

Titanium Silicate Molecular Sieve (TS-1) induced Catalytic Cleavage of Tosylhydrazones†

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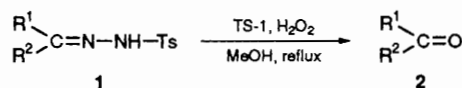
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Titanium silicate molecular sieve, having MFI (TS-1) topology, efficiently catalyses the oxidative cleavage of various tosylhydrazones to the corresponding carbonyl compounds in moderate to good yields, using dilute hydrogen peroxide (30%) as an oxidising agent and involving a unique electrophilic species; mechanistically, the intermediacy of oxaziridine has been established.

The efficiency of heterogeneous catalytic transformations, transition-state shape and size selectivity involving 1 Å level precision, the ability to recognise, discriminate and organise molecules at the active site, the unique properties of framework metal ions, *e.g.* acid (Lewis and Brønsted), base and oxidising properties, coupled with the ease of operation and consequent industrial applications has made the interface of organic synthesis and zeolite catalysis an important research area. A recent account¹ of zeolite catalysis considers it as a mimic of metalloenzymes² and antibody catalysed³ conversions. There is a close connection between the microscopic structures at the active site of zeolites and the macroscopic properties of the catalysts. The commercial success of zeolites is mainly due to the continued discovery of new materials that have enabled process improvements and developments of new technologies. One of the latest arrivals on the zeolite scene is crystalline microporous titanium silicate molecular sieve (TS-1).⁴ Recently, microbial type⁵ oxyfunctionalisation of the C–H bond^{6,7} has been reported in various organic molecules including *n*-alkanes, which are normally resistant to oxidation by hydrogen peroxide.⁸ Subsequently, we have reported the oxidation of sulfur in thioethers⁹ and the cleavage of carbon–

carbon double bonds¹⁰ using these catalysts. From the reactivity patterns in these studies,^{9,10} it is reasonable to assume that the active species in many of these transformations is electrophilic in nature. If it is so, then this should cleave carbon–nitrogen double bonds as well. We report here the successful implementation of our idea in terms of the unprecedented use of TS-1 catalyst for the oxidative cleavage of toluene-*p*-sulfonylhydrazones to their corresponding carbonyl compounds. Additionally, the cleavage of normal imines to the corresponding carbonyl compounds and the intermediacy of oxaziridines during this catalytic transformation has been established.

Thus, a variety of tosylhydrazones and imines were prepared according to literature procedures.^{11,12} As shown in Tables 1 and 2, when the tosylhydrazones **a–i** and imines **j–l** were subjected to oxidative cleavage using TS-1 catalyst, the corresponding carbonyl compounds **2** were obtained in moderate to good yields (Scheme 1). The present procedure for oxidative cleavage involves an easy workup. The use of other zeolites such as NaY, [UCIL Bombay (India)] H-ZSM-5¹³ and 4 Å or 5 Å molecular sieves failed to accomplish the above transformations. Additionally either pure silicalite-2¹⁴ or TiO₂ (both amorphous and crystalline), or amorphous Ti-silicate⁴, or a physical mixture of silicalite-2 and TiO₂ were inactive in this reaction. These control experiments suggest that Ti ions associated with the zeolite framework are responsible for the observed catalytic activity.^{7,9,10} It is noteworthy that no Baeyer–Villiger product of regenerated ketone or epoxy ketone from regenerated enone (Table 1, entry **h**) could be observed under the reaction conditions. Consequently it can be argued that initially there is preferential chemoselective epoxidation of C=N bond (entry **h**). Additionally, the absence of epoxy enones indicates the electrophilic nature of the reactive species. However, with aldehyde (Table 1, entry **i**)§ further oxidation to the carboxylic acid and subsequent reaction with the solvent methanol to give the ester was observed. Thus, esterification seems to be a facile process under our reaction conditions, but no ketalisations of deprotected ketones could be observed.



Scheme 1 (Ts = *p*-MeC₆H₄SO₂)

Table 1 Oxidative cleavage of tosylhydrazones by TS-1 catalyst

Entry	Tosylhydrazones of 1	Conversion (%)	Reaction time/h	Carbonyl compounds 2 ^a yield (%) ^b
a	Butan-2-one	100	4	84
b	Cyclopentanone	100	10	80
c	Cyclohexanone	100	10	75
d	Acetophenone	100	6	73
e	Benzophenone	66	18 ^{d,e}	70 ^c
f	Menthone	80	18 ^{d,e}	60 ^c
g	α-Tetralone	80	18 ^d	70 ^c
h	Cyclohexenone	80	10	65 ^c
i	Benzaldehyde	60	15 ^d	60 ^c

^a Products were characterized by IR, ¹H NMR and mass spectral data and also by comparison with authentic samples. ^b Yields refer to isolated pure product. ^c Yields based on starting material consumed. ^d The equivalent amount (by mass) of TS-1 catalyst with respect to tosylhydrazone was used in order to get the maximum conversion. ^e Reaction was performed in acetone.

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‡ Although highly concentrated H₂O₂ is known to be explosive, 30% or less concentrated H₂O₂ is normally utilised industrially with appropriate precaution.⁸ Also in our reaction condition, the concentration (v/v) of H₂O₂ falls to <10% because of solvent dilution.

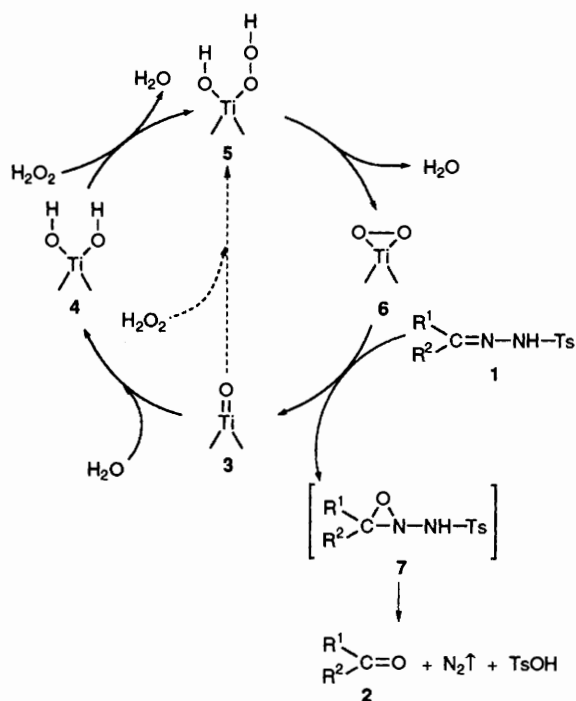
Table 2 Oxidative cleavage of imines by TS-1 catalyst

Entry	Imines	Conversion (%)	Reaction time/h	Carbonyl compounds ^a yield (%) ^b
j	PhCH=N–Ph	85	10	74 ^c
k	PhCH=N–Me	85	10	65 ^c
l	PhC=N–Ph	100	10	67

|
Me

^a Products were characterized by IR, ¹H NMR and mass spectral data and also by comparison with authentic samples. ^b Yields refer to isolated pure product. ^c Yields based on starting material consumed.

§ In a control experiment, benzaldehyde was transformed to an ester under the experimental conditions.



Scheme 2

In a typical reaction procedure, to a stirred solution of tosylhydrazone or imine (1.74 mmol) in methanol (10 ml) were added TS-1 catalyst (0.5 parts by mass to that of substrate) and 30% H_2O_2 (2.1 mmol),[‡] the mixture was refluxed with stirring for the specified period of time (see Tables 1 and 2). The reaction was monitored by GC and/or TLC. After the reaction was complete, the zeolite was filtered off and the solvent removed under reduced pressure. After extraction with dichloromethane followed by sodium bisulfite and sodium bicarbonate wash, the organic layer was dried over anhydrous sodium sulfate. Removal of solvent and subsequent column chromatography provided pure carbonyl compounds.

The present method for the cleavage of **1** involves an electrophile as an active species, which is present in hydroperoxy **5** or peroxy **6** (Scheme 2). A tentative mechanism for the catalytic cleavage of carbon–nitrogen double bond is attributed to the presence of the randomly distributed Ti^{4+} ion in the lattice.¹⁵ According to the proposed mechanism^{7,9,10} the species **3** reacts with H_2O_2 and leads to the peroxy species **6** via an intermediate hydroxy peroxy titanium complex **5**, which eventually provides the reactive electrophilic oxygen species for the oxidation of imino double bond of tosylhydrazones **1** to oxaziridine derivatives **7**. Subsequent oxidative H-abstraction either by **5** or **6**, radical H-abstraction by OH^* or by usual fragmentation due to instability of **7** in our reaction conditions, leads to transformation of oxaziridines into carbonyl compounds (Scheme 2).[¶] An authentic sample¹² similar to **7** was found to be unstable under our reaction conditions and gave the carbonyl compound (Table 2, entry k).

Deprotection of tosylhydrazones is a commonly used transformation in synthetic organic chemistry. Based on the nature of reactive species involved in these methods, one can classify them in four main categories: nucleophilic (sodium hypochlorite¹⁷ and superoxide¹⁸), electrophilic (*m*-chloroperbenzoic acid¹⁹), radicaloid (*N*-bromosuccinimide,²⁰ sodium methoxide–dimethyl sulfoxide²¹ and lead tetraacetate²²) and

miscellaneous (UF_6 ²³ and baker's yeast²⁴). However, many of the conventional procedures for regeneration of the carbonyl function from such nitrogen derivatives have several limitations, viz, toxicity of reagent *e.g.* $(\text{PhSeO})_2\text{O}$ ²⁵ and pyrophoric nature of Na_2O_2 ⁸ *etc.* In this context, the present heterogeneous catalytic method should be a useful addition to synthetic organic chemistry.

In summary, a facile heterogeneous catalytic method for the oxidative cleavage of tosylhydrazones to ketones or aldehydes, has been developed. The obvious advantages of heterogeneous catalysis in terms of easy separation, consistent yield and recyclability of the catalyst are noteworthy. A mechanistic insight regarding the nature of the reactive species as electrophilic in a highly complex reaction of TS-1 and H_2O_2 is proposed,⁴ which can serve as a model for future planning and prediction.

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[¶] The instability of oxaziridines in aqueous acidic media is reported.¹⁶ Since our reaction provides toluene-*p*-sulfonic acid as a side product, this appears to be the most natural course.

[‡] The recovered zeolite was reactivated for reuse by heating at 500 °C in presence of air. The same zeolite was recycled for all the reactions without loss of activity and selectivity. This is one of the normal features of TS-1.^{1–10}