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# TELLURIUM DIOXIDE CATALYZED SELECTIVE OXIDATION OF SULFIDES TO SULFOXIDES WITH HYDROGEN PEROXIDE

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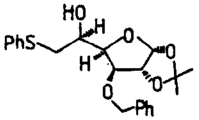
**Summary:** $TeO_2$-$H_2O_2$ system was found to be an efficient and selective reagent for the oxidation of sulfides to sulfoxides in the presence of other common functional groups. Over-oxidation of sulfoxides to sulfones was not observed.

Oxidation of sulfide to sulfoxide is an important transformation in organic systhesis. Although there are various reagents available for this purpose[1], there still exists a need for new methods, especially for complex polyfunctional compounds. The most widely used hydrogen peroxide, *m*-chloroperbenzoic acid, and sodium metaperiodate sometimes cause over-oxidation of sulfoxides to sulfones or oxidation of other functional groups such as double bonds, carbonyl groups, and vicinal diols. Recently reported other oxidizing agents such as sodium perborate[2], sodium bromite[3], potassium hydrogen persulfate[4], and acyl nitrates[5] have also similar drawbacks and are not generally applicable for the oxidation of sulfides to sulfoxides. We have reported that $SeO_2$-$H_2O_2$ system is an efficient and chemoselective system for the oxidation of sulfides to sulfones[6,7] whereas other workers reported earlier that $SeO_2$-$H_2O_2$ was a selective oxidizing agent for sulfides to sulfoxides[8].

Herein we report $TeO_2$-$H_2O_2$ system as a remarkably selective oxidizing agent for the oxidation of sulfides to sulfoxides. Thus, sulfides were transformed into sulfoxides in high yields by treatment with hydrogen peroxide in the presence of the catalytic amount of tellurium dioxide at room temperature. A representative example is the oxidation of crotyl phenyl sulfide. To a mixture of crotyl phenyl sulfide (0.165g, 1.00mmol) and tellurium dioxide (0.016g, 0.10mmol) in methanol (2.0 ml), aqueous 30% hydrogen peroxide solution (0.227g, 2.00 mmol) was added dropwise at room temperature. After stirring at room temperature for 24h, the reaction mixture was partitioned between methylene chloride and water layers. The product in organic layer was purified by column chromatography of silica gel to afford pure crotyl phenyl sulfoxide (0.126g, 70%).

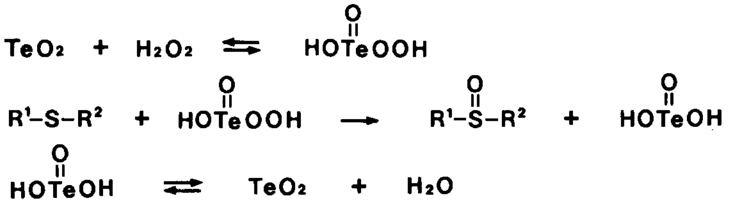
The results of the oxidation are summarized in Table. $TeO_2$-$H_2O_2$ system under the present conditions, and even with on equivalent of $TeO_2$, neither oxidized the resulting sulfoxides further to sulfones nor affected other functional groups. The reaction of cyclohexene, benzaldehyde, acetophenone, geraniol, or ethylene glycol with $TeO_2$-$H_2O_2$ did not give an appreciable amount of products and the starting material was recovered. Entry 4 illustrates that the chemoselective oxidation of a sulfide group in the presence of a double bond in the same molecule. Carbonyl groups and hydroxy groups were not affected under the present conditions as shown in entries 5-7. In this regard, $TeO_2$-$H_2O_2$ system appears to be superior to most widely used mCPBA and $NaIO_4$ which oxidizes olefines and carbonyl groups and cleaves diols, respectively. One problem of the catalytic $TeO_2$-$H_2O_2$ system was that the reaction time was relatively longer. Especially, the oxidations of sulfides having carbonyl groups or hydroxy groups were very sluggish. However, the additon of a small amount of c-HCl[9] (1/100 molar ratio of a sulfide) drastically accelerated the oxidation of sulfides. The effect of c-HCl was especially pronounced in the oxidation of a carbohydrate sulfide(entry 7); it was not oxidized by one equivalent $TeO_2$-$H_2O_2$ system in the prolonged reaction time but oxidized to a sulfoxide in 83% yield in 2h by catalytic $TeO_2$-$H_2O_2$-HCl system. It is also noteworthy that the acid labile isopropylidene group in the carbohydrate sulfide was not affected by the present $TeO_2$-$H_2O_2$-HCl system.

Table. Selective Oxidation of Sulfides to Sulfoxides with $TeO_2$-$H_2O_2$

| Entry | Sulfides | Time, h/Yield, %[a,b] | | |
|---|---|---|---|---|
| | | 1 equiv. of $TeO_2$ | 0.1 equiv. of $TeO_2$ | 0.1 equiv. of $TeO_2$-0.01 equiv. of HCl |
| 1 | $C_6H_5SCH_2CH_3$ | 8/90 | 12/90 | 2/92 |
| 2 | *p*- $ClC_6H_4SC_6H_5$ | 16/80 | 24/84 | 2/85 |
| 3 | $CH_3(CH_2)_3SCH_3$ | 4/90 | 8/95 | 1/95 |
| 4 | $C_6H_5SCH_2CH{=}CHCH_3$ | 16/85 | 24/75(70) | 4/85 |
| 5 |  $CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}CH_2SC_6H_5$ | 48/(67) | | 2/(81) |
| 6 |  $C_6H_5\overset{O}{\overset{\|}{C}}CH_2SC_6H_5$ | 48/(71) | | 2/(82) |
| 7 |  | no reaction | | 2/(83) |

[a] The yields were determined by GLC. [b] The yields in parentheses are isolated ones.

True oxidizing species in $TeO_2$-$H_2O_2$ system would be peroxytellenious acid ($H_2TeO_4$) which would be reduced back to $H_2TeO_3$ and quickly regenerated by $H_2O_2$ during the reaction and hence the catalytic cycle is completed as shown in Scheme 1. The efficiency and the selectivity of $TeO_2$-$H_2O_2$-HCl system indicate that this oxidizing agent would proved to be a useful alternative to other reagents in the selective oxidation of sulfides to sulfoxides.



$$TeO_2 + H_2O_2 \rightleftarrows HO\overset{O}{\overset{\|}{Te}}OOH$$

$$R^1{-}S{-}R^2 + HO\overset{O}{\overset{\|}{Te}}OOH \longrightarrow R^1{-}\overset{O}{\overset{\|}{S}}{-}R^2 + HO\overset{O}{\overset{\|}{Te}}OH$$

$$HO\overset{O}{\overset{\|}{Te}}OH \rightleftarrows TeO_2 + H_2O$$

Scheme 1

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9. Other strong acids such as c-$H_2SO_4$ and c-$HNO_3$ did not affect the reaction rate as much as c-HCl.

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