13 H, cyclohexyl and methylene protons), and 5.5 (m, 1 H, vinyl proton) [lit.⁹ bp 101-102.5° (10 Torr), n²⁵p 1.4640]

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Cooxidation of α Olefins and Arenethiols with Oxygen. Synthesis of β -Hydroxy Sulfoxides

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We have found a new method to transform β -hydroxy sulfoxides (2) into a protected form of α -hydroxy aldehydes (3) by the Pummerer reaction with acetic anhydride in the presence of sodium acetate.¹ Since β -hydroxy



sulfoxides are obtained by the cooxidation of olefins and thiols with oxygen,² a combination of the cooxidation and the subsequent Pummerer reaction will provide an attractive route to α -hydroxy aldehydes from α olefins (1). However, the cooxidation is actually limited to olefins conjugated with electron-attacting groups such as aromatic rings, ester, and nitrile.³ After some experimentation to establish a general method to get 2 from 1, we have found that the irradiation of a black-light fluorescent lamp is most suitable for the cooxidation of 1 and arenethiol with oxygen because the light is effective enough to give the porduct and does not decompose it. The use of approximately 2 equiv of 1 to thiol affords the product in good yield. The various types of 2 were prepared as summarized in Table I.

The similar cooxidation of 1-pentene (4) and p-toluenethiol in hexane did not give the corresponding β -hydroxy sulfoxide (6) but many unidentified substances. The reaction in hexane-ethyl acetate (4:1) or hexane-acetone (4:1)as solvent, however, afforded the corresponding β -hydroperoxy sulfide (5) in good yield. It was found that 5 can be converted into 6 by simply stirring the reaction mixture in the presence of a catalytic amount of V_2O_5 , oxobis(acetvlacetonato)vanadium(IV), or dioxobis(acetylacetonato)molybdenum(VI). The sulfoxide 6 was isolated in 63-67% yields (see Table I). The by-products were the corresponding sulfide 7 and sulfone 8.



Thus, in the cooxidation of olefins and thiols with oxygen, olefins can be classified into three groups: (1) the conjugated olefins such as styrene, acrylonitrile, and methacrylate, which are known to be easily cooxidized to the corresponding β -hydroxy sulfoxides,³ (2) the α olefins as shown in Table I, which are cooxidized under the irradiation of a black-light fluorescent lamp, and (3) 1-alkenes, which need catalyst in the transformation of β -hydroperoxy sulfides to β -hydroxy sulfoxides.

The β -hydroxy sulfoxides (2) obtained here are all new compounds, and this work in conjunction with the Pummerer process¹ constitutes a new and simple two-step synthesis of α -hydroxy aldehyde derivatives (3) from α olefins (1). Recently β -hydroxy sulfoxides were found to be converted to α,β -unsaturated sulfoxides,⁴ β -chloro sulfones,⁵ and α,β -unsaturated sulfones.⁶

Experimental Section

The cooxidation reactions were carried out using freshly distilled olefins. The product is a diastereomeric mixture.

Procedure A-1. Preparation of 3-Acetoxy-2-hydroxypropyl p-Tolyl Sulfoxide (2, $\mathbf{R} = \mathbf{AcOCH}_2$). A solution of p-toluenethiol (0.89 g, 7.15 mmol) and allyl acetate (1.30 g, 13.0 mmol) in hexane (100 ml) contained in a 100-ml cylinder was efficiently bubbled with oxygen by means of a sintered-glass bubbler from the bottom of the container under the irradiation of a black-light fluorescent lamp (Toshiba FL-20BLB)7 at room temperature overnight. The formed white crystals were freed from the solvent by decantation to give 1.515 g (82%) of 2 ($R = AcOCH_2$). The product was recrystallized from chloroform-hexane: ir (Nujol) 1008, 1025, 1243, 1728, and 3265 cm⁻¹; nmr (CDCl₃) § 2.06 (3 H), 2.44 (3 H), 2.55-3.35 (2 H), 4.0-4.65 (4 H), and 7.45 (4 H).

Anal. Calcd for C12H16O4S: C, 56.24; H, 6.29; S, 12.51. Found: C, 56.15; H, 6.10; S, 12.54.

Procedure A-2. Preparation of 2-Hydroxy-3-phenylpropyl p-Tolyl Sulfoxide (2, $\mathbf{R} = \mathbf{PhCH}_2$). A solution of p-toluenethiol (1.13 g, 9.09 mmol) and allylbenzene (2.15 g, 18.2 mmol) in hexane (200 ml) was subjected to the cooxidation under the same condition as above for 2 days. The formed crystals were collected to afford 1.83 g (73%) of 2 ($R = PhCH_2$). The mother liquor was stirred with ca. 30 mg of V_2O_5 for 5 hr to give 0.25 g (10%) of the additional product as insoluble crystals. The product was recrystallized from benzene-hexane: ir (Nujol) 700, 810, 1045, 1085, and 3325 cm⁻¹; nmr (CDCl₃) δ 2.39 (3 H), 2.85 (4 H), 4.00 (1 H), 4.95 (1 H), and 7.30 (9 H).

Anal. Calcd for C16H18O2S: C, 70.04; H, 6.61; S, 11.69. Found: C, 70.05; H, 6.60; S, 11.73.

Procedure A-3. Preparation of 3-Acetoxy-2-hydroxybutyl p-Tolyl Sulfoxide [2, $\mathbf{R} = \mathbf{CH}_3 \mathbf{VH}(\mathbf{OAc})$]. A solution of *p*-toluenethiol (1.00 g, 8.05 mmol) and 3-acetoxy-1-butene (2.21 g, 19.4 mmol) in hexane (300 ml) was stirred in a 500-ml flask under the atmosphere of oxygen and the irradiation of a black-light fluo-

Table I β -Hydroxy Sulfoxides (2) from α Olefins (1) and Arenethiols

Ar ^a	R (equiv) ^b	Registry no.	Mp,° °C	Yield, %	Registry no.
Ci	$AcOCH_2$ (1.0)	591-87-7	140-143	63 ^d	50921-23-8
С	$AcOCH_2$ (2.0)			92 ^d	
\mathbf{T}^{k}	$AcOCH_2$ (1.8)		136 - 145	82^d	50921-24-9
\mathbf{Ph}^{i}	$AcOCH_2$ (1.2)		107 - 109	54 [,]	50921-25-0
т	$HOCH_2(2.4)$	107-18-6	117 - 126	90 ^d	50921-26-1
\mathbf{T}	$CH_3CH(OAc)$ (2.4)	6737-11-7	88-109	76	50921-27-2
\mathbf{T}	$PhCH_2OCH_2(2.1)$	14593-43-2	135-136	87ª	50921-28-3
Ť	$PhOCH_2$ (2.2)	1746-13-0	92-98	80 ^d	50921-29-4
\mathbf{T}	$ClCH_2$ (2,4)	107-05-1	134-136	79 ^d	50921-30-7
\mathbf{T}	$ClCH_2CHCI$ (2.0)	760-23-6	202 - 204	82ª	50921-31-8
\mathbf{T}	$PhCH_{2}(2.0)$	300-57-2	136-141	83	50921-32-9
Т	4-Acetoxy-3-methoxy- benzyl (1.05)	93-28-7	129-138	777	50921-33-0
\mathbf{T}	$CH_3(CH_2)_2$	109-67-1	43-75	670	50921-34-1
\mathbf{T}	$CH_3(CH_2)_2$			66 ^h	
\mathbf{T}	$CH_{3}(CH_{2})_{2}$			63 ⁱ	
\mathbf{T}	$CH_{3}(CH_{2})_{5}$	111-66-0	68-71	68	50921-35-2

^a C = p-chlorophenyl, T = p-tolyl. ^b Equivalent of olefins to thiol. ^c Melting point of diastereometric mixtures after a few recrystallizations. ^d By procedure A-1. ^e By procedure A-2. ^f By procedure A-3. ^g With V₂O₅ by procedure B. ^h With VO(acac)₂ by procedure B. ⁱ With MoO₂(acac)₂ by procedure B. ⁱ Registry no., 106-54-7. ^k Registry no., 106-45-6. ⁱ Registry no., 108-98-5.

rescent lamp overnight. The solvent was evaporated under vacuum to give an oil, which was chromatographed on silica gel with benzene. The elution with benzene-ethanol (95:5) furnished 1.65 g (76%) of 2 [R = CH₃CH(OAc)]. The product crystallized on standing and was recrystallized from benzene-hexane: ir (Nujol) 810, 1040, 1245, 1375, 1735, and 3300 cm⁻¹; nmr (CDCl₃) δ 1.24 (3 H), 2.02 (3 H), 2.42 (3 H), ~3.1 (2 H), 4.2 (1 H), 4.53 (1 H), 5.0 (1 H), and 7.46 (4 H).

Anal. Calcd for C13H18O4S: C, 57.76; H, 6.71; S, 11.86. Found: C, 58.04; H, 6.85; S, 11.90.

Procedure B. Preparation of 2-Hydroxypentyl p-Tolyl Sulfoxide (2, $\mathbf{R} = \mathbf{CH}_3\mathbf{CH}_2\mathbf{CH}_2$). A solution of *p*-toluenethiol (1.00 g, 8.05 mmol) and 1-pentene (1.29 g, 18.4 mmol) in 200 ml of hexane-ethyl acetate (4:1) was stirred in the same condition as procedure A-3 overnight. Then the solution was stirred with ca. 30 mg of V_2O_5 for 5 hr. The solvent was removed under vacuum to give an oil, which was chromatographed with benzene. The elution with benzene-ethyl acetate (8:2) furnished 1.23 g (67%) of 2 $(R = CH_3CH_2CH_2)$. The product crystallized on standing and was recrystallized from benzene-hexane: ir (Nujol) 803, 1026, and 3320 cm⁻¹; nmr (CDCl₃) δ 0.87 (3 H), 1.41 (4 H), 2.36 (3 H), 2.5-3.25 (2 H), 4.06 (1 H), 4.14 (1 H), and 7.1-7.7 (4 H).

Anal. Calcd for C12H18O2S: C, 63.68; H, 8.02; S, 14.16. Found: C, 63.67; H, 8.15; S, 14.00.

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