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Catalytic Oxidation of Ethers with H₂O₂ over Zeolites

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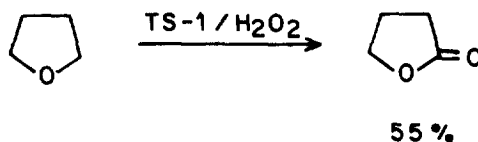
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Abstract : Titanium Silicates (TS-1 and TS-2) catalyzed efficiently the selective oxidation of both linear and cyclic ethers into the corresponding acids and lactones respectively, using dil. H₂O₂ as the oxidant.

The selective oxidative functionalization at the α C-H bonds of ethers is one of the most useful reactions in organic synthesis, because it provides for the efficient preparation of esters (or lactones in the case of cyclic ethers).¹ Such conversions are usually accomplished by the use of either stoichiometric amounts of chromium trioxide, lead tetraacetate, ruthenium tetroxide as oxidants² or the catalytic amounts of RuO₄ in the presence of hypochlorite or periodate.³ Most recently, several new oxidation systems have been described using transition metal complexes of Co, Pd etc. for the transformation of ethers to esters.⁴ Although a number of different reagents have been discovered for the selective oxidation of ethers, few have assumed any synthetic importance because of expense of catalysts, high acidity of the media and poor selectivity in terms of product distribution. The use of heterogeneous catalysts in the liquid phase, on the other hand, offers several advantages compared with their homogeneous counterparts e.g. ease of recovery and recycling and enhanced stability.⁵ Moreover, the α -methylene- γ -butyrolactone structural unit is present in a wide variety of sesquiterpenes and other natural products and has been suggested to be of central importance for the biological activities of those compounds.⁶

In recent years, redox zeolites especially the titanium silicates (TS-1 and TS-2) and other molecular sieves have figured prominently for their remarkable catalytic properties when used with dil. H₂O₂ as oxidant.⁷ Herein, we wish to report our observation of the facile and selective oxidation of several classes of ethers by a new heterogeneous catalytic system, TS-1/H₂O₂ (Scheme 1).



Scheme-1

TS-1^{8a}, TS-2^{8b}, VS-1^{8c}, VS-2^{8d}, CrS-1^{8e} and CrS-2^{8f} were prepared following literature procedures. In a typical reaction, a mixture of tetrahydrofuran (3.6 g, 0.05 mol), TS-1 (360 mg, 10% wt) and 30% H₂O₂ (5.7 ml, 0.05 mol) was heated at 70°C with stirring for 12 h. The catalyst was filtered off, the product distilled to afford γ -butyrolactone (2.36 g, 55%) and characterized.⁹ The results are summarized in Table-1.

Table 1 : TS-1 catalyzed oxidation of various ethers with 30% H₂O₂

Entry	Substrates	Products ^a	Yield ^b (%)
1	Dibutyl ether	Butyric acid	54
2.	Benzyl methyl ether	Benzoic acid	65
3.	Tetrahydrofuran ^c	γ-Butyrolactone	55
4.	Tetrahydropyran	δ-Valerolactone	42
5.	Dihydropyran	δ-Valerolactone	40
6.	1,4-Dioxan	Keto-1,4 - dioxane	5

a : characterized by m.p., IR, ¹H and ¹³C NMR; b : Isolated either by distillation or by chromatographic purification; the rest is essentially unreacted ether; c : The catalyst was recovered and reused three times with no loss of activity and selectivity.

Evidently, linear ethers underwent oxidation selectively to produce the corresponding acids, presumably formed by the hydrolysis of the esters, while cyclic ethers are selectively transformed into lactones in good yields. Even vinylic ether (entry 5) has been successfully oxidized to δ-valerolactone in 40% yield. When the oxidation of tetrahydrofuran with H₂O₂ was carried out with other metal incorporated catalysts such as VS-1, CrS-1 (MFI topology) and VS-2 and CrS-2 (MEL topology), it is found that titanium silicates (TS-1 and TS-2) have exhibited significantly better activity (55%) and selectivity (98%) than chromium silicates (11%) while vanadium silicates totally failed to catalyze the reaction. Mechanistically, the peroxy species Ti (μ-O₂) oxidizes the α C-H bond of ethers producing the α-hydroxylated product, which undergoes further oxidation to give the corresponding lactones and esters.

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- ¹H NMR (200 MHz, CDCl₃); δ 2.1 (2H, m), 2.35 (2H, t, J = 6 Hz), 4.15 (2H, t, J = 7 Hz); ¹³C NMR (200 MHz, CDCl₃) : δ 21.5, 27.2, 68.2 and 177.9.