst maintained high reactivity (Table 14) [35].

The catalyst (**22**) also showed high catalytic activity toward the oxidation of α-hydroxy ketones and a thiol. The desired products were almost quantitatively obtained (Scheme 32) [35].



Scheme 32.

Table 14
TentaGel S OH-supported $VOCl_3$-catalyzed aerobic oxidation of benzoin (**1n**) [34].



Run	Catalyst	Time (h)	Yield of benzil	Recovery of the catalyst (%)
1	**22** (freshly prepared)	1.0	Quant.	84
2	**22** (recovered from run 1)	1.5	Quant.	83
3	**22** (recovered from run 2)	1.5	Quant.	81
4	**22** (recovered from run 3)	1.5	Quant.	81
5	**22** (recovered from run 4)	2.0	Quant.	80

9. Conclusion

The vanadium-catalyzed aerobic oxidations developed by our research group, and related reactions have been summarized in this review. As described in Section 1, vanadium-catalyzed aerobic oxidations are environmentally benign and might be applicable to industrial production. Their further development, including enantioselective oxidation, is strongly desired.

References

[1] Representative papers of aerobic oxidation reactions catalyzed by vanadium compounds:
(a) K. Kikushima, T. Moriuchi, T. Hirao, Tetrahedron Lett. 51 (2010) 340;
S. Takizawa, Chem. Pharm. Bull. 57 (2009) 1179;
(b) T. Moriuchi, K. Kikushima, T. Kajikawa, T. Hirao, Tetrahedron Lett. 50 (2009) 7385;
(c) K. Kikushima, T. Moriuchi, T. Hirao, Chem. Asian J. 4 (2009) 1213;
(d) S. Singhal, S. Jain, B. Sain, Chem. Commun. (2009) 2371;
(e) S. Takizawa, T. Katayama, H. Sasai, Chem. Commun. (2008) 4113;
(f) S. Takizawa, T. Katayama, C. Kameyama, K. Onitska, T. Suzuki, T. Yanagida, T. Kawai, H. Sasai, Chem. Commun. (2008) 1810;
(g) S. Takizawa, T. Katayama, H. Somei, Y. Asano, T. Yoshida, C. Kameyama, D. Rajesh, K. Onitsuka, T. Suzuki, M. Mikami, H. Yamataka, D. Jayaprakash, H. Sasai, Tetrahedron 64 (2008) 3361;
(h) H. Somei, Y. Asano, T. Yoshida, S. Takizawa, H. Yamataka, H. Sasai, Tetrahedron Lett. 45 (2004) 1841;
(i) P.J. Figel, J.M. Sobczak, New J. Chem. 31 (2007) 1668;
(j) N. Jiang, A.J. Ragauskas, Tetrahedron Lett. 48 (2006) 273;
(k) A.T. Radosevich, C. Musich, F.D. Toste, J. Am. Chem. Soc. 127 (2005) 1090;
(l) S.R. Reddy, S. Das, T. Punniyamurthy, Tetrahedron Lett. 45 (2004) 3561;
(m) S. Velusamy, T. Punniyamurthy, Org. Lett. 6 (2004) 217;
(n) Y. Maeda, N. Kakiuchi, S. Matsumura, T. Nishimura, T. Kawamura, S. Uemura, J. Org. Chem. 67 (2002) 6718;
(o) Y. Maeda, N. Kakiuchi, S. Matsumura, T. Nishimura, S. Uemura, Tetrahedron Lett. 42 (2001) 8877;
(p) T. Hirao, M. Mori, Y. Ohshiro, Bull. Chem. Soc. Jpn. 62 (1989) 2399;
(q) T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329.
[2] Reviews on vanadium mediated organic reactions: T. Hirao, Pure Appl. Chem. 77 (2005) 1539;
T. Hirao, Yuki Gosei Kagaku Kyokaishi 62 (2004) 1148;
T. Hirao, Coord. Chem. Rev. 237 (2003) 271;
T. Hirao, Chem. Rev. 97 (1997) 2707.
[3] M. Kirihara, S. Takizawa, T. Momose, J. Chem. Soc. Perkin Trans. 1 (1998) 7.
[4] Representative papers of glycol cleavage except for periodates and lead tetraacetate:
(a) K.H. Pausacker, J. Chem. Soc. (1953) 107;
(b) D.H.R. Barton, J.P. Kitchin, D.J. Lester, W.B. Motherwell, C. Pichon, Tetrahedron 37 (Suppl. 1) (1981) 73;
(c) S.P. Rao, J.N. Gaur, S.K. Sharma, Naturwissenschaften 48 (1961) 98;
(d) S.O. Nwaukwa, P.M. Keehn, Tetrahedron Lett. 23 (1982) 3135;
(e) A. Cisneros, S. Fernandez, J.E. Hernandez, Synth. Commun. 12 (1982) 833;
(f) C. Venturello, M. Ricci, J. Org. Chem. 51 (1986) 1599;
(g) G. Ohloff, W. Giersch, Angew. Chem. Int. Ed. Engl. 12 (1973) 401;
(h) D.H.R. Barton, J.-P. Fiento, W.B. Motherwell, C. Pichon, Tetrahedron 42 (1986) 5627.
[5] Reviews M. Rezaeivalla, Synlett (2006) 3550;
A.J. Faitadi, Synthesis (1974) 220.
[6] Reviews: M.L. Mihailovic, Z. Cekovic, B.M. Mathes, e-EROS Encyclopedia of Reagents for Organic Synthesis, 2001;
M.L. Mihailovic, Z. Cekovic, L. Lorenc, Org. Synth. Oxid. Met. Compd. (1986) 741.
[7] M. Kirihara, T. Nishio, S. Yokoyama, H. Kakuda, T. Momose, Tetrahedron 55 (1999);
T. Momose, T. Nishio, M. Kirihara, Tetrahedron Lett. 37 (1996) 4987.
[8] G.J. Buist, C.A. Bunton, J.H. Miles, J. Chem. Soc. (1957) 456.
[9] M. Kirihara, K. Yoshida, T. Noguchi, S. Naito, N. Matsumoto, Y. Ema, M. Torii, Y. Ishizuka, I. Souta, Tetrahedron Lett. 51 (2010) 3619.
[10] M. Zviely, A. Goldman, I. Kirson, E. Glotter, J. Chem. Soc. Perkin Trans. 1 (1986) 229.
[11] E.L. Eliel, J. Am. Chem. Soc. 77 (1955) 3600.
[12] M. Kirihara, Y. Ochiai, S. Takizawa, H. Takahata, H. Nemoto, Chem. Commun. (1999) 1387.
[13] G.B. Gill, in: G. Pattenden (Ed.), Comprehensive Organic Synthesis, vol. 3, Pergamon, New York, 1991, p. 821.
[14] I. Flament, M. Stoll, Helv. Chim. Acta 50 (1967) 1754;
W.H. Rothkopf, D. Wöhrle, R. Müller, G. Kossmehl, Chem. Ber. 108 (1975) 875;
H. Wynberg, H.J. Kooreman, J. Am. Chem. Soc. 87 (1965) 1739;
W.W. Paudler, J.M. Barton, J. Org. Chem. 31 (1966) 1720.
[15] J.S. Buck, S.S. Jenkins, J. Am. Chem. Soc. 51 (1929) 2163;
A. McKillop, B.P. Swann, M.E. Ford, E.C. Taylor, Tetrahedron Lett. (1970) 5281;
A. McKillop, B.P. Swann, M.E. Ford, E.C. Taylor, J. Am. Chem. Soc. 95 (1973) 3641;
P. Girara, H.B. Kagan, Tetrahedron Lett. (1975) 4513;
R.S. Varma, D. Kumar, R. Dahiya, J. Chem. Res. (S) (1998) 324.
[16] (a) M. Kirihara, H. Kakuda, M. Ichinose, Y. Ochiai, S. Takizawa, A. Mokuya, K. Okubo, A. Hatano, M. Shiro, Tetrahedron 61 (2005) 4831;
(b) M. Kirihara, M. Ichinose, S. Takizawa, T. Momose, Chem. Commun. (1998) 1691.
[17] Reviews:
(a) S. Murai, I. Ryu, N. Sonoda, J. Organomet. Chem. 250 (1983) 121;
(b) I. Kuwajima, E. Nakamura, Top. Curr. Chem. 155 (1990) 1;
(c) I. Ryu, S. Murai, in: A. deMeijere (Ed.), Methoden der Organisches Chemie (Houben-Weyl), vol. E17, Georg Thieme, New York, 1997, p. 1985;
(d) O.G. Kulinkovich, Chem. Rev. 103 (2003) 2597.
[18] (a) M. Kirihara, S. Yokoyama, H. Kakuda, T. Momose, Tetrahedron Lett. 36 (1995) 6907;
(b) M. Kirihara, S. Yokoyama, T. Momose, Synth. Commun. 28 (1998) 1947;
(c) M. Kirihara, S. Yokoyama, H. Kakuda, T. Momose, Tetrahedron 54 (1998) 13943;
(d) M. Kirihara, M. Shimizu, S. Yokoyama, H. Kakuda, ITE Lett. 3 (2003) 215;
(e) M. Kirihara, T. Kambayashi, T. Momose, Chem. Commun. (1996) 1103;
(f) M. Kirihara, H. Kakuda, M. Tsunooka, A. Shimajiri, T. Takuwa, A. Hatano, Tetrahedron Lett. 44 (2003) 8513;
(g) M. Kirihara, T. Noguchi, H. Kakuda, T. Akimoto, A. Shimajiri, M. Morishita, A. Hatano, Y. Hirai, Tetrahedron Lett. 47 (2006) 3777;
(h) M. Kirihara, H. Kakuda, Yuki Gosei Kagaku Kyokaishi 62 (2004) 919.
[19] V. Morisson, J.-P. Barnier, L. Blanco, Tetrahedron Lett. 40 (1999) 4045.
[20] (a) L. Blanco, A. Mansouri, Tetrahedron Lett. 29 (1988) 3239;
(b) K.I. Booker-Milburn, Synlett (1992) 809.
[21] N. Iwasawa, S. Hayakawa, K. Isobe, K. Narasaka, Chem. Lett. (1991) 1193.
[22] R.A. Rowe, M.M. Jones, Inorg. Synth. 5 (1957) 113.
[23] M. Kirihara, Y. Ochiai, N. Arai, S. Takizawa, T. Momose, H. Nemoto, Tetrahedron Lett. 40 (1999) 9055.
[24] J. Romo, G. Rosenkranz, C. Djerassi, J. Am. Chem. Soc. 73 (1951) 4961;
V.K. Yadav, A.G. Fallis, Tetrahedron Lett. 29 (1988) 897.
[25] K. Fuji, M. Ueda, E. Fujita, J. Chem. Soc. Chem. Commun. (1977) 814;
K. Fuji, M. Ueda, K. Sumi, K. Kajiwara, E. Fujita, T. Iwashita, I. Miura, J. Org. Chem. 50 (1985) 657;
K. Fuji, M. Ueda, K. Sumi, E. Fujita, Tetrahedron Lett. 22 (1981) 2005;
K. Fuji, M. Ueda, E. Fujita, J. Chem. Soc. Chem. Commun. (1983) 49.
[26] C. Djerassi, M. Shamma, T.Y. Kan, J. Am. Chem. Soc. 80 (1958) 4723;
R.H. Mazur, E.A. Brown, J. Am. Chem. Soc. 77 (1955) 6670;
E.J. Corey, B.W. Erickson, J. Org. Chem. 36 (1971) 3553;

D.W. Emerson, H. Wynberg, Tetrahedron Lett. (1971) 3445;
K. Fuji, K. Ichikawa, E. Fujita, Tetrahedron Lett. (1978) 3561;
S.V. Frye, E.L. Eliel, Tetrahedron Lett. 26 (1985) 3907;
J. Nakayama, H. Sugiura, A. Shiotsuki, M. Hoshino, Tetrahedron Lett. 26 (1985) 2195;
T. Ravindranathan, S.P. Chavan, J.P. Varghese, S.W. Dantale, R.B. Tejwani, J. Chem. Soc. Chem. Commun. (1994) 1937;
K. Nishide, K. Yokota, D. Nakamura, T. Sumiya, M. Node, M. Ueda, K. Fuji, Tetrahedron Lett. 34 (1993) 3425;
K. Nishide, D. Nakamura, K. Yokota, T. Sumiya, M. Node, M. Ueda, K. Fuji, Heterocycles 44 (1997) 393.

[27] M. Kirihara, K. Okubo, T. Uchiyama, Y. Kato, Y. Ochiai, S. Matsushita, A. Hatano, K. Kanamori, Chem. Pharm. Bull. 52 (2004) 625.

[28] For example, see:
(a) A. Ogawa, Y. Nishiyama, N. Kambe, S. Murai, N. Sonoda, Tetrahedron Lett. 28 (1987) 3271;
(b) S. Antebi, H. Alper, Tetrahedron Lett. 26 (1985) 2609;
(c) L. Bischoff, C. David, L. Martin, H. Meudal, B.-P. Roques, M.-C. Fournié-Zaluski, J. Org. Chem. 62 (1997) 4848.

[29] M. Bodanszky, Principles of Peptide Synthesis: Reactivity and Structure Concepts in Organic Chemistry, Springer Verlag, Hiderberg, 1984, p. 307.

[30] T. Aida, T. Akasaka, N. Furukawa, S. Oae, Bull. Chem. Soc. Jpn. 49 (1976) 1441;
X. Wu, R. Reike, L. Zhu, Synth. Commun. 26 (1996) 191;
J. Drabowicz, M. Mikolajczyk, Synthesis (1980) 32;
N.A. Noureldin, M. Caldwell, J. Hendry, D.G. Lee, Synthesis (1998) 1587;
V. Kesavan, D. Bonnet-Delpon, J.-P. Bégué, Synthesis (2000) 223;
J.P. Tam, C.-R. Wu, W. Liu, J.-W. Zhang, J. Am. Chem. Soc. 113 (1991) 6657;
R. Sanz, R. Aguado, M.R. Pedrosa, F.J. Arnáiz, Synthesis (2002) 856;
B. Karimi, H. Hazarkhani, D. Zareyee, Synthesis (2002) 2513.

[31] For example:
(a) K.-T. Liu, Y.-C. Tong, Synthesis (1978) 669;
(b) L.I. Simándi, S. Németh, N. Rumelis, J. Mol. Catal. 42 (1987) 357;
(c) A. Cervilla, A. Corma, V. Fornes, E. Llopis, P. Palanca, F. Rey, A. Ribera, J. Am. Chem. Soc. 116 (1994) 1595;
(d) N. Iranpoor, B. Zeynizadeh, Synthesis (1999) 49;
(e) T.V. Rao, K.N. Rao, S.L. Jain, B. Sain, Synth. Commun. 32 (2002) 1151;
(f) S.T.A. Shah, K.M. Khan, M. Fecker, W. Voelter, Tetrahedron Lett. 44 (2003) 6789.

[32] Recently, we developed the mild and environmentally benign oxidation of thiols to disulfides with a catalytic amount of molecular iodine or iodocation equivalent generated from iodide and hydrogen peroxide: M. Kirihara, Y. Asai, S. Ogawa, T. Noguchi, A. Hatano, Y. Hirai, Synthesis (2007) 3286.

[33] (a) J. Hill, A. McAuley, J. Chem. Soc. A (1968) 2405;
(b) W.F. Pickering, A. McAuley, J. Chem. Soc. A (1968) 1173.

[34] S. Raghavan, A. Rajender, S.C. Joseph, M.A. Rasheed, Synth. Commun. 31 (2001) 1477.

[35] M. Kirihara, Y. Torii, K. Sato, R. Takizawa, A. Hatano, ITE Lett. 5 (2004) 479.

[36] Studies of immobilized vanadium compounds achieved by other groups:
A. Lattanzi, N.E. Leadbeater, Org. Lett. 4 (2002) 1519;
S. Bhaduri, H. Khwaja, V. Khanwalkar, J. Chem. Soc. Dalton Trans. (1982) 447;
A. Kumar, S.K. Das, J. Catal. 166 (1997) 108;
T. Yokoyama, M. Nishizawa, T. Kimura, T.M. Suzuki, Chem. Lett. (1983) 1703;
T. Yokoyama, M. Nishizawa, T. Kimura, T.M. Suzuki, Bull. Chem. Soc. Jpn. 58 (1985) 3271;
G.L. Linden, M.F. Farona, Inorg. Chem. 16 (1977) 3170;
D.R. Pesiri, D.K. Moritia, T. Walker, W. Tumas, Organometallics 18 (1999) 4916.