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Facile Oxidation of Silyl Enol Ethers with Hydrogen Peroxide Catalyzed by Methyltrioxorhenium

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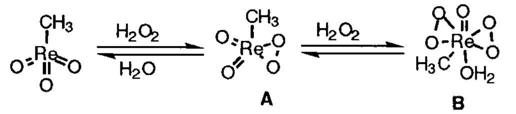
In the presence of catalytic amounts of MTO, silyl enol ethers are oxidized with hydrogen peroxide to afford α-hydroxy and α-siloxy ketones. On treatment of the mixture with potassium fluoride, the former are obtained in high yields.

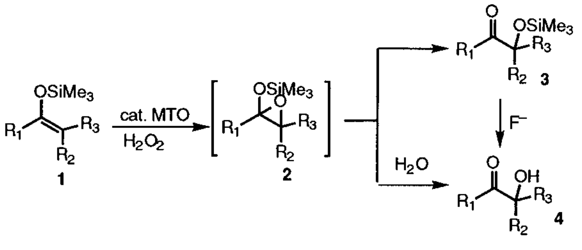
Methyltrioxorhenium (CH_3ReO_3, abbreviated as MTO) is a well-established catalyst for the reactions of hydrogen peroxide,[1,2] including the epoxidation of alkenes.[3−6] The active forms of the catalyst are the monoperoxo and diperoxo complexes formed in reversible equilibria, eq 1:



A **B**

(1)

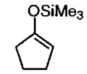
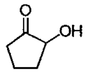
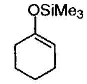
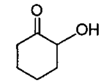
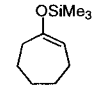
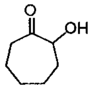
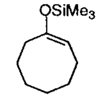
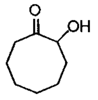
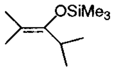
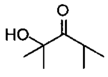
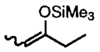
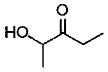
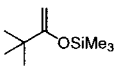
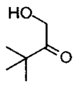
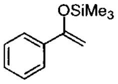
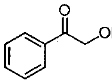
We have devised a convenient and efficient method for preparing α-hydroxy ketones from silyl enol ethers with H_2O_2 as the oxidizing agent and MTO as the catalyst in acetonitrile. The silyl enol ethers **1** were converted to the α-hydroxy ketones **4**, accompanied by the corresponding α-hydroxy siloxy ketones **3**, presumably through the epoxide **2**, which partitions by hydrolysis to **4** or silyl rearrangement to **3**, eq 2.[7−9] Successive disilylation of the crude reaction mixtures afforded **4** in high yields. The compounds are presented in Table 1.



(2)

This conversion was best carried out in acetonitrile solutions containing pyridine and acetic acid. The ethers **1** are moisture-sensitive compounds, especially when acids or bases are present. Indeed, our initial attempts with H_2O_2/MTO but lacking pyridine and acetic acid failed, giving only hydrolysis to ketones; apparently, MTO or **A** or **B** are strong enough Lewis acids to catalyze hydrolysis. Recently, it has been shown that pyridine is able to suppress the Lewis acidity of MTO and its peroxo adducts and prevent the hydrolysis of epoxides formed by the oxidation of alkenes with a hydrogen peroxide/MTO system.[10] Also, pyridine accelerates peroxo complex formation as in eq 1. The use of pyridine alone is not satisfactory, since MTO is concurrently deactivated by conversion to perrhenate.[11] To stabilize the catalyst and to allow higher levels of the enol ether and lower catalyst concentrations, acetic acid was added along with pyridine as a component of the solvent mixture. With 5% HOAc, 0.2 mol % MTO sufficed, with little or no hydrolysis of the ether. Pyridine is necessary, however, as HOAc alone gives only total hydrolysis. This system constitutes a buffer, with each component having a separate role. Pyridine reduces the Lewis acidity of the catalyst, thus preventing the hydrolysis of **1**; HOAc lowers the basicity

Table 1. Synthesis of α-Hydroxy Carbonyl Compounds

Entry	Trimethylsilyl enol ether	Product	Yield [a]
1			96
2			97 (90)[b]
3			99 (91)[b]
4			99
5			95
6[c]			99
7			100
8			60

[a] Combined GC/MS yields of both α-hydroxy and α-siloxy ketones, the balance being the corresponding ketone formed by the hydrolysis of the starting trimethylsilyl enol ether. In two cases, entries 2 and 3, the GC/MS yield was confirmed from the amount of the nonoxidized ketone, which was determined by the method of standard addition. [b] Isolated yield from a reaction on a scale of ∼2 g. [c] Mixture of isomers, trans/cis 97:3 from GC−MS.

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of the solution, prolonging the catalyst's lifetime. The ratio HOAc/Py was ~9:1.

As shown in eq 2, **3** accompanies the desired product in an amount depending on the substrate. These materials were not isolated, but were observed in the GC−MS. Under the experimental conditions, slow hydrolysis of **3** to **4** was found when the potassium fluoride workup was delayed.

The method works efficiently when **1** does not have an electron-withdrawing group conjugated with the enol ether double bond. In the case of 1-phenyl-1-(trimethylsiloxy)ethene (Table 1, entry 8), the yield is only 60%, presumably due to its lower reactivity toward oxidation, allowing hydrolysis to compete. The even less reactive 4-(trimethylsiloxy)-3-penten-2-one gave hydrolysis only, resulting in 2,4-pentanedione.

The literature reports such reactions, utilizing reagents such as peracids,[7−9] chromyl chloride,[12] hypervalent iodine,[13] dimethyldioxirane,[14] sulfonyloxaziridines,[15] osmium tetraoxide,[16] triphenyl phosphite ozonide,[17] lead tetrabenzoate,[18] and molecular oxygen.[19] Optically active α-hydroxy carbonyl compounds have been prepared from silyl enol ethers using a number of oxidants with (salen)-Mn(III) complex as a catalyst.[20] The method described here has the advantage over most of the mentioned methods because aqueous hydrogen peroxide, a cheap and readily available oxidizing agent, was used; also, MTO is commercially available and the procedure gives high yields in reasonable reaction times. Recently, a moderately successful oxidation of silyl enol ethers with aqueous hydrogen peroxide catalyzed by peroxotungstophosphate has been reported.[21]

Experimental Section

General Experimental Procedures. **1** (0.10 mmol) was added to a rapidly stirred solution of MTO (0.2 mM), hydrogen peroxide (0.2 M, added as a 30% solution in water), and pyridine (0.1 M) in 1.0 mL of acetonitrile/HOAc, 95:5 by volume. After 15 min, most of the acetonitrile was removed by rotary evaporation and the residue poured into 5 mL of saturated KF in methanol. Stirring was continued for 2 h and the solution dissolved in ether and washed first with saturated sodium bicarbonate and then water. The ether layer was dried and the product obtained by evaporation after column chromatography (*n*-hexane/acetone). This procedure was successfully scaled up by a factor of 100 to obtain the isolated yields reported in Table 1.

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Supporting Information Available: ^{1}H and ^{13}C data of **4** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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