Oxidation reactions catalysed by titanium- and chromium-containing silicalites

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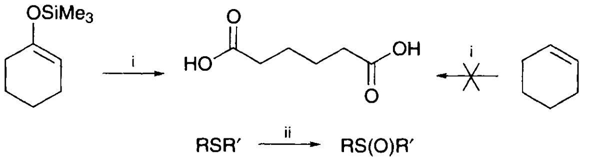
While the titanium silicalite-1 (TS-1)–*tert*-butyl hydroperoxide (TBHP) combination exhibits remarkable activity and selectivity in the oxidative cleavage of the C–C double bond of silyl enol ethers to produce dicarboxylic acids, the chemoselective oxidation of thioethers to sulfoxides without generation of sulfones is achieved using chromium silicalite-2 (CrS-2)–H_2O_2.

Oxidative cleavage of the carbon–carbon double bond of alkenes to form the corresponding carboxylic acids is a useful reaction for both fundamental and industrial applications because it is often employed to degrade large compounds or to introduce different functionality into complex molecules.[1] Traditionally, such transformations under stoichiometric conditions have been conveniently performed with ozone[2] and transition metal oxidants such as $KMnO_4$,[3] RuO_4[4] and CrO_3.[5] The $MoO_2(acac)_2$–TBHP system has recently been shown to oxidize silyl enol ethers to dicarboxylic acids under homogeneous and anhydrous conditions.[6] However, a heterogeneous metal catalyst such as a transition metal incorporated zeolite in conjunction with a cheap, readily available oxygen source like *tert*-butyl hydroperoxide (TBHP) offers the advantages of being both cheap and environmental friendly.

Of late, redox zeolites such as titanium, vanadium and chromium silicates with Mobile Five (MFI) and Mobile Eleven (MEL) topologies have been shown to possess unique catalytic properties in oxidation reactions with H_2O_2 and TBHP.[7] Here we report that 70% TBHP in conjunction with a catalytic amount of titanium silicate-1 (TS-1) provides a synthetically useful procedure for the highly selective cleavage of the carbon–carbon double bond of silyl enol ethers to carboxylic acids, while chromium silicalite-2 (CrS-2) has been found to be an excellent catalyst for the chemoselective oxidation of thioethers to sulfoxides without the generation of sulfones, Scheme 1. Interestingly, it may be noted that cyclohexene under the same reaction conditions (TS-1–TBHP) failed to undergo epoxidation.

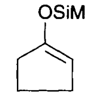
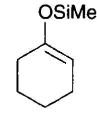
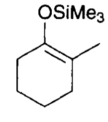
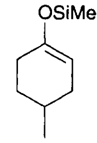
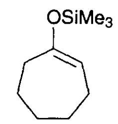
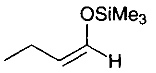
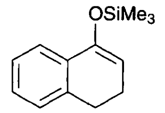
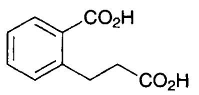
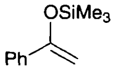
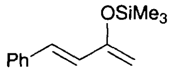
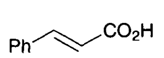
TS-1 (Si/Ti = 32)[8] and CrS-2 (Si/Cr = 140)[7b] were synthesized following literature procedures. In a typical reaction, a mixture of α-tetralone silyl enol ether (2.04 g, 10 mmol), 70% TBHP (9 ml, 66 mmol) and TS-1 (204 mg, 10% by mass) was gently refluxed for 24 h. The progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was cooled to room temperature, diluted with acetone (20 ml) and the catalyst filtered off. The filtrate containing solvent and excess TBHP was evaporated under reduced pressure to afford a viscous liquid. The addition of light petroleum gave the solid which was then recrystallized from 5% acetone in light petroleum to afford the diacid as colourless crystals (1.76 g, 91%).[†]



Scheme 1 *Reagents and conditions*: i, Bu^tO_2H (70%), TS-1, reflux, 24 h, 74%; ii, H_2O_2 (30%), CrS-2, MeOH, 20 °C; R,R′ = alkyl, aryl, allyl, *etc.*

Table 1 lists a range of silyl enol ethers which underwent oxidative cleavage with the TS-1–TBHP system to produce dicarboxylic acids in high yields. In the absence of Ti-catalyst, cyclohexyl silyl enol ether underwent deprotection to quantitatively furnish cyclohexanone. Considering that the regiospecific generation of silyl enol ethers can be easily achieved by either kinetic or thermodynamic control, the reaction is a powerful method for regiospecific α-cleavage of thermodynamic precursors (entry 3). Both aldehyde and cyclic ketone silyl enol ethers are oxidatively cleaved to give mono- and dicarboxylic acids respectively in high yields whereas the tetrasubstituted silyl enol ether gave the keto acid (entry 3) and the size of the ring did not influence the reactivity of the catalyst system. It is remarkable that the silyl enol ether, prepared from α,β-unsaturated ketone, underwent oxidative cleavage with TS-

Table 1 Oxidative cleavage of C=C of silyl enol ethers with 70% TBHP catalysed by TS-1

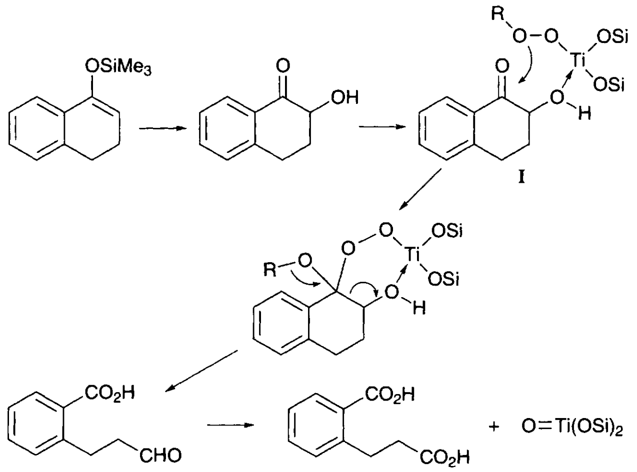
Entry	Substrate	Product[a]	Yield (%)[b]
1		$HO_2C[CH_2]_3CO_2H$	72
2		$HO_2C[CH_2]_4CO_2H$	74
3		$HO_2C[CH_2]_4COMe$	73
4		$HO_2C[CH_2]_2CH(Me)CH_2CO_2H$	76
5		$HO_2C[CH_2]_5CO_2H$	78
6		$EtCO_2H$	82
7			91
8		$PhCO_2H$	89
9			68

[a] Characterized by mp, IR, ^1H and ^{13}C NMR spectroscopy. [b] Isolated after recrystallization; also 5–6% of 2-hydroxy ketones isolated in each case.

1–TBHP in a regioselective manner to give cinnamic acid in 68% yield (entry 9). This high regioselectivity is a sharp contrast to that with ozone which attacks the two double bonds indiscriminately. However, chromium silicalite (CrS-2) showed less activity (45% yield) in the oxidative cleavage of silyl enol ether as compared to TS-1.

In order to obtain more information on the reaction path of this oxidation process, α-tetralone silyl enol ether was subjected to TS-1 catalysed oxidative cleavage with 3 equiv. of TBHP. It was then subsequently found that α-hydroxy tetralone could be isolated (52% yield) and characterized (IR and ^{1}H NMR). Thus, the reaction appears to proceed *via* the initial epoxidation of the electron-rich double bond followed by its transformation to α-hydroxy ketone which then undergoes oxidative cleavage with Ti(μ-O_2) species **I** to furnish the dicarboxylic acid (Scheme 2).

When substrates such as allyl phenyl sulfide and prop-2-ynyl phenyl sulfide are subjected to oxidation with 30% H_2O_2 catalysed by chromium silicalite (CrS-2), it was found that the sulfoxidation proceeded in high yields without affecting the carbon–carbon multiple bonds (Table 2, entries 6 and 7). The results of CrS-2 catalysed oxidations of various thioethers with 30% H_2O_2 at 20 °C in MeOH are presented in Table 2. Transition metal-catalysed sulfoxidations have been reported for oxidants such as H_2O_2,[9] iodylarenes,[10] O_2, CHO[11] and TBHP.[12] Generally, it is important to stop the oxidation at the sulfoxide stage by controlling the electrophilic character of oxidant, but this requirement is often hard to meet and failure results in over-oxidation of the sulfoxides to give sulfones.



Scheme 2

Table 2 Sulfoxidation[a] of various thioethers with H_2O_2 over CrS-2 (Si/Cr = 140)[b]

Entry	Substrate	*t*/h	Conv.[c] (%)	Product yield[d] (%)
1	Me_2S	2	100	96
2	$(Bu)_2S$	2	100	92
3	PhSMe	3	100	91
4	Ph_2S	6	95	88
5	$(PhCH_2)_2S$	2	98	89
6	$PhSCH_2CH{=}CH_2$	6	94	85
7	$PhSCH_2CH{\equiv}CH$	6	96	90
8	Tetrahydrothiophene	2	100	95

[a] In a typical reaction procedure, a mixture of phenyl allyl sulfide (0.50 g, 0.0034 mol), CrS-2 (50 mg, 10% *m*/*m*) and 30% H_2O_2 (0.69 ml, 0.0068 mol) in MeOH (20 ml) was stirred at 20 °C for 6 h. After the reaction was complete (TLC), the catalyst was filtered off and the product purified by flash chromatography (SiO_2, 50% EtOAc–light petroleum) to afford the corresponding sulfoxide (0.470 g, 85%); [b] No reaction in the absence of catalyst and the catalyst was recovered and reused 3 times without any loss of activity and selectivity; [c] Conversions determined by GLC-HP-1 capillary column; [d] Isolated yields; products characterized by IR, ^{1}H and ^{13}C NMR and MS spectroscopy.

As can be seen from Table 2, the sulfoxidation proceeded chemoselectively (entries 6 and 7) and even the sterically hindered diphenyl sulfide underwent sulfoxidation with the CrS-2–H_2O_2 system. However, it should be noted that the TS-1–H_2O_2 combination[9] failed to oxidize sterically hindered thioethers, *e.g.* diphenyl sulfide, and that the reaction was not selective as mixtures of sulfoxides and sulfones were produced. It was found that the choice of solvent (MeOH) for CrS-2 catalysed oxidation of phenyl methyl sulfide with H_2O_2 was critical as the reaction fails when carried out in solvents such as dichloromethane and chloroform. While the sulfoxidations can also be carried out with 70% TBHP instead of 30% H_2O_2 as oxidant, the catalyst failed to activate the molecular oxygen under the reaction conditions. When the oxidation of allyl phenyl sulfide with 30% H_2O_2 was carried out with other catalysts such as TS-1 and CrO_3, no significant formation of sulfoxide (< 5%) was observed even after stirring for 24 h at 20 °C, suggesting that the oxochromium(v) species (the redox potential of Cr^{5+}/Cr^{4+} is 0.50 V) present in the CrS-2 zeolite framework is responsible for the sulfoxidation.

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Footnote

† ^{1}H NMR (200 MHz, [$^{2}H_6$]acetone): δ 2.65 (2 H, t, *J* 6 Hz), 3.3 (2 H, t, *J* 6 Hz), 7.3–7.5 (3 H, m) and 8.0 (1 H, d, *J* 6 Hz); ^{13}C NMR (50.3 MHz, [$^{2}H_6$]Me_2SO): δ 30.3, 36.5, 127.3, 131.5, 131.8, 132.8, 143.0, 169.9 and 175.1.

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