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HYPERVALENT IODINE IN SYNTHESIS X X Ⅲ ;OXIDATION WITH [HYDROXY(TOSYLOXY)IODO]BENZENE: SELECTIVE OXIDATION OF SULFIDES TO SULFOXIDES

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Abstract: Alkyl-and aryl-sulfides can be selectively oxidated to their corresponding sulfoxides with excellent yields under mild conditions by [hydroxy(tosyloxy)iodo]benzene. Morever, [hydroxy (((+)-10-camphorosulfonyl)oxy)iodo]benzene as the chiral oxidizer, can be used to oxidate unsymmetric sulfides to sulfoxides with a few %ee to some extent.

In the course of our studies on the functionalizations of organic compounds with hypervalent iodine reagents, we have found that [hydroxy(tosyloxy)iodo]benzene, Koser's reagent, is useful for a mild, selective oxidation of alkyl-and aryl-sulfides to corresponding sulfoxides. This reaction can be carried out readily at room temperature. (Scheme 1)

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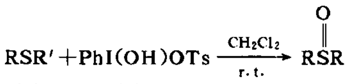


$$RSR' + PhI(OH)OTs \xrightarrow[r.t.]{CH_2Cl_2} R\overset{O}{\overset{\|}{S}}R'$$

(1) (2) (3)

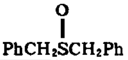
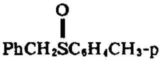
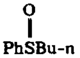
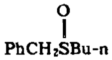
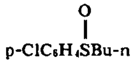
(Scheme 1)

To the stirred suspended solution of PhI(OH)OTs in CH_2Cl_2 was added the solution of the appropriate sulfide in CH_2Cl_2. Then, simple stirring the mixture for a few minutes until it became clear. After workup and isolation, the corresponding sulfoxide was obtained with excellent yield, as shown in Table 1.

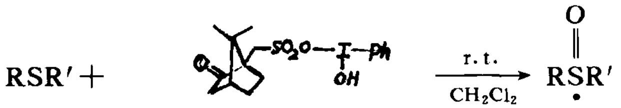
The results show that the reaction is not only suitable for alkyl sulfides but also for aryl sulfides to be oxidated to sulfoxides. The more importance is the reaction has high selectivity which only makes the oxidation stop at the stage of sulfoxides without any furthur oxidation to produce sulfones. As we know, the oxidation of a sulfide R-S-R′ can yield either sulfoxide R-SO-R′ or sulfone $R\text{-}SO_2\text{-}R'$, or the both, depending on the method used.

Usually, most of the methods for the preparation of sulfoxides from sulfides can not avoid the products of sulfones, i. e. peroxytrifluoroacetic acid[1], sodium bromite in aq. dioxane[2], aq. HNO_3 and H_2SO_4 in $MeNO_2$[3], $PhIO_2$ catalyzed by vanadyl acetylacetonate[4], [3—(oxocamphorsulfonyl]oxaziridine[5], etc. Although there are some ways with high selectivity, such as mercury(Ⅱ) oxide-iodine system[6], PhIO catalyzed by metalloporphyrin chloride[7] or by $PhSe_2OH$[8],etc they need either toxic agents or catalysts. Relatively, PhI(OH)OTs is a mild and nontoxic oxidant that can be used to high-selectively oxidate sulfides to sulfoxides with excellent yields under very mild conditions without any catalyst.

Table 1: sulfoxides from sulfides by PhI(OH)OTs:

Products (3)	yield (%)	I.R. (KBr, cm^{-1})	^{1}H-NMR (ppm, CDCl$_3$)
 $\mathrm{PhCH_2\overset{\overset{O}{\vert}}{S}CH_2Ph}$	~100	1500,1460,1035 775,700	3.91(s,4H) 6.77—7.60(m,10H)
 $\mathrm{PhCH_2\overset{\overset{O}{\vert}}{S}C_6H_4CH_3\text{-}p}$	~100	1500, 1040, 800, 765,700	2.33(s,3H) 3.94(s,2H), 6.67—7.33(m,9H)
 $\mathrm{Ph\overset{\overset{O}{\vert}}{S}Bu\text{-}n}$	97	2980, 1460, 1030, 770,700	0.90(t,3H), 1.03—1.77(m,4H) 2.70—2.93(m,2H) 6.80—7.70(m,5H)
 $\mathrm{Ph\overset{\overset{O}{\vert}}{S}CH_2Ph}$	~100	1500,1040,770,700	4.00(s,2H) 6.72—7.40(m,10H)
 $\mathrm{Ph\overset{\overset{O}{\vert}}{S}Et}$	95	1480,1045,770,700	1.30(t,3H) 3.90(q,2H) 6.96—7.43(m,5H)
 $\mathrm{PhCH_2\overset{\overset{O}{\vert}}{S}Bu\text{-}n}$	94	2980, 1450, 1040, 750,690	0.90(t,3H) 1.00—1.80(m,4H) 2.34—2.67(m,2H), 3.90(s,2H) 6.96—7.43(m,5H)
 $\mathrm{p\text{-}ClC_6H_4\overset{\overset{O}{\vert}}{S}Et}$	84	1485,1045,825,740	1.27(t,2H) 3.90(s,2H) 6.83—7.47(m,4H)
 $\mathrm{p\text{-}ClC_6H_4\overset{\overset{O}{\vert}}{S}Bu\text{-}n}$	88	2980, 1485, 1040, 820,740	0.90(t,3H) 1.00—1.77(m,4H) 2.67—2.90(m,2H) 6.80—7.64(m,4H)
 $\mathrm{p\text{-}ClC_6H_4\overset{\overset{O}{\vert}}{S}C_6H_4CH_3\text{-}o}$	92	1480,1030,830,740	2.33(s,3H) 7.33—8.00(m,8H)

Recently, Varvoglis and co-workers has synthesized a chiral reagent, [hydroxy(((+)—10—camphorsulfonyl)oxy)iodo]benzene (4)[10], which has the similar qualities to [hydroxy(tosyloxy)iodo]benzene. Based on our finding about oxidation of sulfides to sulfoxides with PhI(OH)OTs, we think it possible to use the [hydroxy(((+)—10—(camphorsulfonyl)oxy)iodo]benzene to stereoselectively oxidate unsymmetric sulfides to chiral sulfoxides. (Scheme 2)



(1) (4) (5)

(Scheme 2)

As we expected, the reaction could occur rapidly with high chemical yields and some enantioselectivity. The results are shown in Table 2.

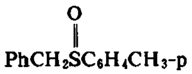
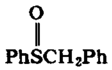
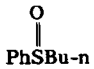
In the summary, PhI(OH)OTs is a mild oxidzing agent which can transfer sulfides to sulfoxides with high selectivity. The reaction has some advantages over others such as mild condition, excellent yields, simple procedure and so on. Moreover, [hydroxy (((+) — 10 — camphorsulfonyl) oxy) iodo] benzene shows some enantioselectivity for the oxidation of unsymmetric sulfides to chiral sulfoxides.

Experimental Section:

I. General procedure for the oxidation of sulfides to sulfoxides with PhI(OH)OTs

At room temperature, under stirring, added the solution of 2mmol appropriate sulfide in 5ml CH_2Cl_2 dropwise to the suspended solution of 2mmol PhI(OH)OTs in 20ml CH_2Cl_2. After about 10 minutes until the mixture became clear, washed it with 10ml water, then dried the CH_2Cl_2 layer with anhydrous magnesium sulphate. After removal of the most solvent, the residue was isolated by TLC with hexane and ether in the ratio of 1 to 3 as the developer to give the product. All the products were identified with I.R. and ^1H-NMR spectral date.

Table 2. Chiral sulfoxides from unsymmetric sulfides with [hydroxy(((+)—10—(camphorsulfonyl)oxy)iodo]benzene

products(5)	yields(%)	$[\alpha]_D^{15}$[a]	%ee[b]	configurations
 $PhCH_2\overset{O}{\overset{\Vert}{S}}C_6H_4CH_3\text{-}p$	92	+3°	13.7	R[9]
 $Ph\overset{O}{\overset{\Vert}{S}}CH_2Ph$	86	+8°	3.17	R[9]
 $Ph\overset{O}{\overset{\Vert}{S}}Bu\text{-}n$	84	−12°	6.2	S[10]
 $Ph\overset{O}{\overset{\Vert}{S}}Et$	82	−5°	2.7	S[11]

[a] $[\alpha]_D^{15}$ was measured in ethanol with $C=0.01g/ml$

[b] $\%ee=\frac{[\alpha]}{[\alpha]_{max}}\times 100\%$

Ⅱ. General procedure for the oxidation of sulfides to chiral sulfoxides with [hydroxy(((+)—10—camphorsulfonyl)oxy) iodo]benzene

Added dropwise the solution of 2mmol appropriate sulfide in 5 ml CH_2Cl_2 to the stirred solution of 2 mmol [hydroxy(((+)—10—camphorsulfonyl)oxy)iodo]benzene in 20ml CH_2Cl_2 at the room temperature. Then dealed with the mixture as the procedure I as the above to give the product.

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