Synthesis and Configurational Assignments of Diastereomeric β-Hydroxy Sulfones

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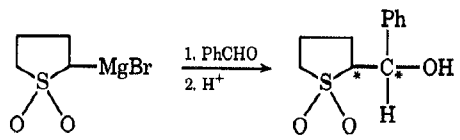
Reported here are the isolations of a number of diastereomeric β-hydroxy sulfones obtained by the condensations of α-sulfonyl carbanions with aldehydes. Configurations were assigned from nmr spectra of the resulting *threo* and *erythro* isomers. Sodium borohydride reductions of β-keto sulfones were found to produce the *threo* isomers in excellent yields. Conversion of *threo* **1** to the β-chloro sulfone by treatment with thionyl chloride proceeds with complete epimerization. Under identical conditions the *erythro* isomer **2** proceeds with complete retention of configuration. Preparation of the exocyclic *cis* olefin **15** was accomplished by dehydration and dehydrohalogenation of **2** and **10**, respectively. The less stable *trans* olefin **16** was prepared *via* the intramolecular cyclization of an acetylenic mercaptan.

While the preparations of α metalated sulfones and their reactions with carbonyl moieties to form β-hydroxy sulfones have been extensively investigated,[1] little of this work has been done with sulfones which can give rise to diastereomers. In cases where such sulfones have been used,[1a,b,d] determination of isomer ratios in the products, isolation of pure *erythro* and *threo*[2] isomers, and assignment of configuration to these isomers have either been ignored or circumvented by oxidation of the mixtures to the β-keto sulfones. It was therefore the purpose of this investigation to isolate pure diastereomeric β-hydroxy sulfones and assign configurations by spectral and chemical methods.

In 1954 the preparation of phenyl(1,1-dioxy-2-thiolanyl)carbinol from 2-thiolanylmagnesium bromide 1,1-dioxide and benzaldehyde was reported (no stereochemistry specified).[1b] As can be readily seen, two



(1)

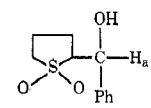
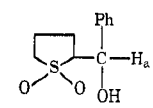
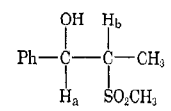
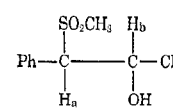
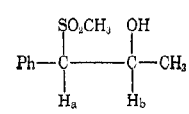
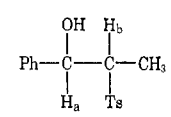
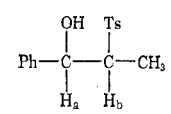
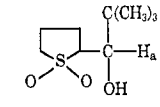
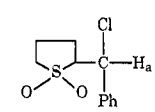
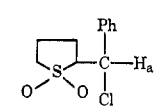
adjacent centers of asymmetry (*) are present which could result in *erythro* and *threo* diastereomers. Upon reinvestigation of this reaction we found that the product was indeed a 50:50 mixture of *threo* (**1**) and *erythro* (**2**) phenyl(1,1-dioxy-2-thiolanyl)carbinol.[3]

Configurational assignments were made on the basis of the magnitude of the coupling constants between the vicinal methinyl protons on the asymmetric centers (Table I). The vicinal coupling constant can be predicted from its relationship to the dihedral angle formed by H–C–C–H.[4] Similar assignment of stereochemistry by nuclear magnetic resonance spectroscopy has been reported for diastereomeric amino alcohols.[5–7]

The large difference in the magnitude of the vicinal coupling constants of the methinyl protons in **1** and **2** (see Table I) suggests preferred residence in different conformations. This requirement is best satisfied by the conformers shown in Chart I. Using theoretical calculations[4] one predicts dihedral angles of 171 and 56°

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA[a]

No.	Compound	Configuration	Chemical shift, δ, H_a	J_{ab}, Hz	Mp, °C
1		*threo*	5.03	9.0	159–159.5
2		*erythro*	5.46	2.2	97–98
3		*threo*	4.87	9.5	130–131
4		*threo*	4.08	9.0	153–154
5		*erythro*	3.97	2.5	114.5–115
6		*threo*	4.90	9.0	104–105
7		*erythro*	5.47	1.5	*b*
8		*erythro*	3.91	1.0	103.5–105
9		*threo*	5.06	10.5	193–194
10		*erythro*	5.22	9.0	159–160

[a] Determined on a Varian Model A-60 (60 MHz) spectrometer in $CDCl_3$ solution. [b] A pure sample, free of **6**, could not be obtained.

(1) (a) L. Field and J. W. McFarland, *J. Amer. Chem. Soc.*, **75**, 5582 (1953); (b) W. E. Truce and K. R. Buser, *ibid.*, **76**, 3577 (1954); (c) H. D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963); (d) D. F. Tavares and P. F. Vogt, *Can. J. Chem.*, **45**, 1519 (1967); (e) E. M. Kaiser and C. R. Hauser, *Tetrahedron Lett.*, 3341 (1967).

(2) The terms *erythro* and *threo* refer to *dl-erythro* and *dl-threo*, respectively.

(3) Isomer ratios were determined by nmr spectroscopy.

(4) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

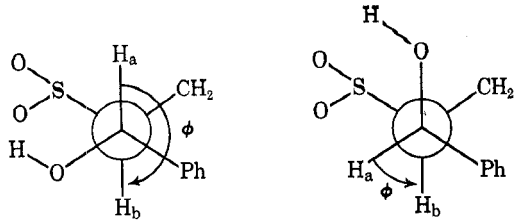
(5) J. B. Hyne, *Can. J. Chem.*, **39**, 2536 (1961).

(6) J. C. Randall, R. L. Vaulx, M. E. Hobbe, and C. R. Hauser, *J. Org. Chem.*, **30**, 2035 (1965).

(7) M. E. Munk, M. K. Meilahn, and P. Franklin, *ibid.*, **33**, 3480 (1968).

CHART I

PREFERRED CONFORMATIONS OF *threo*- AND *erythro*-PHENYL(1,1-DIOXY-2-THIOLANYL)CARBINOL

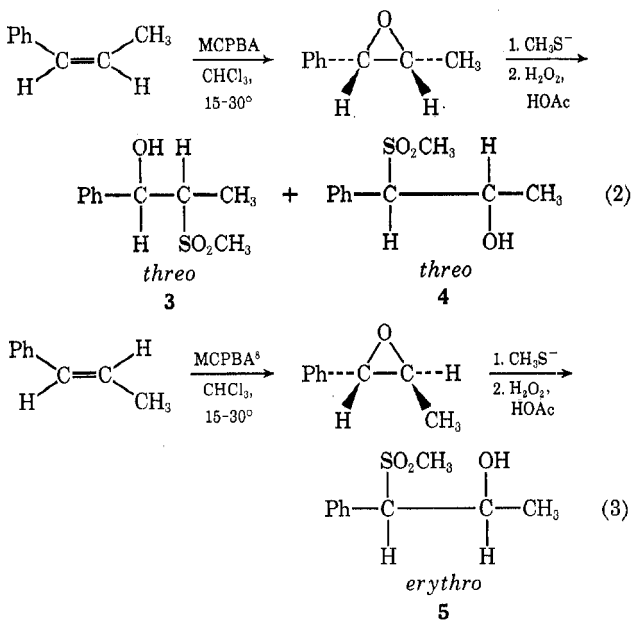


threo — J_{ab} = 9.0 Hz — ϕ_{calcd} = 171°

erythro — J_{ab} = 2.2 Hz — ϕ_{calcd} = 56°

from the coupling constants 9.0 and 2.2 Hz, respectively. On this basis we have assigned the *threo* configuration to the isomer with J_{ab} = 9.0 Hz. This isomer resides primarily in the *anti* conformation (Chart I). The *erythro* isomer resides chiefly in the *gauche* conformation and therefore has the coupling constant of 2.2 Hz. These values are in good agreement with those previously reported in similar conformational studies.[5-7]

In order to confirm these stereochemical assignments and test the generality of this method of assignment of stereochemistry in other β-hydroxy sulfones, it was deemed necessary to synthesize compounds of unambiguous configuration. This was accomplished using *cis*- and *trans*-propenylbenzene. These olefins



threo **3** + *threo* **4** (2)

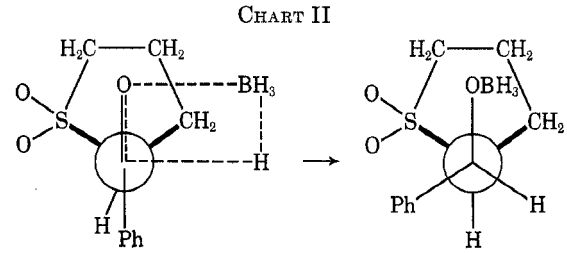
erythro **5** (3)

were converted to the corresponding *cis*- and *trans*-propenylbenzene oxides in near quantitative yields by treatment with *m*-chloroperoxybenzoic acid. Treatment of the *cis* epoxide with sodium methanethiolate in ethanol, followed by oxidation of the β-hydroxy sulfides with peracetic acid, produced a mixture of *threo*-2-methylsulfonyl-1-phenyl-1-propanol (**3**) and *threo*-1-methylsulfonyl-1-phenyl-2-propanol (**4**) (eq 2). Structural assignment of **3** was based on the mass spectrum in which the major ion fragment was *m/e* 107 which corresponds to cleavage of the molecule at the C_1–C_2 bond. The structures of **4** and **5** were established by oxidation of the alcohols to 1-phenyl-1-methylsulfonylacetone with the chromium trioxide–pyridine complex.[9] *erythro*-1-Methylsulfonyl-1-phenyl-2-propanol (**5**) was prepared in a similar fashion from the *trans* epoxide (eq 3). None of the *erythro* benzylic alcohol was isolated from this reaction.[10] The observed vicinal coupling constants of **3** and **4** were 9.5 and 9.0 Hz corresponding closely with that of **1**. A value of 2.5 Hz was observed for **5** which supports the configurational assignment of **2**.

In the course of our investigation it came to our attention that the synthesis and nmr spectrum of 1-phenyl-2-(*p*-tolylsulfonyl)-1-propanol had been recorded previously.[1d] These authors obtained a compound melting from 99 to 100°. A doublet at δ 1.5 with a coupling constant of 7.5 Hz was attributed to the benzylic methinyl proton. We wish to report that this assignment is in error. Treatment of ethyl *p*-tolyl sulfone with *n*-butyllithium in tetrahydrofuran followed by addition of benzaldehyde produced a 93% yield of a mixture composed of 62% *erythro*-1-phenyl-2-(*p*-tolylsulfonyl)-1-propanol (**7**) and 38% *threo* isomer (**6**). The methinyl resonance in question appears at δ 4.90 (J_{ab} = 9.0 Hz) for **6** and δ 5.47 (J_{ab} = 1.5 Hz) for **7** which corresponds closely with compounds previously discussed here. Apparently the authors were dealing with a mixture containing 75% **6** and 25% **7**. The resonance which was attributed to the methinyl proton is in reality due to the alkyl methyl grouping of **7**. The doublet at δ 1.17 corresponds to the methyl grouping of **6**.

Further evidence for the above stereochemical assignments was obtained through the sodium borohydride reduction of α-(*p*-tolylsulfonyl)propiophenone (**11**) and 2-thiolanyl phenyl ketone (**12**). Applying the rule of steric control of asymmetric induction[11] one would predict attack from the least hindered side of the conformer shown in Chart II and production of the

CHART II



threo alcohol. The other conformations of this molecule were ruled out on the basis of severe steric and electrostatic repulsions. Reduction of **12** with sodium borohydride in aqueous methanol produced a nearly quantitative yield of β-hydroxy sulfone. The product contained 95% *threo* isomer **1** and 5% *erythro* isomer **2**. Similarly, reduction of **11** resulted in a 97%

(8) *m*-Chloroperoxybenzoic acid.

(9) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, **75**, 422 (1953).

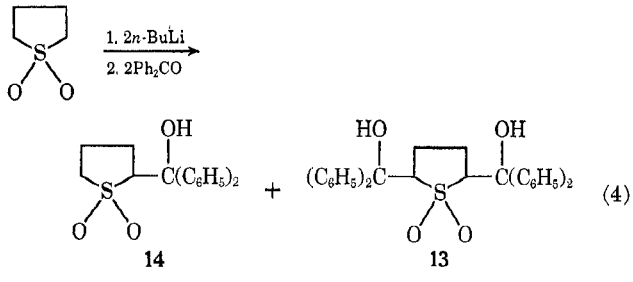
(10) The appearance of the "abnormal" ring opening leading to product **3** may be related to hindered rotation on the part of the phenyl ring in the *cis* epoxide. The resulting noncoplanarity of the phenyl group would hinder attack at the benzylic carbon atom sterically as well as through decreased resonance stabilization of the incipient positive charge in the transition state. Similar results were observed by H. Audier, *et al.*, *Bull. Soc. Chim. Fr.*, 2811 (1966).

(11) For leading references, see H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 28–33.

yield of **6** and 3% **7**. The high degree of stereospecificity indicates the importance of large steric factors present in these molecules.

The metalation of sulfones has been achieved with a wide variety of bases.[1] We have found *n*-butyllithium in THF to be an excellent base–solvent system for metalation and subsequent condensation with carbonyl moieties. Reaction times are short and yields are high. The condensation works well with aldehydes, ketones, and carboxylic acid esters and is not limited by side reactions such as are found with liquid ammonia.[1d] The ratios of diastereomers produced in eq 1 appear to be somewhat influenced by the cation associated with the carbanion although the effect is small, the greatest difference being observed with the *n*-butyllithium–tetramethylethylenediamine complex[12] (65 ± 2% **2** and 35 ± 2% **1**).

When the sulfone is capable of forming an α,α' dicarbanion (*i.e.*, sulfolane), care must be exercised to add the *n*-butyllithium slowly in a dropwise fashion or appreciable quantities of diaddition products may result.



(4)

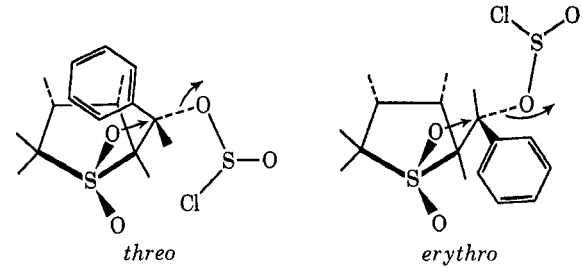
14 **13**

Treatment of sulfolane with 2 equiv of *n*-butyllithium in THF followed by 2 equiv of benzophenone afforded an 80% yield of diadduct **13** and 18% monoadduct **14**. Hauser[1e] has reported that treatment of sulfolane with 2 mol of lithium amide followed by benzophenone produced only monoadduct, while use of sodium amide resulted in a 41% yield of **13** and a 48% yield of **14**. Apparently *n*-butyllithium in THF is a superior system for such 1,3 dicarbanions.

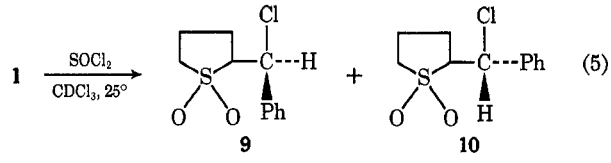
While attempting to assign stereochemical configurations to **1** and **2** we converted them to the *threo* (**9**) and *erythro* (**10**) chlorides with thionyl chloride (eq 5). Treatment of **1** with thionyl chloride in deuteriochloroform resulted in the quantitative conversion to a 1:1 mixture of **9** and **10** in 12 hr. Treatment of **2** under the same conditions provided a quantitative yield of **10** in 72 hr. Use of various solvents (dioxane, thionyl chloride, and pyridine), as well as lower temperatures, had no effect on the products formed. The *threo* isomer always proceeded with epimerization while the *erythro* isomer always proceeded with retention of configuration. These results are perhaps best explained by participation of the sulfonyl oxygens in back-side protection of the incipient carbonium ion (Chart III). This would prevent back-side attack and therefore result in retention of configuration. This conformation is considered the most stable owing to minimal steric interaction. In order for back-side assistance to occur in the *threo* isomer, the molecule must assume a conformation in which the aromatic nucleus is seated directly upon the sulfolane ring. This produces severe steric interaction as well as interfering with the ability

(12) D. J. Peterson, *J. Org. Chem.*, **32**, 1717 (1967).

CHART III



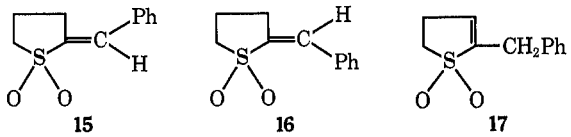
of the aromatic nucleus to attain coplanarity with the incipient carbonium ion thereby interfering with resonance stabilization. Such participation by neighboring groups has been studied for the decomposition of β-phenyl chlorosulfites.[13]



(5)

9 **10**

Further support for these configurational assignments was obtained from the results of base-catalyzed dehydrohalogenation of **9** and **10**. On the basis of earlier observations of bimolecular eliminations of diastereomeric halides,[14] the preferred *trans* elimination of **10** should lead to formation of the *cis* olefin (**15**) as the predominant product. By similar considerations, **9** should be transformed primarily into the *trans* olefin (**16**). These systems are, however, directly analogous to the diastereomeric 2-*p*-tolylsulfonyl-1,2-diphenyl-1-chloroethanes studied by Cristol[15] in which dehydrohalogenation resulted in stereoconvergent eliminations and production of the *cis* olefin from both the *erythro* and *threo* isomers. Similar steric interactions between the sulfonyl and aryl groupings in the transition state should lead to formation of **15** from **9** *via cis* elimination. The rate of elimination should be considerably slower for **9** than for **10** in which a *trans* elimination occurs. Treatment of **10** with triethylamine in chloroform at 25° gave essentially quantitative conversion to **15** in 48 hr. Under the same conditions **9** showed no detectable elimination even after 2 weeks. Attempted dehydrohalogenation of **9** with triethylamine in refluxing benzene for 24 hr again resulted in quantitative recovery of starting material. Treatment of **9** and **10** with potassium *t*-butoxide in benzene gave dehydrohalogenation; however, the olefinic products were isomerized to the endocyclic olefin (**17**). Attempted isomerization of **16** to **15** in refluxing ethanolic sodium hydroxide also produced **17** as the major product.

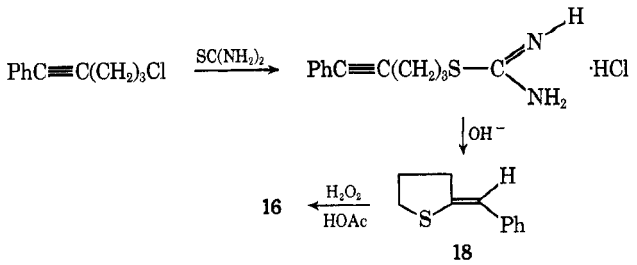


15 **16** **17**

The synthesis of **16** was accomplished by the sequence shown in Scheme I. 5-Chloro-1-phenyl-1-pentyne was converted to the corresponding thiouronium salt by reaction with thiourea. Subsequent treatment with

(13) D. J. Cram, *J. Amer. Chem. Soc.*, **75**, 332 (1953).
(14) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962).
(15) S. J. Cristol and P. Pappas, *J. Org. Chem.*, **28**, 2066 (1963).

SCHEME I



hydroxide resulted in the expected *trans* sulfide (**18**) *via* intramolecular *trans* addition to the acetylenic linkage. Such additions in intermolecular thiolate additions have been extensively studied.[16] Oxidation of **18** with peracetic acid afforded **16** in excellent yields.

Other behavioral differences between *erythro*- and *threo*-hydroxy sulfones were observed upon acid-catalyzed dehydration of **1** and **2**. **2** was converted to **15** in high yield in refluxing 85% phosphoric acid in 1 hr. The *threo* isomer **1** was recovered intact after 1 hr under the same conditions. When treated for 24 hr at reflux, **1** gave extensive decomposition, and the only product isolated was apparently a salt melting above 300°. The *erythro* alcohols and chlorides studied here generally had lower melting points and higher degrees of solubility in organic solvents such as chloroform and benzene than the corresponding *threo* isomers.

Experimental Section[17]

Reagents.—*n*-Butyllithium in hexane was purchased from Foote Mineral Corp. and Alfa Inorganics. Sulfolane was obtained from Eastman Organic Chemicals. Reagent grade THF was distilled from lithium aluminum hydride prior to use. *m*-Chloroperoxybenzoic acid (85%) was purchased from Aldrich Chemical Co.

Phenyl(1,1-dioxy-2-thiolanyl)carbinol. A.—*n*-Butyllithium (0.05 mol) in hexane under a nitrogen atmosphere was cooled below 20°, and 5.8 g (0.05 mol) of TMEDA was added slowly, followed by 6 g (0.05 mol) of sulfolane in 10 ml of THF; stirring was continued for 1 hr. The solution was cooled to −30° and 6.36 g (0.06 mol) benzaldehyde was added and stirring was continued for 1 hr. The mixture was acidified with aqueous NH_4Cl, and the organic phase was separated and dried over Na_2SO_4. Filtration and removal of solvent *in vacuo* gave 10 g of a viscous oil that was shown by nmr to contain 65% *erythro* isomer **2** and 35% *threo* isomer **1**. The oil was dissolved in benzene–hexane and 9.6 g (85%) of a white solid precipitated, mp 80–82°. A second recrystallization raised the melting point to 87–88°. This mixture was submitted for analysis.

Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24; S, 14.17. Found: C, 58.47; H, 6.48; S, 13.96.

Subsequent recrystallization from benzene, benzene–hexane, and benzene–CCl_4 yielded **2** [mp 97–98°; nmr ($CDCl_3$) δ 1.68–2.56 (m, 4, $-CH_2CH_2-$), 2.90–3.50 (m, 4, CH_2SO_2CH and OH), 5.46 (d, 1, $-C(H)(OH)C_6H_5$), and 7.35 (s, 5, aromatic H)] and **1** [mp 159–159.5° (lit.[1b] 159–159.5°); nmr ($CDCl_3$) δ 1.55–2.35 (m, 4, $-CH_2CH_2-$), 2.95–3.50 (m, 3, CH_2SO_2CH), 3.56 (s, 1, OH), 5.03 (d, 1, $-C(H)(OH)C_6H_5$), and 7.47 (s, 5, aromatic H)].

B.—Synthesis was carried out as previously described by Truce and Buser[1b] with the exception that an equimolar amount of benzaldehyde was used. A yield of 20% of a mixture composed of 50% **1** and 50% **2** was obtained.

C.—Sulfolane (18 g, 0.15 mol) in 200 ml of THF under nitrogen was cooled to −30°, and *n*-butyllithium (0.15 mol) in hexane was added dropwise. After 1 hr benzaldehyde (15.9 g, 0.15 mol) in 100 ml of THF was added, and stirring was continued for 3 hr. Work-up as in A produced 26.8 g (79%) of a mixture of 43% **2** and 57% **1**.

trans-**Propenylbenzene Oxide.**—*trans*-Propenylbenzene (11.8 g, 0.1 mol) in 100 ml of $CHCl_3$ was cooled to 15°, and a solution of 85% *m*-chloroperoxybenzoic acid (25 g) in 300 ml of $CHCl_3$ was added dropwise maintaining the temperature below 30°. After stirring 1 hr at room temperature the excess peracid was decomposed with 10% aqueous Na_2SO_3. The organic layer was washed with 10% Na_2CO_3 until basic and then H_2O until neutral. After drying over Na_2SO_4, filtration, and removal of solvent, 12.8 g (95.6%) of the epoxide was obtained: nmr ($CDCl_3$) δ 1.33 (d, 3, CH_3), 2.90 (m, 1, $HCCH_3$), 3.47 (d, 1, HCC_6H_5), 7.20 (s, 5, C_6H_5).

cis-**Propenylbenzene Oxide.**—The *cis* epoxide was prepared from *cis*-propenylbenzene[18] and MCPBA in the same manner as the *trans* isomer in 94% yield: nmr $CDCl_3$, δ 1.00 (d, 3, CH_3), 3.20 (m, 1, $HCCH_3$), 3.95 (d, 1, HCC_6H_5), 7.21 (s, 5, C_6H_5).

threo-**1-Phenyl-2-(methylsulfonyl)-1-propanol (3) and** *threo*-**2-Phenyl-1-(methylsulfonyl)-2-propanol (4).**—To a solution of Na (0.80 g) in 50 ml of ethanol was added 3 ml of methanethiol. After stirring 15 min, 2.6 g (19.4 mmol) *cis*-propenylbenzene oxide was added, and stirring was continued for 2 hr at 35°. After acidification with 10% HCl and extraction with CH_2Cl_2, removal of solvent gave the crude β-hydroxy sulfide. This was dissolved in 20 ml of HOAc, and 15 ml of 30% H_2O_2 was added. The solution was heated at 83° for 2 hr and poured onto ice. The solution was extracted with $CHCl_3$, neutralized with 10% Na_2CO_3, and dried; solvent was removed *in vacuo* to yield 3.1 g (75%) of a white solid, mp 110–130° (31% isomer **3** and 69% isomer **4**). This was dissolved in hot benzene, and 1.6 g of a 1:1 mixture of **3** and **4** precipitated on cooling. Hexane was added to the mother liquor and 200 mg of **3** was obtained: mp 130–131; nmr ($CDCl_3$) δ 1.00 (d, 3, $HCCH_3$), 3.02 (s, 3, SO_2CH_3), 3.18–3.80 (m, 2, OH and $HCCH_3$), 4.87 (d, 1, HCC_6H_5), 7.32 (s, 5, C_6H_5); mass spectrum (70 eV) *m/e* (relative intensity) 214 (2.4), 213 (25.8), 196 (1.7), 107 (100). The 1:1 mixture was recrystallized several times from benzene to obtain **4**: mp 153–154°; nmr ($CDCl_3$) δ 1.08 (d, 3, $HCCH_3$), 2.81 (s, 3, SO_2CH_3), 3.50–3.70 (m, 1, OH), 4.08 (d, 1, SO_2CH), 4.65–5.00 (m, 1, $HCCH_3$), 7.38 (s, 5, C_6H_5).

erythro-**1-Phenyl-1-(methylsulfonyl)-2-propanol (5).**—Sodium (1.2 g) was dissolved in 50 ml of ethanol, and methanethiol (3.0 g, 63 mmol) was added. After stirring 10 min, *trans*-propenylbenzene oxide (5 g, 37.3 mmol) in 20 ml of ethanol was added, and stirring was continued for 2 hr at room temperature (32°). Work-up as with **3** and **4** gave the crude sulfide. This was heated at 85° for 2 hr in a solution of 25 ml of HOAc and 20 ml of 30% H_2O_2. Treatment as above and recrystallization from 95% ethanol gave 5.0 g (58%) of white crystals: mp 114.5–115°; nmr (CCl_3) δ 1.20 (d, 3, $HCCH_3$), 2.68 (s, 3, SO_2CH_3), 3.07 (d, 1, OH), 3.97 (d, 1, $HCSO_2CH_3$), 4.78–5.20 (m, 1, $HCCH_3$), 7.25–7.80 (m, 4, C_6H_5).

Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.59; S, 14.96. Found: C, 56.06; H, 6.67; S, 14.74.

1,1-Dioxy-2-thiolanyl Phenyl Ketone (12).—A solution of sulfolane (12 g, 0.1 mol) in 200 ml of THF under nitrogen was cooled to −68° and *n*-butyllithium in hexane (0.1 mol) was added dropwise with stirring. After 1 hr ethyl benzoate (16 g, 0.107 mol) was added rapidly and stirred 15 min. The solution was acidified with 10% HCl. The organic phase was extracted with 10% NaOH. Cooling of the basic layers and acidification with HCl gave an oil which crystallized on standing. This was recrystallized from 95% ethanol to obtain 9.4 g (42%) of **12**: mp 91–93°; nmr ($CDCl_3$) δ 1.80–2.80 (m, 4, CH_2CH_2), 2.9–3.0 (t, 2, CH_2SO_2), 4.87 (t, 1, $SO_2C(H)(CO)$), 7.20–7.70 (m, 3, aromatic H), and 7.70–8.20 (m, 2, aromatic H).

Reduction of 12.—A solution of **12** (1 g, 4.45 mmol) in 50 ml of methanol was cooled to 15° and $NaBH_4$ (0.8 g) in 10 ml of H_2O was added dropwise keeping the temperature at 10–15°. After 5 hr the reaction was acidified with 15 ml of 10% HCl, and the product was extracted with $CHCl_3$. Removal of solvent produced 0.98 g of a mixture of 95% **1** and 5% **2**, mp 153–155°. Two recrystallizations from benzene–hexane gave 0.93 g (93%) of **1**, mp 159–159.5°.

(16) (a) W. E. Truce and R. F. Heine, *J. Amer. Chem. Soc.*, **79**, 5311 (1957); (b) W. E. Truce, H. G. Klein, and R. B. Kruse, *ibid.*, **83**, 4636 (1961).

(17) All melting points are uncorrected. The nmr spectra were obtained using a Varian A-60 spectrophotometer. Mass spectral data were obtained on a CEC 21110-B spectrometer. Microanalyses were performed by Dr. C. S. Yeh and staff.

(18) The authors wish to express their appreciation to Dr. W. Chaisson for the preparation of the *cis*-propenylbenzene used in this work.

1-Phenyl-2-(*p*-tolylsulfonyl)-1-propanol (6 and 7).—A solution of *p*-tolyl ethyl sulfone (3.7 g, 0.02 mol) in 100 ml of THF under nitrogen was cooled to −28°, and *n*-butyllithium (0.02 mol) in hexane was added with stirring. After 5 min benzaldehyde (2.0 g, 0.019 mol) was added and stirring was continued 15 min. Work-up as above gave 5.3 g (93%) of a mixture of the *erythro* isomer **7** (62%) and the *threo* isomer **6** (38%). Attempts to separate the isomers were unsuccessful. The nmr for **7** was obtained by subtraction of the nmr of **6** from the above mixture: nmr ($CDCl_3$) δ 1.18 (d, 3, $HCCH_3$), 2.42 (s, 3, $CH_3C_6H_4$), 3.10–3.70 (m, 1, $SO_2C(H)(CH_3)$), 4.50 (s, 1, OH), 5.47 (d, 1, HCC_6H_5), 7.20–7.9 (m, 9, aromatic H).

2-(*p*-Tolylsulfonyl)propiophenone (11).—Ethyl *p*-tolyl sulfone (2.0 g) in 40 ml of THF was cooled to −30° under nitrogen, and an equivalent amount of *n*-butyllithium in hexane was added. After 5 min ethyl benzoate (3.0 g) was added and stirring was continued 7 min. Acidification with 10% HCl and subsequent work-up gave 1.6 g of **11**: mp 98.5–99.5° (lit.[1a] 99.5–100.5°); nmr ($CDCl_3$) δ 1.56 (d, 3, $HCCH_3$), 2.40 (s, 3, $CH_3C_6H_4$), 5.18 (q, 1, $HCCH_3$), 7.1–8.1 (m, 9, aromatic H).

***threo*-1-Phenyl-2-(*p*-tolylsulfonyl)-1-propanol (6).**—To a solution of **11** (1 g, 3.52 mmol) in 50 ml of methanol at 15° was added $NaBH_4$ (0.8 g) in 10 ml of H_2O with 3 drops of 10% NaOH. The solution was stirred at 10° for 1.5 hr and at room temperature for 3.5 hr. Work-up with 10% HCl gave 1 g (100%) of white crystals which was a mixture of 97% **6** and 3% **7**. Recrystallization from CCl_4 followed by benzene–hexane produced 0.9 g of **6**: mp 104–105°; nmr ($CDCl_3$) δ 0.83 (d, 3, $HCCH_3$), 2.42 (s, 3, $CH_3C_6H_4$), 3.10–3.70 (m, 1, $SO_2C(H)CH_3$), 4.50 (s, 1, OH), 4.90 (d, 1, HCC_6H_5), 7.20–7.95 (m, 9, aromatic H).

***erythro-t*-Butyl-(1,1-dioxy-2-thiolanyl)carbinol (8).**—Sulfolane (24 g, 0.2 mol) in 500 ml of THF was treated with *n*-butyllithium (0.2 mol) and pivalaldehyde (17.2 g, 0.2 mol) as described above. A viscose oil was obtained which was taken up in 95% EtOH and chilled. The 2,5 diadduct (7.6 g) was obtained: mp 228–229°; nmr (d_6-DMSO) δ 0.81 (s, 18, $C(CH_3)_3$), 1.7–2.3 (m, 4, CH_2CH_2), 2.60–3.70 (m, 4, OH and $CHSO_2CH$), 4.7–5.0 (m, 2, $HCC(CH_3)_3$).

Anal. Calcd for $C_{14}H_{28}O_4S$: C, 57.50; H, 9.65; S, 10.96. Found: C, 57.69; H, 9.73; S, 11.08.

The mother liquor was stripped of solvent and recrystallized from CCl_4–petroleum ether (30–60°) to obtain 47% **8**: mp 103.5–105°; nmr ($CDCl_3$) δ 0.98 (s, 9, $C(CH_3)_3$), 1.9–2.0 (m, 4, CH_2–CH_2), 2.75 (s, 1, OH), 2.80–3.30 (m, 3, CH_2SO_2CH), 3.91 (d, J = 1, 1, $HCC(CH_3)_3$).

Anal. Calcd for $C_9H_{18}O_3S$: C, 52.40; H, 8.80; S, 15.54. Found: C, 52.33; H, 8.77; S, 15.77.

Bis-1,1-diphenyl(1,1-dioxy-2,5-thiolanyl)carbinol (13).—A solution of sulfolane (1.0 g, 8.35 mmol) in 50 ml of THF was treated with *n*-butyllithium (16.7 mmol) and benzophenone (3.04 g, 16.7 mmol) in 50 ml of THF. On acidification with HCl the diadduct **13** precipitated and was removed by filtration. Recrystallization from $CHCl_3$ resulted in 3.02 g (75% yield) of **13**, mp 312–313°.

Anal. Calcd for $C_{30}H_{28}O_4S$: C, 74.35; H, 5.82; S, 6.62. Found: C, 73.92; H, 5.65; S, 6.63.

The solvent was removed from the initial filter solution and recrystallized from ethanol. An additional 5% of **13** was obtained and 0.46 g (18% yield) of the monoadduct **14**, mp 203–204° (lit.[1d] 203.5–204.5°).

***threo*-1-Chloro-1-phenyl(1,1-dioxy-2-thiolanyl)methane (9).**—A solution of **1** (3.8 g, 16.3 mmol) in 100 ml of dry dioxane was cooled to 15° and $SOCl_2$ (4.5 g) was added. The solution was stirred at room temperature for 72 hr, and the solvent and excess $SOCl_2$ were removed *in vacuo* leaving 3.97 g (100% yield) of a 1:1 mixture of **9** and **10**. This was separated on an acid-washed Al_2O_3 column eluting with 50% $CHCl_3$ in CCl_4 to give **9**: mp 193–194°; nmr ($CDCl_3$) δ 1.40–2.32 (m, 4, CH_2CH_2), 2.80–3.90 (m, 3, CH_2SO_2CH), 5.06 (d, 1, ClCH), 7.35 (s, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{13}ClO_2S$: C, 53.98; H, 5.35; Cl, 14.49; S, 13.10. Found: C, 54.25; H, 5.34; Cl, 14.79; S, 13.16.

***erythro*-1-Chloro-1-phenyl(1,1-dioxy-2-thiolanyl)methane (10).**—In an nmr tube was placed 0.1 g of **2** in 0.3 ml of $CDCl_3$ and 0.2 ml of $SOCl_2$. The reaction was allowed to stand in a desiccator filled with Drierite and KOH pellets. Spectra were taken periodically. After 72 hr conversion was complete. Removal of solvent left 0.106 g (98% yield) of **10**, mp 158–159°. One recrystallization from benzene–hexane gave white crystals: mp 159–160°; nmr ($CDCl_3$) δ 1.83–2.85 (m, 4, CH_2CH_2), 2.90–3.32 (m, 2, CH_2SO_2), 3.39–3.98 (m, 1, $CHSO_2$), 5.22 (d, 1, ClCH), 7.38 (s, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{12}ClO_2S$: C, 53.98; H, 5.35; Cl, 14.49; S, 13.10. Found: C, 53.77; H, 5.38; Cl, 14.25; S, 13.15.

An identical reaction with **1** was complete in 12 hr and showed complete racemization to yield **9** and **10** in equivalent amounts.

Dehydrohalogenation of 10.—In an nmr tube were placed 0.1 g of **10**, 0.3 ml of $CDCl_3$, and 0.1 ml of NEt_3. After 48 hr at room temperature conversion to the *cis* olefin **15** was complete. The reaction mixture was worked up with H_2O and $CHCl_3$ and recrystallized from benzene–hexane to give 0.80 g (90% yield) of **15**: mp 83–83.5°; nmr ($CDCl_3$) δ 2.26 (p, 2, CH_2), 3.05 (t, 4, CH_2SO_2 and $CH_2C{=}C$), 7.22 (t, 1, $C{=}CH$), 7.38 (s, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; S, 15.40. Found: C, 63.43; H, 5.78; S, 15.61.

Similar treatment of **9** resulted in quantitative recovery of starting material after 2 weeks.

5-Chloro-1-phenyl-1-pentyne.—To a slurry of $NaNH_2$ (16.0 g) in 400 ml of liquid NH_3 was added dropwise phenylacetylene (Farchan Acetylenic Chemicals) (40.8 g, 0.4 mol). After 1 hr at reflux 1-bromo-3-chloropropane (70 g) was added and stirring was continued for 1 hr. Replacement of NH_3 with ether, acidification with dilute HCl, and distillation gave 33.1 g (47% yield) of **5-chloro-1-phenyl-1-pentyne**: bp 98–100° (0.03 mm); nmr ($CDCl_3$), δ 1.90 (p, 2, $CH_2CH_2CH_2$), 2.49 (t, 2, $C{\equiv}CCH_2$), 3.57 (t, 2, CH_2Cl), 7.02–7.58 (m, 5, C_6H_5).

Reaction of 5-Chloro-1-phenyl-1-pentyne with Thiourea.—5-Chloro-1-phenyl-1-pentyne (30 g, 0.168 mol) and thiourea (12.8 g, 0.168 mol) were refluxed in 100 ml of 95% ethanol for 24 hr. NaOH (10.1 g) in 100 ml of H_2O was added and reflux was continued 2 hr. After cooling to room temperature and extraction with benzene an 86% yield of the *trans* olefin **18** was obtained: bp 110–114° (0.02 mm); nmr ($CDCl_3$) δ 1.91 (p, 2, $CH_2CH_2CH_2$), 2.58–2.95 (m, 2, $CH_2C{=}CH$), 3.10 (t, 2, CH_2S), 6.43 (t, 1, $C{=}CH$); 6.90–7.56 (m, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{12}S$: C, 74.97; H, 6.86; S, 18.16. Found: C, 74.73; H, 7.08; S, 18.06.

Oxidation of 18.—To a solution of **18** (10.0 g, 56.8 mmol) in 57 ml glacial HOAc was added 17 ml of 30% H_2O_2. The reaction was heated at reflux for 1 hr, poured on ice, extracted with $CHCl_3$, and dried (Na_2SO_4), and solvent was removed *in vacuo* leaving a yellow solid. Recrystallization from CCl_4 gave 7.3 g (62% yield) of the *trans*-vinyl sulfone **16**: mp 101–102°; nmr ($CDCl_3$) δ 2.12 (p, 2, $CH_2CH_2CH_2$), 2.79–3.27 (m, 4, CH_2SO_2 and $CH_2C{=}C$), 6.80 (t, 1, $C{=}CH$), 7.20–7.50 (m, 3, aromatic H), 7.52–7.88 (m, 2, aromatic H).

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; S, 15.40. Found: C, 63.38; H, 5.82; S, 15.54.

Dehydration of 2.—The *erythro* alcohol **2** (3 g) was refluxed in 30 ml of 85% H_3PO_4 for 1 hr. This was poured onto ice and extracted with $CHCl_3$. Subsequent work-up and recrystallization from benzene–hexane gave 1.9 g of **15** (69% yield), mp 83–83.5°.

Registry No.—**1**, 24463-72-7; **2**, 24463-73-8; *trans*-propenyl benzene oxide, 23355-97-7; *cis*-propenylbenzene oxide, 21884-74-2; **3**, 24463-76-1; **4**, 24463-77-2; **5**, 24463-78-3; **6**, 24463-79-4; **7**, 24463-80-7; **8**, 24515-54-6; **9**, 24463-81-8; **10**, 24463-82-9; **11**, 14195-15-4; **12**, 24463-84-1; **13**, 24463-85-2; **15**, 24463-86-3; 5-chloro-1-phenyl-1-pentyne, 24463-87-4; **16**, 24463-88-5; **18**, 24463-89-6; 2,5 diadduct, 24463-90-9.

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